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Magnetic Properties and EPR Spectra of Tetranuclear Copper(II) Complexes

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Abstract

The low-temperature EPR powder spectra of four tetrameric oxygen-bridged copper(II) complexes with ligands, (L), derived from pyridoxal and amino-alcohols, $(Cu_4L_4)\cdot xCH_3OH$, are reported. A comparison of the electron paramagnetic resonance study with the magnetic susceptibility measurements provides further informations on the magnetic properties of these compounds. The ferromagnetic nature of the resulting intramolecular exchange coupling into the Cu_4O_4 core is observed for the four complexes. For one peculiar tetramer the evolution of the EPR spectra by gradual loss of the solvent is presented, to show the importance of the solvent molecules and of the resulting hydrogen bond network to maintain the tetrameric structure.

Introduction

Copper(II) tetranuclear complexes are of particular interest to study the relationship between magnetic properties and molecular structure in multinuclear transition metal compounds. Cu(II) tetramers show different core type structures and in the present case we are interested in Cu_4O_4 cubane-like complexes. Such tetramers often contain bridging alkoxide oxygen atoms and different structural studies have been reported [1–11].

Recently we have synthesized copper(II) tetramers derived from iminoalcohols (L^n) which have the general stoichiometry $(Cu_4L_4^n)\cdot xCH_3OH$. The Schiff base ligand H_2L^n is derived from pyridoxal and different phenylethanolamines: 2-amino-1-phenylpropan-1-ol (L^1), 2-amino-1-(3′,4′-dichlorophenyl)ethanol (L^2), 2-amino-1-phenylethanol (L^3) and 2-amino-1-(4′-hydroxyphenyl)ethanol (L^4). X-ray studies and magnetic susceptibility measurements have been reported for compounds 1 (L^1, $x = 8$), 2 (L^2, $x = 9$) and 3 (L^3, $x = 9$) which gave a cubane-like conformation for the Cu_4O_4 core (Fig. 1) and a ferromagnetic ground state [12–15]. These copper tetrameric species are classified as type II complexes [4].

To obtain additional information about the magnetic properties of these compounds, electron spin resonance studies have been carried out. From the magnetic susceptibility measurements and the fitting procedures, some questions were not completely answered. For instance, it was not possible to determine the ground state within 2, which is definitively ferromagnetic in 1 and 3. For 4, the lack of a crystalline form prevented an analysis of the magnetic susceptibility measurements in terms of definite exchange interactions. Finally different magnetic behaviours observed between the crystalline form and the amorphous one, in some cases, were an additional reason to investigate these compounds with EPR spectroscopy.

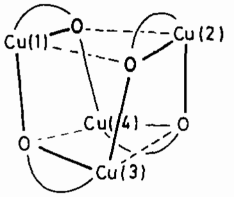

Fig. 1. Principal structure of the Cu_4O_4 core.

The preparation, characterization and magnetic susceptibility measurements are reported for the new copper(II) tetramer (4). The EPR spectra of these different compounds, 1–4, are compared and analysed in a qualitative way.

Experimental

Preparation of 4

The complex was prepared by the same procedure given for 1 and 2 [12, 14]. As amine component of the pyridoxal Schiff base, 2-amino-1-(4′-hydroxyphenyl)ethanol (L^4) was used.

Pyridoxal base prepared from pyridoxal hydrochloride (2.5 mmol) and sodium acetate (5.0 mmol) in methanol (100 cm^3) was reacted with L^4 hydrochloride (2.5 mmol). After adding copper acetate (2.5 mmol) the complex precipitated immediately. The resulting mixture was stirred vigorously until the copper salt dissolved. The powdered precipitate was filtered and washed with methanol. *Anal.* Calc. for $C_{16}H_{16}N_2O_4Cu$: C, 52.81; H, 4.43; N, 7.70; Cu, 17.46. Found: C, 52.39; H, 4.25; N, 7.65; Cu,

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16.82%. Because of the low solubility of 4 in all common solvents, a recrystallization was not possible. λ_{max} (powder reflectance spectra) = 645 nm.

Physical Measurements

The magnetic susceptibilities of 4 were recorded by the Faraday method at *ca.* 10 kG cm^{-1} using mercury tetra(thiocyanato)cobaltate(II) as a susceptibility standard. Experimental susceptibility data were corrected for underlying diamagnetism. To convert into S.I. units, χ/c.g.s.u. should be multiplied by $4\pi \times 10^{-6}$.

The X-band and Q-band EPR spectra were recorded on a Brucker ER 200 D spectrometer at 9.58 GHz or at 35.5 GHz microwave frequency. To prevent loss of the solvent from the polycrystalline forms, samples were kept in methanol.

Powder reflectance spectrum was obtained with a Cary 14 spectrophotometer at room temperature.

Results and Discussion

Magnetic Data

The magnetic susceptibilities of compound 4 in the temperature range from 4.2 to 298 K are shown in Table I. The temperature dependence of its magnetic moment is shown in Fig. 2. While the susceptibility increases steadily with decreasing temperature, the magnetic moment reaches a maximum at about 15 K and decreases at lower temperatures. These magnetic moments are higher than those of monomeric copper(II) complex ions and show a predominant ferromagnetic spin coupling. The lack of molecular structure determination for 4 does not allow the calculation of exchange parameters. However, the temperature dependences of the magnetic susceptibility and of the magnetic moment of 4 are comparable to those of the other three reported tetramers 1, 2 and 3.

TABLE I. Experimental Magnetic Susceptibilities of the Copper(II) Complex Derived from Pyridoxal and Octopamine (4)

T (K)	$10^6\chi$ (cm^3 mol^{-1})
4.2	134103
6.4	95043
10.6	61278
15.3	43221
19.0	34096
25.4	25138
30.6	20429
36.6	16459
42.0	14102
48.8	11998
65.7	8159
78.1	6921
89.6	5941
98.5	5200
112.5	4594
123.5	4084
139.9	3630
161.8	3146
181.8	2729
204.5	2426
215.9	2296
236.9	2110
260.6	1946
298.4	1748

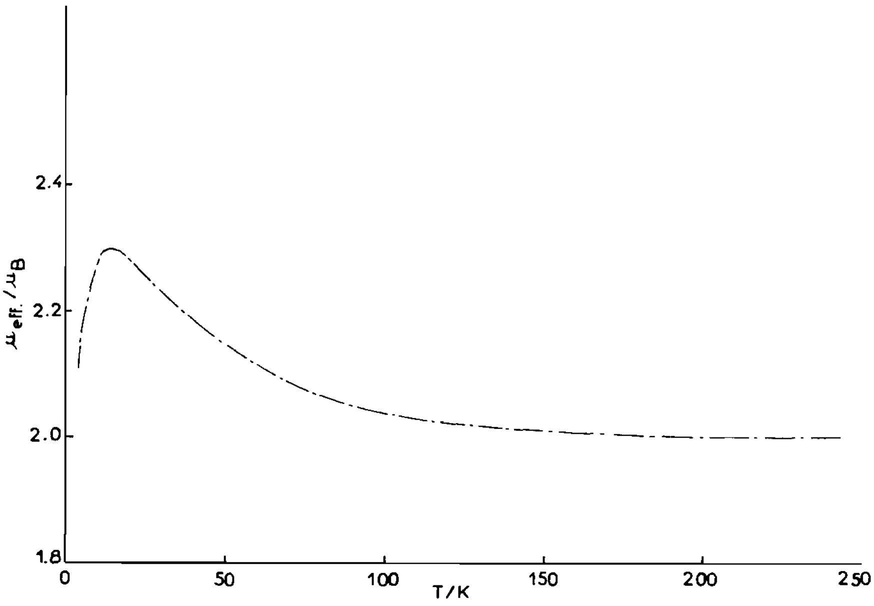

Fig. 2. Temperature dependence of the magnetic moments of $[Cu_4L^4_4]$ (4).

TABLE II. Magnetic Parameters Describing the Exchange Interactions in **1**, **2** and **3**

Compound	Formula	Real symmetry	Symmetry used for calculations	g	J_{12} (cm^{-1})	J_{13} (cm^{-1})	J_{34} (cm^{-1})	Reference
1	$Cu_4L^1_4 \cdot 8MeOH$	S_4	S_4	2.12(0.03)	0 (fixed)	17.1(5.0)		12
1′[a]	$Cu_4L^1_4 \cdot 8CH_3CH_2OH$	S_4	S_4	2.16(0.02)	0 (fixed)	17.4(2.0)		15
2	$Cu_4L^2_4 \cdot 9CH_3OH$	C_1	S_4	2.08(0.02)	−9.9(3.0)	20.5(3.0)		14
2	$Cu_4L^2_4 \cdot 9CH_3OH$	C_1	C_{2v}[b]	2.06(0.02)	−14.8(3.0)	24.9(3.0)	−14.8(3.0)	15
3	$Cu_4L^3_4 \cdot 9CH_3OH$	S_4	S_4	2.085(0.02)	−7.1(2.0)	28.5(2.0)		15

[a] A different solvent was used for the crystallization. [b] The distortion of the molecule is more realistically described in terms of C_{2v} symmetry than S_4 symmetry [15].

Table II lists the previously reported magnetic parameters describing the exchange interactions in **1**, **2** and **3**. Data for a second form of **1**, prepared with a different solvent, (**1′**), are also reported [15]. The reason for preparing a second form of **1** was that different solvents employed for crystallization can lead to different molecular structures. The substitution of the solvent molecules of crystallization (methanol → ethanol) does not change the crystallographic symmetry (**1** → **1′**) [12, 15].

The magnetic properties have been explained on the basis of the isotropic Heisenberg–Dirac–van Vleck model in which the effective Hamiltonian describing the various energy levels with different total spin S has the form (1), where J_{ij} is the exchange integral between the magnetic centers i and j:

$$\mathcal{H} = -2 \sum_{i<j} J_{ij} S_i S_j \qquad (1)$$

Molecular C_1 symmetry implies an effective Hamiltonian with six exchange constants ($J_{12}, \ldots, J_{16}$) but the highest possible molecular symmetry within the Cu_4O_4 core, (S_4), reduces them to two (J_{12}, J_{13}). Compound 2 was the only one not having S_4 symmetry. Calculations were first made with an S_4 symmetry [14]. But structural and magnetic data comparisons between 2 and 3 show that the distortion of molecule 2 could be more realistically described in terms of C_{2v} symmetry which leads to three spin coupling constants (J_{12}, J_{13}, J_{34}) as presented in Table II.

The magnetic order in the ground states has been found from the interpretation of the exchange parameters with the isotropic HDvV model. While **1**, **1′** and 3 definitively have a ferromagnetic ground state, it was not possible to determine whether the spin coupling within 2 is ferromagnetic or antiferromagnetic in the ground state [14]. The EPR studies will help to answer this question.

The susceptibilities and magnetic moments of the amorphous form derived from the crystalline one by loss of solvent molecules of crystallization, have been reported for **1** and **2**. The amorphous form of **1**, $[(CuL^1)_m]$ shows a very weak antiferromagnetic coupling [12]. In contrast, $[(CuL^2)_m]$ does not vary significantly in magnetic properties from its crystalline form [14]. The amorphous form of 3 presents similar magnetic properties to its crystalline form [15].

Thus comparing the magnetic data of **1**, **2** and **3** with those of **4**, shows a comparable magnetic behaviour between the powdered compound **4** and the crystalline or amorphous forms of **2** and **3**. Further conclusions will be provided by the EPR studies.

EPR Studies

There have been few reports on EPR spectra for tetrameric copper(II) complexes which contain μ_4-bridging oxygen atoms in a Cu_4O_4 core [16, 17]. Spectra reproductions failed in other work [18–20]. Recently EPR data have been reported for tetranuclear copper(II) derivatives with different core structures [21].

Some theoretical approaches have been developed for interpreting the fine-structure EPR spectra for $S = 2$ systems [22–24] or for exchange-coupled clusters of paramagnetic ions [24]. Applications of these methods for simulation and interpretation of the EPR powder or single crystal spectra, have until now failed to give convincing explanations of the spectral features for these tetrameric oxygen-bridged copper(II) complexes of the cubane type.

Magnetic investigations have also been made on a different class of tetranuclear copper(II) complexes which have the general stoichiometry $[Cu_4OX_{10-n}L_n]^{n-4}$ where X is a chloride or a bromide ion and L represents a Lewis base ligand. These complexes contain both μ_4-bridging oxygens and μ-bridging halogens between the copper ions [25–32]. The first detailed EPR studies in this series of tetrameric copper compounds were reported by Black and coworkers [31]. It was the first electron paramagnetic resonance study of single crystals for a cubic copper tetramer and the first one in which the cubic zero-field splitting of an $S = 2$ manifold had been measured. The studied complex, $Cu_4OCl_6L_4$ (L = triphenylphosphine oxide) was an example of particular interest since it presents an overall cubic symmetry. The four identical magnetic ions lie at the corners of a regular tetrahedron which leads to the simplest case to construct a model for fitting procedures. Such symmetries are not encountered for μ_4-oxygen bridged copper(II) tetramers, the highest possible one being S_4 and that undoubtedly explains the difficulty in obtaining a fine analysis of observed EPR spectra with fitting procedures for these compounds and the lack of reports in this field.

In the absence of a satisfying model to compute experimental data, a qualitative observation of EPR spectra can provide interesting and complementary informations on the magnetic behaviour of these compounds. The EPR spectra of **1**–**3** recorded at 100 K are shown in Fig. 3 for X-band and in Fig. 4 for Q-band. X-band EPR spectra of **1**–**4** at 4.2 K are compared in Fig. 5.

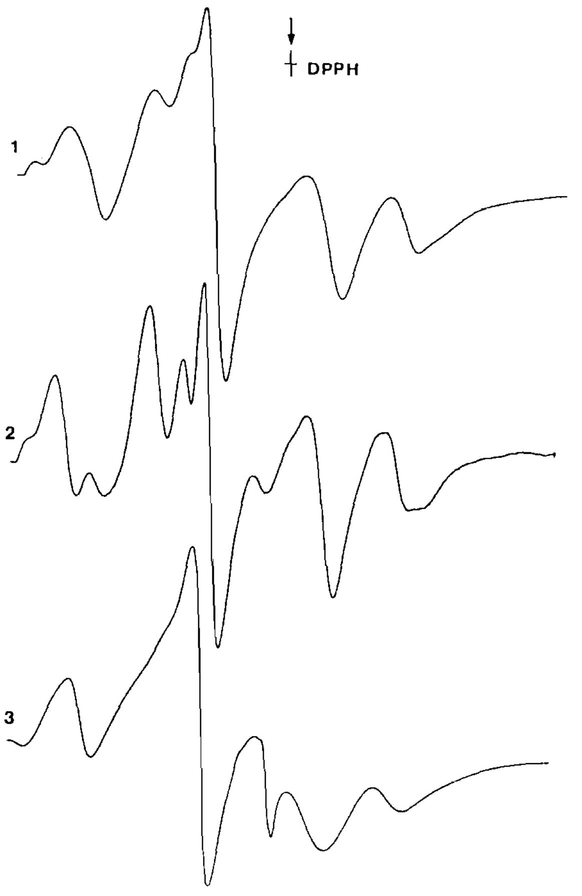

Fig. 3. X-band EPR spectra of **1** ($[Cu_4L^1_4]\cdot 8CH_3OH$); **2** ($[Cu_4L^2_4]\cdot 9CH_3OH$) and **3** ($[Cu_4L^3_4]\cdot 9CH_3OH$) at 100 K.

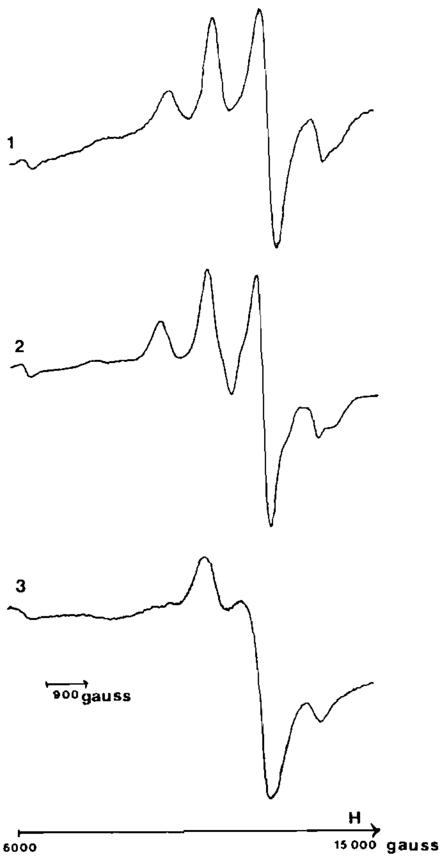

Fig. 4. Q-band EPR spectra of **1**–**3** at 100 K.

The spectra exhibit several EPR signals with different intensities and linewidths. First of all, signals in the 3200–3400 G range arise from transitions in the doublet state ($S = 1/2$) which corresponds to the percent of monomeric impurity (PMI) of copper(II) ions. Their intensities vary together with the sample and with the percent of the impurity connected with the possibility or not to recrystallize the compound. For instance, it was impossible to recrystallize compound **4** and the higher intensity of the corresponding signal indicates a stronger PMI.

A noteworthy feature of these EPR studies is the temperature dependence of the line intensities which globally increase by a hundred factor from 100 to 4.2 K. This confirms that the ground state manifold is paramagnetic and that the intracluster exchange couplings show a predominant ferromagnetic interaction. These observations are in agreement with the calculated exchange integrals of the complexes by using the magnetic susceptibility data and the isotropic HDvV model.

Starting from the X-band spectra recorded at 100 K, the most visible differences between the compounds appear for the 1500–3000 G range lines. Three distinct signals are observed for **2**, while they

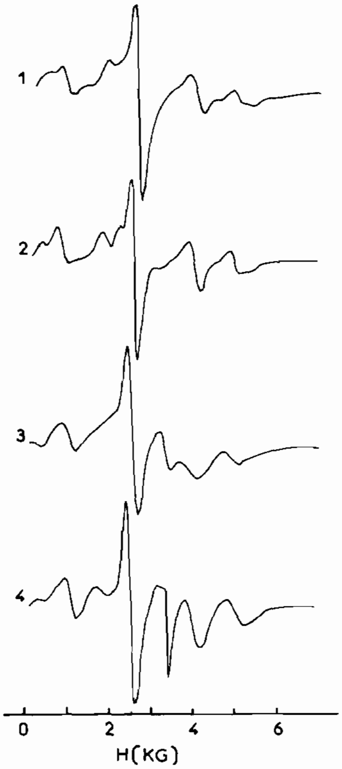

Fig. 5. X-band EPR spectra of **1**–**4** at 4.2 K.

are not so obvious for the other compounds. The Q-band spectra confirm the presence of these three lines for each tetramer in this range. At 4.2 K some new shoulderings appear on the signals of lower intensity. The three signals in the 1500–3000 G range are not affected in the same way by decreasing the temperature. For two of these three apparent lines (~1700, ~2000 G), the intensity decreases while for the third one no significant change is observed. The relative intensities of the other lines remain similar in comparison with the spectra recorded at 100 K. The change in the line intensities could be correlated with a modification of the quintet and triplet state populations with the temperature change. These observations certainly confirm that the sum of the EPR signals arise from the superimposition of EPR transitions within the excited spin states and the ground spin state ($S' = 2, 1, 0$).

The observation and comparison of these spectra allow us to draw some interesting conclusions. First these EPR studies show a similar behaviour for the new reported compound **4**, compared to those of **1**–**3** and definitively confirm its tetrameric structure. The increase in signal intensities on going from 100 to 4.2 K is consistent with a paramagnetic ground-state manifold and a predominance of the ferromagnetic intracluster combination of ferromagnetic and antiferromagnetic exchange coupling in such tetramers.

Magnetic susceptibility measurements did not allow to define the ground spin state for **2**. Considering the increasing of the line intensities with decreasing the temperature, a quintet ground state ($S' = 2$) can be proposed for **2** and not a singlet ground state ($S' = 0$), otherwise the signals would decrease in intensity.

Differences in the susceptibilities and magnetic moments of the amorphous form derived from the crystalline one by loss of solvent molecules of crystallization have been observed for **1**. EPR measurements have been used to study the role of the solvent molecules on the stability of the tetrameric structure and on the resulting magnetic interactions. Starting from micro-crystals of **1** kept in methanol, the solvent was then allowed to evaporate slowly. Figure 6 shows the variation of the EPR spectra together with the progressive loss of the solvent molecules from the poly-crystalline sample (1a) to the amorphous form (1d). The spectrum (1d) clearly shows the typical four signals of an isolated copper(II) ion and confirms the correct attribution of the signal observed at

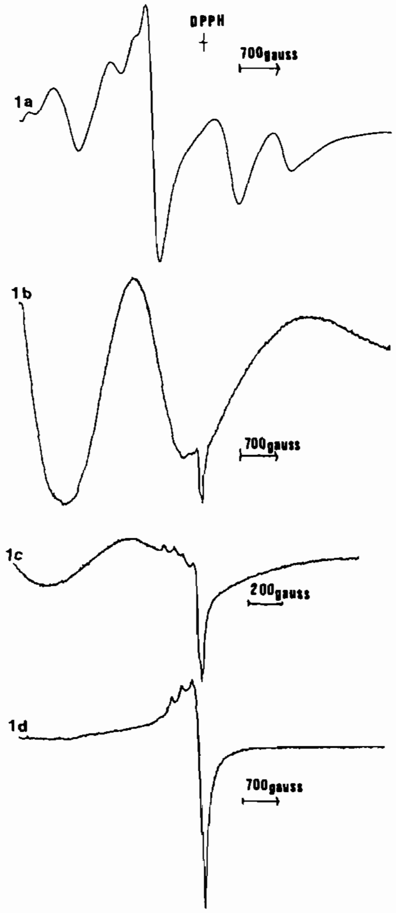

Fig. 6. Evolution of the X-band EPR spectra of $[Cu_4L^1{}_4] \cdot 8CH_3OH$ (**1**) at 100 K by gradual loss of the solvent molecules of crystallization (1a → 1d).

3200–3400 G to a transition in the doublet state in the previously analyzed spectra. The progressive evolution of the ESR spectra by loss of the solvent unambiguously demonstrates the absolute necessity of solvent molecules to maintain the tetrameric molecular structure of **1**. The stabilization of the crystal structures of compound **1** as well as **2** and **3** is dependent on a dense hydrogen-bond network. The three compounds easily lose their solvent of crystallization and decay to amorphous powders. But only **1** has the peculiarity to be unable to preserve a tetrameric form when it turns amorphous. This could be connected to the steric hindrance of the methyl group only present in L^1 which would prevent a tetrameric form in the absence of hydrogen-bond bridges.

Conclusions

To get a further description of the exchange interaction in these small clusters, supplementary EPR experimental data would be necessary, such as studies on single crystals or more detailed studies on the temperature-dependence of the signal intensities. Such measurements have demonstrated their undeniable contribution in explaining the magnetic properties of cubane-like complexes of metal ions [31, 33]. EPR measurements below 4.2 K would be also a test for examining the validity of the model used to interpret the magnetic susceptibility data for these Cu_4O_4-cubane like tetramers [31] and to verify whether the ground spin state is definitively ferromagnetic at a very low temperature for these four compounds [32]. For such investigations, the development of satisfying computational methods for EPR powder or single crystal spectra taking into account the lower symmetries of the Cu_4O_4 cubane-like complexes, such as considered in this present work, are absolutely necessary.

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