Inorganica Chimica Acta, 154 (1988) 31–34

Evidence for a Ferromagnetic Ground State in a Polynuclear Copper(II) Complex Involving CuN_2O Chromophores

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(Received April 1, 1988)

Abstract

The Schiff base resulting from the condensation of pyrrole-2-carboxaldehyde and 2-aminoethanol has been used to prepare a copper(II) complex. The complex has been characterized by chemical analysis and infrared spectroscopy. Analysis of its magnetic properties (susceptibility and ESR spectrum) points to the occurrence of a predominant ferromagnetic interaction resulting in a ferromagnetic ground state. This behaviour would be consistent with a tetranuclear structure.

Introduction

Considerable interest has been given to the Schiff bases L_1H_2 (Fig. 1) deriving from aminoalcohols and offering an NO_2 environment to a metal ion.

Under carefully controlled conditions, these aminoalcohols react with copper and nickel(II) ions to yield either mononuclear or polynuclear complexes, depending on their deprotonation state [1–4]. Furthermore, it is generally accepted that the nuclearity of the resulting complexes is also dependent on the length of the $-N-(CH_2)_n-O-$chain, since dinuclear species are obtained when $n = 2$ whereas a longer chain ($n = 3$) favours the formation of tetranuclear complexes of the cubane type [5–8]. Seemingly, this is also the case for the complexes involving aminoalcohols as ligands [9–17]. However, in a recent paper [18] we have shown that this rationale is no longer valid in the case of the Schiff base L_2H_2 (Fig. 1) with an N_2O donor set. Despite the presence of a short $-N-(CH_2)_2-O-$chain, this ligand reacts with copper ions to afford a dinuclear complex which is characterized by a rather low antiferromagnetic interaction ($-J = 23$ cm^{-1}). This result prompted us to investigate the coordination chemistry of a novel Schiff base, L_3H_2, displaying an N_2O donor set and a short $-N-(CH_2)_2-O-$chain but prepared from pyrrolecarboxaldehyde. From previous works, the homologous ligand L_4H_2, which involves a triethylene chain, is known [19] to yield a dinuclear complex with a very low value (0.5 BM) for the magnetic moment at room temperature.

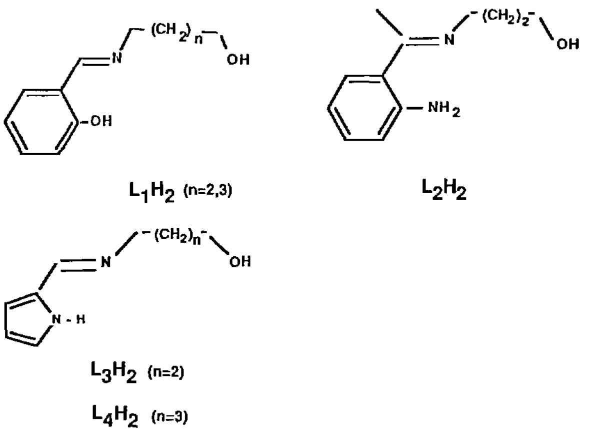

Fig. 1. Examples of tridentate Schiff bases.

Experimental

Preparation

The synthesis of the ligand L_3H_2 was carried out in a Dean and Stark apparatus. A mixture of pyrrolecarboxaldehyde (0.03 mmol) and ethanolamine (0.03 mol) in benzene (100 ml) was kept boiling for 2 h. The solvent was then removed under reduced pressure to yield a brown powder. Recrystallization of this crude product from toluene afforded orange needles. *Anal.* Calc. for $C_7H_{10}N_2O$: C, 41.7; H, 5.9; N, 20.5. Found: C, 41.4; H, 6.0; N, 20.4%.

To prepare the copper complex, a mixture of $Cu(ClO_4)_2$, $6H_2O$ (5×10^{-3} mol) and 2,2-dimethoxypropane (5×10^{-2} mol, excess) dissolved in 20 ml of methanol was slowly added to a methanolic solution of L_3H_2 (5×10^{-3} mol) and triethylamine (5×10^{-3} mol). The mixture was stirred at room temperature for 2 h whereupon the green precipitate which had formed was filtered off, washed with methanol and

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0020-1693/88/$3.50

dried. *Anal.* Calc. for [$CuC_7H_8N_2O$]: C, 42.1; H, 4.0; N, 14.0; Cu, 31.8. Found: C, 41.9; H, 4.1; N, 13.8; Cu, 32.0%. Despite many attempts no crystal suitable for a structural study has yet been obtained.

Physical Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker WH 90 spectrometer using $CDCl_3$ as internal standard. IR spectra were run on a Perkin-Elmer model 984 spectrometer with KBr disks.

Magnetic susceptibility data were collected on powdered samples with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. Mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C: 16.4×10^{-6} cgsu) was used as a susceptibility standard. All data were corrected for diamagnetism (estimated [21] at -56.5×10^{-6} cgsu) and TIP (taken as 60×10^{-6} cgsu/copper atom). EPR spectra were recorded at X-band frequencies (9.4–9.6 GHz) with a Bruker 200 TT spectrometer.

Results and Discussion

In addition to analytical results, ^1H and ^{13}C NMR parameters afford an unambiguous characterization of L_3H_2. The most significant ^{13}C signals are observed at 154.2 ppm (C=N), 62.7 and 61.9 ppm (CH_2 of the diethylene chain) whereas the signals of the pyrrole moiety are located at 109.5, 116.2, 122.5 and 129.2 ppm. Imine formation is also supported by the presence of a characteristic signal at 7.83 ppm (HC=N) in the ^1H spectrum and by the IR data (Table I).

According to analytical data, the copper complex is represented by a simple formula involving one molecule of ligand per metal atom. In the absence of any counterion, charge balance and coordination number considerations strongly suggest that the ligand is actually twice deprotonated and the complex oligomeric. Oligomerization likely occurs through alkoxo-bridges as for copper complexes of L_1H_2, L_2H_2, L_3H_2... These points are borne out by the physical characteristics of the complex.

TABLE I. Relevant IR Data[a]

L_3H_2	$(L_3Cu)_n$	
3400(m)		O–H stretching
3260(s)		N–H stretching
3109(w)	3092(w)	C–H stretching (pyrrole)
2915(m)	2910(m)	
2839(w)	2900(w)	C–H stretching (CH_2)
2749(w)	2840(w)	
1639(vs)	1600(vs)	C=N stretching
1457(m)		C–H out of plane (pyrrole)
1439(m)		
1414(m)		
1366(m)		O–H deformation (alcohol)
1075(s)	1095(s)	N–C deformation
1042(s)	1040(s)	C–O deformation

[a] s, strong; vs, very strong; m, medium; w, weak.

The relevant infrared absorptions are quoted in Table I. Significantly, the ν(OH), ν(NH) and δ(OH) absorptions which appear in the spectrum of the free ligand at 3400, 3263 and 1340 cm^{-1}, respectively, are no longer observed in the spectrum of the complex. The bands characteristic of the perchlorate ion, expected at *ca.* 1100 and 600 cm^{-1}, are merely absent.

The hypothesis of a polynuclear structure is supported by the magnetic behaviour of the complex since neither the thermal variation of the static susceptibility nor the ESR spectrum can be explained in terms of isolated mononuclear species.

The thermal variation of the effective moment μ per copper atom is represented in Fig. 2. Cooling down the sample causes the moment to increase gradually from 1.89 BM at 277 K to a maximum of 2.42 BM at 8 K. Further cooling results in a slight decrease. The graph $\chi_M^{-1} = f(T)$ is linear in this range and shows an intercept at 6.4 K. Obviously, this behaviour cannot be ascribed to a mononuclear complex but must be considered as indicative of an overall ferromagnetic interaction in a polynuclear species. Due to the lack of structural data, the choice of a suitable model is not straightforward. However, an analysis of the literature data related to μ-oxo copper complexes points to two possibilities, *viz.* a dinuclear structure or a tetranuclear cubane-like structure with a Cu_4O_4 core. As a matter of fact, attempts to describe the magnetic behaviour in terms of a dinuclear formulation via the Bleaney and Bower [22] expression have been unsuccessful.

For a tetranuclear entity with C_1 molecular symmetry, six exchange integrals (J_{12}...J_{16}) are involved

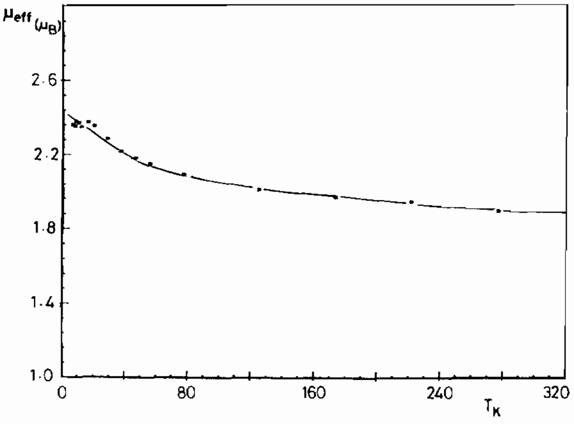

Fig. 2. Magnetic behaviour of $(L_3Cu)_n$.

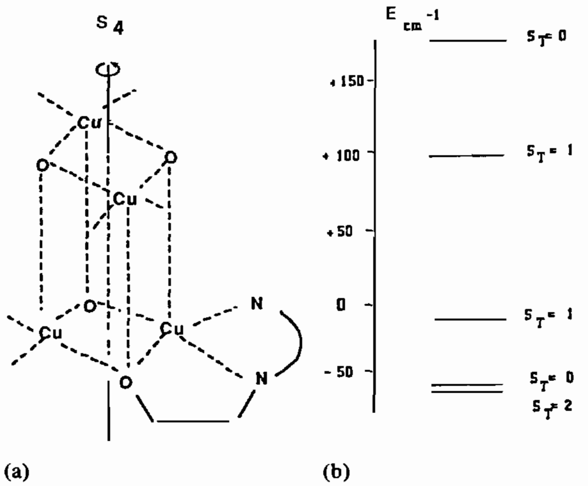

Fig. 3. (a) Schematic structure of the Cu_4O_4 core. (b) Schematic energy splitting diagram for $(L_3Cu)_4$.

in the theoretical expression of the susceptibility. To avoid overparametrization, we assume that the symmetry is S_4 so that the number of coupling constants involved in the calculation is restricted to two (J_{12} and J_{13}) [23–25]. In this idealized geometry (Fig. 3), the susceptibility is given by the expression

$$X = \frac{Ng^2\beta^2}{4kT}\,\frac{10e^{2u} + 2e^{-2u} + 4e^{-2v}}{5e^{2u} + 3e^{-2u} + e^{-4v}}$$

where $u = J_{13}/kT$ and $v = J_{12}/kT$. Terms corresponding to temperature-independent paramagnetism ($N\alpha = 60 \times 10^{-6}$ per copper atom) and, eventually, the contribution of a small amount (p) of a non-coupled impurity, have to be added.

In Fig. 2, the best-fitted curve ($g = 2.08(1)$, $J_{13} = 40.0 \pm 1.0$ cm^{-1}, $J_{12} = -19.5 \pm 1.0$ cm^{-1} and $p = 0$) is represented by a solid line and it can be seen that the agreement with the experimental data is good in the range 8–280 K.

Due to the difficulties in fitting theoretical susceptibility expression to experimental values in ferromagnetically coupled systems, this agreement does not afford a definitive evidence for the occurrence of a cubane-like structure with a Cu_4O_4 core as represented in Fig. 3.

Furthermore, the magnitude of the J values has to be considered with caution since other sets of values lead to scarcely lower agreement with experimental data. Very similar remarks have yet been done by other investigators [14, 26–28]. One way to solve this problem would be to assume a molecule symmetry lower than S_4 but doing so would leave us with the problems of overparametrization. Clearly, structural data are needed to analyze fully the magnetic behaviour of $(L_3Cu)_n$ but we can say that a ferromagnetic interaction is predominant. Interestingly, the simple assumption of a Cu_4O_4 core with S_4 symmetry does not allow a determination of the magnetic order in the ground state which, according to the J values, may be either ferromagnetic ($S_T = 2$) or antiferromagnetic ($S_T = 0$). This ambiguity can be relieved by a qualitative study of the ESR spectra. In the absence of a satisfactory model to simulate ESR spectra of tetranuclear complexes [29], no attempt has been made to perform a quantitative analysis. At 120 K as well as at 4 K, the spectrum of $(L_3Cu)_n$ displays a broad absorption centred at $g \sim 3.0$ and devoid of any structure. However, the intensity of this signal strongly increases on lowering the temperature so that a quintet ground state ($S_T = 2$) can be proposed. This is without doubt the most interesting result of the present study since, to our knowledge, this is the first example of a polynuclear complex involving CuN_2O chromophores and having a ferromagnetic ground state.

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