7430 *Inorg. Chem.* **1996,** *35,* 7430−7439

Allopurinol− and Hypoxanthine−Copper(II) Compounds. Spectral and Magnetic Studies of Novel Dinuclear Coordination Compounds with Bridging Hypoxanthine

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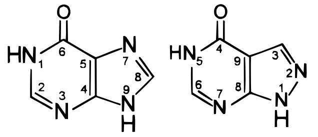
Received February 23, 1996[⊗]

The synthesis in aqueous solution and pH = 1.0 of several novel Cu(II) compounds with allopurinol and hypoxanthine as heterocyclic ligands and X = Cl^-, Br^-, NO_3^-, SO_4^{2-}, and ClO_4^- as anions, together with their spectral and magnetic characterization, is reported. The studies of the Cu(II) systems with these heterocycles and Cl^- or Br^- support their $Cu^{II}(L)_2(X)_2$ character and their interactions through halogen atoms as bridging ligands, leading to a very weak antiferromagnetic coupling. For the Cu(II) compounds with hypoxanthine and X = NO_3^-, SO_4^-, or ClO_4^-, new examples of the cupric acetate type are obtained, showing in all cases similar strong antiferromagnetic coupling. These three cases are new examples of the scarce Cu(II) dinuclear compounds with bridging hypoxanthine which have been reported up to now.

Introduction

The family of purinic type heterocycles, their structural analogues and isomers are relevant in biochemical and pharmacological processes,[1] and its coordination chemistry is a topic of present-day research.[2] The specific role that several transitional metals play in the nucleic acid processes have prompted several research groups to study the bonding behavior of these heterocycles in metal−heterocycle reactions.[3] Within the class of these heterocycles, the isomers 6-oxopurine (hypoxanthine) and 1*H*-pyrazolo[3,4-*d*]pyrimidin-4-one (allopurinol) (Figure 1) are interesting ligands from very different points of view. The diverse metallic coordination capability they show lies in great measure both in the existence of several electronic donor atoms and their disposition in the respective frameworks. Surprisingly, the coordination chemistry of both molecules has not been explored similarly, since the coordination chemistry of 6-oxopurine[2] has been much more extensively studied than that of its purinic isomer.[4]

As part of our study on purine derivative and isomer transition metal interactions and the physical properties of the respective coordination compounds, our attention has been focused on the interactions of the above two heterocycles with Cu(II), under the same reaction conditions and several others systematically modified. Our objective has been to explore the capability of the N atoms of both ligands in the construction of Metal−N bonds in systematically modified reaction conditions. In addition, the magnetic interactions (at intramolecular and intermolecular levels) between the metallic centers and the role played by the ligands in the type and strength of these couplings are topics which interest us. In this paper we report the synthesis in aqueous solution (pH = 1.0) of novel Cu(II) coordination compounds containing respectively the ligands hypoxanthine and allopurinol and their characterization.



I **II**

Figure 1. Schematic drawing and numbering for hypoxanthine (**I**) and allopurinol (**II**).

Experimental Section

(A) Reagents and Buffer Solution. The heterocyclic ligands, Cu(II) salts and buffer constituents were commercially supplied and were used with no further purification. The buffer solution employed was prepared with 0.168 g of glycine, 0.132 g of NaCl and 4.456 g of HCl in 1 L of aqueous solution. The value pH = 1.0 was potentiometrically corroborated.

(B) Single and Competitive Interactions. (i) Single Allopurinol− and Hypoxanthine−Cu(II) Interactions. Each single heterocycle−Cu(II) reaction was carried out by the same procedure except when quoted. One mmol of the heterocyle was dissolved in *ca.* 100 mL of the buffer solution.

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1996.

(1) (a) Hughes, M. N.; *The Inorganic Chemistry of Biological Processes*; 2nd. ed.; John Wiley & Sons: New York, 1981. (b) Stryer, L. *Biochemistry*; 3rd ed.; Freeman: New York, 1988.

(2) *CRC Handbook of Nucleobase Complexes*; Lusty, J. R., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. I and references therein.

(3) For example: *Nucleic Acid-Metal Ion Interactions*; Spiro, T. G. Ed.; John Wiley & Sons: New York, 1980; Vol. 1 and references therein.

(4) Acevedo-Chávez, R.; Costas, M. E.; Escudero-Derat, R. *J. Solid State Chem.* **1994**, *113*, 21 and references therein.

S0020-1669(96)00200-5 CCC: $12.00

Table 1. Analytical Results of the Cu(II) Coordination Compounds (L_1 = Allopurinol; L_2 = Hypoxanthine)

		calcd			found		
compound	color	% C	% H	% N	% C	% H	% N
$Cu(L_1)_2(Cl)_2 \cdot H_2O$	pale green	28.28	2.37	26.38	28.20	2.50	26.10
$Cu(L_2)_2(Cl)_2 \cdot 2H_2O$	blue	27.13	2.73	25.31	27.10	2.60	25.29
$Cu(L_2)_2(Br)_2 \cdot 2H_2O$	green-yellow	22.59	2.27	21.08	22.65	2.60	21.15
$Cu(L_2)_2(NO_3)_2 \cdot 2H_2O$	deep blue	24.22	2.44	28.25	24.71	2.71	28.40
$Cu(L_2)_2(SO_4) \cdot H_2O$	blue	26.70	2.24	24.91	26.79	2.33	25.04
$Cu(L_2)_2(ClO_4)_2 \cdot 2H_2O$	blue	21.05	2.12	19.36	21.36	2.13	19.88

To this, 1 mmol of the respective Cu(II) salt ($X = Cl^-$, Br^-, NO_3^-, SO_4^{2-}, or ClO_4^-) previously dissolved in *ca.* 10 mL of buffer solution was added. The reaction mixture was maintained under stirring at room temperature for *ca.* 2 weeks, and then was kept at *ca.* 40 °C and slow evaporation. From this, a solid product was initially formed, isolated, and carefully washed with H_2O ($T = 4$ °C). The solid product was kept at *ca.* 50−60 °C for 48 h, without color changes (see Results and Discussion). For allopurinol and $CH_3CO_2^-$ a blue suspension was formed. The product was isolated, washed with H_2O and kept at 50−60 °C for several days, resulting in a deep blue product. Its characterization was in full agreement with the polynuclear system Cu^{II}(allopurinolate$^-$)(OH^-), previously synthesized under several experimental conditions.[4] For hypoxanthine and $X = Br^-$, a second minor fraction was isolated, which was not characterized. Also for this heterocycle and $X = SO_4^{2-}$ or ClO_4^-, a second solid product was respectively formed, which was isolated and treated as before (see Results and Discussion).

(ii) Competitive Heterocycle−Cu(II) Interactions. Competitive reactions of the heterocycles in study toward the metallic center were systematically performed. The reactions scheme employed was as follows:

$$[M + L_1] + L_2 \overset{X}{\rightleftharpoons}$$

$$[M + L_2] + L_1 \overset{X}{\rightleftharpoons}$$

$$(L_1 + L_2) + M \overset{X}{\rightleftharpoons}$$

The brackets correspond to the previously established chemical equilibria in solution, while the parentheses correspond to the previously dissolved heterocycles, X is the metallic counterion systematically modified ($X = Cl^-$, Br^-, NO_3^-, SO_4^{2-}, ClO_4^- and $CH_3CO_2^-$), M = Cu(II), and L_1 and L_2 represent the heterocyclic ligands allopurinol and hypoxanthine, respectively. All the competitive reactions were performed at the same pH and temperature values. For the first and second type of competitive reactions, the initial step was performed as mentioned in point i; the solution obtained by adding the second heterocyclic ligand was maintained for another 2 weeks. After this time, the respective reaction mixture was maintained at slow evaporation ($T = 40$ °C), and the solid products formed were isolated and treated as before. For the last type of competitive reactions the two ligands previously dissolved in the buffer solution were allowed to react simultaneously with each metallic salt. For this case also each competitive reaction was maintained for the same period of time and treated with the same technique.

It is important to point out that the high chemical complexity of the reaction mixtures and the evaporation conditions from which the different fractions were separated made it very difficult to obtain single crystals for any of the compounds, which could be employed in diffraction studies.

(C) Physical Measurements. Infrared (IR) spectra in the 4000−200 cm^{-1} range (Nujol mulls, CsI windows) were obtained by using a 599-B Perkin-Elmer spectrometer. IR data in the 600−70 cm^{-1} range (high density polyethylene pellets) were obtained by using a 740 FT IR Nicolet equipment.

Electronic spectra in the 200−1100 nm range (quartz windows and $BaSO_4$ as reference) of the powdered solid samples were recorded by the specular reflectance method by employing a 160-A Shimadzu spectrometer.

Thermogravimetric studies (room temperature−600 °C) were carried out in a DT-30 Shimadzu equipment by using N_2(g) as carrier fluid and 5 °C/min as heating rate.

X-band EPR spectra of the powdered solid samples (room temperature and 77 K) were recorded by employing a 200-D Bruker spectrometer, with DPPH as reference.

Magnetic susceptibility of powdered samples as a function of temperature at different magnetic fields was obtained with a SQUID MPMS-5 Quantum Design Magnetometer, from 2 to 300 K, and magnetic fields of 100, 1000, 5000, 10000, and 30000 G. The equipment was previously calibrated with very fine standards (Pd, Ni, Al). The magnetic measurements (for each field) were carried out under both increasing and decreasing temperature. Each magnetic measurement was corrected due to the cell and sample diamagnetic contributions and showed an average standard deviation 3 orders of magnitude lower than the respective reading reported.

Microanalyses (C,H,N) were performed at the Chemistry Department of the University College of London, and by means of a 240-C Perkin-Elmer elemental analyzer.

Results and Discussion

(A) Analytical Results. The products isolated and characterized in this study were systematically confirmed by elemental analysis. The results shown in Table 1 are the representative values obtained.

(B) Summary of the Single and Competitive Heterocycle−Cu(II) Interactions. The single and competitive heterocycle−Cu(II) interactions carried out yield several coordination compounds. Table 2 shows these results for the different counterions employed.

In this table, a remarkable preponderance of Cu(allopurinol)$_2$(Cl)$_2 \cdot H_2O$ from the single reactions is observed, irrespective of the metallic counterion employed (except for $X = CH_3CO_2^-$). The higher basicity of $CH_3CO_2^-$ may play a significant role in the heterocyclic ligand deprotonation and in the stabilization of Cu(allopurinolate$^-$)(OH^-), in which the allopurinol is dissociated even at this very low pH value. The behavior, however, is different for hypoxanthine: for the single reactions, a clear influence of the metallic counterion is found due to the formation of several coordination compounds. It is possible that the lower coordination capability of the polyatomic counterions leads to the formation of other products, such as Cu(hypoxanthine)$_2$(Cl)$_2 \cdot 2H_2O$. The most significant case is for $X = CH_3CO_2^-$, in which only this last product was formed. Again, the higher basicity of this anion appears to play a critical role in this behavior. The higher stability of Cu(allopurinol)$_2$(Cl)$_2 \cdot H_2O$ arises again in the competitive heterocycle−Cu(II) interactions,

Table 2. Cu(II) Compounds Obtained Employing (a) X = Cl^-, Br^-, and NO_3^-, and (b) SO_4^{2-}, ClO_4^- and $CH_3CO_2^-$ as Metallic Counterions[a]

Part a

reaction	Cl^-	Br^-	NO_3^-
$Cu+L_1 \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$
$Cu+L_2 \rightleftharpoons$	$Cu(L_2)_2(Cl)_2\cdot 2H_2O$	$Cu(L_2)_2(Br)_2\cdot 2H_2O$ (A)	$Cu(L_2)_2(NO_3)_2\cdot 2H_2O$
$[Cu+L_1]+L_2 \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$
$[Cu+L_2]+L_1 \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$
$(L_1+L_2)+Cu \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$ (B)	$Cu(L_1)_2(Cl)_2\cdot H_2O$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$ $Cu(L_2)_2(NO_3)_2\cdot 2H_2O$

Part b

reaction	SO_4^{2-}	ClO_4^-	$CH_3CO_2^-$
$Cu+L_1 \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1^-)(OH^-)$
$Cu+L_2 \rightleftharpoons$	$Cu(L_2)_2(SO_4)\cdot H_2O$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$	$Cu(L_2)_2(ClO_4)_2\cdot 2H_2O$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$	$Cu(L_2)_2(Cl)_2\cdot 2H_2O$
$[Cu+L_1]+L_2 \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$ (C, D, E)	$Cu(L_1)_2(Cl)_2\cdot H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$
$[Cu+L_2]+L_1 \rightleftharpoons$	$Cu(L_1)_2(Cl)_2\cdot H_2O$ (F, G)	$Cu(L_2)_2(ClO_4)_2\cdot 2H_2O$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$	$Cu(L_1)_2(Cl)_2\cdot H_2O$
$(L_1+L_2)+Cu \rightleftharpoons$	$Cu(L_2)_2(SO_4)\cdot H_2O$ (H)	$Cu(L_1)_2(Cl)_2\cdot H_2O$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$	$Cu(L_1^-)(OH^-)$ $Cu(L_2)_2(Cl)_2\cdot 2H_2O$

[a] A to H represent scarce minor fractions not characterized. Abbreviations are the same as in Table 1.

almost without any influence of the $[M + L_i]$ equilibrium carried out in the first step.

For the last type of competitive reactions, the coordination compounds obtained in both single heterocycle−Cu(II) interactions are mainly formed, suggesting the influence of both kinetic and thermodynamic stabilities in these very complex interactions.

(C) IR Spectral Results. IR bands characterization of free allopurinol[5] and hypoxanthine[6−8] was employed in this study. A meticulous and systematic comparison between the bands of these respective ligands and those of the Cu(II) compounds was carried out.

(i) $Cu^{II}(allopurinol)_2(Cl)_2\cdot H_2O$. From the IR data (1700 cm^{-1} for $\nu_{C=O}$ in the free ligand; 1705 cm^{-1} for $\nu_{C=O}$ in the coordinated ligand), noninvolvement of O(4) in the metallic bonding is inferred; the same behavior is deduced for the N(5)−H group (1595 *vs* 1605 cm^{-1}). Of the changes in the spectral data, those corresponding to endocyclic perturbations of the pyrazolic fragment are noticeable. The perturbations where several C−H group vibrational modes in the spectrum of the coordination compound are involved, suggest the participation of the N(2) atom in the metallic bonding of allopurinol. This proposition might be in agreement with this most favorable metallic bonding site shown by this ligand (in the neutral form) in its coordination compounds with unfilled d-shell metallic centers reported up to now.[4] The IR data suggest the noninvolvement of the H_2O molecule in the metallic bonding. The ν_{Cu-Cl} and ν_{Cu-N} vibrational modes could be associated to the broad and complex bands centered at 290 cm^{-1} and 242 cm^{-1} respectively. Finally, the spectral data for this compound show differences with respect to that for $Cu(allopurinol)_2(Cl)_2(H_2O)_2$, previously synthesized in ethanolic medium,[5] for which the coordination of H_2O molecules was suggested.

(ii) $Cu^{II}(hypoxanthine)_2(Cl)_2\cdot 2H_2O$. The spectral data (1670 cm^{-1} for $\nu_{C=O}$ in the free ligand; 1680 cm^{-1} for $\nu_{C=O}$ in the coordinated ligand) suggest the noninvolvement of O(6) in the metallic bonding; the same behavior is deduced for the N(1)−H group (1583 *vs* 1600 cm^{-1}). Of the changes in the spectral data, those involving endocyclic perturbations of the imidazolic fragment are inferred. Considering the existence of N(7)−H/N(9)−H tautomerism for hypoxanthine in aqueous solution, it is difficult to dilucidate the specific nature of the N atom involved in the metallic bonding (N(7) or N(9)). However, considering the spectral behavior of the band assigned to $\nu_{C=O}$, and its differences with respect to that shown by the same band for the cases of Cu(II) compounds with hypoxanthine and polyatomic anions (where the N(3) and N(9) atoms are involved in the metallic bonding, as is discussed below), the involvement of the N(7) atom in the metallic coordination is suggested for the case under discussion.

The involvement of the H_2O molecules in the metallic bonding is not evident. The band appearing at 310 cm^{-1} is assigned to ν_{Cu-Cl}. The coordination of hypoxanthine through N is supported by the broad and complex band with peaks at 295 and 285 cm^{-1}.

(iii) $Cu^{II}(hypoxanthine)_2(Br)_2\cdot 2H_2O$. The IR spectrum in the 4000−400 cm^{-1} range is very similar to that shown by the preceding compound with X = Cl^-; this suggests analogue electronic perturbations of the heterocyclic ligand in both coordination compounds. This same argument can be extrapolated to the nature of the H_2O molecules. The complex and broad band with peaks at 290 and 283 cm^{-1} is assigned to the ν_{Cu-N} vibrational mode; the one centered at 230 cm^{-1} is attributed to the ν_{Cu-Br} vibrational mode. In this compound, as in the X = Cl^- system, a distortion of the metallic plane containing the coordinated Br^- and hypoxanthine ligands is proposed.

(iv) $Cu^{II}(hypoxanthine)_2(NO_3)_2\cdot 2H_2O$. Heterocycle IR Bands. The spectral pattern of this compound is very different from the two systems described above. From the spectral data, the shift to higher frequencies of the band associated with $\nu_{C=O}$ (1710 cm^{-1} for X = NO_3^-, 1680 cm^{-1} for X = Cl^-, and 1685 cm^{-1} for X = Br^-) can be observed. Also, the band associated with $\delta_{N(1)-H}$ is shifted to a higher frequency (1620 cm^{-1} for X = NO_3^-, 1600 cm^{-1} for X = Cl^- or Br^-). These spectral

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(5) Acevedo-Chávez, R.; Behrens, N. B. *Transition Met. Chem.* **1990**, *15*, 434 and references therein.

(6) Mulet, D.; Calafat, A. M.; Fiol, J. J.; Terron, A.; Moreno, V. *Inorg. Chim. Acta* **1987**, *138*, 199.

(7) Dubler, E.; Hänggi, G.; Bensch, W. *J. Inorg. Biochem.* **1987**, *29*, 269.

(8) Mikulski, C. M.; Grossman, S.; Bayne, M. L.; Gaul, M.; Staley, D. L.; Renn, A.; Karayannis, N. M. *Inorg. Chim. Acta* **1989**, *161*, 29.

characteristics suggest the noninvolvement of both the O(6) atom and the N(1)−H group in the metallic bonding. The spectral analysis is in agreement with a noticeable electronic perturbation of endocyclic groups, suggesting the existence of a different metallic bonding behavior of the heterocyclic ligand. In this respect, the IR characteristics of the bands attributed to the C═O and N(1)─H groups suggest the involvement of endocyclic N atoms (possibly the N(3) and N(9) atoms) in addition to those for X = Cl^- or Br^-. The spectral data permit us to propose the noninvolvement of the H_2O molecules in the bonding, as for X = Cl^- and Br^-.

NO_3^- IR bands. The IR bands for this system are located in the 1800−600 cm^{-1} range. The spectral characterization is indicative of the presence of both ionic and coordinated[9,10] NO_3^-. The existence of the coordinated NO_3^- (C_{2v} symmetry) is deduced from the partial splitting of the complex and strong band in the 1750−1725 cm^{-1} range (peaks at 1750, 1744, 1740, and 1725 cm^{-1}). This band corresponds to the $\nu_1 + \nu_4$ vibrational mode. This same behavior is deduced from the band at 1565 cm^{-1} (ν_4), and from the partial splitting of the complex band in the 1395−1300 cm^{-1} range (peaks at 1380, 1360, and 1345 cm^{-1}). The band corresponding to ν_1 might be masked by the band at 1273 cm^{-1}, which in turn is associated with ring, ν_{C-N}, and δ_{N-H} vibrational modes of the coordinated hypoxanthine. Also, ν_2 might be masked by the bands at 980 and 935 cm^{-1} (assigned to ring and C−H vibrational modes of the same heterocyclic ligand). ν_6 is associated with the band at 830 cm^{-1}. Finally, the bands at 730 and 696 cm^{-1} might contain the ν_3 and ν_5 vibrational modes, respectively, although they are also attributed to vibrational modes of the heterocyclic ligand. The existence of the ionic NO_3^- group is inferred from the band at 1050 cm^{-1} (ν_1). The bands corresponding to ν_2, ν_3, and ν_4 for the NO_3^- group in D_{3h} symmetry might be contained respectively in the bands corresponding to the vibrational modes for the coordinated NO_3^-. The $\nu_1 + \nu_4$ vibrational mode for the ionic NO_3^- group might also be contained in the same 1750−1725 cm^{-1} range. The ν_{Cu-ONO_2} vibrational mode is associated with the band at 343 cm^{-1}, although heterocyclic ligand vibrational modes cannot be discarded. The band at 290 cm^{-1} is attributed to the ν_{Cu-N} vibrational mode.

(v) Cu^{II}(hypoxanthine)$_2$(SO_4)·H_2O. Heterocycle IR Bands. The IR information for the 4000−1400 cm^{-1} range is very similar to that corresponding to X = NO_3^-; this suggests an analogous metallic bonding behavior for hypoxanthine in both cases, which is corroborated by the related bands (except those corresponding to SO_4^{2-} vibrational modes) appearing in the 1300−600 cm^{-1} range and by the low-energy IR spectrum. From the spectral analysis, the H_2O molecules show the same behavior for both cases.

SO_4^{2-} IR Bands. The spectral data of the IR active bands are indicative of the existence of coordinated SO_4^{2-}. ν_3 shows splitting with broad bands at 1175 and 1100 cm^{-1}. ν_1 can be associated to the broad band at 970 cm^{-1}, without excluding in this band the participation of ring and C−H vibrational modes of the coordinated heterocyclic ligand. ν_4 is associated to the band centered at 623 cm^{-1}, which is also split at 600 cm^{-1}; these bands seem to be also produced by the skeletical and C−H vibrational modes. Finally, the very weak band at 490 cm^{-1} could be assigned to ν_2. With this spectral information, the participation of the SO_4^{2-} group in a monocoordinated (C_{3v} symmetry) form can be suggested.[9,10] This metallic coordination might be supported by the band at 348 cm^{-1}, which is attributed to ν_{M-OSO_3}, and which is also suggested to be produced, in part, by heterocyclic vibrational modes. The metallic bonding of hypoxanthine could be supported by the broad band at 290 cm^{-1}, assigned to the ν_{Cu-N} vibrational mode.

(vi) Cu^{II}(hypoxanthine)$_2$(ClO_4)$_2$·2H_2O. Heterocycle IR Bands. The IR data are very similar to that for X = SO_4^{2-}; therefore, we can suggest an equivalent behavior for the coordinated hypoxanthine and H_2O molecules in the three cases (X = NO_3^-, SO_4^{2-}, and ClO_4^-).

ClO_4^- IR Bands. The spectral data for this group are in agreement with its existence in both ionic and coordinated forms. For the coordinated ClO_4^-, the strong and broad band (peaks at 1140, 1116, and 1060 cm^{-1}) is respectively assigned to ν_4 and ν_1 of ClO_4^- in a C_{3v} symmetry. The broad and asymmetric band at 932 cm^{-1} is attributed to the ν_2 of ClO_4^- in this same symmetry, although the contribution to this band of ring and C−H vibrational modes is not discarded. ν_3 is associated with the broad band at 680 cm^{-1}. The contribution of ν_5 is attributed to the broad band at 620 cm^{-1}, in addition to the contribution of skeletical and C-H vibrational modes. ν_6 could be associated to the weak band at 500 cm^{-1}. These spectral data are in agreement with the presence of ClO_4^- in a monocoordinated form (C_{3v} symmetry).[9,10] On the other hand, the presence of the ν_3 and ν_4 vibrational modes for ClO_4^- in a T_d symmetry could be masked respectively, by the bands attributed to ν_4 and ν_1, and to ν_5 for ClO_4^- in a C_{3v} symmetry. The IR activated ν_1 for the ionic ClO_4^- could be assigned[9,10] to the broad and weak band at 860 cm^{-1}. The asymmetric and broad band at 345 and 338 cm^{-1} could be assigned in part to the ν_{M-OClO_3} vibrational mode. The contribution of the heterocyclic ligand skeletal vibrations in this band must also be considered. The band at 285 cm^{-1} is assigned to the ν_{Cu-N} vibrational mode.

With the above spectral information, two types of metallic bonding for the heterocycles can be proposed. For the Cu(II) compounds with allopurinol and hypoxanthine respectively (X = Cl^- or Br^-), the first type is through one of the N atoms of the five-membered ring. The second type is deduced for the cases with X = NO_3^-, SO_4^{2-}, and ClO_4^-, with the involvement of N(3) and N(9) atoms of hypoxanthine. For all the cases, counterions are suggested to be coordinated to the Cu(II) atoms, the polyatomic ones in a monocoordinated form. For the systems with NO_3^- and ClO_4^- the presence of ionic groups is also proposed. In all the cases, the participation of H_2O molecules in the metallic bonding is excluded.

(D) Thermogravimetric Results. The thermogravimetric results are summarized in Table 3.

For the first and the last compounds, the first mass loss step corresponds respectively to the following processes:

$$\mathrm{Cu(allopurinol)_2(Cl)_2{\cdot}H_2O \rightarrow Cu(allopurinol)_2(Cl)_2}$$

$$\mathrm{Cu(hypoxanthine)_2(SO_4){\cdot}H_2O \rightarrow Cu(hypoxanthine)_2(SO_4)}$$

For the other three, this step is in agreement with the sample dryness process. For all the cases, the temperature range in which the initial step takes place is suggestive of the nonexistence of H_2O molecules in the metallic coordination sphere, in agreement with the low-energy IR spectral information. In trying to corroborate our results related to the nature of the H_2O molecules (crystalline lattice type) and the thermal stability

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(9) Ferraro, J. R. *Low-frequency vibrations of Inorganic and Coordination Compounds*; Plenum Press: New York, 1971 and references therein.

(10) Nakamoto, K. *Infrared and Raman spectra of Inorganic and Coordination Compounds*, 2nd. ed.; John Wiley & Sons, Inc.: New York, 1978 and references therein.

Table 3. Summary of Thermogravimetric Results[a]

compound	initial step	second step	third step	stability limit
$Cu(L_1)_2(Cl)_2\cdot H_2O$	room temp to 100 °C	195−340 °C (a)	340−570 °C	≈195 °C
$Cu(L_2)_2(Cl)_2\cdot 2H_2O$	room temp to 115 °C	215−280 °C (a, n)	280−530 °C	≈215 °C
$Cu(L_2)_2(Br)_2\cdot 2H_2O$	70−135 °C	185−260 °C (a)	260−600 °C (n)	≈185 °C
$Cu(L_2)_2(NO_3)_2\cdot 2H_2O$	35−100 °C	200−275 °C (a)	275−515 °C (n)	≈200 °C
$Cu(L_2)_2(SO_4)\cdot H_2O$	room temp to 110 °C 110−220 °C (vs)	220−430 °C (a, n)	430−550 °C (a, n)	≈220 °C

[a] Key: a = abrupt, n = noticeable, and vs = very smooth.

limits, a hydrated compound was randomly selected (Cu^{II}(hypoxanthine)$_2$(Cl)$_2\cdot$2H$_2$O), was kept at *ca.* 115 °C and analyzed. Anal. Calcd for Cu^{II}(hypoxanthine)$_2$(Cl)$_2$: C, 29.53; H, 1.98; N, 27.55. Found: C, 30.30; H, 1.92; N, 27.45. The IR spectrum of the anhydrous compound was the same in the low-energy region as the one corresponding to the hydrated compound. These results confirm the interpretation of the IR and thermal data and support the considerations made for the properties of the other coordination compounds studied here. With regard to the thermal stability limit for all the anhydrous compounds, this lies in the 185−220 °C range.

Finally, with this thermal information it is difficult to assure the detailed nature of the second and third steps for each compound. However, considering the thermal characteristics of the free heterocyclic ligands, it is possible to speculate that, in the second step, chemical processes involving counterions dissociation may be included and, in the third step, heterocyclic transformations might be involved.

(E) Electronic Spectroscopy Results. (i) Cu^{II}(allopurinol)$_2$(Cl)$_2\cdot$H$_2$O, Cu^{II}(hypoxanthine)$_2$(Cl)$_2\cdot$2H$_2$O and Cu^{II}(hypoxanthine)$_2$(Br)$_2\cdot$2H$_2$O. These compounds show two bands at 361 and 700 nm, 367 and 621 nm, and 392 and 702 nm, respectively. The spectral pattern for the three compounds is suggestive of a distorted tetracoordinated geometry (roughly planar) for the Cu(II) center. In comparing the spectra of Cu^{II}(hypoxanthine)$_2$(Cl)$_2\cdot$2H$_2$O and Cu^{II}(hypoxanthine)$_2$(Br)$_2\cdot$2H$_2$O, the existence of Cl^- and Br^- as coordinated ions to the respective metallic centers is confirmed.

(ii) Cu^{II}(hypoxanthine)$_2$(NO$_3$)$_2\cdot$2H$_2$O and analogue compounds ($X = SO_4^{2-}$ and ClO_4^-). The spectrum of the Cu(II) compound with $X = NO_3^-$ shows, in the blue region, a low-energy tail of a band from the near-UV region. This tail shows an absorbance minimum at *ca.* 485 nm. The spectrum also shows a broad and asymmetric band centered at *ca.* 620 nm. The Cu(II) compounds with $X = SO_4^{2-}$ and ClO_4^- also show the same spectrum. All this information is indicative of the same ligand field intensity in these coordination compounds, and related to this, an isostructural character is suggested for them. The spectral pattern might be suggestive of a pentacoordinated geometry for Cu(II).

(F) EPR Spectral Results. (i) Cu^{II}(allopurinol)$_2$(Cl)$_2\cdot$H$_2$O, Cu^{II}(hypoxanthine)$_2$(Cl)$_2\cdot$2H$_2$O and Cu^{II}(hypoxanthine)$_2$(Br)$_2\cdot$2H$_2$O. The EPR spectra of these three compounds are shown in Figure 2.

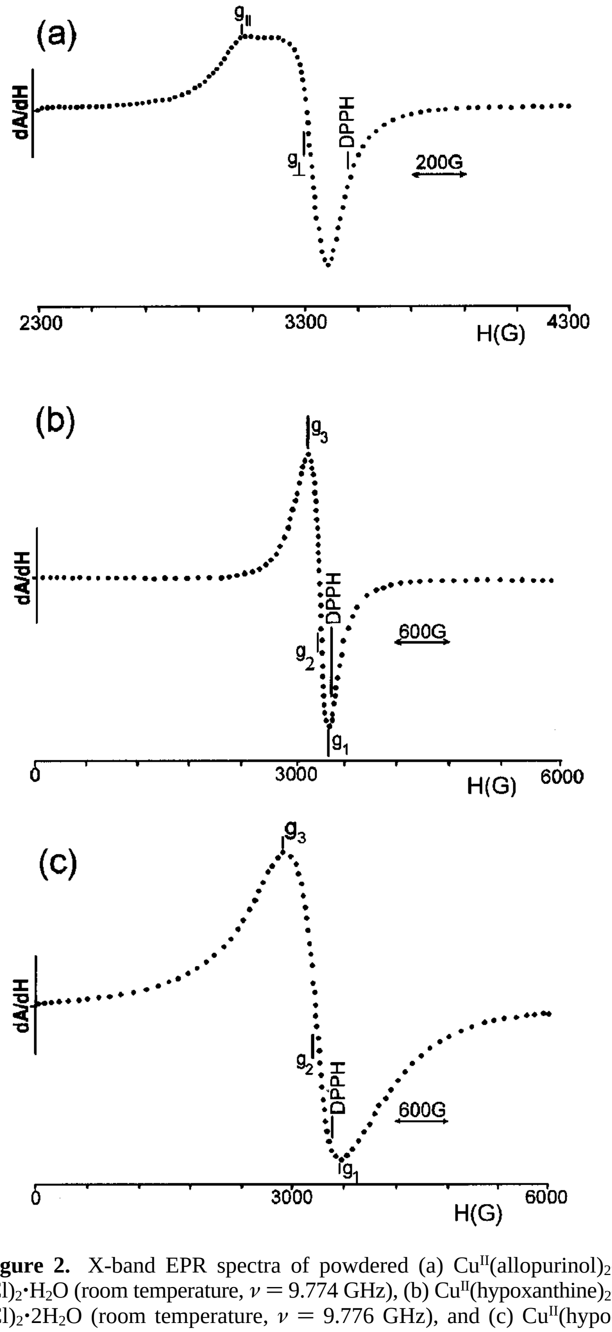

Figure 2. X-band EPR spectra of powdered (a) Cu^{II}(allopurinol)$_2$(Cl)$_2\cdot$H$_2$O (room temperature, $\nu = 9.774$ GHz), (b) Cu^{II}(hypoxanthine)$_2$(Cl)$_2\cdot$2H$_2$O (room temperature, $\nu = 9.776$ GHz), and (c) Cu^{II}(hypoxanthine)$_2$(Br)$_2\cdot$2H$_2$O (room temperature, $\nu = 9.778$ GHz).

The EPR spectrum at room temperature of Cu^{II}(allopurinol)$_2$(Cl)$_2\cdot$H$_2$O shows (Figure 2a) an asymmetric signal in the middle magnetic field region, indicative of an anisotropic **g** tensor, with $g_\perp = 2.09$ and $g_\parallel \approx 2.24$. These values allow us to consider the existence of a distorted tetracoordinated geometry[11−14] around the Cu(II) center ($g_\parallel \gg g_\perp > 2.0$). Besides this, the shape of the signal for $g_\parallel$ indicates the possibility of weak axial interactions. The d-type orbitals involved in the ground electronic state, are suggested to be the $d_{x^2-y^2}$ or d_{xy} orbitals. Under these conditions, the spectral pattern is not indicative of Cu(II)−Cu(II) interactions. With a lowering of the temperature (77 K, $\nu = 9.264$ GHz), the EPR spectrum shows essentially

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(11) Hathaway, B. J.; Procter, I. M.; Slade, R. C.; Tomlinson, A. A. G. *J. Chem. Soc. A* **1969**, 2219.

(12) Foley, J.; Tyagi, S.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1.

(13) Foley, J; Kennefick, D.; Phelan, D.; Tyagi, S; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2333.

(14) Wilson, R. B.; Wasson, J. R.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1978**, *17*, 641.

the same general pattern. The only difference lies in the resolution of the signal for $g_{\|}$ (with g components of 2.24 and 2.16), which supports the considerations on the structural features and axial interactions quoted above for the Cu(II) center. Again, under these conditions, a Cu(II)−Cu(II) magnetic coupling is discarded.

The EPR spectrum of $Cu^{II}(hypoxanthine)_2(Cl)_2 \cdot 2H_2O$ shows (Figure 2b) a signal in the middle magnetic field region, suggestive of an anisotropic g tensor, with $g_1 = 2.025$, $g_2 = 2.103$ and $g_3 = 2.247$ ($R = (g_2 - g_1)/(g_3 - g_2) = 0.5$ (<1.0)), with no evidence at these conditions of Cu(II)-Cu(II) interactions. The spectral data could be associated to a distorted octahedral rombic environment for Cu(II). The ground electronic state is suggested to be associated to the $d_{x^2-y^2}$ and d_{z^2} orbitals. With a decrease in temperature (77 K, $\nu = 9.264$ GHz) the spectrum gives $g_1 = 2.029$ and $g_2 = 2.072$ and shows a resolution of the signal for $g_{\|}$ (with g components of 2.22 and 2.14). This result, joined to the value $g_{\perp} = 2.072$, is associated to axial interactions and to the suggestion of an elongated octahedral rombic environment for Cu(II). Also, under these conditions, there is no evidence of Cu(II)−Cu(II) interactions.

Finally, the EPR spectrum at room temperature ($\nu = 9.778$ GHz) of the anhydrous $Cu^{II}(hypoxanthine)_2(Cl)_2$ was obtained in the hope of corroborating the isostructural character for this system and the former hydrated analogous. For the anhydrous compound, essentially the same pattern is obtained ($g_1 = 2.02$, $g_2 = 2.09$, $g_3 = 2.20$), in agreement with the spectral and thermal results (*i.e.*, the noninvolvement of H_2O molecules in the Cu(II) coordination sphere of $Cu^{II}(hypoxanthine)_2(Cl)_2 \cdot 2H_2O$).

The EPR spectrum of $Cu^{II}(hypoxanthine)_2(Br)_2 \cdot 2H_2O$ (Figure 2c) shows differences with respect to the two preceding cases. The spectral pattern consists of a very broad and non symmetric signal ($g_1 = 1.96$, $g_2 = 2.14$, $g_3 = 2.38$), which is associated with an anisotropic **g** tensor[15] and to the existence of Cu(II)−Cu(II) interactions. With a lowering of the temperature (77 K, $\nu = 9.264$ GHz) the spectrum shows the same general features ($g_1 = 1.98$, $g_2 = 2.15$, $g_3 = 2.36$). Interestingly, a broad and unresolved signal in the low-field region is also detected (600−1500 G), supporting the existence of Cu(II)−Cu(II) interactions, although without excluding its origin due to the presence of magnetic impurities of $S = {}^1/_2$ spins in the ground state.

The analysis of the EPR spectral results described for these three compounds, suggests the structural features for them. For $Cu^{II}(allopurinol)_2(Cl)_2 \cdot H_2O$, it is possible to consider the existence of mononuclear $Cu^{II}(allopurinol)_2(Cl)_2$ units in a distorted square planar geometry, possibly with very weak axial interactions in the crystalline lattice, as is schematically shown in Figure 3.

For $Cu^{II}(hypoxanthine)_2(Cl)_2 \cdot 2H_2O$ the existence of a distorted octahedral rombic geometry for Cu(II), with the hypoxanthine and Cl^- ligands in the equatorial plane is proposed. Weak axial interactions occur possibly through the heterocyclic ligand (*i.e.*, the exocyclic O(6) atoms) or through the halogen atoms of neighboring Cu(II) units, this last one in a similar way to that postulated for $Cu^{II}(allopurinol)_2(Cl)_2 \cdot H_2O$. For $Cu^{II}(hypoxanthine)_2(Br)_2 \cdot 2H_2O$, it is possible to consider the existence of Cu(II)-Cu(II) interactions through the Br^- ligands, in a similar form to that suggested for $Cu^{II}(allopurinol)_2(Cl)_2 \cdot H_2O$.

(ii) $Cu^{II}(hypoxanthine)_2(NO_3)_2 \cdot 2H_2O$ and analogue compounds ($X = SO_4^{2-}$ and ClO_4^-). The EPR spectrum of $Cu^{II}(hypoxanthine)_2(NO_3)_2 \cdot 2H_2O$ at room temperature (Figure 4) shows absorptions at resonance fields both well above and below

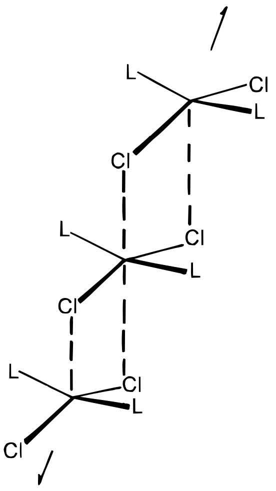

Figure 3. Schematic drawing of the distorted tetracoordinated environment proposed for $Cu^{II}(allopurinol)_2(Cl)_2 \cdot H_2O$ and its interactions.

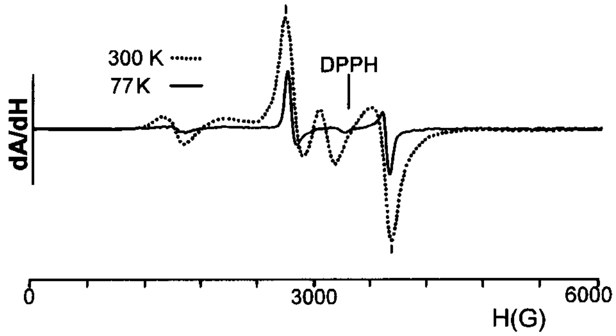

Figure 4. X-band EPR spectra of powdered $Cu^{II}(hypoxanthine)_2(NO_3)_2 \cdot 2H_2O$ at room temperature (dotted line) and 77 K (solid line) at $\nu = 9.264$ GHz.

the region (g_{eff} *ca.* 2) where signals are normally found for Cu(II) with $S = {}^1/_2$ spins in the ground state. In fact, the spectral pattern at 77 K fully resembles the one shown by dinuclear Cu(II) systems with N,N-bridging ligands in a square-pyramidal geometry for the Cu(II) centers, showing ligands bonded in the axial positions.[16−18]

For the spectrum at room temperature, the pair of bands quoted are assigned to the two $\Delta m = 1$ transitions H_{xy1} and H_{xy2} of a triplet electronic state. From these, the dipolar splitting (dipolar interaction between the electronic spins of the Cu(II) centers) is *ca.* 1125 G. The g values are $g_{\perp} = 2.09$ and $g_{\|} = 2.19$. The spectrum also shows, in the low-field region, the expected absorption $\Delta m = 2$ for dinuclear Cu(II) systems in the same triplet electronic state. In short, the spectrum shows the $\Delta m = 1$ and $\Delta m = 2$ transitions for a triplet state and nearly axial symmetry for Cu(II) in a dinuclear framework. The unpaired spins of the Cu(II) centers are suggested to lie upon the $d_{x^2-y^2}$ orbitals. The E splitting parameter appears to be zero, or at least negligible, due to the fact that the xy bands do not split in the spectra at 300 and 77 K. The spectrum at 77 K shows a general pattern that closely resembles the one shown at low temperature by this type of dinuclear systems. The lowering in the intensities of the signals is in agreement with the depopulation of a $S = 1$ state and the population of a $S = 0$ state associated with the existence of an antiferromagnetic coupling between the unpaired electrons of the Cu(II) atoms in the dinuclear compound. At this temperature, the almost

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(15) Hecht, H. G.; Frazier, J. P., III. *J. Chem. Phys.* **1966**, *44*, 1718.

(16) Goodgame, D. M. L.; Price, K. A. *Nature* **1968**, *220*, 783.

(17) Duerst, R. W.; Baum, S. J.; Kokoszka, G. F. *Nature* **1969**, *222*, 665.

(18) Sonnenfroh, D.; Kreilick, R. W. *Inorg. Chem.* **1980**, *19*, 1259 and references therein.

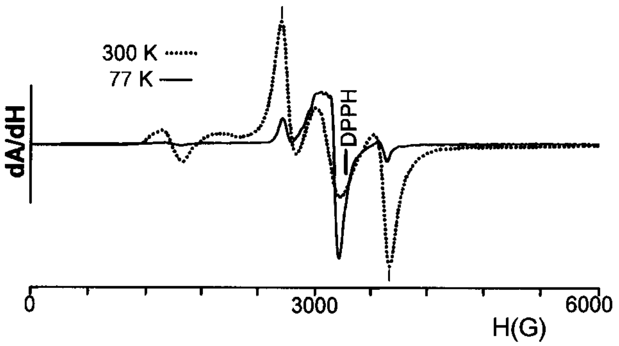


Figure 5. X-band EPR spectra of powdered $Cu^{II}(hypoxanthine)_2(SO_4)\cdot H_2O$ at room temperature (dotted line) and 77 K (solid line) at $\nu = 9.264$ GHz.

symmetric absorption in the low-field region also shows a decrease of intensity, with only a partial resolution of the hyperfine structure (only five of the expected seven components were resolved, with $A = 60$ G). The observation of more than four hyperfine components confirms that this band arises from the dinuclear unit and not from a magnetic impurity.

The EPR spectrum of $Cu^{II}(hypoxanthine)_2(SO_4)\cdot H_2O$ (Figure 5) at room temperature resembles closely the one shown by the preceding system ($X = NO_3^-$). The pair of bands quoted are also assigned to the two $\Delta m = 1$ transitions. From these, a dipolar splitting D parameter of 1155 G is obtained. The g values are $g_\perp = 2.05$ and $g_\parallel = 2.20$. In the low-field region, this spectrum also shows the expected $\Delta m = 2$ transition for dinuclear Cu(II) systems in a triplet electronic state. As before, the unpaired spins are suggested to be associated with the Cu(II) $d_{x^2-y^2}$ orbitals. The E parameter also appears to be zero or at least very small, because the xy bands do not split when the temperature is decreased.

The spectrum at 77 K also shows a decrease of intensity of the signals in the low and high field regions, in agreement with the depopulation of the $S = 1$ electronic state and the population of the $S = 0$ ground state. The $\Delta m = 2$ absorption shows a low resolution (only four components, $A = 60$ G) supporting, however, the dinuclear character of the Cu(II) system. The almost symmetric signal appearing above 3000 G in the room temperature EPR spectrum does not show a decrease in intensity. In fact, it appears as the most important band in the EPR spectrum at 77 K, suggesting that it is a result of the existence of a magnetic impurity with a $S = {}^1/_2$ ground state.

The EPR spectrum of $Cu^{II}(hypoxanthine)_2(ClO_4)_2\cdot 2H_2O$ at room temperature (Figure 6) is also in agreement with a dinuclear system in a $S = 1$ electronic state. Besides, the almost symmetrical signal in the middle-field region found in the $X = NO_3^-$ and SO_4^{2-} spectra at the same temperature is almost absent here. For this case, the signals quoted lead to the parameter $D = 1125$ G.

When the temperature is decreased to 77 K ($\nu = 9.264$ GHz), a noticeable decrease of intensity of all the signals is observed, confirming the population of the $S = 0$ ground state at these conditions.

With all the EPR spectral information for these three Cu(II) compounds, a clear structural proposition can be made: each one consists of a dinuclear system, with the Cu(II) atoms bridged by four hypoxanthine ligands and two monocoordinated polyatomic groups ($X = NO_3^-$, SO_4^{2-}, or ClO_4^-) in the axial positions of the metallic centers, as is schematically shown in Figure 7.

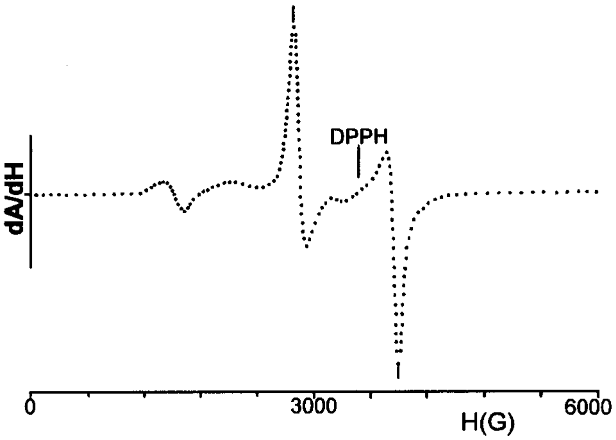
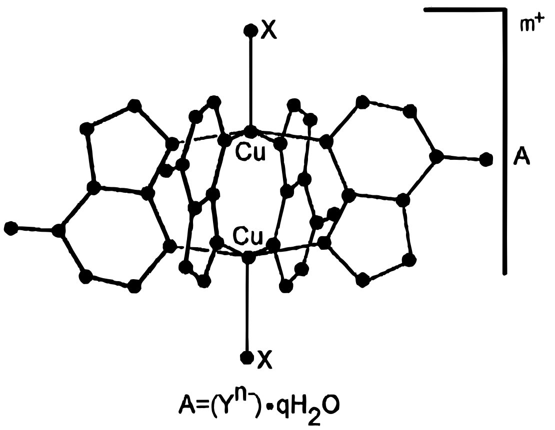


Figure 6. X-band EPR spectrum (room temperature, $\nu = 9.778$ GHz) of powdered $Cu^{II}(hypoxanthine)_2(ClO_4)_2\cdot 2H_2O$.



X	NO_3^-	SO_4^{2-}	ClO_4^-
m^+	2	0	2
(Y^{n-})	$(NO_3^-)_2$	-	$(ClO_4^-)_2$
q	4	2	4

Figure 7. Schematic drawing of the structural proposition for the dinuclear Cu(II) compounds with the bridging ligand hypoxanthine and polyatomic anions bonded in the axial positions.

This structural arrangement might be in close analogy with that shown by several dinuclear Cu(II) compounds containing bridging adenine or bridging hypoxanthine and other ligands bonded in the axial positions of the metallic centers.[16–20] The above spectral information is in agreement with the existence of antiferromagnetic coupling between the unpaired electrons of the Cu(II) atoms (ground state, $S = 0$; first excited state, $S = 1$).

In comparing the D values for these dinuclear Cu(II) compounds (1125 G for $X = NO_3^-$, 1155 G for $X = SO_4^{2-}$, and 1125 G for $X = ClO_4^-$) with that found (1111 G) for the dinuclear compound $[Cu^{II}(\mu\text{-hypoxanthine})_2(Cl)]_2Cl_2\cdot 6H_2O$,[18] a noticeable similarity arises, suggesting the existence of analogue dipolar interactions between the unpaired spins of the Cu(II) centers in these cases. This could be associated to the close similarity of the Cu(II)−Cu(II) distances, stereochemical arrangements and ligand field intensities in these Cu(II) compounds, supporting again the dinuclear character and stereochemical features proposed for the three last Cu(II) compounds discussed here.

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(19) Asakawa, T.; Inoue, M.; Hara, K. I.; Kubo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1054 and references therein.

(20) Inoue, M.; Kubo, M. *Coord. Chem. Rev.* **1976**, *21*, 1 and references therein.

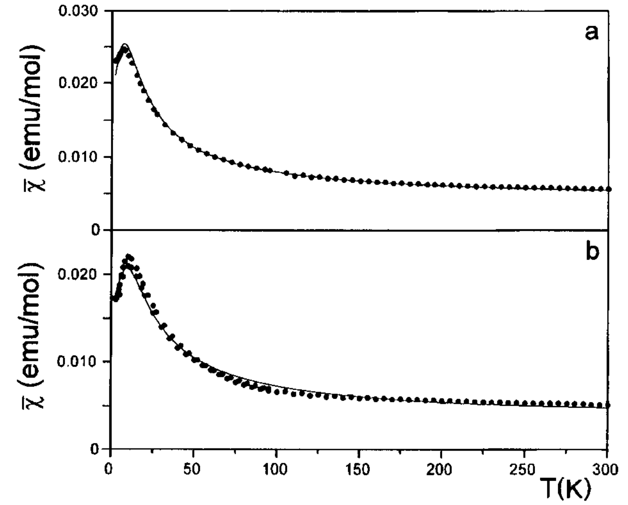

Figure 8. $\bar{\chi}$ (emu/mol) -*T* (K) curves for powdered (a) $Cu^{II}(allopurinol)_2(Cl)_2{\cdot}H_2O$ ($H = 100$ G) and (b) $Cu^{II}(hypoxanthine)_2(Cl)_2{\cdot}2H_2O$ ($H = 100$ G). Dotted lines are experimental data; solid lines are theoretical results.

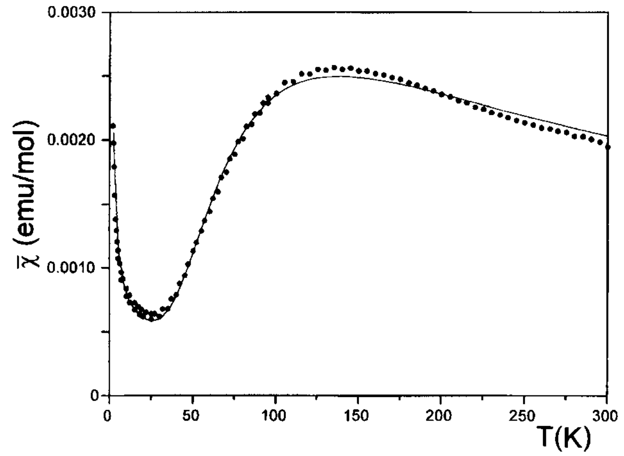

Figure 9. $\bar{\chi}$ (emu/mol) -*T* (K) curves ($H = 1000$ G) for powdered $Cu^{II}(hypoxanthine)_2(Br)_2{\cdot}2H_2O$. Dotted line are experimental data; solid line are theoretical results.

(G) Magnetic Studies Results. In order to study in detail the behavior of the Cu(II) centers, magnetic measurements of the different coordination compounds were made.

(i) $Cu^{II}(allopurinol)_2(Cl)_2{\cdot}H_2O$ and $Cu^{II}(hypoxanthine)_2(Cl)_2{\cdot}2H_2O$. The molar magnetic susceptibility $\bar{\chi}$ (emu/mol) values as a function of *T* (K) were obtained at the three magnetic fields of 100, 1000 and 10000 G for both compounds. The results for $H = 100$ G are shown in Figure 8 for (a) $Cu^{II}(allopurinol)_2(Cl)_2{\cdot}H_2O$ and (b) $Cu^{II}(hypoxanthine)_2(Cl)_2{\cdot}2H_2O$. A very small decrease of $\bar{\chi}$ is observed with the increase of the magnetic field, but without any changes in the general trend of the magnetic response, which in turn is associated in both cases to very weak antiferromagnetic coupling. The presence of a magnetic impurity is excluded in both systems due to the form of the $\bar{\chi} - T$ curves at low temperature (at least up to 2 K).

In order to analyze the magnitude of the magnetic interactions (not detected in the EPR data, not even at 77 K), and considering the distorted geometry and axial interactions suggested for these systems, a linear chain magnetic model of antiferromagnetically coupled $S = {}^1/_2$ spins was selected, for which the $\bar{\chi}$ values can be calculated with the Bonner–Fisher equation

$$\bar{\chi} = \frac{Ng^2\beta^2}{kT}\left[\frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} + \bar{\chi}_0\right](1 - \rho) + \frac{Ng^2\beta^2}{2kT}\rho \qquad (1)$$

where $x = |J|/kT$ and the other symbols have their usual meaning.

For $Cu^{II}(allopurinol)_2(Cl)_2{\cdot}H_2O$, setting $g = 2.09$ and $\rho = 0$ as fixed parameters, a very good fit was obtained (Figure 8a, solid line). The magnetic parameters obtained are the following: $J = -3.9088$ cm^{-1} and $\bar{\chi}_0 = 0.004167$ emu/mol. The fitting process was performed for the other two values of the magnetic field (1000 and 10000 G), and very similar parameters were obtained. When the same fitting procedure was carried out fixing only the *g* parameter, very similar *J* and $\bar{\chi}_0$ values were also obtained. Other magnetic models (i.e, a dinuclear magnetic model of coupled $S = {}^1/_2$ spins) were studied, without successful results both in the fitting process and in the physical meaning of the magnetic parameters obtained.

When the same model and eq 1 for $Cu^{II}(hypoxanthine)_2(Cl)_2{\cdot}2H_2O$ were employed, a good fit was obtained, which is shown as a solid line in Figure 8b. For this process with $g = 2.10$ and $\rho = 0$, the values $J = -4.85$ cm^{-1} and $\bar{\chi}_0 = 0.003534$ emu/mol were obtained. For $H = 10\,000$ G, the same procedure gave $J = -4.69$ cm^{-1} and $\bar{\chi}_0 = 0.001562$ emu/mol. With the employment of a dinuclear system of coupled $S = {}^1/_2$ spins, and the Bleaney–Bowers equation, the fitting process was good (for $H = 100$ G), with $J = -5.77$ cm^{-1} and $\bar{\chi}_0 = 0.0034$ emu/mol, but with a very low (unphysical) *g* (=1.22) value.

The magnitude of the *J* parameter for both compounds ($J = -3.9088$ cm^{-1} for $Cu^{II}(allopurinol)_2(Cl)_2{\cdot}H_2O$ and $J = -4.85$ cm^{-1} for $Cu^{II}(hypoxanthine)_2(Cl)_2{\cdot}2H_2O$) is indicative of very weak antiferromagnetic coupling between the unpaired electrons of the Cu(II) centers, without an important dependence on the magnetic field intensity. These magnetic results joined to the spectral information for both systems suggest the participation of certain ligands in the magnetic coupling discussed. From these, the allopurinol and hypoxanthine molecules are excluded, respectively, and the ligands that play an important role in the magnetic coupling pathway could be the Cl^- atoms. Thus, the suggestion of the structural arrangement for both $Cu^{II}(allopurinol)_2(Cl)_2{\cdot}H_2O$ and $Cu^{II}(hypoxanthine)_2(Cl)_2{\cdot}2H_2O$ would be analogous (Figure 7).

(ii) $Cu^{II}(hypoxanthine)_2(Br)_2{\cdot}2H_2O$. The $\bar{\chi}$(emu/mol) $- T$ (K) values for this compound were obtained at magnetic fields of 1000, 10000, and 30000 G, and only shown for $H = 1000$ G in Figure 9. The general pattern is in agreement with an antiferromagnetic coupling, higher in intensity than that shown for the former two cases. With an increase of the intensity of the magnetic field, a very small lowering of the $\bar{\chi}$ values is obtained, but without a modification of the general trend of the magnetic response. The tail at the low-temperature region, which follows a Curie–Weiss behavior, is associated to a magnetic impurity of non coupled $S = {}^1/_2$ spins.

With respect to the spectral information for this compound, several magnetic models were explored. The first was the dinuclear model of coupled $S = {}^1/_2$ spins with the Bleaney–Bowers equation:

$$\bar{\chi} = \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3 + e^{-2J/kT}} + \bar{\chi}_0\right](1 - \rho) + \frac{Ng^2\beta^2}{2kT}\rho \qquad (2)$$

The attempts to fit this equation to the experimental data completely revealed a poor agreement between the calculated (with realistic magnetic parameters) and experimental susceptibilities; when the fitting was good, unrealistic parameters (*i.e.*, $g = 1.7$) were obtained. An appreciable improvement was obtained considering the Weiss correction in the Bleaney–Bowers equation; from the fitting procedure, an intradinuclear antiferromagnetic coupling is corroborated ($J = -54.32$ cm^{-1}), together with interdinuclear magnetic interactions, also of antiferromagnetic type.

As the interdinuclear coupling was suspected, the dinuclear model with a mean-field correction for the interdinuclear interaction was selected

$$\bar{\chi} = \bar{\chi}'\left(1 - \frac{2zJ'\bar{\chi}'}{Ng^2\beta^2}\right)^{-1} \qquad (3)$$

where $\bar{\chi}'$ is the molar magnetic susceptibility calculated from eq 2, J' is the mean-field interdinuclear magnetic coupling parameter, and z is the number of nearest neighboring dinuclear units. With this approximation and with $H = 1000$ G and $g = 2.14$, a good fitting was obtained (Figure 9, solid line), with the following parameters: $J = -77.25$ cm^{-1}, $\rho = 0.0053$, $\bar{\chi}_0 = 4.336 \times 10^{-4}$ emu/mol, and $zJ' = -3.35$ cm^{-1}. From these good results, both intra- and interdinuclear antiferromagnetic couplings are inferred, the last type of lower intensity.

In a second step, considering the interdinuclear magnetic interactions, a linear chain magnetic model was selected and the Bonner–Fisher equation (eq 1) was employed. The fitting process was not successful, even when the Curie–Weiss correction was included. From these results, a linear chain of interacting units was excluded as a possible structural arrangement. In a third step, tetranuclear arrangements of different symmetries were studied, but unsuccessful results were obtained. These results allow us to consider the limitations of modeling the magnetic properties through tetranuclear systems of certain symmetry. Perhaps the more realistic results are those concerning mononuclear Cu(II) units interacting through Br$^-$ bridges, in this way allowing the construction of dinuclear units, and these last interacting in the same way, in a picture roughly reminiscent of a cubane-like tetranuclear framework.

(iii) Cu^{II}(hypoxanthine)$_2$(NO$_3$)$_2$·2H$_2$O and Analogue Compounds (X = SO$_4^{2-}$ and ClO$_4^-$). The $\bar{\chi}_0$ (emu/mol of dinuclear unit) values as a function of T (K) were obtained at magnetic fields of 5000 and 10000 G for Cu^{II}(hypoxanthine)$_2$(NO$_3$)$_2$·2H$_2$O, and at 100, 1000, and 10000 G for its analogue compounds (X = SO$_4^{2-}$ and ClO$_4^-$). A very small dependence of $\bar{\chi}$ with the magnetic field intensity was observed for the three compounds, but without any changes in the general trend of the magnetic responses. Figure 10 shows the $\bar{\chi} - T$ curves for (a) X = NO$_3^-$ at 10000 G, (b) X = SO$_4^{2-}$ at 10000 G, and (c) X = ClO$_4^-$ at 100 G. The general patterns are suggestive of antiferromagnetic coupling between the unpaired electrons of the Cu(II) centers. For these three systems, the maxima lie at a higher temperature that the ones shown by the Cu(II) compounds discussed before, indicating for these cases a higher intensity of the magnetic coupling. In the region of low temperatures, a tail (Curie–Weiss type) is observed, associated to noncoupled $S = {}^1/_2$ spins, possibly as magnetic impurities. Considering all the spectral information about the three compounds under discussion, the dinuclear model of coupled $S = {}^1/_2$ spins, eq 2, was employed.

For Cu^{II}(hypoxanthine)$_2$(NO$_3$)$_2$·2H$_2$O a good fit was obtained, shown in Figure 10a as a solid line. The parameters obtained from this fitting procedure were $g = 2.27$, $\rho = 0.000746$, $J = -142.56$ cm^{-1}, and $\bar{\chi}_0 = 8{,}7689 \times 10^{-6}$ emu/mol of dinuclear unit. When $g = 2.09$ was fixed, non significative changes in the values of the magnetic parameters were observed. The same good results were obtained for the other magnetic field value.

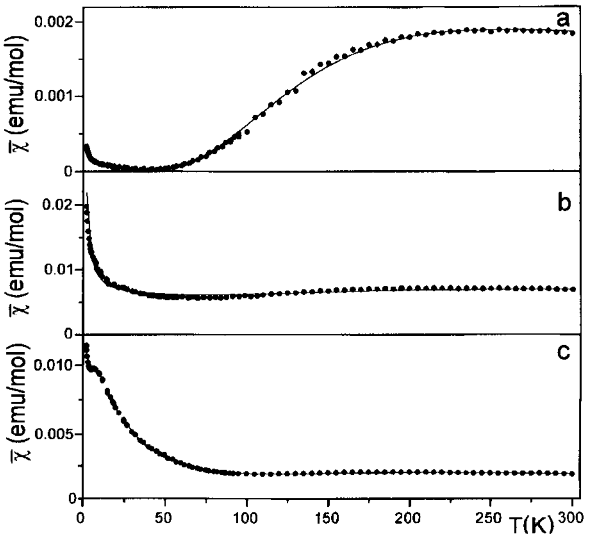

Figure 10. $\bar{\chi}$ (emu/mol of dinuclear unit) – T (K) curves for powdered (a) Cu(II)(hypoxanthine)$_2$(NO$_3$)$_2$·2H$_2$O at $H = 10000$ G, (b) Cu^{II}(hypoxanthine)$_2$(SO$_4$)·H$_2$O at $H = 10000$ G, and (c) Cu^{II}(hypoxanthine)$_2$(ClO$_4$)$_2$·2H$_2$O at $H = 100$ G. Dotted lines are experimental data; solid lines are theoretical results.

For Cu^{II}(hypoxanthine)$_2$(SO$_4$)·H$_2$O, the maximum lies upon nearly the same region as the one for the X = NO$_3^-$ system, suggesting a similar magnetic coupling intensity. However, there are differences in the region of low temperatures with respect to that same system; for the compound under consideration here a noticeable tail (Curie–Weiss behavior) of the $\bar{\chi}$ values is observed for the 2–115 K range. This suggests a higher contribution of magnetically non coupled $S = {}^1/_2$ spins. Using the same model and eq 2 as before, the fitting process for fixed $g = 2.05$ gave the following magnetic parameters: $\rho = 0.0412$, $J = -162.03$ cm^{-1}, and $\bar{\chi}_0 = 0.005922$ emu/mol of dinuclear unit. The theoretical results are also shown in Figure 10b as a solid line. Very similar fitting results and magnetic parameters were obtained for the other magnetic fields.

Finally, for Cu^{II}(hypoxanthine)$_2$(ClO$_4$)$_2$·2H$_2$O, a remarkable tail (Curie–Weiss behavior) of the $\bar{\chi}$ values in the 2–100 K range is observed. As before, this behavior is associated to non coupled $S = {}^1/_2$ spins, possibly as magnetic impurity. The maximum appears to lie upon nearly the same region as the one for the X = SO$_4^{2-}$ system. Also, and as before, in a typical fitting process and selecting the 25–300 K range, a good fit was obtained. From this, the magnetic parameters were $g = 2.17$, $\rho = 0.166$, $J = -160.16$ cm^{-1} and $\bar{\chi}_0 = 2.2264 \times 10^{-4}$ emu/mol of dinuclear unit. The results are also shown in Figure 10c as a solid line. Good fitting results and very similar values of the magnetic parameters were obtained for the other magnetic fields.

From the magnetic study for these three compounds, a strong antiferromagnetic coupling is found, in agreement with the EPR spectral results (the ground state, $S = 0$; the first excited state $S = 1$ for a dinuclear system). Also, all the spectral and magnetic studies are in full agreement with the structural arrangement proposed before for the three Cu(II) compounds discussed here.

Regarding the magnetic studies carried out on homologue dinuclear Cu(II) systems with 6-aminopurine in neutral form as unique bridging ligand and several ligands (Cl$^-$, Br$^-$, ClO$_4^-$, and H$_2$O) in the axial positions, the J values[17–19] range from -152.5 to -142 cm^{-1}, which indicates the existence of strong antiferromagnetic coupling. Homologue dinuclear Cu(II) systems with 6-aminopurinolate as bridging ligand and several axial ones appear to show lower $|J|$ values,[16–20] ranging from -127 to -107 cm^{-1}, showing the influence that the anionic character of the heterocyclic ligand has on the decrease of the antiferromagnetic coupling effectiveness between the unpaired electrons of the metallic centers.

With respect to the few (only three) magnetic studies on dinuclear Cu(II) systems reported up to date with 6-oxopurine (hypoxanthine) in neutral form as unique bridging ligand and anions ($X = Cl^-$ or Br^-) in the axial positions,[18,19] the J values range from -142.1 to -105.5 cm^{-1}. There are no reports of homologue dinuclear systems and anionic or cationic 6-oxopurine.

In relation to the three dinuclear Cu(II) compounds reported here with the unique bridging ligand 6-oxopurine, the J values (-141.76 to -142.56 cm^{-1} for $X = NO_3^-$; -162.03 to -167.02 cm^{-1} for $X = SO_4^{2-}$; and -153.89 to -160.16 cm^{-1} for $X = ClO_4^-$) are of the same type as those for the analogue systems with 6-aminopurine or the few reported with 6-oxopurine ($X = Cl^-$ or Br^-). The similarity in the J parameter for all these cases is suggestive of strongly related structural features and electronic architecture between them.

In the absence of crystalline data for these dinuclear compounds, we cannot make statements about the nature of the magnetic coupling pathway that produces the antiferromagnetic behavior we have found. For the examples quoted before,[16–20] the Cu(II)-Cu(II) distance is such that a direct metal–metal interaction has been discarded, as in the cupric acetate type systems, and a ligand-mediated process is proposed. The similarity of the magnetic behavior they show with respect to the three dinuclear compounds reported here let us suggest that the magnetic coupling pathway in these last ones could be also through the bridging hypoxanthine molecules, in the N(1)–H, N(7)–H tautomeric form.

In order to explore this possibility at a molecular level, we have recently performed exhaustive density functional theory calculations for hypoxanthine and its tautomers, and we have found interesting results for the N(1)–H, N(7)–H tautomeric form. The electrostatic potential with respect to a positive charge, shows an attractive region located at the N(3) and N(9) atoms. The total electron density shows pseudoaromaticity in both rings, and for still high density values ($\rho = 0.27$) these nitrogen atoms are electronically communicated through the fragment N(3)–C(4)–N(9). The molecular orbital analysis is also interesting, because the d-orbitals of two Cu(II) atoms can present respectively potential effective overlap with the N(3) and N(9) atoms: for the σ bonding MO the overlap could be suggested to be with the $d_{x^2-y^2}$ orbitals; the HOMO (Π -type) could overlap with the d_{xz} orbitals, and finally, the LUMO (Π-type located at the C(2), C(4), and C(8) atoms) could overlap with the d_{yz} orbitals, favoring a Π-type backbonding process. The first two overlaps postulated would form σ/Π bonds between the two Cu(II) atoms and the deprotonated nitrogen atoms, which suggest a possible communication between these Cu(II) centers through the fragment N(3)–C(4)–N(9) of the bridging ligands. This communication could be enhanced by the backbonding process from the third type of overlap considered.

Concluding Remarks. In the study reported here, new Cu(II) coordination compounds with the heterocyclic ligands allopurinol and hypoxanthine, respectively, and several anions were synthesized in aqueous solution and at low pH value. In the competitive reactions of these heterocycles by the Cu(II) center, the fact that $Cu^{II}(allopurinol)_2(Cl)_2 \cdot H_2O$ is the predominant compound is relevant, almost without influence (except for $X = CH_3CO_2^-$) of the metallic counterion employed in the syntheses.

With regard to the Cu(II) compounds with allopurinol and hypoxanthine ($X = Cl^-$ or Br^-), respectively, the correspondent characterization supports the existence of both the MN_2X_2 character and nearest neighbor interactions, which lead to a very weak antiferromagnetic coupling. This type of coupling is conceived through both a linear chain (Cu(II) compounds with allopurinol and hypoxanthine with $X = Cl^-$), and a dinuclear system (Cu(II) compound with hypoxanthine and $X = Br^-$), with the participation of the halogen atoms as bridging ligands.

For the Cu(II) compounds with hypoxanthine and $X = NO_3^-$, SO_4^{2-}, or ClO_4^-, the characterization supports the existence of dinuclear units, of the cupric acetate type, with bridging hypoxanthine and polyatomic anions as axial ligands. The unpaired electrons on the pairs of Cu(II) atoms are strongly antiferromagnetically coupled in all these cases. The three systems are incorporated within the few examples reported up to date with this heterocycle as unique bridging ligand in dinuclear Cu(II) compounds.

The magnetic study carried out for the $Cu^{II}(N)_2(X)_2$ systems has contributed to the exploration of both the role played by the halogen atoms on the magnetic coupling pathway between the Cu(II) units and some features of their structural arrangements in the crystalline lattices. For the dinuclear $Cu^{II}(N)_4\,(O)_1$ systems the same study let us suggest the role played by the bridging hypoxanthine ligands in the effectiveness of the antiferromagnetic coupling pathway when anionic and polyatomic O-donor groups are simultaneously bonded to Cu(II) centers in axial form.

Noticeable differences in the metallic bonding behavior for the two isomeric heterocyclic ligands have been deduced from the study. This is particularly remarkable for hypoxanthine, where the N(3) and N(9) atoms are in some cases involved in this bonding, irrespective of the strong acid conditions and the N(7)–H/N(9)–H tautomerism for the free ligand in solution. All this could be of potential biochemical significance in the study of their catalytic metal center–ligand interactions, because both heterocycles are substrates of the metalloenzyme xanthine oxidase.[1,4]

With regard to the Cu(II) compounds studied here, the synthetic dinuclear compounds could be proposed to potentially mimic some physical property of dinuclear copper centers of protein sites,[21,22] which could contribute to an improved understanding of their biological analogues.

Finally, this study also represents a contribution about the exploration of the chemical behavior of Cu(II) toward two isomeric heterocyclic ligands under systematically modified reaction conditions. Related studies are in progress, in the hope to advance in the correspondent comprehensive understanding of this problem.

Acknowledgment. We thank Max Azomoza-Palacios (UAM-Iztapalapa), Jorge Ramírez-Salcedo (IFC-UNAM), and Francisco Morales-Leal (IIM- UNAM) for the thermal results, the EPR spectra of the Cu(II) compounds and the magnetic susceptibility measurements, respectively. We also acknowledge CONACyT (Grant 3170-E) for partial financial support.

IC9602005

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(21) Urbach, F. L. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker, Inc.: New York, 1981; Vol. 13.

(22) Solomon, E. I.; Baldin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521.