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Octahedral Trinuclear Complexes with Aminothiolates. Crystal Structure of Hexakis(3-Amino-1-propanethiolate)tricobalt(III) Chloride

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Abstract

The crystal structure of the complex $\{Co_3[S(CH_2)_3NH_2]_6\}Cl_3$ was determined by X-ray diffraction methods. It is composed of discrete trinuclear cation and chloride anions linked by NH...Cl hydrogen bonds. All the ligands are chelated to metal atoms, and the cation can be described as being formed by three octahedra sharing two opposite faces. Electronic spectroscopy indicates that the structure of the complex $\{Co_3[S(CH_2)_2NH_2]_6\}Cl_3$ should be very similar.

The homologous iron(III) complexes $\{Fe_3[S(CH_2)_3NH_2]_6\}Cl_3$ and $\{Fe_3[S(CH_2)_2NH_2]_6\}Cl_3$ were synthesized and their infrared spectra show that the same structure could be considered for these complexes.

Introduction

There are several reports in the literature of trinuclear complexes $[M(CoL_3)_2]^{m+}$ with 2-aminothiolate as a chelate ligand, and Co(III), Zn(II) and Ni(II) as the central metal atom M [1–3].

In our study with γ-mercaptoamines we observed some interesting differences in behaviour between these ligands and the homologous β-mercaptoamines [4, 5]. To our knowledge, there are no reports in the literature about the molecular structure of the above mentioned trinuclear complexes. Therefore, in order to verify the geometry of the central atom** we solved the structure of the complex $[Co_3(MPA)_6]Cl_3$ (MPA = $SCH_2CH_2CH_2NH_2$) by X-ray analysis.

Experimental

Material

The ligand MPAH and the complex $[Co_3(MPA)_6]Cl_3$ were made according to previously published procedures [7]. Single crystals of the above complex were prepared from a saturated solution by slow evaporation.

Physical Methods

The electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer using aqueous solutions of the cobalt complexes. The infrared spectra were measured in a Beckman IR-20A spectrophotometer as KBr pellets.

Crystal Data

$Co_3(C_3H_8NS)_6Cl_3\cdot 2H_2O$, Fw = 829.96, monoclinic, $a = 15.680(2)$, $b = 12.964(1)$, $c = 17.608(2)$ Å, $\beta = 106.44(2)°$, $V = 3433(1)$ Å^3, $C2/c$, $Z = 4$, $F(000) = 1664$, $\mu(MoK_\alpha) = 21.0$ cm^{-1}.

Crystal Data and Intensity Measurements

An equidimensional crystal (0.2 × 0.2 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit cell was measured from 25 reflections ($4 \leqslant \theta \leqslant 8°$) and refined by least-squares. Intensities were collected with MoK_α radiation monochromatized by reflexion from a graphite crystal, using the ω-scan technique (scan width 1°, scan speed 0.03° s^{-1}). Three reflections were measured each two hours as orientation and intensity control. Significant differences were not observed. 2685 intensities were measured in the range $2 \leqslant \theta \leqslant 25°$, 2662 of which were assumed as 'observed' applying the condition $I \geqslant 2.5\sigma(I)$. Lorentz polarization corrections were made, but no absorption.

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**A trigonal prismatic geometry was found in a similar trinuclear complex with the ligand 2-aminoethanol. This was attributed to steric requirements of the ligands [6].

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Crystal Structure Determination and Refinement

The structure was solved by direct methods using the MULTAN system of computer programs [8]. An E-map computed from the set of phases with the highest combined figure of merit revealed peaks for the eight heaviest atoms. A subsequent Fourier synthesis revealed the position of the remaining non-hydrogen atoms. The structure was refined by the full-matrix least-squares method, using the SHELX 76 computer program [9]; f, f' and f'' were taken from the International Tables of Crystallography [10] and the function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0102\,|F_o|^2)^{-1}$. Isotropic and anisotropic refinements lead to $R = 0.076$. A difference synthesis revealed the position of 24 hydrogen atoms (of 26), which were refined with an overall isotropic temperature factor and anisotropically the remaining atoms. The final R was 0.044 ($Rw = 0.048$) with all observed reflections. Final atomic parameters have been deposited with the Editor as supplementary data.

Preparation of [Fe_3L_6]Cl_3 (L = MEA, MPA; MEA = $SCH_2CH_2NH_2$)

All solvents were reagent grade and were dried by distillation from suitable agents. All reactions and manipulations were carried out under dry nitrogen. A methanolic solution of $LiCH_3O$ (9 mmol) was added to a solution of LH·HCl (5 mmol) in methanol (50 ml). The resulting solution was cooled to 0 °C and added with stirring to a cold solution of $FeCl_2 \cdot 4H_2O$ (2.5 mmol in 50 ml) in methanol. At this point, a stream of dry air was passed through the mixture for 15 minutes and the solution became purple. A precipitate of this colour which formed after a few minutes was filtered off and washed with cold ethanol. *Anal.* Calcd. for $C_{12}H_{36}N_6Cl_3Fe_3S_6$: C, 19.7; H, 4.9; N, 11.5 Found: C, 19.7; H, 4.8; N, 11.1. Calcd. for $C_{18}H_{54}N_6Cl_3Fe_3O_3S_6$: C, 24.9; H, 6.2; N, 9.7. Found: C, 24.2; H, 5.9; N, 9.4.

Results and Discussion

Intramolecular bond lengths and angles are listed in Table I, the numbering system is displayed in Fig. 1. The crystal structure consists of discrete trinuclear cations $[Co_3(MPA)_6]^{3+}$ and chloride anions linked by NH...Cl hydrogen bonds and weak interionic forces (Table II). The central metal atom Co(1) is located on a crystallographic inversion centre and imposes to the cation C_i symmetry. The Co(1) atom is surrounded

TABLE I. Bond Distances and Bond Angles.

Bond Distances (Å)		Bond Angles (°)	
Co(1)–S(1)	2.264(1)	S(1)–Co(1)–S(2)	80.2(1)
Co(1)–S(2)	2.263(1)	S(1)–Co(1)–S(3)	81.4(1)
Co(1)–S(3)	2.262(1)	S(2)–Co(1)–S(3)	80.8(1)
Co(2)–S(1)	2.247(1)	S(1)–Co(2)–S(2)	81.0(1)
Co(2)–S(2)	2.242(1)	S(1)–Co(2)–S(3)	82.2(1)
Co(2)–S(3)	2.243(1)	S(2)–Co(2)–S(3)	81.6(1)
Co(2)–N(1)	2.021(3)	N(1)–Co(2)–N(2)	90.1(2)
Co(2)–N(2)	2.022(3)	N(2)–Co(2)–N(3)	88.8(2)
Co(2)–N(3)	2.031(3)	N(1)–Co(2)–N(3)	90.0(2)
S(1)–C(11)	1.823(4)	Co(2)–S(1)–C(11)	109.3(2)
S(2)–C(21)	1.815(4)	Co(2)–S(2)–C(21)	109.7(2)
S(3)–C(31)	1.826(4)	Co(2)–S(3)–C(31)	109.7(2)
C(11)–C(12)	1.505(6)	Co(2)–N(1)–C(13)	123.5(3)
C(21)–C(22)	1.526(6)	Co(2)–N(2)–C(23)	122.8(3)
C(31)–C(32)	1.498(6)	Co(2)–N(3)–C(33)	122.1(3)
C(12)–C(13)	1.510(7)	S(1)–C(11)–C(12)	113.9(3)
C(22)–C(23)	1.511(6)	S(2)–C(21)–C(22)	112.3(3)
C(32)–C(33)	1.493(6)	S(3)–C(31)–C(32)	113.6(3)
C(13)–N(1)	1.486(5)	C(11)–C(12)–C(13)	114.3(4)
C(23)–N(2)	1.486(5)	C(21)–C(22)–C(23)	112.2(4)
C(33)–N(3)	1.475(5)	C(31)–C(32)–C(33)	114.6(4)
		C(12)–C(13)–N(1)	113.4(4)
Co(1)–Co(2)	2.974(1)^a	C(22)–C(23)–N(2)	113.7(4)
S(1)–S(2)	2.917(1)^a	C(32)–C(33)–N(3)	114.3(4)
S(1)–S(3)	2.951(1)^a	Co(1)–S(1)–Co(2)	82.5(1)
S(2)–S(3)	2.931(1)^a	Co(1)–S(2)–Co(2)	82.6(1)
		Co(1)–S(3)–Co(2)	82.6(1)

^{a}No bonding distances.

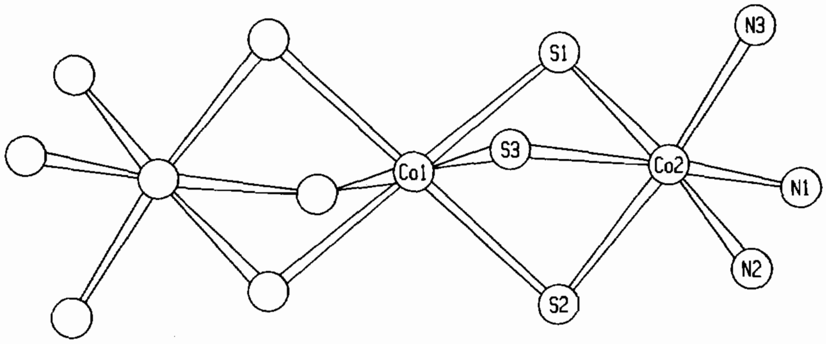

Fig. 1. A simplified view of the cation $[Co_3(MPA)_6]^{3+}$ showing the numbering scheme. Carbon atoms are labeled as S(n)–C(n1)–C(n2)–C(n3)–N(n).

TABLE II. Shortest Interionic Distances (Å).

N(1)......Cl(1)^{i}	3.278
N(1)......Cl(1)^{ii}	3.404
N(2)......Cl(1)^{iii}	3.278
N(3)......Cl(1)^{iii}	3.360
N(3)......Cl(2)^{iv}	3.356
OW.......Cl(1)^{ii}	3.341
OW.......Cl(2)^{iv}	3.383

Symmetry code:
i $= 1 - x, y, \frac{1}{2} - z$
ii $= x, 1 - y, z + \frac{1}{2}$
iii $= x, y, z$
iv $= x - \frac{1}{2}, y - \frac{1}{2}, z$

by six bridging sulphur atoms and the geometry around this atom is octahedral with trigonal distortion (the S–Co(1)–S angles between crystallographic independent sulphur atoms average 80.4°). Terminal Co(2) atoms are also in an octahedral arrangement but in this case only the S–Co(2)–S angles show lower values than the right angle. Consequently, the structure can be described as being formed by three octahedra sharing two opposite faces, where the S–S edges have been constrained. This fact has been observed in several thiolate complexes, and it has been attributed to steric requirements of the bridging atoms or attractive forces between sulphur atoms, among other possibilities [4, 11]. In our case, perhaps non-bonding interactions between the metal atoms could also be considered. All the Co–S bond lengths are in accordance with literature data [12, 13]. As in other Co(III) complexes with aminothiolates, the Co–N distances appear significantly lengthened as a result of sulphur trans effects [13]. The Co_2S_2 rings show an anti isomerism as can be seen in Fig. 2 [11]. All the chelate rings of the cation have chair conformation (Fig. 2). The rings S(1)C(11)C(12)C(13)N(1)Co(2) and S(3)C(31)C(32)C(33)N(3)Co(2) are very similar while S(2)C(21)C(22)C(23)N(2)Co(2) has a slightly different geometry (Table III). These chair conformations are significantly flattened in comparison with the chelate rings in the same conformation in the complex $[Ni_3(MPA)_4]Cl_2$. It has been attributed to interactions between the ligands in the tris chelate octahedral complexes [14].

TABLE III. Dihedral angles.

Mean Planes	Dihedral Angles (°)
C(11)C(12)C(13), C(11)C(13)S(1)N(1)	62.4
C(21)C(22)C(23), C(21)C(23)S(2)N(2)	65.4
C(31)C(32)C(33), C(31)C(33)S(3)N(3)	62.1
S(1)Co(2)N(1), S(1)N(1)C(11)C(13)	27.6
S(2)Co(2)N(2), S(2)N(2)C(21)C(23)	24.3
S(3)Co(2)N(3), S(3)N(3)C(31)C(33)	27.1

Fig. 2. A stereoscopic view of $[Co_3(MPA)_6]^{3+}$.

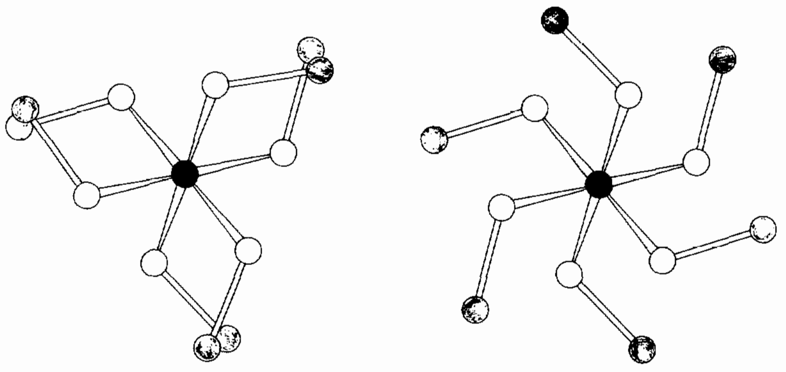

Fig. 3. A view of the fragment [$Co(1)S_6$] along the Co(1)–Co(2) axis showing the carbon atoms attached to sulphur atoms. Sulphur, carbon and cobalt are white, grey and black respectively. a) In the hypothetical complex with optical activity. b) In the complex [$Co_3(MPA)_6]Cl_3$.

TABLE IV. Electronic Spectra.

Complex	λ^a (ϵ)
[$Co_3(MEA)_6]Cl_3$ ^{b}	546sh (2140) 438 (5620) 347 (18190) 275 (25560)
[$Co_3(MPA)_6]Cl_3$	525sh (~2000) 420sh (~6400) 361 (18500) 250 (28500)

^{a}In nm. ^{b}Reference 2.

The electronic spectra of [$Co_3L_6]Cl_3$ complexes (L = MEA, MPA), are very similar (Table IV). On the contrary, the spectra of trinuclear square-planar complexes [$Ni_3L_4]Cl_2$ show significant differences which were attributed to the different Ni–Ni distances (2.733 Å in the complex with MEA and 3.104 Å in the complex with MPA) [4]. Therefore, the addition of another methylene group to the chelate ring in the octahedral trinuclear complexes does not cause important modifications between the chromophores, and the structures of both complexes should be very similar. Nevertheless, there is one difference that should be emphasized. The complex with MEA was prepared in both the meso and optically active forms [2]. However, with MPA only the meso form has been obtained. The optically active isomers could be destabilized with respect to the meso form as a result of steric hindrance between the methylene groups attached to sulphur atoms (Fig. 3). This fact would probably be enhanced in the complex with MPA.

Finally, iron(III) complexes with the same stoichiometry as the above Co(III) complexes have been prepared with the ligands MEA and MPA. The infrared spectra of these iron complexes are practically identical to those of the homologous Co(III) complexes. Consequently it is reasonable to think of an octahedral trinuclear structure for these iron(III) complexes. We were unable to register the X-ray powder diagram of the iron complexes for comparison purposes, since they decompose during the data collection. Further work on the magnetic interactions in the latter complexes is in progress.

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