A Unique Heterotopic Ligand for Sequential Synthesis of Polymetallic Complexes

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A new organic ligand bearing four coordination sites that may be metallated in a stepwise manner is described, together with its Cu^{II} and Fe^{II} derivatives. This may be considered as the first ligand precursor for trimetallic systems.

Introduction

The design of new coordination complexes that play the role of ligands in the elaboration of polymetallic complexes is one of the challenging issues in the domain of modern inorganic chemistry.[1] The preparation of such complexes using a "step-by-step" approach is a prerequisite to building molecular extended systems with new architectures or even discrete molecules containing an increasing number of metallic centres with predetermined physical properties.[2−13]

Oxamato ligands have been extensively used to generate families of polymetallic compounds according to a sequential strategy.[2−7] However, the pitfall of this generation of oxamato complexes was the isolation of only heterobimetallic complexes. In order to overcome this drawback, it seems evident that the ligand must embody predetermined instructions that will, under the supervision of the chemist, lead toward the desired edifice. Recently, Chaudhuri et al. described a well-founded route leading to the formation of discrete heterotrimetallic complexes in a stepwise fashion.[14] Thus, in comparison to the chemistry described for instance with $[Cu(opba)]^{2-}$ [opba = *o*-phenylenebis(oxamato)],[2,3] an additional chelating anchor in the initial building block should consequently allow us to synthesize molecules of higher nuclearity and dimensional arrays.

In this communication, we describe the synthesis of an organic ligand that contains three different types of coordination sites. The chemical difference in the binding nature of the three coordination sites of the ligand renders the metalation process selective, allowing stepwise reactions that may lead to novel higher nuclearity trimetallic systems, be it discrete or extended in nature. Herein we report the preparation and the crystal structure of the first coordination complex $[\mathbf{L}Cu]^{2-}$ where $H_4\mathbf{L}$ stands for *N*,*N*′-(dipyrido[3,2-*a*:2′,3′-*c*]phenazine-11,12-diyl)bis(oxamic acid). The versatility of this ligand **L** towards selective metalation is also shown with the characterisation of the $[Fe(\mathbf{L_1})_3]^{2+}$ complex together with the tetranuclear $[Fe(\mathbf{L}Cu)_3]^{4-}$ adduct.

The synthesis of the heterotopic ligand follows the condensation of *o*-diones with aromatic *o*-diamines as shown in Scheme 1.[15] The ethyl ester derivative, noted $\mathbf{L_1}$, was isolated quantitatively as a yellow powder by condensation of equimolar amounts of **1**[16] and 1,10-phenanthroline-5,6-dione[17] in refluxing methanol.

Selective metalation of the bis(oxamato) cavity with a copper(II) ion was carried out in basic medium by slow addition of a copper(II) salt in solution, and the corresponding phosphonium salt was obtained by metathesis. Insertion of a copper ion in the bis(oxamato) cavity was evidenced by a red shift of about 50 cm^{-1} for the C=O stretching. Crystallisation in a mixture of acetonitrile and water gave red tablets that were analysed by X-ray diffraction. The structure of $[\mathbf{L}Cu](PPh_4)_2 \cdot 0.5CH_3CN$ consists of the dianionic copper(II) complex, tetraphenylphosphonium cations, and acetonitrile molecules of crystallisation. As shown in Figure 1, a perspective side view of the dianion complex $\mathbf{L}Cu^{2-}$ indicates an almost planar structure of the ligand skeleton with maximum deviation from the mean molecular plane of 0.317(3) Å for atom O(17).

The copper atom sits in a planar-trapezoidal N_2O_2 coordination environment. The average bond lengths between

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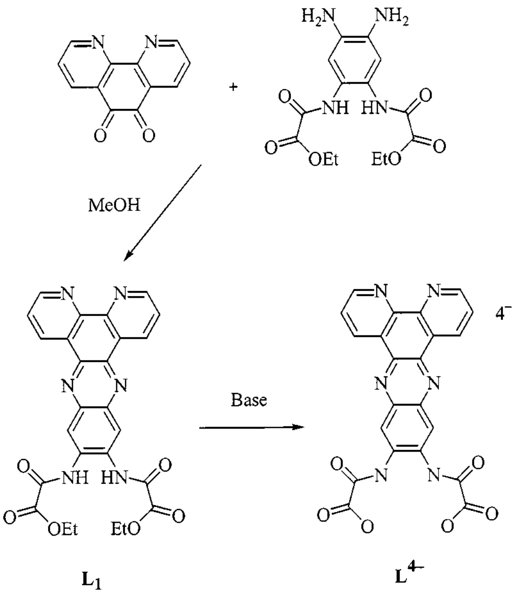
1434−1948/02/0202−0323 $ 17.50+.50/0



Scheme 1

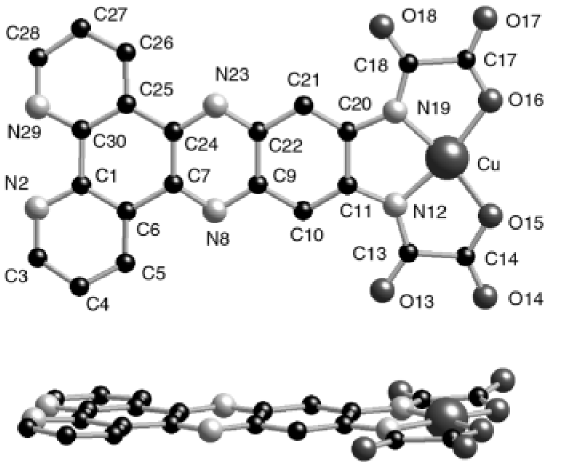


Figure 1. Different views of $[\mathbf{L}Cu]^{2-}$ with the atom numbering scheme (H atoms have been omitted)

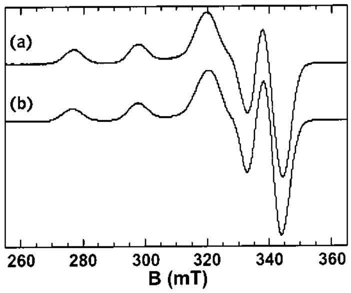


Figure 2. Solid-state EPR spectra (100 K) of $[\mathbf{L}Cu](PPh_4)_2{\cdot}0.5CH_3CN$: (a) experimental; (b) simulated

the copper and the two deprotonated nitrogen atoms of the amide functions and the two oxygen atoms from the carboxylate groups are 1.898 and 1.936 Å, respectively. Comparatively, these bond lengths are in agreement with those found for similar environments of copper(II).[18] To the best of our knowledge, this is the first X-ray structure whereby a phenanthroline-carrying ligand is not involved in the coordination sphere of the metal ion. The solid-state EPR spectrum (100 K) of this copper complex, shown in Figure 2, is characteristic of a copper(II) ion in a square-planar geometry. The best agreement between the experimental solid-state spectrum and the simulated one was obtained for the following parameters: $A_{\perp} = 33.275$ G, $A_{\|} = 214.587$ G, $g_{\perp} = 2.040$, and $g_{\|} = 2.191$.

Benefiting from the high affinity constant of the iron(II) ion for phenanthroline to form the tris(phenanthroline) complex ($K_c = 10^{21}$),[19] we set out to metallate the phenanthroline end of the $\mathbf{L_1}$ ligand. The ^{1}H NMR spectrum of the $[Fe(\mathbf{L}_1)_3]^{2+}$ clearly indicates that the compound is diamagnetic and all signals of the ligand are present. The less resolved signals and the chemical shifts for the protons carried by the phenanthroline skeleton are attributable to the presence of the iron(II) ion. No apparent shift was observed for the proton signals of the ethyl groups indicating that no metal ion was coordinated to this cavity. This was also confirmed by infrared spectroscopy where no shift in the vibration frequencies of the carbonyl groups was observed.

Finally, treatment of $[Fe(\mathbf{L}_1)_3]^{2+}$ with an adequate amount of tetramethylammonium hydroxide in an aqueous solution, followed by addition of a copper(II) salt, gave, after conventional work up, a deep red solid. The infrared spectrum of $(NMe_4)_4[Fe(\mathbf{L}Cu)_3]{\cdot}10H_2O$ indicates the presence of a tetramethylammonium cation and metalation of the oxamato cavity. The pattern of the signals is similar to that of the mononuclear counterpart, bringing thus a solid evidence that all the oxamate groups are coordinated in the same fashion. The more convincing piece of evidence of the content of copper ions for complex $(NMe_4)_4$-$[Fe(\mathbf{L}Cu)_3]{\cdot}10H_2O$ comes from the magnetic susceptibility measurement where the χT value for a wide range of temperatures equals to the sum of three spins $S = 1/2$ for each corresponding copper(II) ion.

We have shown in this report the versatility of this new heterotopic ligand in the design of multinuclear compounds in a rationale way. We are currently using the tetranuclear complex as ligand to bind a third generation of metal ions through the external oxygen atoms of the oxamato groups to give discrete molecules or an extended network of heteropolymetallic compounds.

Experimental Section

Diethyl *N,N′*-(Dipyrido[3,2-*a*:2′,3′*c*]phenazine-11,12-diyl)bis(oxamate) ($\mathbf{L_1}$): To a stirred solution of 1,10-phenanthroline-5,6-dione[17] (0.42 g, 2 mmol) in methanol (100 mL) under reflux was added dropwise a slurry of the diamine **1**[16] (0.68 g, 2 mmol) in methanol (50 mL). After the addition was completed, the mixture was kept under constant stirring for 30 min. The deep yellow precipitate was filtered off, washed with ether and dried under vacuum (0.92 g, 90%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 1.38$ (t, 3 H), 4.40 (q, 4 H), 7.95 (dd, 2 H), 8.64 (s, 2 H), 9.26 (dd, 2 H), 9.55 (dd, 2 H), 10.9 (s, 2

H). IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} (NH), 1755 and 1695 cm^{-1} (C=O).

$(PPh_4)_2[CuL]$: To a suspension of **L_1** (513 mg, 1 mmol) in water (25 mL) was added a methanolic solution of Me_4NOH (25%) (1.7 mL, 4 mmol). After complete dissolution, an aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (246 mg, 1 mmol) was added dropwise with stirring. The dark brown solution was filtered to remove any insoluble material and concentrated under reduced pressure. To the solution was added an excess of Ph_4PCl and the complex extracted twice with dichloromethane. The organic phase was dried with $MgSO_4$, filtered and the solvents were evaporated to dryness yielding a red solid. Crystallisation in a mixture of acetonitrile and water (90:10) afforded well-shaped crystals of the copper complex suitable for X-ray analysis. IR (KBr): $\tilde{\nu}$ = 1675 and 1645 cm^{-1} (C=O).

$[Fe(L_1)_3](BF_4)_2{\cdot}2H_2O$: In methanol (30 mL), **L_1** (154 mg, 0.3 mmol) was suspended and a methanolic solution (10 mL) of $Fe(BF_4)_2{\cdot}6H_2O$ (33 mg, 0.1 mmol) was added dropwise, giving a deep red solution. A red solid was isolated after concentration of the reaction mixture and precipitation with diethyl ether (90%). ^{1}H NMR ([D$_6$]DMSO): δ = 1.38 (t, 3 H), 4.46 (q, 4 H), 7.82 (dd, 2 H), 7.95 (dd, 2 H), 8.74 (s, 2 H), 9.62 (dd, 2 H), 11.2 (s, 2 H). IR (KBr): $\tilde{\nu}$ = 3415 cm^{-1} (NH), 1745 and 1710 cm^{-1} (C=O). $C_{78}H_{64}N_{18}O_{20}B_2F_8Fe$ (1802.9): calcd. C 51.96, H 3.58, N 13.98; found C 50.99, H 3.49, N 14.14.

$(NMe_4)_4[Fe(CuL)_3]{\cdot}10H_2O$: The synthesis of $[Fe(\mathbf{L}Cu)_3]^{6-}$ was similar to that of $[\mathbf{L}Cu]^{2-}$, starting with $[Fe(\mathbf{L_1})_3]^{2+}$ in methanol and adding 12 equiv. of base and 3 equiv. of the copper(II) salt. It was isolated as a red solid by concentration of the filtered solution and precipitation with diethyl ether. IR (KBr): $\tilde{\nu}$ = 1670 and 1635 cm^{-1} (C=O). $C_{72}H_{60}Cu_3FeN_{22}O_{28}$ (2080.3): calcd. C 47.35, H 4.46, Cu 9.16, Fe 2.68, N 14.81; found C 47.18, H 4.86, Cu 9.22, Fe 2.56, N 14.86.

Crystal Data for $(PPh_4)_2[CuL]{\cdot}0.5CH_3CN$: $C_{71}H_{49.5}CuN_{6.5}O_6P_2$, M = 1433.11, $P\bar{1}$, a = 11.141(3), b = 14.724(5), c = 19. 586(6) Å, α = 75.617(2), β = 75.43(2), γ = 84.592(2) °, V = 3010.3(16) Å^3, T = 220 K, Z = 2, 14106 reflections measured, of which 10676 were unique (R_{int} = 0.0190). Data collection, solution, and refinement: ω-θ, standard Patterson methods with subsequent full-matrix least-squares refinement. Shelxl-97.[20] The final $wR(F^2)$ was 0.1893 (all data). The crystal drawings were carried out with the Crystal Maker program.[21] Crystallographic data (excluding structure factors) reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC-164965. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1ZZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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