

Unusual Dinuclear Copper(II) and Nickel(II) Complexes of a Novel Schiff Base Deriving from 2-Aminoethanol

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Abstract

It is generally accepted that copper(II) complexes involving 2-aminoethanol or a Schiff base deriving from this aminoalcohol display a tetranuclear structure with a Cu_4O_4 'cubane' core. Using a Schiff base obtained by reacting 2'-aminoacetophenone with 2-aminoethanol, we have prepared copper(II) and nickel(II) complexes whose properties are fully consistent with a dinuclear structure. The copper complex is characterized by a low antiferromagnetic interaction.

Introduction

The alkoxo-bridged copper(II) complexes form a large class of polynuclear compounds. Many have been structurally and magnetically investigated [1]

and the variety of this class of complexes led to the possibility of correlating their magnetic properties with their structures. A particular attention has been paid to the di-, tetra- and polynuclear complexes of polydentate ligand such as aminoalcohols [2–6] and/or iminoalcohols [7–11]. Much more widely studied are the complexes deriving from ligands with an NO_2 donor set such as L_4 in Fig. 1 [12–20].

The present paper is devoted to the copper(II) and nickel(II) complexes of a new Schiff base (L in Fig. 1) resulting from the condensation of 2'-aminoacetophenone with 2-aminoethanol. The main interest of this ligand originates in its N_2O donor set which is rather uncommon since, to our knowledge, only two such species have been previously reported [21–23] (L_2 and L_3 in Fig. 1). However it may be recognized that L_1 differs from L_2 and L_3 in the extracyclic situation of the nitrogen atom and the length of the $-\text{N}-(\text{CH}_2)_n-\text{O}-$ Chain.

Experimental

Preparation

The synthesis of the ligand was carried out in a Dean and Stark apparatus. A mixture of 2'-aminoacetophenone (10^{-1} mol) and 2-aminoethanol (1.2 mol, excess) and ZnCl_2 (traces) in benzene (300 ml) was kept boiling for two hours. The solvent and the excess of aminoalcohol were removed under reduced pressure and a yellow oil was obtained.

The preparation of Ni and Cu complexes was performed directly from the crude ligand. In a typical procedure, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (10^{-2} mol) and 2,2-dimethoxypropane ($6 \cdot 10^{-2}$ mol) in CH_3OH (20 ml) were added to a methanolic solution (40 ml) of the ligand (1.5×10^{-2} mol, excess) and NEt_3 ($2 \cdot 10^{-2}$ mol). A light green precipitate appeared readily then gradually turned to yellow green. The crude product was filtered out and washed with ethanol.

Anal. Calc. for $[\text{NiC}_{10}\text{H}_{12}\text{N}_2\text{O}]_2(\text{CH}_3\text{OH})_2$: Ni, 22.0; C, 49.5; H, 6.0; N, 10.5. Found: Ni, 22.2; C, 49.6; H, 5.9; N, 10.8%. Calc. for $[\text{CuC}_{10}\text{H}_{12}\text{N}_2\text{O}]_2$: Cu, 26.6; C, 49.9; H, 6.6; N, 11.6. Found: Cu, 26.4; C, 49.5; H, 6.4; N, 11.2%.

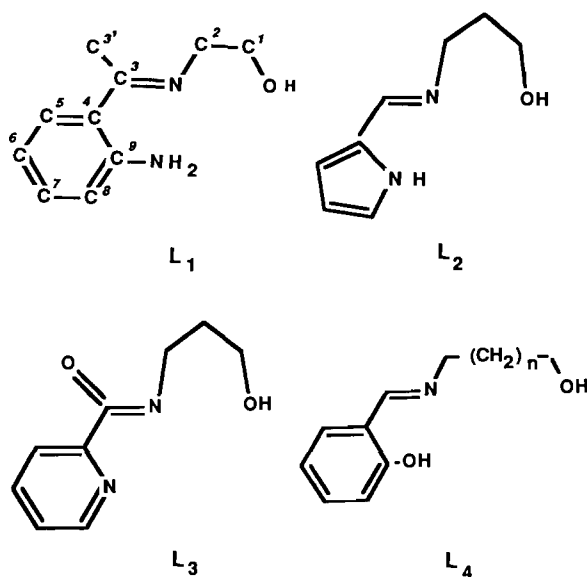


Fig. 1. Examples of tridentate Schiff bases.

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TABLE 1. Relevant IR Data^a

| Ligand | Ni complex | Cu complex | |
|-----------|------------|------------|---|
| 3420(s) | | | O-H and N-H stretching |
| 3320(s) | 3320(w) | 3320(w) | N-H stretching |
| 3040(w) | 3020(w) | 3000(w) | C-H (aromatic) stretching |
| 2910(w) | 2890(w) | 2900(w) | C-H stretching (CH ₂ and CH ₃ groups) |
| 2820(w) | 2840(w) | 2820(w) | |
| 1640(vs) | | | NH ₂ deformation |
| 1620(vs) | 1600(s) | 1600(s) | C=C (aromatic) stretching |
| 1580(vs) | 1560(s) | 1560(s) | C=N stretching |
| 1540(s) | 1520(s) | 1530(s) | |
| 1240(u.s) | 1260(s) | 1260(s) | C-N deformation |
| 1020(m) | 1060(m) | 1060(m) | C-O (alcohol) deformation |
| 750(s) | 730(s) | 730(s) | C-H out of plane (aromatic) deformations |

^avs = very strong, s = strong, m = medium, w = weak, b = broad.

Physical Measurements

Microanalyses and mass spectra were performed by the Service Central de Microanalyse du CNRS (Lyon). ¹³C NMR spectra of the ligand were run on a Bruker WH 90 instrument using CDCl₃ as internal reference. Chemical shifts are given in ppm *versus* TMS using CDCl₃ as solvent. IR spectra were recorded on a Perkin-Elmer model 984 spectrometer with KBr disks or with KBr pellets. Visible and UV spectra were measured on 1 × 10³ M methanolic solutions on a Cary 2300 instrument.

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: 16.44 × 10⁻⁶ cgsu) was used as a susceptibility standard. All data for copper complexes were corrected for diamagnetism [24] (estimated at -120.5 · 10⁻⁶ cgsu) and TIP (taken as 60 × 10⁻⁶ cgsu/copper atom).

Results and Discussion

In contrast with the rapid condensation of 2-aminoethanol with salicylaldehyde, the reaction with 2'-aminoacetophenone proceeds smoothly even when an excess of aminoalcohol and traces of ZnCl₂ are present in the reaction mixture. The ligand is recovered as a yellow oil and characterized by ¹³C NMR and IR. The most significant ¹³C signals are observed at 169.3 ppm (C=N) and 16.4 ppm (CH₃-CN) [25, 26]. The CH₂ groups of the ethylene chain give signals at 62.2 and 53.7 ppm whereas the signals of the aromatic carbons are located at 115.8 (C8), 116.6 (C6), 121.2 (C4), 128.9 (C5), 129.8 (C7) and 147.2 (C9) ppm. Imine formation is also supported by IR data (Table I).

The yellow oil is then reacted, without further

purification, with nickel acetate or copper perchlorate to afford the corresponding complexes. They are isolated as yellow green (Ni) and apple green (Cu) powders. Analytical data point to a simple formula involving one molecule of ligand per metal atom. From the absence of any counterion, charge balance and coordination number considerations lead to the conclusion that the ligand actually is twice deprotonated and the complexes polymeric through alcoxyl-bridges as it is the case for complexes of the L₄ [13-20] and L₃ [22] ligands. Structural determinations performed on the copper complex of L₂ have also pointed to a dinuclear structure with bridging oxygen [23]. These points are borne out by the physical properties of the complexes which are reported below.

The main infrared absorptions are reported in Table 1. Comparing the data characterizing both complexes with those related to the uncomplexed ligand yields convincing proofs of the ligand being twice deprotonated. Significantly the ν(OH) absorption at 3440 cm⁻¹ in the free ligand spectrum is no longer observed in the spectra of the complexes whereas the symmetric and antisymmetric ν(NH) (3420 and 3320 cm⁻¹, respectively) are replaced by a single band of medium intensity at 3320 cm⁻¹. The absence of counterion (acetate or perchlorate) is confirmed since none of their characteristic absorptions can be detected.

Very similar electronic spectra are displayed by both complexes with a d-d band at 600 nm (ε = 250) and 650 nm (ε = 200) for the nickel and copper complexes, respectively. These positions are consistent with a square-based geometry [27, 28]. However, one may notice that the d-d absorption for the copper complex is rather low in energy (15 400 cm⁻¹) suggesting that the geometry around the metal ion may be tetrahedrally distorted [29, 30].

TABLE II. Assignment of Major Fragments in the Mass Spectra^a of the Complexes [NiL]₂ and [CuL]₂^b

| <i>m/e</i> | [CuL] ₂ | | [NiL] ₂ | |
|------------|--|--------------------|--------------------------------------|--------------------|
| | Assignment | Relative intensity | Assignment | Relative intensity |
| 479 | [(Cu) ₂ + 1] ⁺ | 7.1 | | |
| 478 | [(CuL) ₂] ⁺ | 1.0 | | |
| 468 | | | [(NiL) ₂] ⁺ | 87.4 |
| 466 | | | [(NiL-H) ₂] ⁺ | 26.8 |
| 236 | | | [NiLH ₂] ⁺ | 100.0 |
| 235 | | | [NiLH] ⁺ | 18.8 |
| 234 | | | [NiL] ⁺ | 64.7 |
| 233 | | | [NiL-H] ⁺ | 9.8 |
| 232 | | | [NiL-2H] ⁺ | 8.3 |
| 181 | [(L + 2H) + 1] ⁺ | 3.1 | | |
| 180 | [L + 2H] ⁺ and [(L + H) + 1] ⁺ | 40.2 | [L + 2H] ⁺ | 1.4 |
| 179 | (L + 1) ⁺ and [L + H] ⁺ | 100.0 | [L + H] ⁺ | 4.9 |
| 178 | [L] ⁺ and [(L-H) + 1] ⁺ | 22.7 | [L] ⁺ | 8.7 |
| 177 | [L-H] ⁺ and [(L-2H) + 1] ⁺ | 23.1 | [L-H] ⁺ | 14.2 |
| 176 | [L-2H] ⁺ and [(L-3H) + 1] ⁺ | 3.4 | [L-2H] ⁺ | 18.5 |
| 175 | [L-3H] ⁺ | 15.4 | [L-3H] ⁺ | 15.5 |

^aObtained by electron ionization for the Ni complex and by desorption/chemical ionization (NH₃) for the Cu complex. ^bL = dideprotonated ligand.

TABLE III. Comparison of Observed and Calculated Isotope Patterns for the Fragments [(NiL)₂]⁺ + [(NiL-H)₂]⁺ and [NiL]⁺

| <i>m/e</i> | Relative intensity | |
|---|--------------------|-------------------------|
| | Observed | Calculated ^a |
| [(NiL) ₂] ⁺ + [(NiL-H) ₂] ⁺ | | |
| 476 | 1.1 | 1.4 |
| 475 | 1.2 | 1.2 |
| 474 | 5.7 | 5.9 |
| 473 | 5.4 | 5.1 |
| 472 | 21.5 | 20.8 |
| 471 | 16.0 | 16.2 |
| 470 | 59.1 | 59.6 |
| 468 | 87.4 | |
| 466 | 26.8 | |
| [NiL] ⁺ | | |
| 243 | | 0.1 |
| 242 | 1.1 | 1.3 |
| 241 | 0.7 | 0.7 |
| 240 | 5.4 | 6.0 |
| 239 | 6.0 | 6.0 |
| 238 | 34.0 | 34.5 |
| 237 | 15.8 | 16.1 |
| 236 | 10.0 | |
| 235 | 18.8 | |
| 234 | 64.7 | |
| 233 | 9.8 | |
| 232 | 8.3 | |

^aComputed from the relative abundances of the naturally occurring isotopes: ¹²C, 98.888%; ¹³C, 1.112%; ⁶³Cu, 69.1%; ⁶⁵Cu, 30.9%; ⁵⁸Ni, 67.77%; ⁶⁰Ni, 26.16%; ⁶²Ni, 3.66%; ⁶⁴Ni, 1.16%.

Due to low solubility and limited stability, molecular weight determinations are performed through mass spectroscopy. The data are reported in Table II and III. In both cases, molecular ions corresponding to dinuclear species are clearly observed but the overall spectral patterns differ according to the nature of the metal centres. It may be underlined that different ionization techniques are used, *i.e.* electron ionization for the nickel complex and, due to a lower stability, desorption/chemical ionization (NH₃) for the copper complex. In the former case, isotopic cluster patterns characteristic of di- and mononuclear species are observed with rather similar overall intensities. In addition, ions deriving from the ligand moiety are detected in the 180–175 a.m.u. area. For the copper complex, the overall intensity of the ions related to the ligand largely prevails over the intensity of the ions related to the dinuclear species while ions corresponding to the mononuclear species are merely absent.

The hypothesis of a dinuclear structure is further supported by magnetic data in the case of the copper complex. The results obtained for the copper complex are represented in Fig. 2 in the form of χ_{corr} versus *T*. Decreasing the temperature causes the susceptibility first to increase. It passes through a maximum at *ca.* 40 K and then decreases. This behaviour is typical of an antiferromagnetically coupled system. At low temperature, the presence of a Curie tail may be ascribed to a mononuclear impurity. Interestingly, the χ values can be fitted to the Bleaney–Bower [31] expression for isotropic exchange in a copper(II) dimer including corrections for a small amount (*p*) of paramagnetic species and

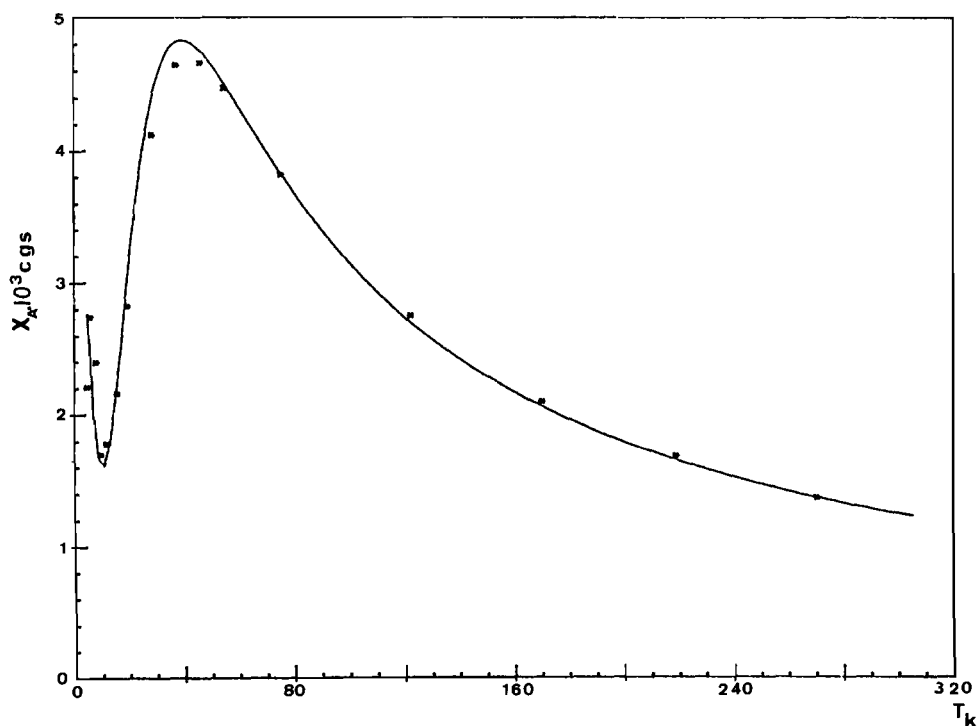


Fig. 2. Magnetic behaviour of $[L_1Cu]_2$.

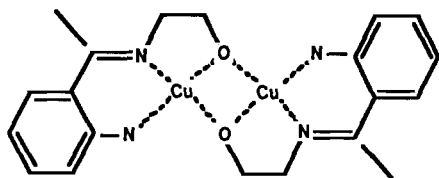


Fig. 3. Proposed structure for the complex $(L_1Cu)_2$.

temperature-independent paramagnetism ($N\alpha = 60 \times 10^{-6}$ cgsu per copper atom). In Fig. 2, the best-fitted curve (with $p = 3\%$, $g = 2.003$, $J = -23$) is represented by a solid line and it can be seen that the fit to experimental data is very good in the whole range of temperatures. Therefore, the temperature variation of the magnetic susceptibility is entirely consistent with the mass spectra to indicate a dinuclear structure in which the metal ions are bridged by two oxygen atoms (Fig. 3). In this instance, the present copper complex has to be compared with the complexes derived from the L_2 and L_3 ligands (Fig. 1). Common features of the three species are the presence of a Cu_2O_2 ring and N_2O_2 environments for the copper ions. However, as previously noted, a striking difference between the L_1 complex on the one hand and the L_2 and L_3 complexes on the other hand originates in the size of the $Cu-O-(CH_2)_n-N$ chelating ring and in the nature of the nitrogen atoms occurring in the donor sets. Moreover, tridentate Schiff base ligands result-

ing from the condensation of aminoethanol with a keto precursor such as salicylaldehyde (L_4 with $n = 2$) lead either to mononuclear ($CuLX$) paramagnetic species or to polynuclear ferromagnetic species [17, 18]. Tetranuclear complexes also are obtained when a copper halogenide or pseudohalogenide is reacted with aminoethanol; these complexes display an overall ferromagnetic behaviour [3]. The dicopper complexes of L_2 and L_3 are characterized by strong antiferromagnetic interaction with singlet-triplet separation of 560 and 555 cm^{-1} , respectively [17-20] whereas both antiferromagnetic and ferromagnetic interactions are observed for the tetranuclear complexes. Obviously, an antiferromagnetic behaviour is not unexpected for the present complex owing to its dinuclear structure. The problem at hand is to explain why a dinuclear structure is observed in spite of the presence of a short $-N-(CH_2)_n-O-$ chain and why the resulting $|J|$ value is low with respect to the values generally observed for dinuclear complexes with a Cu_2O_2 core. The lack of structural determination prevents any firm conclusion to be drawn. However, concerning the reduction of the antiferromagnetic interaction, some possible causes are suggested by considering the reported magnetostructural relationship [32-34]. These causes may be related either to the influence of the geometry within the Cu_2O_2 network ($O-Cu-O$ angle, $O-Cu$ bond lengths, dihedral angle between the two O , Cu , O planes...) or to the effect of coordination

geometry. It is noteworthy that some degree of tetrahedral distortion of the coordination planes would be consistent with the electronic spectrum. However, it is generally accepted that the tetrahedral deformation related to the shorter $-N-(CH_2)_2-O-$ chains is accompanied by a rehybridization of the bridging oxygens and association between dinuclear units to yield tetranuclear species with a Cu_4O_4 'cubane' core. Seemingly, this is not the case for the present complex which therefore may be considered as the first example of a dinuclear complex involving a short diethylene bridge.

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