

Antiferromagnetic Coupling in the Polynuclear Compound [Cu(II) (Allopurinolate) (OH⁻)]_n

Rodolfo Acevedo-Chávez

Centro de Química, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Apartado Postal 1613, Puebla, Puebla, México

and

María Eugenia Costas^{*,1} and Roberto Escudero-Derat[†]^{*}Facultad de Química, and [†]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México 04510, Distrito Federal, Mexico

Received August 25, 1993; in revised form December 10, 1993; accepted January 10, 1994

Synthetic, spectral, and magnetic studies of the Cu(II) polynuclear coordination compound [Cu(HL)(OH⁻)]_n with bridging OH⁻ and HL (allopurinolate; C₅H₃N₄O⁻) ligands are reported. The compound is obtained from aqueous media (at several pH values and from Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, ClO₄⁻, and CH₃CO₂⁻ Cu(II) salts), from DMSO at ca. 70°C using several of the above salts, and under refluxing methanol employing Cu(SO₄) or Cu(CH₃CO₂)₂. The results suggest that the compound [Cu(HL)(OH⁻)]_n has a polynuclear form in which the bridging allopurinolate is coordinated through the N(1) and N(2) atoms of the pyrazolic moiety. All attempts to grow crystals suitable for X-ray studies were unsuccessful, and an amorphous compound was always obtained. Magnetic studies show the existence of a strong antiferromagnetic coupling, which may be associated with a favorable structural arrangement between the metallic centers and the bridging ligands. This magnetic behavior is remarkable for a Cu(II) polynuclear coordination compound. Spectral and magnetic results together with the coordination modes of the bridging groups let us postulate as a possible arrangement a cyclic polynuclear structure presenting the allopurinolate and OH⁻ bridging ligands in a mutually *trans* configuration. This work is the first EPR spectral and magnetic study reported for a coordination compound with the allopurinol heterocycle as a ligand and, thus for the first example of a polynuclear coordination compound combining allopurinolate and OH⁻ as bridging groups. © 1994 Academic Press, Inc.

INTRODUCTION

Heterocycles with pyrimidine- and azole-type rings fused in their structure are molecules of interest in biochemistry (1), its related areas (2), and coordination chemistry (3-5). This interest is due in part to the fact that

they have several donor atoms, binding arrangements, and structural dispositions, and their coordination compounds have novel spectral and magnetic properties. In particular, several of these heterocycles, purine-type molecules and their structural analogues and isomers, are of special biochemical and biomedical interest, since they are heterocyclic substrates of the Mo metalloenzyme xanthine oxidase, for which oxidation in almost all of these substrates takes place in the Mo center (2). In relation to the structural properties, donor atomic dispositions, and coordinating capability of these heterocycles, a refined understanding of the heterocycle-metallic center interactions is an open field of systematic studies, including kinetic, thermodynamic, structure, and spectral studies, as well as in magnetochemical and quantum mechanical research. Among the compounds that contain these heterocycles, only a few examples have been found (3, 4, 6) that have polynuclear structures. A member of this family, allopurinol (H₂L, 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-one), is a structural isomer of hypoxanthine (6-oxopurine), as is shown in Fig. 1.

Figure 1 shows in 1 a pyrazolic moiety and in 2 an imidazolic moiety as five-membered rings. This characteristic leads to remarkable differences in their behavior with Lewis acids, e.g., transition metal centers. From previous and more recent studies with allopurinol and its derivatives (5-11), and depending on the metallic systems and the experimental conditions, the N atoms of the five-membered ring, and in particular the N(2) atom, are the most favorable coordinating sites of the heterocycle, in agreement with the donor properties (12-14) of N(2). In a previous work (5) the ethanolic synthesis and some properties of the compound [Cu(HL)(OH⁻)]_n were reported. The suggested polynuclear nature of this product and its low magnetic moment at room temperature are

¹ To whom correspondence should be addressed.

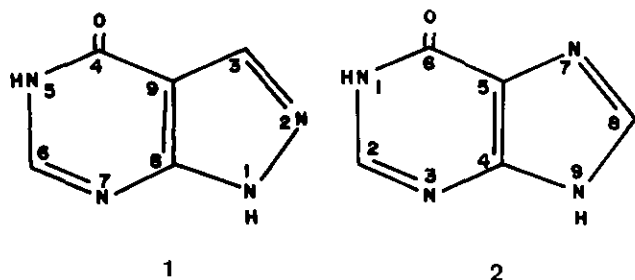


FIG. 1. Formulae and numbering schemes of allopurinol (1) and hypoxanthine (2).

properties that could be associated with an effective magnetic coupling pathway, particularly of an antiferromagnetic character. All these facts prompted us to explore alternative synthetic routes and to carry out a more detailed characterization and magnetic study of this coordination compound.

In this paper, other synthetic routes and spectral (EPR), thermogravimetric, and further magnetic results for $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ are reported. From these results we propose a possible structural arrangement based on a cyclic framework for $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$. This represents the first example of a polynuclear system with allopurinolate and OH^- as bridging groups.

EXPERIMENTAL

1. Materials

The cupric salts, solvents, and buffer solution reagents were analytical grade products from Aldrich and Merck. Allopurinol was from Sigma. All these products were used without further purification.

2. Synthesis

Aqueous medium. Metallic salts with $X = \text{Cl}^-$, Br^- , NO_3^- , SO_4^{2-} , ClO_4^- , and CH_3CO_2^- , in 1:1, 2:1, 3:1, 1:2, and 1:3 metal:allopurinol molar ratios, were used (mmole scale). pH values were 4, 7, and 13. In all syntheses 1 mmole (136.11 mg) of allopurinol was dissolved in about 100 ml of the respective buffer aqueous solution ($\text{CH}_3\text{COOH}/\text{NaCH}_3\text{CO}_2$ for pH 4, $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ for pH 7, and KCl/NaOH for pH 13) with stirring and heating. After ligand dissolution, the corresponding cupric salt was added to the colorless solution at room temperature and the reaction mixture was stirred for about 1 hr. The deep blue product obtained was isolated by filtration, washed with water and hot ethanol, and then dried at 110°C for 4 hr. The same product was also obtained for pH 1 (glycine/HCl) for a 1:1 $\text{Cu}(\text{CH}_3\text{CO}_2)_2$:allopurinol molar ratio at boiling temperature.

Methanol medium. In this technique SO_4^{2-} and CH_3

CO_2^- , as counterions and stronger bases, were used. A 1:1 metal:allopurinol molar ratio (mmole scale) was employed. The heterocycle was dissolved in about 100 ml of boiling methanol under reflux. The respective metallic salt was added to the colorless solution, and the mixture was maintained under reflux for 10 days. The corresponding product was isolated by filtration from the hot mixture and washed with hot methanol. The resulting deep blue solid was dried at 110°C for 4 hr. For both techniques, the compounds obtained were preserved in a desiccator under vacuum with CaCl_2 .

Dimethyl sulfoxide medium. In this technique several of the metallic salts employed in the aqueous media synthesis were used. A 1:1 metal:allopurinol molar ratio (mmole scale) was applied. The ligand was dissolved under stirring in ca. 20 ml of DMSO and the respective cupric salt was added. The reaction mixture was maintained at ca. 70°C for several days. The deep blue compound obtained was filtered, washed with hot methanol, dried, and preserved as mentioned above.

3. Physical Measurements

Infrared (IR) spectra were obtained as nujol mulls using CsI plates in the $4000\text{--}200\text{ cm}^{-1}$ range employing a 598 Perkin-Elmer spectrometer. Electronic spectra (350–1100 nm) of the powdered samples were measured by the specular reflectance method in a 160-A Shimadzu spectrometer. Magnetic susceptibility at room temperature was measured by the modified Gouy method using a Johnson Matthey magnetic susceptibility balance and employing $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrating agent. Thermogravimetric measurements were carried out in DT-30 Shimadzu equipment using N_2 as the carrier gas and a heating rate of $5^\circ\text{C}/\text{min}$. The variable-temperature magnetic susceptibility measurements were carried out using a SQUID Quantum Design magnetometer, from 5 to 300 K under a magnetic field of 100 G. EPR spectra (X band) of the solid samples were obtained in a 200-D Bruker spectrometer at liquid nitrogen and room temperature. An EPR spectrum (X band) of the frozen solution (DMSO) of the solvated compound was obtained at liquid nitrogen temperature only. The g values obtained were standardized against the absorption of diphenylpicrylhydrazine (DPPH) at $g = 2.0043$. X-ray powder diffraction patterns of allopurinol and several samples of the coordination compound were taken in a XD-5A Shimadzu and a D-500 Siemens diffractometer, the latter using a secondary monochromator with $\text{CuK}\alpha$ radiation. Scanning electronic microscopy of solid $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ samples, treated under several thermal and pressure conditions, was carried out in JEOL 5400-LV equipment, employing an Ag thin layer as electric conductor medium. Microanalysis confirmation (C, H, N) was performed by the Chemistry Department at the University College, London.

RESULTS AND DISCUSSION

The coordination compound studied was obtained by several synthetic routes and corresponds to the formula $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ (calculated: 27.8, C; 1.8, H; 25.9, N; found: 27.5, C; 1.9, H; 25.8, N). The reaction was ca. 100% quantitative in all cases. The product is insoluble in common organic solvents and shows a thermogravimetric curve that corresponds to an anhydrous sample, its thermal decomposition starting at around 310°C. The same thermal behavior was observed even when the Cu(II) compound was exposed to humid air. X-ray powder diffraction patterns of several samples of $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ obtained by different synthetic routes are identical and show remarkable differences with respect to the free heterocycle. The former show scarce, weak, and broader signals, indicative of a poor-crystalline nature. It is important to mention that this poor crystallinity was not overcome by the different product syntheses, by modifying the formation and the precipitation rates, nor by the redissolution attempts of the same compound in several solvents at different temperature conditions. The scanning electronic microscopy results for several samples of solid $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ do not show the topology and the morphology of a crystalline product. The electronic spectrum of the solid shows a broad band at around 590 nm and a low energy tail of a band in the limit of the blue region. The position of the broad band could be associated with Cu(II) $d-d$ transitions, and the pattern of the spectrum is suggestive of near-planar geometry around Cu(II).

The IR spectrum of $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ shows a strong band close to 3500 cm^{-1} , which can be assigned to the $\nu(\text{OH}^-)$ bridge (15). It is interesting that the splitting band of the $\nu(\text{OH}^-)$ mode can be associated with the presence of OH^- groups simultaneously bridging two metallic centers in a mutually *cis* configuration; this spectral behavior has been reported (16) for the dinuclear system $[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\text{OH}^-)_2]^{2-}$ and is absent in the spectrum under discussion, suggesting that this type of configuration does not exist for the OH^- groups. The complex and broad signal in the 1130–1010 cm^{-1} region is associated with the $\delta(\text{OH}^-)$ bridge mode. Also, as previously noted (5), the IR spectrum shows bands at 1700 cm^{-1} ($\nu(\text{C} = \text{O})$) and 1610 cm^{-1} ($\delta(\text{N}(5)-\text{H})$), therefore excluding these groups of the organic ligand as coordinating sites in the compound. Signals at 486 cm^{-1} ($\nu(\text{Cu}-\text{OH}^-)$ bridge) and at 295 and 265 cm^{-1} ($\nu(\text{Cu}-\text{N})$) are also shown. The presence of these two latter bands in the low-energy region, attributed to the $\nu(\text{metal}-\text{N})$ mode, is in agreement with the participation of the N atoms of the pyrazolic moiety of allopurinolate as coordinating sites in a bridging fashion (17). In summary, IR data are suggestive of the participation of the pyrazolic fragment of allopurinolate and OH^- as bridging

groups between Cu(II) centers in a polynuclear arrangement.

Although in principle two arrangements of the bridging ligands are feasible (one in the mutually *cis* configuration of the pyrazolic moiety of allopurinolates and the OH^- groups, and the other in the mutually *trans* configuration), the IR data are in agreement with a mutually *trans* configuration, which has been found previously in a triazolic ligand with Cu(II) in a polynuclear system (18), and recently in the interesting cyclic compound $[\text{Cu}(3,5\text{-dmpz}^-)(\text{OH}^-)]_8$ (19).

The room-temperature EPR spectrum of powdered $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ shows a complex pattern. A reliable assignment of the bands is difficult, but it indicates the existence of strong metal-metal interactions. The approximate g value is 2.27. Although the EPR spectrum at 77 K shows (Fig. 2) a relatively better resolution, its pattern is complicated because, among other features (a nonflat baseline and a long tail at the high-field side of the g_\perp feature), it seems to contain overlapped signals in the middle-field region. With a g_\perp value of ca. 2.08, the region for g_\parallel (ca. 2.4) shows several bumps. This last characteristic could be associated with magnetic impurity signals or exchange averaging of magnetically nonequivalent sites. With this spectral information it is difficult to conclude anything about the possibilities mentioned above. However, the general pattern in the middle-field region could correspond to a predominant axial line shape and principally $d_{x^2-y^2}$ ground state ($g_\parallel > g_\perp > 2.0$) in a dominant tetragonal stereochemistry (20). The underlying broad signal of the ERP spectrum is suggestive of the existence of Cu(II)-Cu(II) interactions in a polynuclear arrangement.

The EPR spectrum at 77 K of the DMSO frozen solution of the solvated sample shows (Fig. 3) the existence of an anisotropic g tensor, with an axial line shape and values of $g_\perp = 2.07$ and $g_\parallel = 2.4$. The spectrum exhibits bands in the low-field region related to a hyperfine structure. It is interesting to point out that the EPR pattern (axially symmetric signal) resembles that shown by some copper(II) compounds in solution with a pentacoordinated environment (square pyramidal) in the solid state, e.g., $[\text{Cu}(\text{Cl})(\text{DMF})(\text{HB}((3,5\text{-}i\text{-propyl})_2\text{pz})_3)]$ in DMF frozen solution (77 K), which presents, in solid state, a DMF molecule coordinated to Cu(II) (21). The hyperfine constant value (≈ 130 G) in the EPR spectrum under discussion is related to significant e^- -nuclei coupling. It may be that the ground state of the metallic centers is mainly due to the $d_{x^2-y^2}$ orbitals, although it is possible that the EPR spectrum characteristics could be due to mononuclear species that appear after a dissociative process induced by temperature and solvent nature has taken place.

Since there are no magnetic studies reported for polynuclear coordination compounds with purine-type ligands and their isomers, and since the room-temperature effec-

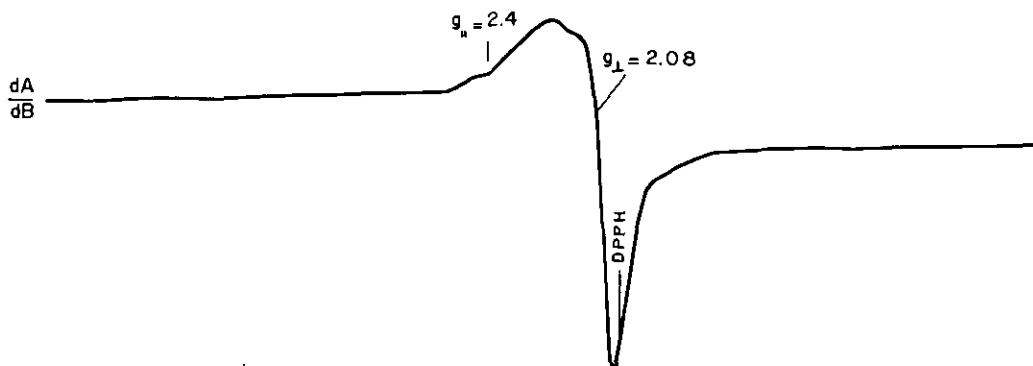


FIG. 2. X-band (9.25 GHz) EPR spectrum at 77 K of solid $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$.

tive magnetic moment of powdered $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ is $0.9 \mu_B$, it was of great interest to explore its magnetic behavior. Figure 4 presents the experimental molar magnetic susceptibility (per $\text{Cu}(\text{HL})(\text{OH}^-)$) as a function of temperature.

From these results we observe interesting qualitative features, such as the increase of the molar susceptibility close to room temperature, which is suggestive of the existence of a strongly antiferromagnetic coupled system (22). In the low-temperature region a Curie-Weiss behavior is observed, very probably associated with magnetically noncoupled $\text{Cu}(\text{II})$ centers as a magnetic impurity. This result was reproducible for all samples studied.

In a preliminary study, the experimental low-temperature magnetic susceptibility was analyzed employing the Curie-Weiss law. For the range 5–30 K, the parameters $\chi_0 = 4.27 \times 10^{-4}$, $C = 11.06 \times 10^{-3}$, and $\theta = -0.2233$ K were obtained. Also, and for the range 5–80 K, the antiferromagnetic coupling behavior results from the same equation. For this case, we obtained the values $\chi_0 = 4.42 \times 10^{-4}$, $C = 10.73 \times 10^{-3}$, and $\theta = -0.096$ K. This same magnetic characteristic is confirmed when the relation $\chi^{-1}-T$ for the low-temperature region is studied.

In order to study the magnetic properties of $[\text{Cu}$

$(\text{HL})(\text{OH}^-)]_n$, several models were selected, corresponding to two principal categories of systems: (a) dinuclear units for paired spins (23–26) and (b) linear chains of interacting spins, including interchain interactions (27–29). From a fitting process, the expression that corresponds to a Bleaney-Bowers-type equation (i.e., dinuclear systems of paired spins) gave the best results:

$$\chi(T) = \frac{2N\beta^2g^2}{k_B T} \left[3 + \exp\left(\frac{-2J}{k_B T}\right) \right]^{-1} (1 - \rho) + 2n\alpha(1 - \rho) + \rho \frac{N\beta^2g^2}{2k_B T} \quad [1]$$

In this equation, N is the Avogadro number, g the Lande splitting factor, β the Bohr magneton, k_B the Boltzmann constant, T the temperature in Kelvin, J the interaction exchange energy between metallic nearest neighbors, ρ the mole fraction of the magnetically noncoupled $\text{Cu}(\text{II})$ impurity, and $n\alpha$ the temperature-independent paramagnetism term. A fitting of the experimental values with Eq. [1] (Fig. 4) was carried out using as the criterion of best fit the minimum value of $\sum_i (\chi_i^{\text{calc}} - \chi_i^{\text{obs}})^2 / (\chi_i^{\text{calc}})^2$, with the following resulting parameters: $g = 2.25$, $\rho = 0.0097$, $J = -492 \text{ cm}^{-1}$, and $2n\alpha = 480 \times 10^{-6} \text{ emu/mole}$. It is



FIG. 3. X-band (9.204 GHz) EPR spectrum of DMSO frozen solution of $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ at 77 K.

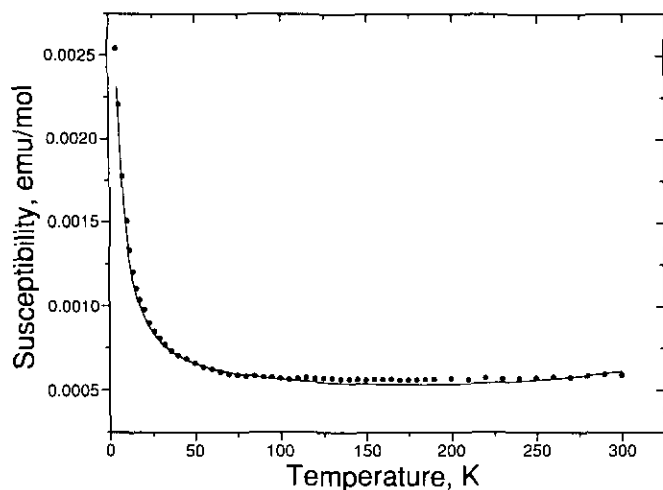


FIG. 4. Experimental (circles) and theoretical (solid line) values of the molar magnetic susceptibility vs temperature of $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$.

interesting that the theoretical g value is in close agreement with the experimental one (2.27). The ρ value is indicative of a very small contribution from magnetically noncoupled Cu(II) centers. The presence and nature of this magnetic impurity were observed in several samples, and they seem to be inherent to the nature of the polynuclear compound. Regarding the J value, its negative character (joined to the same property for θ) may be associated with the existence of a singlet ground state, that is, an antiferromagnetic coupling between the Cu(II) atoms. The magnitude of J is attributed to an appreciable band gap between the ground and the excited states (22). Similar results were obtained when the χT - T behavior was analyzed with Eq. [1] (Fig. 5). In this case, the following

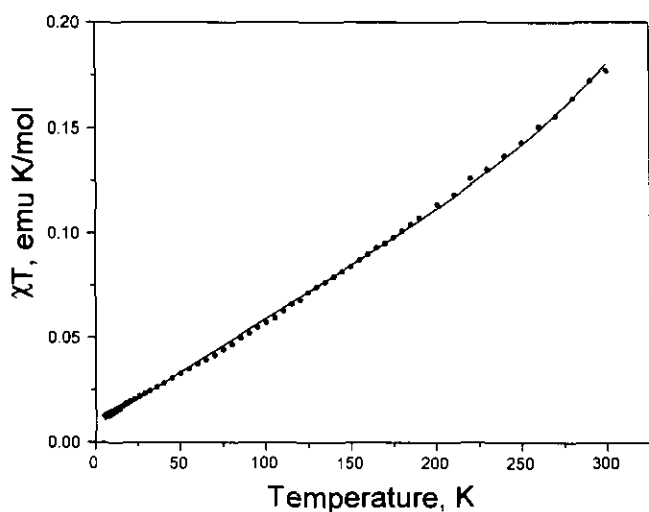


FIG. 5. Experimental (circles) and theoretical (solid line) values of χT vs temperature values of $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$.

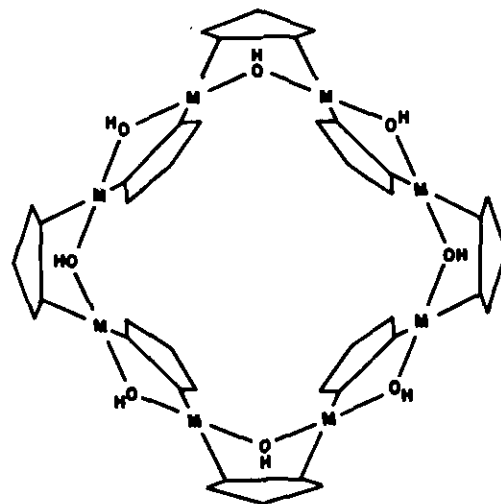


FIG. 6. Schematic drawing of the cyclic framework proposition for $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ in a mutually *trans* configuration.

results were obtained: $g = 2.24$, $\rho = 0.00857$, $J = -549.7 \text{ cm}^{-1}$, and $2n\alpha = 515.6 \times 10^{-6} \text{ emu/mole}$.

The good fitting shown by our results suggests a remarkable intrachain spin coupling between the Cu(II) centers by the bridging ligands due to an arrangement that makes efficient connection between the magnetic orbitals possible. As has been previously discussed (30), the planarity and efficient overlap between the metallic and the bridging in-phase orbitals gives, in general, this strong antiferromagnetic coupling. In our case it is probable that the participation of the Cu(II) $d_{x^2-y^2}$ orbitals in sigma bonding with N and O atomic orbitals of the bridging groups, and the d_{yz} and/or d_{xz} orbitals of Cu(II) overlapping with $p\pi$ orbitals of N atoms of the pyrazolic moiety of allopurinolate, may be relevant to the J value.

Keeping these aspects in mind as well as the structural and configurational arrangement possibilities for $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$, it is interesting to note that the mutually *trans* configuration is a favorable arrangement for the coordination chemistry of pyrazolate⁻ (pz^-), its derivatives, and OH^- , OR^- , and X^- ligands as bridging groups (14, 16, 19). The fact that the pyrazolic moiety N atoms are participating as a bridge in the coordination of allopurinolate, together with the existence of the bridging OH^- ligand in $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ and the same metal:ligands stoichiometry with respect to $[\text{Cu}(3,5\text{-dmpz}^-)(\text{OH}^-)]_8$, makes it possible in principle to suggest analogous configurational and structural features in these two coordination compounds. A schematic drawing of this possible structure is shown in Fig. 6.

This possible structure is supported also by the fact that the chemical behavior of the allopurinolate in the compound $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ is established essentially by

the pyrazolic ring, which is a structural analogue of the 3,5-dmpz⁻ model system ligand.

CONCLUSIONS

Alternative experimental conditions for the synthesis of the polynuclear compound $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ have been established. The critical factors in these routes of synthesis are the presence of water in the reaction media, the nature and basic properties of the counterions, and the pH and temperature. We found that the coordination compound $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ is kinetic and thermodynamically stable toward other competitive reactions (31). Concerning the magnetic studies carried out on $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$, the results show strong antiferromagnetic coupling, and the J average value obtained let us suggest the existence of a favorable structural arrangement, in which the disposition and orientation of metallic and bridging donor atomic orbitals are critical for the superexchange coupling pathway. The influence of the pyrimidinic ring of allopurinolate on the magnetic behavior previously discussed was studied by analyzing the magnetic results for the molar susceptibility temperature dependence of $[\text{Cu}(\text{pz}^-)(\text{OH}^-)]_n$ obtained under selected conditions (31). This compound shows magnetic properties analogous to those of $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$. This allows us to postulate that the principal heterocyclic ring involved in the magnetic coupling of the metallic centers in $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ is the pyrazolic moiety. On the structural arrangement for $[\text{Cu}(\text{HL})(\text{OH}^-)]_n$ the results suggest a possible cyclic framework in a mutually *trans* configuration, in which the superexchange coupling pathway could be favorable. The magnitude of this antiferromagnetic coupling is remarkable for a polynuclear coordination compound. This is the first report of EPR spectral and magnetic studies of an allopurinol coordination compound, and of one of the few polynuclear coordination compounds with these types of heterocycles reported thus far. Also, this is the first example of a polynuclear system with allopurinolate and OH^- as bridging groups.

ACKNOWLEDGMENTS

We thank Jorge Ramírez-Salcedo (IFC-UNAM), Max Azomoza-Palacios (UAM-Iztapalapa), Leticia Baños-López (IIM-UNAM), Francisco Morales-Leal (IIM-UNAM), and Rutilo Silva-González (IFBUAP) for the EPR spectra of samples, thermal results, X-ray diffraction patterns, magnetic susceptibility measurements, and scanning electronic microscopy studies, respectively. We also acknowledge Hugo Torrens (FQ-UNAM) for his helpful comments on this manuscript. Secretaría

de Educación Pública de México Grants C88-01-0143 and C89-01-0160 are gratefully acknowledged by R. A. Ch. R.E.D. thanks DGAPA (UNAM), CONACyT, and AEO for financial support.

REFERENCES

1. L. Stryer, "Biochemistry," 3rd. ed. Freeman, New York, 1988.
2. R. K. Robins, G. R. Revankar, D. E. O'Brien, R. H. Springer, T. Novinson, A. Albert, K. Senga, J. P. Miller, and D. G. Streeter, *J. Heterocyclic Chem.* **22**, 601 (1985).
3. E. Dubler and E. Gyr, *Inorg. Chem.* **27**, 1466 (1988).
4. E. Dubler, G. Hänggi, and H. Schmalle, *Inorg. Chem.* **29**, 2518 (1990), and references therein.
5. R. Acevedo-Chávez and N. Barba-Behrens, *Transition Met. Chem.* **15**, 434 (1990).
6. W. S. Sheldrick and P. Bell, *Z. Naturforsch. B* **42**, 195 (1987).
7. W. S. Sheldrick and P. Bell, *Inorg. Chim. Acta* **137**, 181 (1987).
8. G. Hänggi, H. Schmalle, and E. Dubler, *Inorg. Chem.* **27**, 3131 (1988).
9. G. Hänggi, H. Schmalle, and E. Dubler, *Acta Crystallogr. Sect. C* **44**, 1560 (1988).
10. W. S. Sheldrick and B. Günther, *Inorg. Chim. Acta* **151**, 237 (1988).
11. G. Hänggi, H. Schmalle, and E. Dubler, *Acta Crystallogr. Sect. C* **47**, 1609 (1991); *J. Chem. Soc. Dalton Trans.*, 941 (1993).
12. A. D. Mighell, C. W. Reimann, and A. Santoro, *Acta Crystallogr. Sect. B* **25**, 595 (1969).
13. C. W. Reimann, A. Santoro, and A. D. Mighell, *Acta Crystallogr. Sect. B* **26**, 521 (1970).
14. S. Trofimenko, *Prog. Inorg. Chem.* **34**, 115 (1986).
15. G. López, J. Ruíz, G. García, C. Vicente, V. Rodríguez, G. Sánchez, J. A. Hermoso, and M. M. Ripoll, *J. Chem. Soc. Dalton Trans.*, 1681 (1992).
16. G. López, G. García, G. Sánchez, J. García, J. Ruíz, J. A. Hermoso, A. Vegas, and M. M. Ripoll, *Inorg. Chem.* **31**, 1518 (1992).
17. J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta* **24**, 123 (1977).
18. J. A. J. Jarvis and A. F. Wells, *Acta Crystallogr.* **13**, 1027 (1960).
19. G. A. Ardizzoia, M. A. Angaroni, G. la Monica, F. Cariati, S. Cenini, M. Moret, and N. Masciocchi, *Inorg. Chem.* **30**, 4347 (1991).
20. L. Mishra and A. K. Pandey, *Polyhedron* **11**, 423 (1992).
21. N. Kitajima, K. Fujisawa, and Y. Moro-oka, *J. Am. Chem. Soc.* **112**, 3210 (1990).
22. S. S. Tandon, S. K. Mandal, L. K. Thompson, and R. C. Hynes, *Inorg. Chem.* **31**, 2215 (1992).
23. C. G. Pierpont, L. C. Francesconi, and D. N. Hendrickson, *Inorg. Chem.* **16**, 2367 (1977).
24. M. S. Haddad, S. R. Wilson, D. J. Hodgson, and D. N. Hendrickson, *J. Am. Chem. Soc.* **103**, 384 (1981).
25. I. E. Dickson and R. Robson, *Inorg. Chem.* **13**, 1301 (1974).
26. A. Escuer, R. Vicente, T. Comas, J. Rivas, M. Gomez, and X. Solans, *Inorg. Chim. Acta* **177**, 161 (1990).
27. W. E. Estes, W. E. Hatfield, J. A. C. van Ooijen, and J. Reedijk, *J. Chem. Soc. Dalton Trans.*, 2121 (1980).
28. M. Inoue, S. Emori, and M. Kubo, *Inorg. Chem.* **7**, 1427 (1968).
29. B. C. Gerstein, F. D. Gehring, and R. D. Willett, *J. Appl. Phys.* **43**, 1932 (1972).
30. E. Colacio, J. M. D. Vera, J. P. Costes, R. Kivekäs, J. P. Laurent, J. Ruíz, and M. Sundberg, *Inorg. Chem.* **31**, 774 (1992).
31. R. Acevedo-Chávez, M. E. Costas, and R. Escudero-Derat, in preparation.