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Synthesis, Characterization and Magnetic Properties in Trinuclear Complexes of Cu(II) Derived from 2-Hydroxy-1,3-propylenebis(oxamato)

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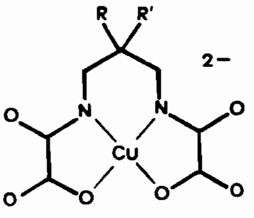
Abstract

The aim of this paper is to vary the magnetic coupling between three copper(II) ions through the oxamato bridge in a predictable manner. Starting from the planar monomeric fragment $[Cu(pbaOH)]^{2-}$ (where pbaOH is 2-hydroxy-1,3-propylenebis(oxamato)) we have synthesized four trinuclear complexes of Cu(II): $\{[Cu(dien)]_2[Cu(pbaOH)]\}(ClO_4)_2$ (**1**); $\{[Cu(pmedien)]_2[Cu(pbaOH)]\}(ClO_4)_2$ (**2**); $\{[Cu(petdien)]_2[Cu(pbaOH)]\}(ClO_4)_2$ (**3**) and $\{[Cu(bipy)]_2[Cu(pbaOH)]\}(ClO_4)_2$ (**4**) with dien = diethylenetriamine; pmedien = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine; petdien = *N,N,N′,N′,N″*-pentaethyldiethylenetriamine and bipy = 2,2′-bipyridyl. According to the literature data and electronic spectra we propose that terminal Cu(II) ions in **1** and **2** are close to a square pyramid environment with a basal plane perpendicular to the basal plane of the Cu(II) central. In **3** the suggested environment is an intermediate between a square pyramid and a trigonal bipyramid. Finally, in **4** the two copper(II) terminal ions are in planar or square-pyramid surroundings. The values of J in **1**–**4** were deduced from the temperature dependence of the magnetic susceptibility. J was found to be equal to -93.2 cm^{-1} in **1**, -111.6 cm^{-1} in **2**, -196 cm^{-1} in **3** and -358 cm^{-1} in **4**. This agrees with our hypothesis about the geometry of terminal Cu(II) ions.

Introduction

There is in the literature a great number of papers in which factors affecting the magnitude of the singlet-triplet gap, J, in dinuclear Cu(II) complexes have been reported [1–5]. We emphasize the work of Kahn who has studied these factors from several points of view during the last decade [6, 7]. One of the most important and easy to control factors was found to be the coordination geometry around the Cu(II) ions: the tendency of certain nitrogenated ligands to create a particular geometry around Cu(II) is well known. The organic ligands 2,2′-bipyridyl, 2,2′-phenanthroline and *N,N,N′,N′*-tetramethylethylenediamine tend to give a planar or square-pyramid coordination; on the other hand, triamines such as diethylenetriamine or similar, give distorted pentacoordination around Cu(II) [1, 4, 5]. The geometry of this five-coordination depends on the nature of the N-substituents: *N,N,N′,N′,N″*-pentamethyldiethylenetriamine gives a distorted square-pyramid geometry with the basal plane perpendicular to the molecule as a whole; *N,N,N′,N′,N″*-pentaethyldiethylenetriamine gives an intermediate geometry between a square pyramid and a trigonal bipyramid. Generally, bulkier N-substituents have a great tendency to pass from a square-pyramid to a trigonal-bipyramid geometry [4, 8–12]. This allows the control of the so-called 'magnetic orbital', following the terminology of Kahn *et al.* [7, 13] and, consequently, of the synthesis of polynuclear complexes with predictable magnetic coupling. In spite of the great number of trinuclear Cu(II) complexes reported in recent years [14] there has never been a systematic study about the relationship between the geometry around the terminal Cu(II) ions and magnetic coupling. It seems logical to suppose that this influence must be very similar to that observed in dinuclear complexes. In order to synthesize this kind of trinuclear Cu(II) complexes in a systematic way we proposed to start from several mononuclear complexes of Cu(II) which are able to link together two terminal Cu(II) ions blocked with the nitrogenated ligands mentioned above. The central ligands chosen were [15]



I R=R'=H

II R=H; R'=OH

III R=R'=CH$_3$

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Two of these ligands have been used by Kahn *et al.* to synthesize one-dimensional Cu–Ni and Cu–Mn polymers [16–18] and heterotrinuclear Ni–Cu–Ni and Mn–Cu–Mn complexes [19].

We present in this paper four new homotrinuclear Cu(II) complexes with several amines as terminal ligands, starting from the mononuclear complex **II**. The amine ligands selected to demonstrate the influence of the coordination on the magnetic properties were bipy, dien, pmedien and petdien, which normally give a different geometry around Cu(II).

Experimental

Syntheses

$Na_2[Cu(pbaOH)] \cdot 4H_2O$

This was prepared as indicated elsewhere [17].

$\{[Cu(dien)]_2[Cu(pbaOH)]\}(ClO_4)_2 \cdot 3H_2O$

To 10 ml of an aqueous solution of 0.74 g (2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ was added an aqueous solution of 0.21 g (2 mmol) of diethylenetriamine (dien). The blue solution was stirred at room temperature and filtered. To this solution was added an aqueous solution of 0.41 g (1 mmol) of $Na_2[Cu(pbaOH)]_2 \cdot 4H_2O$ with constant stirring. A blue precipitate was immediately formed. After filtering, the precipitate was recrystallized in a small amount of water. The new complex is very soluble in water but insoluble in other common organic solvents. *Anal.* Calc. for $C_{15}H_{32}N_8O_{15}Cl_2Cu_3 \cdot 3H_2O$: C, 20.45; H, 4.32; N, 12.72; Cu, 21.66. Found: C, 20.5; H, 4.3; N, 12.8; Cu, 21.5%.

$\{[Cu(pmedien)]_2[Cu(pbaOH)]\}(ClO_4)_2$

To 10 ml of an aqueous solution of 0.19 g (0.51 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ was added an aqueous solution of 0.90 g (0.51 mmol) of N,N,N',N',N''-pentamethyldiethylenetriamine (pmedien). The blue solution was stirred at room temperature and filtered. To this solution was added an aqueous solution of 0.10 g (0.25 mmol) of $Na_2[Cu(pbaOH)] \cdot 4H_2O$ with constant stirring. After several minutes a dark blue precipitate was formed. After filtering it was dissolved in hot methanol and left to crystallize at room temperature. Complex **2** is soluble in water, acetonitrile, nitromethane and methanol. *Anal.* Calc. for $C_{25}H_{52}N_8O_{15}Cl_2Cu_3$: C, 31.07; H, 5.38; N, 11.60; Cu, 19.73. Found: C, 31.0; H, 5.4; N, 11.5; Cu, 19.6%.

$\{[Cu(petdien)]_2[Cu(pbaOH)]\}(ClO_4)_2$

To 10 ml of an aqueous solution of 0.75 g (2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ was added an aqueous solution of 0.48 g (2 mmol) of N,N,N',N',N''-pentaethyldiethylenetriamine (petdien). The blue solution was stirred at room temperature and filtered. To this solution was added an aqueous solution of 0.41 g (1 mmol) of $Na_2[Cu(pbaOH)] \cdot 4H_2O$ with constant stirring. No precipitate was immediately formed. The greenish solution was left to stand at room temperature for several days. After solvent evaporation, microcrystals of **3** were formed, which were dissolved in hot ethanol and left to crystallize at room temperature. Complex **3** is very soluble in water, acetonitrile, methanol, nitromethane, acetone and hot ethanol. *Anal.* Calc. for $C_{35}H_{72}N_8O_{15}Cl_2Cu_3$: C, 37.99; H, 6.51; N, 10.13; Cu, 17.23. Found: C, 38.0; H, 6.5; N, 10.1; Cu, 17.2%.

$\{[Cu(bipy)]_2[Cu(pbaOH)]\}(ClO_4)_2 \cdot H_2O$

To 10 ml of an aqueous solution of 0.74 g (2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ was slowly added 0.33 g (2 mmol) of 2,2-bipyridyl in 10 ml of water/acetone (1:1) with constant stirring. The blue solution was filtered after several minutes. It was cooled in an ice-cold bath and an aqueous solution of 0.41 g (1 mmol) of $Na_2[Cu(pbaOH)] \cdot 4H_2O$ was slowly added, with constant stirring. A green precipitate was immediately formed. This was filtered, washed with ethanol and ether and air dried. This compound cannot be recrystallized due to its decomposition problems in all common solvents. *Anal.* Calc. for $C_{27}H_{22}N_6O_{15}Cl_2$-$Cu_3 \cdot H_2O$: C, 34.14; H, 2.52; N, 8.85; Cu, 20.07. Found: C, 33.8; H, 2.4; N, 8.6; Cu, 19.8%.

All the reagents were used as purchased without further purification.

Techniques

Infrared spectra were recorded on a Beckmann IR-20A spectrophotometer. Samples were prepared by using the KBr technique. Vis–UV spectra were recorded in solution and solid form with a Perkin-Elmer 550 S spectrophotometer with Integrating sphere attachment. Polycrystalline powder EPR spectra were recorded at room temperature with a Varian E-109-E spectrometer.

Magnetic measurements were carried out in a Faraday type magnetometer with a continuous-flow cryostat. The polycrystalline powder samples weighed about 30 mg. The independence of the susceptibility against the magnetic field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections were estimated as -384×10^{-6}, -464×10^{-6}, -580×10^{-6} and -411×10^{-6} cm^3 mol^{-1} for **1**, **2**, **3** and **4** respectively.

Voltammetric measurements were performed with a DACFAMOV 05-03 instrument. Rigorously deaerated acetonitrile was used as a solvent and (n-$Bu_4N)ClO_4$ (0.1 M) as supporting electrolyte. Solutions were deaerated by means of a stream of argon bubbling for 15 min and an argon blanket was maintained above the solutions during the electrochemical measurements.

Potentials were referenced versus an Ag/AgCl (0.1 M KCl) electrode separated from the bulk of the solution by a medium porosity fritted disk. The potential for the one-electron oxidation of ferrocene is 420 and 460 mV versus the Ag/AgCl (0.1 M KCl) electrode with or without ohmic resistance compensation, respectively. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working electrode (Tacussel Edi rotating electrode, area 3.14 mm^2).

Results and Discussion

The four new trinuclear Cu(II) complexes were characterized by chemical analysis, infrared and visible spectroscopy and cyclic voltammetry. Magnetic measurements up to liquid helium temperature were recorded to study the influence of external ligands on the coupling constant *J*. Room temperature EPR measurements were also recorded. All our efforts to obtain single crystals suitable to X-ray structure determination have been unsuccessful up to now.

Infrared Spectra

All the IR spectra are very similar. Bands attributable to amine ligands (bipy, dien, pmedien and petdien) and the two strong characteristic bands attributable to ClO_4^- anion (*c.* 1100 and 600 cm^{-1}) appear at normal frequencies [20]. Bands attributable to the central bridging oxamato ligand appear at 1600–1620 cm^{-1} (vs, broad) which can be split at lower frequencies, as in the case of dien and bipy ligands; two sharp and medium bands centered at 1300 and 1450 cm^{-1}, and, finally, a group of very sharp bands centered at 800 cm^{-1}.

Visible Spectra

Lacking in structural data, visible spectra are important for characterizing the geometry of the terminal Cu(II) ions. According to the literature [21], when Cu(II) is coordinated to similar ligands but with a different geometry, the trigonal-bipyramid geometry shifts the visible spectra towards lower frequencies; square-pyramid geometry towards medium frequencies and, finally, square-planar geometry towards higher frequency. For example, it is well known that the geometries of $CuCl_5^{3-}$ [21] and $[Cu(bipy)Cl]^+$ ions [22] depend on the counterion in the crystal lattice. Our starting complex $Na_2[Cu(pbaOH)]\cdot 4H_2O$ presents only one maximum in the visible zone, centered at 580 nm. The structure of this complex is not known, but its Mn–Cu polymer has been described [17] as a square-pyramid geometry around the Cu(II) ion (the pentacoordination is achieved using one molecule of water). The trinuclear complex mentioned here, with dien as terminal ligand, presents only one wide and symmetrical maximum, centered at 610 nm (diffuse reflectance and water solution); with pmedien this maximum is shifted to 630–640 nm (diffuse reflectance and water or ACN solution) and with petdien the same d–d maximum is shifted to 715–720 nm (diffuse reflectance and water or ACN solution). This shift may indicate the tendency of square-pyramid geometry to change to trigonal-bipyramid geometry when we pass from non-substituted to bulky-substituted triamines. The complex with bipy as the terminal ligand is more difficult to assign. One symmetrical and wide band centered at 620 nm is observed (diffuse reflectance and water or ACN solution). Taking into account the usual planar coordination of the bipy ligand, the observed shift, almost equal to that observed for pmedien, can be attributed to the pentacoordination produced by a solvent molecule, as has been reported for this kind of planar ligand. Crystal structures of dinuclear complexes of Cu(II) with oxalato and derivatives as bridging ligands corroborate our assignment [1, 4, 5]. In all cases dien and pmedien triamine produce a square-pyramid geometry with four short and one long distance, the latter corresponding to one Cu–O(oxalato) bond. With petdien the geometry is always an approximately distorted trigonal bipyramid; with bipy the geometry is square planar or square pyramid the basal plane being coplanar to the molecule.

Cyclic Voltammetry

The four new complexes do not present any reversible peak. Complexes **1**, **2** and **3** only present several non-reversible decomposition processes, which are very complicated to interpret, especially when the amine is pentamethyl or pentaethyldien. When the terminal ligand is bipy (**4**) there is only one non-reversible peak in the reduction zone. This behaviour can indicate the great stability of this kind of trinuclear complex versus redox processes.

Magnetic Measurements

A magnetic investigation was carried out on complexes **1**, **2**, **3** and **4**. The temperature dependence of the product $\chi_M T$ is represented in Fig. 1. When complexes **1**, **2** and **3** are cooling down from room temperature, $\chi_M T$ decreases gradually to reach a plateau with $\chi_M T$ *c.* 0.4 cm^3 mol^{-1} K. This plateau corresponds to the Curie law expected for a doublet ground state. The bipy complex presents a more complicated behaviour at low temperature (Fig. 1). There is a gradual decrease of $\chi_M T$ up to 20 K approximately. At this temperature the $\chi_M T$ value is 0.41 cm^3 mol^{-1} K; at lower temperatures, $\chi_M T$ gradually increases up to 0.47 at 5 K. This is described in detail below.

The spin Hamiltonian appropriate to describe the magnetic properties of **1**–**4** is

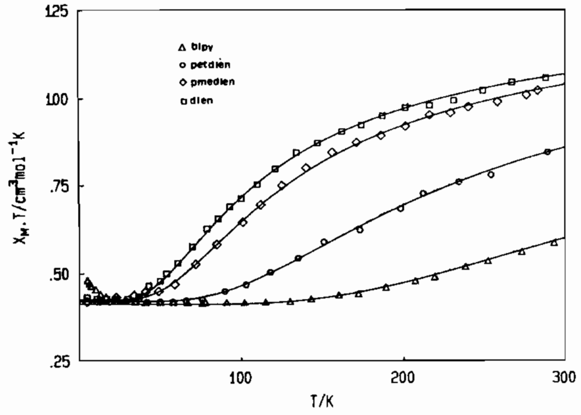


Fig. 1. Temperature dependence of $\chi_M T$.

$$\mathcal{H} = -J(S_1S_2 + S_2S_3) - jS_1S_3 + \beta gSH$$

where J and j denote the exchange parameters between the nearest-neighbor and terminal copper(II) ions, respectively. g denotes the average g factor for the three Cu(II) ions. In a first approximation, taking into account the structure of the mononuclear Cu(II) central complex [17], we can neglect the j parameter ($j = 0$) supposing a quasi-linear structure. Other studies about trinuclear Cu(II) complexes [14, 23] found this j factor to have a negligible effect on the magnetic properties. With this approximation the low-lying states are a spin doublet taken as energy origin, a second spin doublet located at $-J$ and a spin quartet at $-3J/2$. The expression of the magnetic susceptibility is then

$$\chi_M = \frac{N\beta^2g^2}{3kT} \times \frac{1.5 + 1.5\exp(J/kT) + 15\exp(3J/2kT)}{2 + 2\exp(J/kT) + 4\exp(3J/2kT)}$$

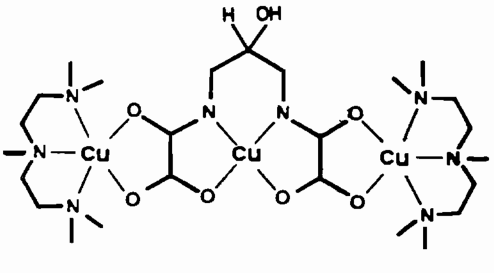
An excellent agreement between calculated and experimental data was obtained by making $j = 0$. The parameters were found to be

Complex **1**: $J = -93.2$ cm^{-1} $g = 2.12$
Complex **2**: $J = -111.6$ cm^{-1} $g = 2.13$
Complex **3**: $J = -196.0$ cm^{-1} $g = 2.12$
Complex **4**: $J = -358.0$ cm^{-1} $g = 2.10$

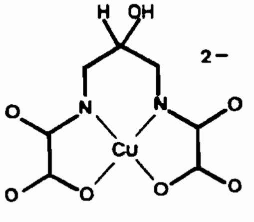
In the latter case the fitting was made only up to 20 K. In all cases the agreement factor defined as $\Sigma(\chi_M T_{calc} - \chi_M T_{obs})^2/\Sigma(\chi_M T_{obs})^2$ is less than 10^{-4}.

The X-band powder EPR spectra at room temperature confirm the average g values obtained by the fitting of susceptibility data. Effectively, the dien complex **1** exhibits a broad band with $g_{\parallel} = 2.11$ and $g_{\perp} = 2.06$; for the pmedien complex **2** there is only a broad and symmetrical band centered at $g = 2.09$; for the petdien complex **3** g values are $g_{\parallel} = 2.12$ and $g_{\perp} = 2.04$ and, finally, for the bipy complex **4** the values of g are $g_{\parallel} = 2.12$ and $g_{\perp} = 2.04$.

These magnetic results agree with those reported by Kahn and coworkers for similar dinuclear oxalato and oxamato complexes [1, 2, 4, 5]. The bipy ligand creates the strongest coupling; petdien shows an intermediate coupling and dien or pmedien the lowest one. If we suppose that the most probable structure in our complexes is

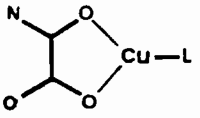


then we can define a monomeric fragment



[A-]

which will remain unchanged throughout the series, and two other monomeric fragments

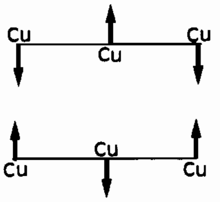


[-B]

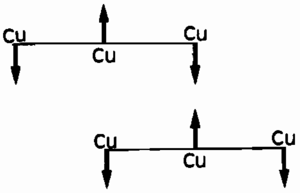
which may be modified by changing L. The two magnetic orbitals may be defined as the highest occupied molecular orbitals for the monomeric fragments [A–] and [–B] in their ground state [7]. In [A–] the copper(II) ion is in a quasi-planar surrounding [17] and the magnetic orbital is located in the molecular plane and points towards the nearest-neighbor O, N atoms [17]. As for the orientation of the magnetic orbital in [–B], it depends on the nature of L. More precisely, the copper(II) ion in [–B] will tend to adopt a 4 or 4 + 1 configuration. Taking into account the visible spectra and magnetic results, when L is a diamine, like bipy, the magnetic orbital is located in the plane of the oxamato bridge, and when L is a non-bulky triamine, like dien, it will be located in a plane perpendicular to the plane of the oxamato bridge. With pmedien the situation should be very similar. In this latter case, the environment of copper(II) ions may take some trigonal-bipyramid character and the magnetic orbital may acquire some d_{z^2} character with a non-zero spin density on the apical site [1, 11]. When L is the bulkiest triamine petdien, owing to the eventual steric hindrance, we can suppose that this presents a more pronounced trigonal-bipyramid character and the magnetic orbital will have a greater percentage of d_{z^2} character as in other reported complexes [1, 11].

We have the same situation described by Journaux *et al.* in the so-called tunable interaction [4] in some dinuclear complexes. In that work molecular structures have been solved so that magnetic orbitals may be visualized. The overlap between magnetic orbitals is very high with the bipy ligand, is lower with the petdien ligand and even lower with dien and pmedien ligands. Consequently, J_{AF}, which is the most important term in J value, follows the same order.

Finally, the anomalous behaviour of the bipy complex at low temperature may be due to packing effects. If the packing of the trinuclear entities is



the magnetic susceptibility would tend to zero at low temperature due to the global antiferromagnetic coupling between two or more entities. This is the case reported by Journaux *et al.* [14] in bis(*N*,*N'*-bis(3-aminopropyl)oxamido)tricopper(II) perchlorate. But if the packing was slipped as shown



total S, at very low temperature, has to be greater than 1/2, because the ground state has two electrons which tend to align in a parallel way. Although highly speculative, this could be an explanation for the anomalous behaviour of bipy complex.

Conclusions

Lacking in structural data, the variation of magnetic susceptibility measurements together with visible spectra of the trinuclear species, confirm the expected coordination and geometry of terminal Cu(II) ions. The geometries we propose are: Coordination 4 or 4 + 1 (square planar or square pyramid) in the bipy complex; the two magnetic orbitals indicated in the 'Discussion' will be coplanar and, consequently, the antiferromagnetic coupling should be very strong. Coordination 5 with triamine, being a square pyramid with the magnetic orbital perpendicular to the oxamato bridge in dien and pmedien species and a trigonal bipyramid with magnetic orbital centered in d_{z^2} orbital, in the petdien complex. This explains the low value of J for complexes **1** and **2** and the intermediate value of J for complex **3**.

Acknowledgements

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