Unprecedented Architecture of the Linear (μ -Cl)-Tetranuclear Cobalt Complex with Quaterpyridine Ligand

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Received: 15 December 2010 / Accepted: 26 September 2011 / Published online: 8 October 2011
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Abstract The cationic tetranuclear cobalt complex of the geometry Cl-CoL-Cl-CoL-Cl-CoL-Cl-CoL (where L is 6,6'''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine) has been synthesized and structurally characterized. The structural unit contains one cationic ligand, two $\text{Eu}(\text{NO}_3)_5$ dianions, two solvent acetonitrile molecules and some disordered water molecules. The salt crystallizes in the monoclinic space group $C2/c$ with $a = 17.405(3) \text{ \AA}$, $b = 28.700(5) \text{ \AA}$ and $c = 23.350(5) \text{ \AA}$, $\beta = 95.14(2)^\circ$. The cation is C_2 -symmetrical, the central Cl atom lies on the twofold axis. This structure is another example of centro-noncentro ambiguity: in the centrosymmetric model, the terminal Cl in the cation is disordered between the two ends of the chain. The Eu ion is coordinated by five nitro groups, the coordination number is 10—two oxygen atoms of every nitro group are involved in the coordination with the mean Eu–O distance of $2.52(3) \text{ \AA}$. The quaterpyridine ligands are folded, the dihedral angle between the terminal ring planes is $29.3(2)$ and $32.8(3)^\circ$ in the two symmetry independent ligands. In the crystal structure the coulombic attraction between the cations and anions seems to be a driving force; the ionic species make a chessboard-like pattern, the voids in such created structure are filled with the solvent-acetonitrile molecules as well as by some disordered waters.

Keywords Co complexes · Eu complexes ·
Centro-noncentro ambiguity · Crystal packing

Results and Discussion

The use of transition metal ions capable of bridging multidentate ligands to construct pre-programed, self-assembled small inorganic systems and multi-dimensional infinite supramolecular networks is an area of chemistry which has received ever-increasing attention over recent years. Up to date, many fascinating supramolecular structures have been obtained by using metal ions and ligands containing nitrogen-donor atoms, for instance bipyridine [1], terpyridine [2] or tetrapyridine [3], to name a few.

In the present work, we extend these studies of the metalo-ligand complexes based on tetrapyridine ligand coordinated with d- and f-metal ions, obtained in one-pot reaction. The crystals contain cation with four organic ligands coordinated to the four cobalt ion bridged by chloride ions and two penta-nitrato anionic species with nitrate oxygen atoms coordinated to trivalent europium ion. The formation of this type of complex may be understood considering the large stability of polynitrato counter ions [4]. The high affinity of the europium ions for nitrato anions does not allow heterometallic Co-Eu complexes to be prepared from N_4 -donor ligand if the latter anions are present in solution [5].

The investigated complex may be of use in several fields of coordination chemistry. In particular, d- and f-polynuclear complexes might be used to fabricate nanomagnetic materials of the potential use in many fields, [6] and due to their electronic properties such as high conductivity as molecular devices in the field of nano-electronics [7, 8].

Figures 1 and 2 show the ionic components of the crystal structure. Table 1 lists some relevant geometrical parameters.

The cation has the unprecedented geometry of linear four-metal-centered chain. In the Cambridge Crystallographic Database [9] we have not found any complex of similar

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Fig. 1 Anisotropic ellipsoid representation of the cation together with atom labeling scheme [19]. The ellipsoids are drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. Prime denotes the symmetry code $1-x, -y, 1/2-z$

Fig. 2 Anisotropic ellipsoid representations of the anion together with atom labeling scheme [19]. The ellipsoids are drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii

geometry, besides two anionic metal halides: tris(μ_2 -iodo)-decakis(iodo)-tetra-mercury(ii) [10] and tris(μ_2 -fluoro)-dodecafluoro-tetra-antimony [11]. There are also infinite, sometimes branched chains of the $\sim \text{Me-X-Me-X} \sim$ disposition, also with the other ligands connected with metal centers but such a strange disposition is observed—to the best of our knowledge—for the first time. The cation is C_2 -symmetrical, the central Cl atom lies on the twofold symmetry axis. This symmetry constitutes the problem of its own, in fact one of the most important problems of the X-ray crystallography: the centro-noncentro ambiguity (for instance, [12, 13] and references therein). In the present case

Table 1 Selected geometrical parameters ($\text{\AA}$, $^\circ$)

Eu1–O12	2.518 (7)	Eu1–O13	2.561 (8)
Eu1–O22	2.534 (8)	Eu1–O23	2.527 (7)
Eu1–O32	2.521 (7)	Eu1–O33	2.486 (7)
Eu1–O42	2.462 (7)	Eu1–O43	2.523 (7)
Eu1–O52	2.519 (7)	Eu1–O53	2.507 (7)
Co1–N1B	2.222 (10)	Co1–N8B	2.113 (8)
Co1–N14B	2.107 (8)	Co1–N20B	2.227 (8)
Co1–Cl1A	2.312 (5)	Co1–Cl1	2.509 (3)
Co2–N1A	2.241 (8)	Co2–N8A	2.067 (9)
Co2–N14A	2.110 (8)	Co2–N20A	2.230 (8)
Co2–Cl1	2.534 (3)	Co2–Cl2	2.519 (2)
Cl1B–Co1–Cl1	164.19 (15)	Co1–Cl1–Co2	132.27 (11)
Cl1–Co2–Cl2	169.93 (11)	Co2–Cl2–Co2 ⁱ	130.45 (18)
Angles between mean planes	Ligand 1	Ligand 2	
A/B	8.5 (3)	8.0 (4)	
B/C	11.6 (3)	14.7 (3)	
C/D	10.3 (3)	11.0 (4)	
A/D	29.3 (2)	32.8 (3)	

this ambiguity leads to the choice between one of the two possible models which can be deduced from the same experimental data:

- centrosymmetric one with the cation in a special position and the terminal chlorine atom with half occupancy (assuming disorder between two oppositely oriented molecules).
- non-centrosymmetric model in which the space group symmetry is lowered to Cc and the chlorine atom is fully occupied at one of the ends of the molecule.

Fig. 3 The neighbouring chains of the cations [20]; for clarity only the “backbone” atoms are shown

Of course in principle these two models lead to the same packing; in reality one position of terminal chlorine enforces the same orientation of the neighboring molecule, in order to avoid impossibly short Cl...Cl contacts. So, we have the “homodromic” chains of cations $\sim\text{Co}-\text{Cl}\sim\text{Co}-\text{C}\cdots\text{Co}-\text{Cl}\sim\text{Co}-\text{Cl}\cdots\text{Co}-\text{Cl}\sim\text{Co}-\text{Cl}\sim$, and the neighboring chains have different orientations (cf. Fig. 3). Due to the space- and time-averaging nature of diffraction experiment both these models lead to the same experimental results. The structure could be solved in both C2/c and Cc space groups, and refinements go more or less properly, but the non-centrosymmetric model leads to large correlations and has no other advantages over the centrosymmetric model; therefore the final refinement was done in the C2/c space group with half-occupied terminal Cl atom. Similar situation, but connected with the hydrogen-bonded chains, was observed for instance in the crystal structure of 1,2-dimethyl-4-nitro-5-morpholino-imidazole hydrate [14].

The conformation of the backbone of the cation is far from linear, the torsion angles along the chain of Co and Cl atoms are 159.4(4), 143.1(4), 153.9(4), 143.1(4), and 159.4(4)°. The three Co atoms are six-coordinated (by four nitrogen atoms of L and two Cl), and this coordination is close to square bipyramid (Co–Cl distances are significantly longer than Co–N, cf. Table 1). Only one terminal Co atom (cf. the discussion above) is five-coordinated, with the square pyramidal coordination. The aromatic rings in both symmetry-independent ligands are to a good approximation planar, however the ligands as a whole are far from planarity. The dihedral angles between terminal ring planes, which may serve as a measure of overall twist of

Table 2 Crystal data, data collection and structure refinement

Formula	$\text{C}_{88}\text{H}_{72}\text{Cl}_4\text{Co}_4\text{N}_{16}\cdot 2(\text{EuN}_5\text{O}_{15})\cdot 2(\text{C}_2\text{H}_3\text{N})\cdot 3(\text{H}_2\text{O})$
Formula weight	2807.26
Crystal system	Monoclinic
Space group	C2/c
a (Å)	17.405(3)
b (Å)	28.700(5)
c (Å)	23.350(5)
β (°)	95.14(2)
V (Å ³)	11617(4)
Z	4
d_x (g cm ^{−3})	1.58
F (000)	5560
μ (mm ^{−1})	1.80
Θ range (°)	2.43–25.00
Hkl range	$-20 \leq h \leq 20$ $-31 \leq k \leq 33$ $-27 \leq l \leq 27$
Reflections	
Collected	44542
Unique (R_{int})	9357 (0.148)
With $I > 2\sigma(I)$	4893
Number of parameters	748
R (F) [$I > 2\sigma(I)$]	0.073
wR (F ²) [$I > 2\sigma(I)$]	0.152
R (F) [all data]	0.148
wR (F ²) [all data]	0.164
Goodness of fit	1.050
Max/min $\Delta\rho$ (e Å ^{−3})	1.16/−0.70

these fragments, are 29.3(2) and 32.8(3)°. More information about the conformation of ligands can be found in Table 2.

In the anion the Eu atom is ten-coordinated (Fig. 2), each nitro group donates two oxygen atom to the coordination sphere. The distances Eu–O with the typical mean value of 2.52(3) Å show only moderate spread (2.461–2.560 Å), what proves that in fact all ten oxygen atoms take part in the coordination. As expected, the asymmetry in the N–O bond distances is clearly seen: the bonds involving atoms that are engaged in the coordination are significantly longer (mean value 1.285(20) Å) than those which are involved in intermolecular interactions, if any (1.234(10) Å).

In the crystal structure these ionic fragments are packed mainly by means of Coulombic interactions; the chessboard-like disposition of cations and anions (Fig. 4) attempts to minimize the repulsion and maximize attraction. The voids in such created structure are filled with ordered solvent (acetonitrile) molecules and some additional electron density which in some instances might be interpreted as

Fig. 4 Fragment of the crystal packing of **1** as seen along *x*-direction [20]

disordered water molecules, but there is also some unmodelled residual electron density (cf. Table 2), which is probably caused by totally disordered water and which can be responsible for relatively high *R* factor of otherwise quite reasonable structure.

Experimental

Preparation

The metal salts were used without further purification as supplied from Aldrich. The ligand **L** and the complex were prepared as described previously [3]. Solvents were freshly distilled under argon from CaH_2 . Mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were determined using a Waters Micromass ZQ spectrometer. Sample solutions were introduced into the mass spectrometer source with a syringe pump at a flow rate of $40 \mu\text{L min}^{-1}$ with a capillary voltage of +3 kV and a desolvation temperature of 300°C . The source temperature was 120°C . The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 200$ to 1,000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained using a Perkin Elmer 2400 CHN microanalyzer.

Preparation of complex: a mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (6.3 mg, $27 \mu\text{mol}$), $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (9.5 mg, $27 \mu\text{mol}$) and ligand **L** (18 mg, $54 \mu\text{mol}$) in 2:1 $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ (18 mL) was stirred at room temperature for 48 h under argon atmosphere. The volume was reduced under vacuum until crystallization commenced and the mixture was then allowed stand to equilibrate. The pale pink complex was isolated in quantitative yield by evaporation of the solvent

Table 3 Crystal data, data collection and structure refinement

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(88%). ESI-MS (+): m/z (%) $\delta = 432$ (100) $[\text{CoLCl}]^+$, 199 (20) $[\text{CoL}]^{2+}$, ESI-MS (−): m/z (%) = 399 (100) $[\text{Eu}(\text{NO}_3)_4]^-$, 231 (20) $[\text{Eu}(\text{NO}_3)_5]^-$. Elemental analysis (%) calcd for $[\text{Co}_4(\text{C}_{22}\text{H}_{18}\text{N}_4)_4\text{Cl}_4][\text{Eu}(\text{NO}_3)_5]_2 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$ (2807.26): C 39.33; H 3.09; N 13.96; found: C 39.41; H 3.05; N 13.93.

Crystallography

Blue transparent prism-like crystals (0.25, 0.1, 0.1) were used for data collection. Diffraction data were collected at 100 (1) K by the ω -scan technique, on a KUMA KM4CCD diffractometer [15] with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ Å}$). The temperature was controlled by an Oxford instruments cryosystems cooling device. The crystal quality deteriorated during data collection, which together with the troubles with selecting the specimen of appropriate quality, resulted with the relatively low completeness of the data. Complete room temperature data are of inferior quality. The data were

corrected for Lorentz-polarization and absorption effects [15]. Accurate unit-cell parameters were determined by a least-squares fit of 7290 reflections of highest intensity, chosen from the whole experiment. Precision of the diffractometer was also taken into account in order to avoid unphysically small standard uncertainties [16]. The structure was solved by direct methods with SIR92 [17] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [18]. Scattering factors incorporated in SHELXL97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (0.06P)^2]$. Disordered oxygen atoms were refined isotropically, all other non-hydrogen atoms were refined anisotropically, hydrogen atoms were put in the calculated positions difference Fourier map, and refined as a “riding” model with the isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times the U_{eq} value for appropriate non-hydrogen atom. No attempts to find the hydrogen atoms from disordered water molecules were performed. Relevant crystal data are listed in Table 3, together with refinement details.

CCDC-804372 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgment This research was carried out as part of the Polish Ministry of Higher Education and Science project (Grant No. NN 204 2716 33).

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