# A Novel Example of a Dinuclear Copper(II) Complex Bridged Only by One Pyrazolate Ion. Preparation, Spectroscopic and Magnetic Properties, and MMX Force Field Study

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The pyrazolate-bridged dinuclear copper(II) complex, $K[Cu_2L_2(pz)]\cdot H_2O$ [where $H_2L$ = 6-amino-1,3-dimethyl-5-(2′-carboxyphenyl)azouracil] has been prepared and characterized by means of magnetic susceptibility and spectroscopic measurements. The compound exhibits antiferromagnetic behaviour with a $2J$ value of $-5.4$ cm$^{-1}$. Because of the lack of suitable crystals for single-crystal X-ray analysis, we have performed MMX force field calculations to obtain the structure having the lowest energy. The magnitude of the magnetic interaction is discussed based upon these results.

The magnetic properties of dinuclear copper(II) compounds have been the subject of intensive study over the past decades. Useful correlations between the singlet–triplet splitting and structural parameters have been made.[1,2] Empirical data on a large variety of compounds including hydroxo, alkoxo, chloro, bromo and thio bridges are in agreement with theoretical approach.

Other interesting aspects of these compounds are their potential use as models for biological materials involving dimetallic sites[3–5] and the ability of copper(II) complexes to act as catalysts in oxidation of organic molecules.[6–9]

It is known that the diazole and diazine groups function as a bridge by their two nitrogens to afford bi- and polynuclear metal complexes. However, pyrazolate bridges in binuclear copper(II) complexes generally appear in combination with alcoholate, phenolate, acetate, thiolate or azide bridging groups.[10–17] Well characterized dinuclear copper(II) complexes containing only pyrazolate bridges are still rare.[18] To the best of our knowledge, only one example of a dinuclear copper(II) complex bridged only by a single pyrazolate ion has been reported.[19] Its structure was deduced from magnetic studies. Any explanation for the magnitude of the magnetic interaction was not given, however.

Thus, quantitative discussions on the correlation between the magnetic coupling and structural parameters were not given. For this, a series of structurally comparable di- or polynuclear copper(II) complexes, with related ligands having different bonding properties, is needed. Therefore the syntheses of these compounds have received relatively more attention.

In this paper we describe the synthesis and magnetic properties of a dinuclear copper(II) complex involving the ligand 6-amino-1,3-dimethyl-5-(2′-carboxyphenyl)azouracil (hereafter abbreviated as $H_2L$) and a pyrazolate (pz) bridge. Moreover, the magnetic interaction is discussed in the light of the optimized structure obtained by semiempirical MMX force field calculations.

## Experimental

*Syntheses.* The ligand $H_2L$ was prepared by coupling diazotized anthranilic acid with 6-amino-1,3-dimethyluracil according to the method described earlier.[20]

The $K[Cu_2L_2(pz)]\cdot H_2O$ complex was prepared by the following procedure: $Cu(NO_3)_2\cdot 3H_2O$ (0.87 g, 3.60 mmol), a solution of pyrazol (0.12 g, 1.80 mmol) and KOH (0.01 g, 1.80 mmol) in MeOH/$H_2O$ (20/1, 25 ml) were added successively to a heated and stirred suspension of $H_2L$ (1.09 g, 3.60 mmol) in MeOH/$H_2O$ (20/1, 100 ml). After 10 min a black homogeneous solution was obtained, which was allowed to stand at room temperature for 1 h, whereupon dark green crystals separated. They were filtered, washed with methanol and ether and then air-dried; yield 80%. Anal. Calc. for $C_{29}H_{27}Cu_2KN_{12}O_9$: C, 40.80; H, 3.19; Cu, 14.89; N, 19.69. Found: C, 40.83; H, 2.95; Cu, 14.53; N, 19.72.

In spite of many attempts, no crystals suitable for X-ray single-crystal determination were obtained. Either the crys-

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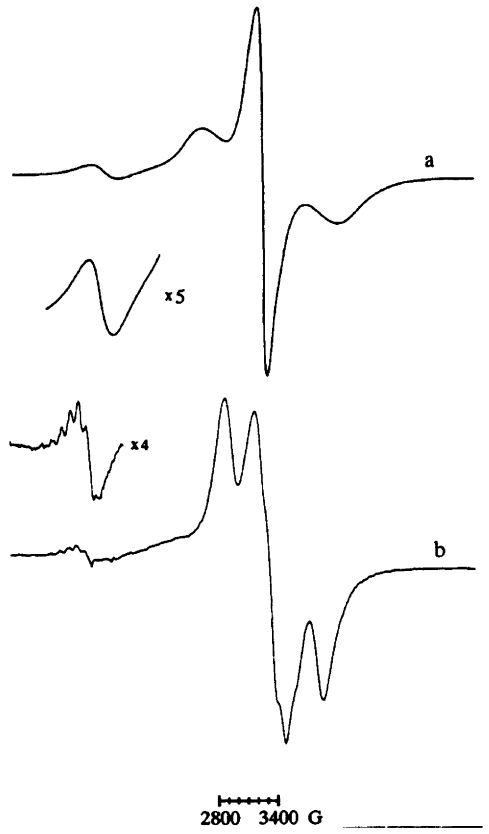


*Fig. 1. X*-band ESR spectrum of $K[Cu_2L_2(pz)]\cdot H_2O$: (a) polycrystalline sample at 90 K; (b) frozen solution (1/1 $H_2O$/DMSO) at 90 K.

tals were too small, or they had diffraction power that was too weak, perhaps due to disorder.

*Physical measurements.* Microanalyses of C, H and N were performed with a Perkin–Elmer 240C analyzer. Copper was determined thermogravimetrically as CuO with a Mettler TG-50 thermobalance.

Magnetic susceptibility data were collected on powdered samples with the use of a Faraday-type magnetometer using mercury tetrakis(thiocyanate)cobaltate(II) (susceptibility at 20°C, $16.44\times10^{-6}$ $cm^3$ $mol^{-1}$) as a standard. Data were corrected for the diamagnetism of the ligands estimated from Pascal's constants and for TIP.

EPR spectra were obtained with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz (X-band).

*Structure optimization.* The program used was PC Model version 3.0, which makes use of an MMX force field, including the π-VESCF calculations.[21] The initial assumption in creating a starting model was that a copper(II) ion is coordinated to the dideprotonated ligand via one of the carboxylate oxygens, the azo nitrogen and the amide nitrogen atoms in the uracil ring. This is the coordination observation in all complexes studied that contain the ligand. Based on the magnetic properties, pyrazole was considered to act as a bridge. Two basic alternatives remained: the ligands lie either *cis* or *trans* to each other. The optimized structure with the *cis* conformation clearly produces a more negative value for the energy minimum, and thus it was considered the most probable structure.

## Results and discussion

The polycrystalline powder EPR spectra of $K[Cu_2L_2(pz)]\cdot H_2O$ at 90 and 4 K are very similar (Fig. 1). The spectra are typical for copper(II) dimers and can be interpreted as triplet state spectra originating from exchange-coupled pairs of copper(II) ions. The absence of hyperfine structure is probably due to the small size of the counter-ion ($K^+$), which does not provide a magnetically dilute environment for the dimers.

Each of these spectra shows, in the $\Delta M = \pm1$ region, two features of a zero-field split transition with $g$ values of 2.90 and 1.90, as well as a broad and strong absorption at $g = 2.10$ G. Moreover, a $\Delta M = \pm2$ absorption (half-field signal) is observed at $g = 4.20$. The magnitudes of $D$ and $E$, which contribute to the zero-field splitting, are 0.066 $cm^{-1}$ and approximately zero, respectively. The zero-field splitting parameter can also be evaluated from the position of the half-field transition through eqn. (1).[22] The resultant value is $D = 0.061$ $cm^{-1}$, in reasonable agreement with the aforementioned value.

$$H_{min} = [(h\nu)^2 - 4/3D^2]^{1/2}/2g\beta \quad (1)$$

In solution (1/1 $H_2O$/DMSO) the complex exhibits a triplet spectrum at 90 K. As seen in Fig. 1, the $\Delta M = \pm2$ transition displays a seven-line hyperfine pattern. Obviously the dimeric structure is retained, at least partly, in solution.

To investigate the magnetic exchange coupling between the two copper centers in the dimer, the magnetic susceptibility of the title compound was investigated in the temperature range 4.4–282 K. The temperature dependence of $\chi^{-1}$ is well fitted to the Curie–Weiss law with $C = 0.90$ and $\theta = -6.12$. From the negative value of θ an overall antiferromagnetic behaviour can be deduced. This is also apparent from a consideration of the thermal variation of $\chi_M T$, which

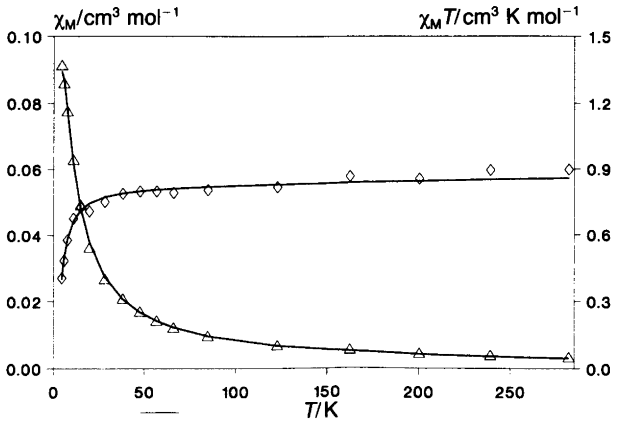


*Fig. 2.* Experimental and calculated dependences of $\chi_M$ and $\chi_M T$ for $K[Cu_2L_2(pz)]\cdot H_2O$.

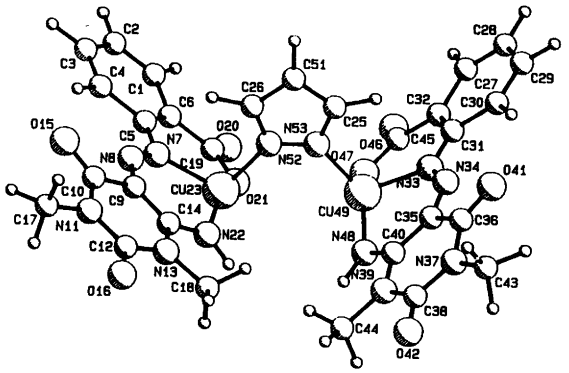


*Fig. 3.* A perspective view of the complex unit $[Cu_2L_2(pz)]^-$, optimized by means of MMX force field calculations.

is presented in Fig. 2. From 282 to 160 K, $\chi_M T$ remains practically constant and equal to 0.89 emu K $mol^{-1}$, which is the value expected for two isolated copper(II) ions with $g = 2.18$. On a further lowering of the temperature, $\chi_M T$ decreases to a value of 0.09 emu K $mol^{-1}$ at 4.45 K. This behaviour is characteristic of a weakly spin-coupled copper(II) dinuclear complex with a singlet ground state.

The experimental susceptibilities corrected for the diamagnetism of the ligands were fitted to the Bleaney–Bowers equation.[23] A reasonable agreement was obtained, with $2J = -5.4$ $cm^{-1}$, $g = 2.10$ and $p = 0.01$ with $N\alpha$ fixed at $120 \times 10^{-6}$ cgsu.

Recently, two closely related dinuclear complexes, **1** and **2** {**1**: $(NBu_4)_2Cu(Dcp)_2$], $H_3Dcp$ = 3,5-pyrazoledicarboxylic acid; **2**: $[CuL]_2(BPh_4)_2$, $H_2L^1$ = 3,5-bis[(2-diethylamine)ethylaminoethyl]pyrazole}, were reported in the literature,[24,25] which exhibited strong antiferromagnetism with $|2J|$ values of 200 and 428 $cm^{-1}$, respectively. In both compounds the copper ions display planar coordination bridged by *two* planar pyrazole ligands. The experimental values for the $|2J|$ values are in good agreement with the extended Hückel calculations performed by Bencini and co-workers.[26] Their results show clearly that the deviation of the pyrazolato ligands from strict planarity in the model compound $[Cu(pz)Cl_2]_2^{2-}$ has the greatest effect on the predicted antiferromagnetic interaction.

In $K[Cu_2L_2(pz)] \cdot H_2O$ there is only *one* pyrazolate bridge, and the exchange integral is significantly lower than in the complexes **1** and **2**. Owing to the lack of suitable single crystals for an X-ray structure determination, we have optimized the structure for the complex anion by means of semiempirical MMX force fields.[21] Molecular mechanics, or force field, calculations treat a molecule as an array of atoms governed by a set of classical-mechanical potential functions. Nevertheless, it can already be considered to have achieved chemical accuracy.[27,28] A perspective view of the optimized structure is given in Fig. 3. The atomic coordinates, bond distances and angles are available from one of the authors (M.R.S.) on request.

The copper ions display distorted tetrahedral geometry. The dideprotonated ligand L affords three coordination sites. For each copper atom, the fourth coordination site is afforded by a nitrogen atom from the pyrazole molecule. Interestingly, the pyrazole ring is far from being coplanar with the two tridentate ligands. This configuration of the $CuN_3O$ chromophores has been observed for a dinuclear complex $[CuLPy]_2 \cdot 0.5H_2O$ which we have reported recently.[29] In this compound the conformation of the $CuN_3O$ chromophore is midway between the $D_{4h}$ and $T_d$ geometries.

Owing to the strong deviation from coplanarity of the pyrazole ring and the coordination planes of the copper ions in the present complex, the overlap density of the magnetic orbitals in the bridging region is expected to be small, and consequently the antiferromagnetic interaction may be low. An experimental $2J$ value of $-24.6$ $cm^{-1}$ was calculated from magnetic susceptibility data for an analogous compound $Ca[Cu_2(pz)_2(GlyGly)_2] \cdot H_2O$.[19] Based upon spectroscopic data, the authors of Ref. 19 propose a structure similar to ours. Interestingly, the $CuN_3O$ chromophores discussed in Ref. 19 deviate less from square-planar geometry than in our complex. This might well be a reason why a higher $|2J|$ value was obtained in the case of $Ca[Cu_2(pz)_2(GlyGly)_2] \cdot H_2O$. However, further studies are needed to decipher more precisely the influence of the different geometric parameters on the importance of the exchange interaction in pyrazolato-bridged copper(II) dimers.

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