A linear mixed oxidation state trinuclear cobalt complex with six bridging sulfito ligands

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Abstract

A linear mixed oxidation state trinuclear cobalt complex $\{Co^{II}[(O_3S)_3Co^{III}(NH_3)_3]_2\}^{4-}$ (**1**), having six bridging sulfito ligands, was obtained by the reaction between $Na_2S_2O_4$ and an oxidized solution of $CoCl_2$ in ammonia. The structure of **1**, as found in the crystals of $[(NH_3)_5CoSO_3]_4 \cdot \mathbf{1} \cdot 16H_2O$, was determined by X-ray crystallography. The compound is triclinic, space group $P\bar{1}$ with $a = 11.956(2)$, $b = 13.260(3)$, $c = 11.480(2)$ Å, $\alpha = 96.50(3)$, $\beta = 111.86(3)$, $\gamma = 81.61(3)°$, $V = 1668(1)$ Å^3 and $Z = 1$. Complex **1** can be regarded as two tridentate $[(NH_3)_3Co(SO_3)_3]^{3-}$ ligands, oxo coordinated to a Co^{2+} ion, forming an octahedral geometry. The dimensions of **1** correspond closely to full D_{3d} symmetry.

Introduction

The ability of a sulfito ligand to bridge two metal atoms as shown in Fig. 1 was postulated in the past [1], but was structurally substantiated only recently. Fukuhara *et al.* showed the existence of such a bridge in a mixed oxidation state, trinuclear cobalt complex, namely, $[Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}L)_2\text{-}Co_2^{III}(Pr^nOH)_2]$ where L = propane-1,3-diylbis(α-methylsalicylideneiminate) (α,α'-Me$_2$-Salpd) [2]. This complex was obtained by the reaction between $[Co^{III}(L')L]$ (L' = acetylacetonate, salicylaldehyde, etc.) and SO_2 in an alcoholic solvent.

We report here the preparation and structure of a new mixed oxidation state, linear trinuclear cobalt(III, II, III) complex with six bridging sulfito ligands. The complex, $[(H_3N)_3Co^{III}(\mu\text{-}SO_3)_3Co^{II}(\mu\text{-}SO_3)_3Co^{III}(NH_3)_3]^{4-}$ (**1**) is prepared in aqueous solution by using $S_2O_4^{2-}$ to reduce Co(III) and an SO_3^{2-} source.

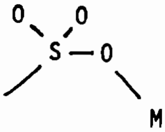

Fig. 1. Bridging SO_3^{2-} ligand.

Experimental

Preparation

$CoCl_2 \cdot 6H_2O$ (10 g), $(NH_4)_2CO_3$ (25 g) and concentrated ammonia (125 ml) were dissolved in 125 ml H_2O. Air was bubbled through the solution for 8 h. $Na_2S_2O_4$ (3 g) was added and the solution was kept at 5 °C for 3 days. The brown crystals of $NH_4[Co(NH_3)_4(SO_3)_2] \cdot 2H_2O$ were filtered and the mother liquor was kept at 5 °C for 8 more days. The orange crystals of $[(NH_3)_5CoSO_3]_4 \cdot \mathbf{1} \cdot 16H_2O$ were collected and washed with acetone and ether. Yield 0.3 g.

X-ray crystallography

Data were collected on a PW1100 Philips diffractomer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 22 reflections in the range of $12 < \theta < 16°$. Data were measured by using ω–2θ motion. Crystallographic data and other pertinent information are given in Table 1. Lorentz and polarization corrections were applied. The heavy atom positions were obtained by using the results of SHELX-86 direct method analysis.

The structure was refined** in space group $P\bar{1}$ to convergence by using anisotropic thermal parameters

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**All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

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TABLE 1. Crystallographic data for $[Co(NH_3)_5SO_3]_4$-$[Co_3(SO_3)_6(NH_3)_6]\cdot 16H_2O$

Formula	$Co_7H_{110}N_{26}O_{46}S_{10}$
Formula weight	1944.17
Space group	$P\bar{1}$
a (Å)	11.956(2)
b (Å)	13.260(3)
c (Å)	11.480(2)
α (°)	96.50(3)
β (°)	111.86(3)
γ (°)	81.61(3)
V (Å^3)	1668(1)
Z	1
D_{calc} (g cm^{-3})	1.936
μ (cm^{-1})	20.20
Range of 2θ (°)	4–46
No. unique data	4520
Data with $F_o^2 > 3\sigma(F_o^2)$	2926
No. parameters	313
R	0.0709
R_w	0.0847

TABLE 2. Positional parameters and e.s.d.s for **1**

Atom	x	y	z
Co(1)	0.50000	0.50000	0.50000
Co(2)	0.6831(2)	0.4561(2)	0.2787(2)
S(1)	0.4840(3)	0.4905(3)	0.2064(3)
S(2)	0.6874(4)	0.3445(3)	0.4103(4)
S(3)	0.7051(3)	0.5843(3)	0.4230(3)
O(11)	0.4309(9)	0.5175(9)	0.3072(9)
O(12)	0.4475(9)	0.5764(8)	0.1257(9)
O(13)	0.4332(9)	0.3987(8)	0.1345(9)
O(21)	0.5853(9)	0.3622(8)	0.457(1)
O(22)	0.801(1)	0.346(1)	0.520(1)
O(23)	0.685(1)	0.2416(9)	0.350(1)
O(31)	0.6438(9)	0.5766(8)	0.5117(8)
O(32)	0.8356(9)	0.5874(9)	0.4965(9)
O(33)	0.658(1)	0.6798(9)	0.361(1)
N(1)	0.865(1)	0.421(1)	0.335(1)
N(2)	0.668(1)	0.346(1)	0.140(1)
N(3)	0.693(1)	0.553(1)	0.161(1)

for all cobalt, sulfur, SO_3^{2-} oxygen atoms and the nitrogen atoms of **1** and isotropic ones for all the rest of the oxygen and nitrogen atoms. The discrepancy indices $R=\Sigma|F_o|-|F_c|/\Sigma|F_o|$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table 1.

Results and discussion

The positional parameters of the atoms in **1** are presented in Table 2. Table 3 gives some important bond distances and angles. Figure 2 shows the numbering scheme in **1**. With $Z=1$ in space group $P\bar{1}$ there is only half a $\{Co[(O_3S)_3Co(NH_3)_3]_2\}^{4-}$ ion in the asymmetric unit, with the other half related to it by a crystallographic center of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Complex **1** can be regarded as an octahedral complex of Co^{2+} coordinated to two tridentate $[(NH_3)_3Co(SO_3)_3]^{3-}$ ligands. The dimensions of **1** correspond closely to full D_{3d} symmetry. The net charge of 4− requires that there be two Co^{3+} ions and one Co^{2+} in **1**. The average Co–S and Co–O distances, 2.208(2) and 2.07(1) Å, respectively, are very similar to those found in $[Co_3(SO_3)_2(\alpha,\alpha'$-$Me_2$-salpd$)_2(Pr^nOH)_2]$, 2.213(2) and 2.032(6) Å, indicating a similar Co^{III}–Co^{II}–Co^{III} arrangement [2]. The shorter Co...Co distance of 3.066 Å in the salpd complex, compared to 3.872(2) Å in **1**, is probably the result of two μ-phenoxo bridges. The 4− charge of **1** is balanced by four $[Co(NH_3)_5SO_3]^+$ ions in the lattice having a similar structure to that found in the crystal of the chloro salt [3].

175.6(3)0

TABLE 3. Important bond lengths (Å) and bond angles (°) for **1**

Co(1)–O(11)	2.08(1)		
–O(21)	2.06(1)		
–O(31)	2.08(1)		
Co(2)–S(1)	2.205(4)		
–S(2)	2.213(5)		
–S(3)	2.208(4)		
–N(1)	2.02(1)		
–N(2)	2.01(1)		
–N(3)	2.01(1)		
O(11)–Co(1)–O(21)	85.6(5)	S(2)–Co(2)–S(3)	92.8(2)
–O(31)	87.9(4)	–N(1)	86.5(4)
O(21)–Co(1)–O(31)	91.7(4)	–N(2)	91.3(4)
O(11)–Co(1)–O(21)′	94.4(5)	–N(3)	175.5(5)
–O(31)′	92.1(4)	S(3)–Co(2)–N(1)	90.9(4)
O(21)–Co(1)–O(31)′	88.3(4)	–N(2)	175.6(3)
S(1)–Co(2)–S(2)	94.7(2)	–N(3)	88.3(4)
–S(3)	92.0(2)	N(1)–Co(2)–N(2)	87.6(6)
–N(1)	176.8(4)	–N(3)	89.1(6)
–N(2)	89.4(5)	N(2)–Co(2)–N(3)	87.6(5)
–N(3)	89.7(5)		

The dithionite ion, $S_2O_4^{2-}$, used in the preparation of **1** undergoes decomposition in aqueous solution according to eqn. (1).

$$2S_2O_4^{2-} + H_2O \longrightarrow S_2O_3^{2-} + 2HSO_3^- \qquad (1)$$

Subsequently, some of the Co^{3+}, which is produced by air oxidation of $CoCl_2$ in ammonia, is probably reduced by the thiosulfate ion according to eqn. (2).

$$2Co^{3+} + 2S_2O_3^{2-} \longrightarrow 2Co^{2+} + S_4O_6^{2-} \qquad (2)$$

1 is one of the few examples of a mixed oxidation state, linear tricobalt compound. Other examples of this group are $[Co_3(OCH_2CH_2NH_2)_6]^{2+}$ [4] and $Na_4[Co_3(NH_3)_6(SO_4)_6]\cdot 6H_2O$ [5].

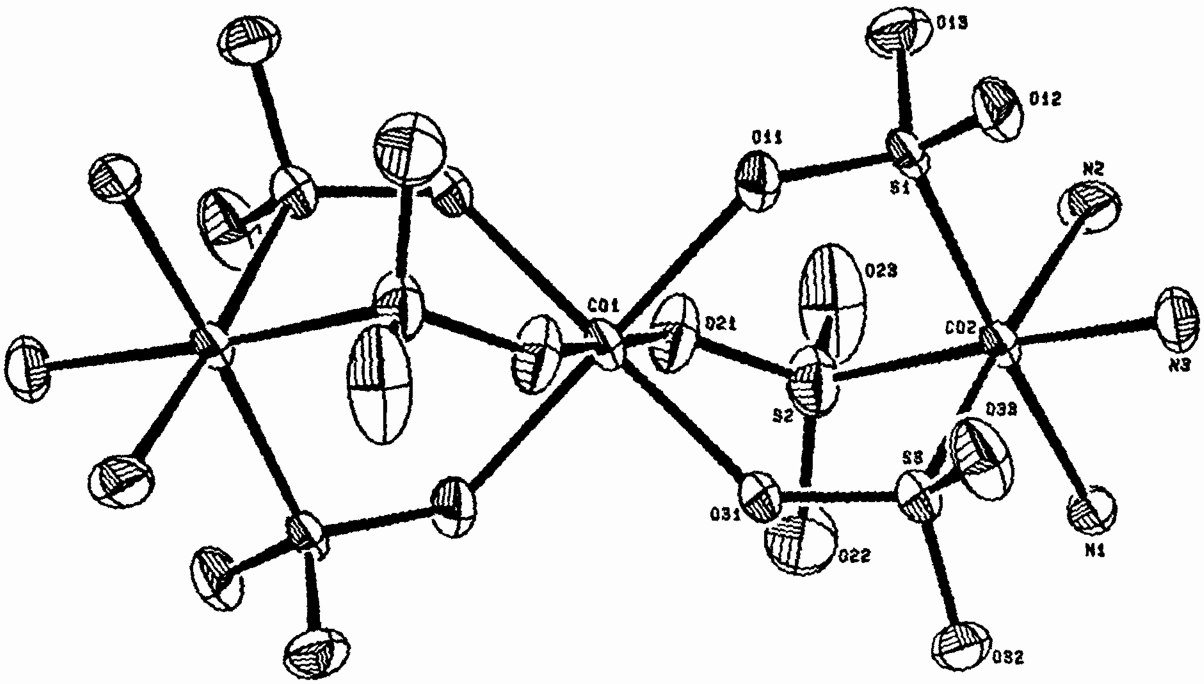

Fig. 2. The structure of $[(H_3N)_3Co(\mu\text{-}SO_3)_3Co(\mu\text{-}SO_3)_3Co(NH_3)_3]^{4-}$ (1).

Supplementary material

Positional parameters of all atoms, thermal parameters, and a table of bond distances and angles are available from the authors.

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References

1 R. Eskenazi, J. Raskovan and R. Levitus, *J. Inorg. Nucl. Chem.*, *27* (1965) 371.

2 C. Fukuhara, E. Asato, T. Shimoji, K. Katsura, M. Mori, K. Matsumoto and S. Ooi, *J. Chem. Soc., Dalton Trans.*, (1987) 1305.

3 R. C. Elder and M. Trkula, *J. Am. Chem. Soc.*, *96* (1974) 2635.

4 J. A. Bertrand, J. A. Kelley and E. G. Vassian, *J. Am. Chem. Soc.*, *91* (1969) 2394.

5 V. M. Novotortsev, O. G. Ellert, T. S. Kapanadze and A. Y. Buslaev, *Koord. Khim.*, *14* (1986) 856.