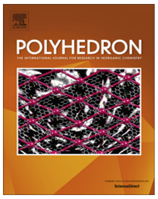
Polyhedron 111 (2016) 101–108

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Use of azido ligands in the syntheses of different homo- and hetero-complexes

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ARTICLE INFO

Article history:
Received 20 January 2016
Accepted 19 March 2016
Available online 25 March 2016

Keywords:
Coordination chemistry
Azido ligands
Copper
Structural determinations
Magnetic properties

ABSTRACT

The reaction of neutral “half-unit” copper azido complexes, made of “half-unit ligands” resulting from a monocondensation of different diamines with an aldehyde function and of end-on azido ligands, with diverse gadolinium or sodium salts, is not straightforward. The resulting complexes are mainly homodinuclear copper complexes. Heterodinuclear Cu–Gd complexes devoid of azido bridges necessitate use of gadolinium nitrate or gadolinium hexafluoroacetylacetonate. A heterotrinuclear Cu–Na–Cu by-product in which the Cu and Na ions are linked by double phenoxo-end-on azido bridges has also been structurally characterized. The decrease of the acidic character of positive ions in protic solvents in going from naked gadolinium to gadolinium nitrate, gadolinium complex and to sodium ions can explain the diverse reaction pathways and formation of the different final products.

1. Introduction

Preparation of Cu–Gd complexes of low nuclearity has allowed to evidence presence of ferromagnetic interactions in a large majority of complexes [1–4]. It has been shown that phenoxo bridges, which are bridges involving a single oxygen atom, transmit ferromagnetic interactions in Cu–Gd complexes. Such complexes are very often obtained thanks to Schiff base ligands resulting from reactions of ovanillin with diverse diamine, so that the Cu and Gd ions are linked by a double phenoxo bridge [5,6]. In the case of deprotonated amide bridges implying three atoms (OCN bridge), single bridges have been structurally characterized and ferromagnetic interactions are observed again but they are weaker than the ones transmitted through the phenoxo bridge [7–9]. Contrary to that, the oximato bridge made up two atoms (NO bridge), transmits antiferromagnetic interaction, whatever presence of one or two oximato bridges [10–13]. In the past we developed syntheses of ligands called “half-unit” ligands for they result from reaction of an aldehyde or a ketone function with only one amine function of a diamine [14–16]. Although these ligands are not easily obtained in organic chemistry, template synthesis with copper (II) ions is really helpful for their preparation. So we decided to use such complexes as ligands to build Cu–Gd complexes having a single phenoxo bridge. Our first trial allowed us to obtain a complex involving a “half-unit”Cu–Gd complex with a non symmetric phenoxo–hydroxo bridge [17]. In the present work we first characterize by X-ray diffraction “half-unit” copper azido complexes and extend their reactions in diverse conditions in order to isolate the expected Cu–Gd complex possessing a unique Cu–Gd phenoxo bridge.

2. Experimental

2.1. Materials

The [L^{1}CuPy]ClO$_4$ complex (L^1 being the half-unit ligand corresponding to the monocondensation of trans-1,2-diaminopropane to orthovanillin) was prepared according to an experimental process previously described [17]. The metal and alkaline salts Cu(ClO$_4$)$_2$·6H$_2$O, NaN$_3$, NaClO$_4$, Na(CF$_3$SO$_3$) were used as purchased. High-grade methanol (Normapur, VWR) and acetone (Normapur, VWR), were used for preparing the complexes.

Caution! Perchlorate and azide salts are potentially explosive especially in presence of organic ligands. Therefore, these compounds must be handled with care and prepared only in small amounts.

2.2. Complexes

2.2.1. [LCuPy]ClO$_4$ **1**

To a stirred solution of ortho-vanillin (1.52 g, 10 mmol) in methanol (50 ml) was first added copper perchlorate (3.7 g,

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http://dx.doi.org/10.1016/j.poly.2016.03.038
0277-5387/

10 mmol) dissolved in water (10 ml) and then pyridine (1.6 g, 20 mmol). A few minutes later, a methanolic solution (10 ml) of 1,2-diaminoethane (0.6 g, 10 mmol) was added at once with stirring at ambient temperature. Two hours later, the precipitate was filtered off, washed with cold methanol and diethyl ether. Yield: 3.0 g, 70%. *Anal.* Calc. for $C_{15}H_{18}ClCuN_3O_6$ (435.3): C, 41.4; H, 4.2; N, 9.6. Found: C, 41.0; H, 4.0; N, 9.4%. IR (ATR): 3320 m, 3260w, 2963w, 1639s, 1604m, 1470w, 1444s, 1398w, 1293m, 1246m, 1224m, 1170w, 1139w, 1093m, 1074s, 1043m, 961m, 851w, 746m, 699m, 619m cm^{-1}.

2.2.2. $[LCuN_3]_2{\cdot}(H_2O)_2$ **2**

Addition of NaN_3 (0.06 g, 1 mmol) to a stirred suspension of $[LCuPy]ClO_4$ (0.27 g, 0.5 mmol) in water (10 mL) at room temperature induced dissolution of the copper complex and precipitation of a new product with colour change. 30 min later, the dark blue precipitate was isolated by filtration and dried. Yield: 0.15 g (95%). *Anal.* Calc. for $C_{20}H_{30}Cu_2N_{10}O_6$ (633.6): C, 37.9; H, 4.8; N, 22.1. Found: C, 38.0; H, 4.7; N, 22.8%. IR (ATR): 3466m, 3261m, 3132m, 2931w, 2039s, 1633s, 1603m, 1470m, 1445s, 1400m, 1317m, 1283m, 1238m, 1213s, 1166w, 1120w, 1078m, 1050m, 967m, 854w, 785w, 741m, 619w cm^{-1}.

2.2.3. $[(LCuN_3(H_2O)CuL](ClO_4)$ **3**

Method A. NaN_3 (0.1 g, 1.5 mmol) was added at room temperature to a stirred solution of $[LCuPy]ClO_4$ (0.43 g, 1 mmol) in methanol (20 mL). The green precipitate that appeared was filtered one hour later and dried. Yield: 0.27 g (80%). Method B. Addition at room temperature of $NaClO_4$ (0.12 g, 1 mmol) to a stirred methanol solution (15 mL) of $[LCuN_3]_2{\cdot}(H_2O)_2$ (0.16 g, 0.5 mmol) yielded an immediate green precipitate that was filtered off 30 min later and dried. Yield: 0.14 g (83%). The infrared spectrum and analytical data are similar to the data obtained with method A. *Anal.* Calc. for $C_{20}H_{28}ClCu_2N_7O_9$ (673.0): C, 35.7; H, 4.2; N, 14.6. Found: C, 35.8; H, 4.1; N, 14.3%. IR (ATR): 3559m, 3348m, 3287m, 3154w, 2944w, 2066s, 1635s, 1604m, 1470m, 1443s, 1402w, 1339w, 1293m, 1245m, 1216s, 1080m, 1044m, 1021m, 966m, 855w, 783w, 742m, 679w, 620m cm^{-1}.

2.2.4. $[(LCuN_3(H_2O)CuL](CF_3SO_3)(H_2O)$ **4**

Method A. Addition at room temperature of gadolinium triflate (0.03 g, 0.05 mmol) to a stirred methanol solution (5 mL) of $[LCuN_3]_2{\cdot}(H_2O)_2$ (0.032 g, 0.1 mmol) yielded a blue solution that was filtered and kept undisturbed. The green crystals that appeared three days later were filtered off and dried while a few ones were put into oil for XRD. Yield: 0.018 g (48%).

Method B. Addition at room temperature of sodium triflate (0.034 g, 0.2 mmol) to a stirred methanol solution (15 mL) of $[LCuN_3]_2{\cdot}(H_2O)_2$ (0.063 g, 0.2 mmol) yielded an immediate green precipitate that was filtered off 30 min later and dried. Yield: 0.04 g (54%). The infrared spectrum and analytical data are similar to the data obtained with crystals of method A. *Anal.* Calc. for $C_{21}H_{24}Cu_2F_3N_7O_9S$ (740.6): C, 34.0; H, 4.1; N, 13.2. Found: C, 33.7; H, 3.9; N, 13.0%. IR (ATR): 3569m, 3339m, 3282m, 3156w, 2951w, 2067s, 1636s, 1605m, 1471m, 1439s, 1405w, 1313w, 1295m, 1267m, 1246s, 1215s, 1083m, 1043m, 1028m, 969w, 854w, 783w, 745m, 639m, 620w cm^{-1}.

2.2.5. $[(LCuN_3)_2Na](ClO_4)$ **5**

NaN_3 (0.1 g, 1.5 mmol) was added at room temperature to a stirred solution of $[LCuPy]ClO_4$ (0.43 g, 1 mmol) in methanol (20 mL). The green precipitate that corresponds to complex **2** was filtered off and the filtrate was kept undisturbed until red crystals appeared a few days later. They were isolated by filtration and dried. Yield: 0.02 g (6%). *Anal.* Calc. for $C_{20}H_{26}ClCu_2N_{10}NaO_8$ (720.0): C, 33.4; H, 3.6; N, 19.5. Found: C, 33.2; H, 3.5; N, 19.3%. IR (ATR): 3326m, 3301m, 3276m, 2966w, 2044s, 1635s, 1604m, 1471m, 1450m, 1438m, 1318m, 1294m, 1239m, 1220m, 1094m, 1079s, 1045s, 971m, 856w, 785w, 745m, 620m cm^{-1}.

2.2.6. $LCuGd(hfa)_3(N_3)$ **6**

$[LCuN_3]_2{\cdot}(H_2O)_2$ (0.016 g, 0.025 mmol) and $Gd(hfa)_3{\cdot}(H_2O)_2$ (0.041 g, 0.05 mmol) were added in a test tube and dissolved in methanol (3 mL) and set aside. Four days later partial solvent evaporation yielded a precipitate that was filtered off and washed with iPrOH and dried. Yield: 0.04 g (74 %). *Anal.* Calc. for $C_{25}H_{16}CuF_{18}GdN_5O_8$ (1077.2): C, 27.9; H, 1.5; N, 6.5. Found: C, 27.4; H, 1.4; N, 6.4%. IR (ATR): 3306w, 3264w, 2956w, 2093s, 1649s, 1638m, 1557m, 1530m, 1505m, 1470m, 1446m, 1298w, 1252m, 1193s, 1134s, 1097m, 1053 m, 1043w, 962w, 796m, 740w, 659m cm^{-1}. Mass spectrum (FAB^+): *m*/*z* 1035 (30) $[LCuGd(hfa)_3]^+$, 980 (100) $[LCuGd(hfa)_2(N_3)–CF_3COH]^+$, 828 (55) $[LCuGd(hfa)_2]^+$.

2.2.7. $[L^1CuN_3(MeOH)]_2{\cdot}(CH_3OH)_2$ **7**

Addition of NaN_3 (0.06 g, 1 mmol) to a stirred suspension of $[L^1CuPy]ClO_4$ (0.25 g, 0.5 mmol) in water (10 mL) at room temperature induced dissolution of the copper complex and precipitation of a new product with colour change. 30 min later, the green precipitate was isolated by filtration and dried. Recrystallization from methanol gave crystals suitable for X-ray diffraction. Yield: 0.17 g (84%). *Anal.* Calc. for $C_{32}H_{54}Cu_2N_{10}O_8$ (833.9): C, 46.1; H, 6.5; N, 16.8. Found: C, 45.6; H, 6.2; N, 16.4%. IR (ATR): 3235m, 3147m, 2939w, 2049s, 1634s, 1600m, 1469m, 1447s, 1216s, 973m, 748m cm^{-1}.

2.3. Physical measurements

Elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France, for C, H, and N IR spectra were recorded with a Perkin-Elmer Spectrum 100FTIR using the ATR mode. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. All samples were 3 mm diameter pellets molded from ground crystalline samples. Magnetic susceptibility measurements were performed in the 2–300 K temperature range in a 0.1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants [18]. Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibilities have been computed by exact calculations of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry [19], and with the MAGPACK program package [20] in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT [21]. Positive ion FAB mass spectra were recorded on a Nermag R10-10 spectrometer using dimethylformamide (dmf) as solvent and m-nitrobenzyl alcohol (NBA) as matrix.

2.4. Crystallographic data collection and structure determination for the complexes **1**, **2**, **4**, **5** and **7**

Crystals of **1**, **2**, **4**, **5**, **7** 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 180 K (**1**, **2**, **4**, **5**, **7**). The selected crystals of **1** (green, 0.20 × 0.14 × 0.05 mm^3), **2** (blue, 0.60 × 0.50 × 0.075 mm^3) and **4** (green, 0.20 × 0.075 × 0.05 mm^3), **5** (red, 0.35 × 0.30 × 0.20 mm^3), **7** (green, 0.40 × 0.25 × 0.12 mm^3) were mounted on a Bruker Kappa Apex II (**1**), Stoe IPDS (**2**, **4**, **5**, **7**) using a graphite monochromator ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems cooler device. The unit cell determination and data integration were carried out using XRED [22], CrysAlis