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Role of the kinetic template effect in the preparation of an original copper complex

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ABSTRACT

Reaction of diethylenetriamine with phenol derivatives possessing a phenyl ester function yields a ligand corresponding to the monocondensation of diethylenetriamine with the phenol derivative. In a following step, its coordination to copper ions gives a neutral complex that is able to react with orthovanillin in order to yield an original complex made of a non symmetric ligand possessing three nitrogen, amide, imine and secondary amine, and four oxygen, amide, phenol (2) and methoxy donor atoms, thanks to the kinetic template effect. In our example, the copper center brings the three reactive functions (first primary amine and aldehyde, then amide) in close vicinity so that the formation of an imine function and the protonation of the amide function can occur. The structural determination of the resulting complex confirms an unexpected copper coordination.

1. Introduction

Some years ago a new class of non symmetric ligands involving amide, imine and phenol functions were used in the syntheses of complexes associating 3d and 4f ions [1,2]. They have several advantages. First of all they are trianionic for they have three functions that can be deprotonated. Then they possess two coordination sites showing different affinities for metal ions, so that 3d-4f complexes can be isolated. Presence of supplementary donor atoms that do not belong to these coordination sites allows association of these 3d-4f entities. Such ligands are prepared in a two step process: the first step results in the reaction of phenol derivatives possessing ester functions (phenyl salicylate or phenyl-3-methoxysalicylate) with one primary amine of a diamine synthon, which yields ligands very often called as "half-unit" ligands for they still have a primary amine function that can be reacted in a second step with aldehyde derivatives possessing again phenol functions. These "half-unit" ligands present one phenol and one amide functions that can be deprotonated and at least three donor atoms, so that they are likely to coordinate 3d ions in their oxidation state II to give neutral complexes. The present work is directed toward the syntheses of "half-unit" ligands derived from diethylenetriamine along with the structural determination of one of these neutral copper complexes. In a following step we try to verify if the coordinated primary amine of the neutral copper complex is able to further react with the aldehyde function of a phenol derivative in order to check if the kinetic template effect is still working. A positive response would open a way yielding original copper complexes.

2. Experimental

2.1. Materials

Phenyl salicylate, *ortho*-vanillin (Hovan), 3-methoxysalicylic acid, 1,3-dicyclohexylcarbodiimide, diethylenetriamine, piperidine, picric acid, phenol, $Cu(OAc)_2{\cdot}2H_2O$, $NaClO_4$ (Aldrich) were used as purchased. High-grade solvents (diethyl oxide, 2-propanol, acetone, THF, methanol) and distilled water were used for the syntheses of ligands and complexes.

Caution! *Because of their explosive character, perchlorate salts and picric acid should be handled with care and in low amounts.*

2.2. Ligand

L^1H_2. A mixture of phenyl salicylate (2.14 g, 1×10^{-2} mol) and diethylenetriamine (1.03 g, 1×10^{-2} mol) was refluxed for 30 min and then cooled to room temperature with stirring. The resulting pasty product was dissolved in methanol. Addition of picric acid induced a quick precipitation that was separated by filtration. The new precipitate that appeared in the filtrate was filtered off, washed with diethyl oxide and dried. This precipitate corresponds to the picrate salt of the desired ligand. Yield: 1.3 g (29%). *Anal.*

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Calc. for $C_{17}H_{20}N_6O_9$ (452.38): C, 45.14; H, 4.46; N, 18.58. Found: C, 44.81; H, 4.33; N, 18.23. ^{1}H NMR (250 MHz, 20 °C, dmso d_6): δ 3.22 (m, 4H, CH_2N), 3.39 (m, 2H, CH_2N), 3.61 (m, 2H, CH_2N), 6.90 (t, J = 7 Hz, 1H, C(5)H), 6.91 (d, J = 7 Hz, 1H, C(3)H), 7.41 (t, J = 7 Hz, 1H, C (4)H), 7.81 (d, J = 7 Hz, 1H, C(6)H), 8.10 (l, 3H, NH), 8.59 (s, 2H, CH pic), 8.92 (t, J = 6 Hz, 1H, OCNH), 12.20 (l, 2H, OH). ^{13}C{^{1}H} NMR (62.896 MHz, 20 °C, dmso d_6): δ 35.67 (s, CH$_2$NH), 36.16 (s, CH$_2$NH), 44.65 (s, CH$_2$NH$_2$), 47.36 (s, CH$_2$NHCO), 115.89 (s, ArC(1) H), 117.75(s, ArC(3)), 119.17 (s, ArC(5)H), 124.90 (s, pic$C$pNO$_2$), 125.72 (s, pic$C$H), 128.74 (s, ArC(6)H), 134.35 (s, ArC(4)), 142.22 (s, pic$C$oNO$_2$), 159.94 (s, ArC(2)OH), 161.32 (s, pic$C$O), 169.80 (s, OCNH).

2.3. Complexes

[CuL^1·H$_2$O] (1). A mixture of phenyl salicylate (2.14 g, 1×10^{-2} mol) and diethylenetriamine (1.03 g, 1×10^{-2} mol) was refluxed for 30 min and then cooled to room temperature with stirring. The resulting pasty product was dissolved in acetone (50 mL). Copper acetate (2.0 g, 1×10^{-2} mol) and piperidine (2 mL, 2×10^{-2} mol) were added and the solution was refluxed and stirred for 1 h. The resulting violet precipitate was filtered off from the cooled solution and dried. Yield: 0.9 g (31%). *Anal.* Calc. for $C_{11}H_{15}CuN_3O_2$ (284.80): C, 46.39; H, 5.31; N, 14.75. Found: C, 46.03; H, 5.18; N, 14.48. IR (ATR): 3248s, 3103m, 2930m, 2876m, 1592m, 1558s, 1520s, 1461m, 1440m, 1385s, 1324m, 1316m, 1258m, 1237w, 1155m, 1145w, 1099m, 1091m, 1038m, 961w, 890w, 842w, 760m, 704w, 651w.

[CuL^2·H$_2$O] (2). A mixture of 3-methoxysalicylic acid (1.68 g, 1×10^{-2} mol), phenol (2.82 g, 3×10^{-2} mol) and 1,3-dicyclohexylcarbodiimide (2.06 g, 1×10^{-2} mol) in THF (100 mL) was stirred for 24 h at room temperature. The solution was filtered off and THF eliminated with use of a rotavapor. The resulting oil was poured into 2-propanol (40 mL) and diethylenetriamine (1.03 g, 1×10^{-2} mol) in 2-propanol (10 mL) was added dropwise, refluxed for thirty minutes and then cooled down to room temperature under stirring. Addition of diethyl oxide (60 mL) induced formation of a white precipitate which was filtered off, and washed with diethyl oxide. A mixture of this crude precipitate (0.25 g, 1×10^{-3} mol) with copper acetate (0.20 g, 1×10^{-3} mol) and piperidine (0.2 mL, 2×10^{-3} mol) in acetone (30 mL) was refluxed and stirred for 30 min. The resulting violet precipitate was filtered off from the cooled solution. Crystals suitable for X-ray diffraction were obtained by slow diffusion of acetone to a methanol/water solution of the isolated complex. Note that the colour change from violet (CuL^2) to blue (CuL^2·H$_2$O) observed during the crystallization process is due to water coordination. Yield: 0.10 g (30%). *Anal.* Calc. for $C_{12}H_{23}CuN_3O_6$ (368.88): C, 39.07; H, 6.28; N, 11.39. Found: C, 38.91; H, 6.18; N, 11.28. IR (ATR): 3221m, 3119m, 2911m, 2872m, 1591w, 1566s, 1532s, 1448m, 1433s, 1391s, 1336m, 1259w, 1225s, 1202s, 1149w, 1106w, 1080m, 1064m, 1001w, 964w, 853w, 804w, 739m, 614w.

[(CuL^{3}H)$_2$NaClO$_4$] (3). A methanol solution (10 mL) of [CuL^2·H$_2$O] (0.28 g, 1×10^{-3} mol), *ortho*-vanillin (0.15 g, 1×10^{-3} mol), sodium perchlorate (0.12 g, 1×10^{-3} mol) and piperidine (0.30 mL, 3×10^{-3} mol) was stirred and refluxed for 20 min. The resulting green solution was cooled down, filtered and left aside. Crystals suitable for X-ray appeared three days later. They were isolated by filtration and dried. Yield: 0.30 g, 62.5%. Calc. for $C_{38}H_{42}ClCu_2N_6NaO_{12}$ (960.32): C, 47.53; H, 4.41; N, 8.75. Found: C, 47.23; H, 4.32; N, 8.52. IR (ATR): 3262w, 3183w, 1628s, 1606m, 1593w, 1551w, 1537w, 1463m, 1449s, 1439s, 1399w, 1313m, 1289w, 1243m, 1219s, 1195w, 1154w, 1081s, 1066s, 1023m, 995w, 970m, 884w, 856w, 818w, 778w, 760m, 736m, 696m, 622m cm^{-1}.

Physical measurements: C, H, and N elemental analyses were carried out at the Laboratoire de Chimie de Coordination, Microanalytical department, in Toulouse, France. IR spectra were recorded with a Perkin-Elmer Spectrum 100FTIR using the ATR mode. Magnetic data of complex **3** were obtained with a Quantum Design MPMS SQUID susceptometer, in the 2–300 K temperature range and a 0.1 T applied magnetic field. Diamagnetic corrections were applied by using Pascal's constants [3].

2.4. Crystallographic data collection and structure determination for complexes *2* and *3*

Crystals of complexes **2** and **3** were kept in the mother liquor until they were dipped into oil. The chosen crystals were mounted on a Mitegen micromount and quickly cooled down to 100 K (**2**) or 140 K (**3**). Selected crystals of **2** (blue, $0.06 \times 0.10 \times 0.25$ mm^3) and **3** (dark green, $0.20 \times 0.20 \times 0.20$ mm^3) were mounted on an Oxford Diffraction Gemini (**2**) or a Bruker Kappa APEX II (**3**) using molybdenum (λ = 0.71073 Å) radiation and equipped with an Oxford Cryosystems cooler device (**2**) or an Oxford Cryosystems Cryostream Cooler Device (**3**). The unit cell determination and data integration were carried out using CrysAlis RED package (**2**) or SAINT APEX II (**3**) [4–6]. The structures have been solved using SIR92 [7], SUPERFLIP [8] or SHELXS-97 [9] and refined by least-squares procedures using the software packages CRYSTALS [10] or WinGX version 1.63 [11]. Atomic Scattering Factors were taken from the International tables for X-ray Crystallography [12]. All hydrogen atoms were refined by using a riding model. All non-hydrogen atoms were anisotropically refined. Drawings of molecules have been performed with the program Mercury [13]. For **3**, it was not possible to resolve accurately residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON [14] resulted in a smooth refinement. Cif data for **2** and **3** have been deposited at CCDC with references CCDC 1842689–1842690.

Crystal data for 2. $C_{12}H_{23}CuN_3O_6$, M = 368.88, monoclinic, C2/c, Z = 8, a = 20.9842(6), b = 7.36425(18), c = 20.1435(5) Å, $\alpha = \gamma = 90°$, β = 108.237(3)°, V = 2956.47(14) Å^3, 39819 collected reflections, 4633 unique reflections (R_{int} = 0.023), R-factor = 0.022, weighted R-factor = 0.024 for 4208 contributing reflections [$I > 3\sigma$ (I)] and 199 parameters. CCDC 1842690.

Crystal data for 3. $C_{38}H_{42}ClCu_2N_6NaO_{12}$, M = 960.32, monoclinic, $P2_1/n$, Z = 4, a = 13.7780(3), b = 14.0751(3), c = 21.8194(4) Å, $\alpha = \gamma = 90°$, β = 94.1770(10)°, V = 4220.13(15) Å^3, 61973 collected reflections, 16540 unique reflections (R_{int} = 0.0497), R-factor = 0.047, weighted R-factor = 0.051 for 11401 contributing reflections [$I > 3\sigma$ (I)] and 541 parameters. CCDC 1842689.

3. Results

The ligands prepared in the present work are reported on the following Scheme 1. The L^{1}H$_2$ and L^{2}H$_2$ ligands result from reaction of diethylenetriamine (dien) with the phenyl ester of salicylic acid or 3-methoxy-salicylic acid. Only L^{1}H$_2$ has been isolated as a picrate salt and characterized by ^{1}H and ^{13}C NMR while L^{2}H$_2$ has been directly reacted with copper ions. A structural determination confirms monocondensation of diethylenetriamine and presence of a primary amine function coordinated to the copper ion that should be able to react with an aldehyde function to give original non symmetric ligands. This is exemplified by the reaction of CuL^2·H$_2$O with *ortho*-vanillin (Hovan) that yields the [(CuL^{3}H)$_2$Na]ClO$_4$ complex. Its structural determination demonstrates the non symmetry of the ligand coordinated to the copper ion along with the role of the kinetic template effect in the original coordination of such a ligand.