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Crystal and Molecular Structure of a Triply-thiolate-bridged Binuclear Cobalt(III) Complex, $[Co_2\{SCH(CH_2CH_2NH_2)_2\}_3](ClO_4)_3 \cdot H_2O$

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Synopsis. The crystal structure of tris[μ-(1,5-diamino-3-pentanethiolato)-*N,N'*, μ-*S*]-dicobalt(III) perchlorate monohydrate was determined by the single-crystal X-ray diffraction method. The binuclear complex has a novel type of binuclear structure in which the two cobalt atoms are bridged by three thiolate sulfur atoms forming a face-shared bioctahedron.

Metal compounds with thiolate ligands are now regarded as an important class of complex in the field of bioinorganic chemistry.[1] A number of compounds containing metal atoms bridged by thiolate sulfur have been reported, but little effort has been devoted toward the isolation of discrete binuclear metal complexes as yet.[2] Recently, Murase *et al.* reported the synthesis of binucleating ligand, 1,5-diamino-3-pentanethiol (Hdpet), and its binuclear complexes, $[M_2(dpet)_2](ClO_4)_2$ (M=Ni, Pd) and $[Co_2(dpet)_3](ClO_4)_3$.[3] Based on the analytical, spectral and magnetic data, they concluded that the cobalt(III) complex possesses a binuclear structure in which the two cobalt atoms are bridged by three thiolate sulfur atoms forming a face-shared bioctahedron. To our knowledge, this is the first example of a triply-thiolate-bridged binuclear cobalt(III) complex. In this study, we have confirmed the structure of $[Co_2(dpet)_3](ClO_4)_3$ by the single-crystal X-ray diffraction method.

Experimental

Black crystals of $[Co_2(dpet)_3](ClO_4)_3 \cdot H_2O$ were prepared by method previously reported.[3] A crystal with dimensions of 0.20×0.40×0.42 mm was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo*Kα* radiation (λ=0.71069 Å) at 23±1 °C.

Crystal Data: $Co_2(C_5H_{13}N_2S)_3(ClO_4)_3 \cdot H_2O$, F.W.=833.93, monoclinic; $P2_1/c$; a=11.101(4), b=28.619(6), and c=10.692(2) Å; β=113.66(2)°; V°=3111(1) Å^3; D_m=1.78, D_c=1.78 g cm^{-3}; Z=4.

The intensity data were collected by the 2θ—ω scan technique with a scan rate of 4° min^{-1}. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. A total of 5960 reflections with $2\theta < 50°$ were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. Independent 4439 reflections with $|F_o| \geq 3\sigma(F_o)$ were considered as "observed" and were used for the structure analysis.

TABLE 1. FRACTIONAL POSITIONAL PARAMETERS (×10^4) AND THERMAL PARAMETERS OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2
Co(1)	3072(1)	1011(1)	6343(1)	2.6
Co(2)	1301(1)	1362(1)	7586(1)	2.7
Cl(A)	4922(2)	3612(1)	7489(2)	4.3
Cl(B)	−975(2)	2037(1)	10025(3)	4.7
Cl(C)	−2659(2)	293(1)	6781(3)	4.5
S(A)	2417(2)	1732(1)	6555(2)	3.2
S(B)	975(2)	830(1)	5926(2)	3.7
S(C)	3171(2)	949(1)	8487(2)	3.4
OW	3417(8)	−1097(3)	10014(8)	7.3
O(A1)	5217(9)	3479(5)	8803(8)	10.0
O(A2)	4759(20)	3246(4)	6631(13)	17.0
O(A3)	5935(14)	3845(5)	7403(14)	13.2
O(A4)	3850(13)	3865(7)	6988(11)	18.0
O(B1)	260(10)	2198(5)	10733(13)	11.9
O(B2)	−1829(11)	2178(5)	10568(12)	12.1
O(B3)	−945(14)	1573(4)	9930(16)	13.1
O(B4)	−1388(15)	2181(7)	8714(12)	16.5
O(C1)	−1713(7)	286(3)	6209(9)	6.9
O(C2)	−2365(10)	610(4)	7830(12)	10.5
O(C3)	−3890(8)	421(4)	5750(9)	8.6
O(C4)	−2849(15)	−153(4)	7123(13)	11.9
N(1A)	4952(7)	1222(3)	6964(8)	4.0
N(2A)	1897(8)	1818(3)	9145(8)	4.1
N(1B)	2802(8)	1071(3)	4385(7)	4.3
N(2B)	−343(7)	1730(3)	6625(8)	4.6
N(1C)	3639(8)	349(3)	6310(8)	4.1
N(2C)	346(7)	986(3)	8471(8)	4.2
C(1A)	5229(9)	1715(4)	6747(10)	4.5
C(2A)	4966(10)	2065(3)	7648(10)	4.5
C(3A)	3840(10)	1976(3)	8024(10)	4.4
C(4A)	3420(11)	2368(3)	8679(10)	4.9
C(5A)	2172(11)	2300(4)	8877(11)	5.1
C(1B)	1563(11)	1269(4)	3353(9)	5.2
C(2B)	381(11)	982(9)	3171(9)	5.4
C(3B)	−198(10)	1046(4)	4242(10)	5.2
C(4B)	−811(11)	1501(4)	4238(10)	5.6
C(5B)	−1366(9)	1561(4)	5321(11)	5.4
C(1C)	4230(12)	78(4)	7598(13)	6.1
C(2C)	3305(12)	−30(4)	8195(13)	5.9
C(3C)	2899(13)	349(4)	8941(12)	5.9
C(4C)	1649(12)	262(4)	9090(12)	5.5
C(5C)	1073(10)	654(4)	9592(9)	4.6

The structure was solved by the direct method. Refinement was carried out by the block-diagonal least-squares method. Hydrogen atoms were inserted in their calculated positions and included in the refinement. The final R value was $R=\sum||F_o|-|F_c||/\sum|F_o|$=0.071. Final difference Fourier map was featureless except for three peaks of 1.26—1.78 e/Å^3 in the vicinity of the sulfur atoms, S(A), S(B), and S(C). All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version[4] of the UNICS-III and the ORTEP programs. The final positional and thermal parameters with their estimated standard deviations are given in Table 1. The coordinates and isotropic temperature factors of the hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, bond lengths and bond angles, and the F_o-F_c tables have been deposited as a Document No. 8528 at the Office of the Editor.

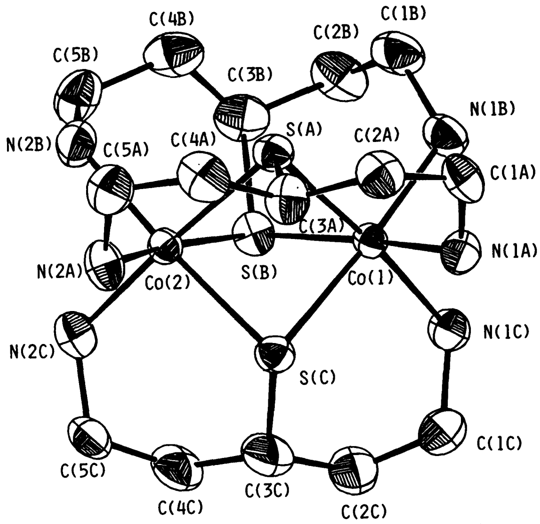

Fig. 1. A perspective view of [Co$_2$(dpet)$_3$]$^{3+}$ ion. Selected bond lengths (l/Å) and angles (ϕ/°) are: Co(1)–Co(2) 2.955(2), Co(1)–S(A) 2.229(3), Co(1)–S(B) 2.247(3), Co(1)–S(C) 2.257(3), Co(2)–S(A) 2.229(3), Co(2)–S(B) 2.256(3), Co(2)–S(C) 2.243(3), Co(1)–N(1A) 2.013(8), Co(1)–N(1B) 2.000(8), Co(1)–N(1C) 2.003(8), Co(2)–N(2A) 2.008(8), Co(2)–N(2B) 1.997(8), Co(2)–N(2C) 1.996(10); Co(1)–S(A)–Co(2) 83.04(9), Co(1)–S(B)–Co(2) 82.03(8), Co(1)–S(C)–Co(2) 82.09(8).

Results and Discussion

The crystal structure consists of discrete binuclear clusters, [Co$_2$(dpet)$_3$]$^{3+}$, perchlorate ions and crystal water molecules. A perspective view of the complex ion, [Co$_2$(dpet)$_3$]$^{3+}$, is shown in Fig. 1. As has been anticipated, the complex ion consists of two distorted octahedra sharing the face formed by the three thiolate sulfurs.

The Co–S bond lengths (2.229—2.257 Å) fall in the range of those of other cobalt(III)-mercaptide complexes.⁵⁾ The Co–N bond lengths (1.996—2.013 Å) are significantly longer than those of ordinary cobalt(III)-amine complexes. The observed lengthening seems to be due to the trans influence of the thiolate sulfur coordination as was observed for cobalt(III) complexes containing 2-aminoethanethiol.⁵⁾

The Co–Co distance is 2.955(2) Å and the Co–S–Co angle 82.0—83.1°. For some tri(μ-hydroxo)dicobalt(III) complexes Co–Co distances of 2.55—2.58 Å, and Co–O–Co angles of 81—86° were reported.⁶⁾ Thus, the substitution of the thiolate sulfur for the hydroxo oxygen leads to an appreciable lengthening of the metal-metal separation.

The water molecules and perchlorate ions are in the vicinity of the amino groups of the dpet ligands by hydrogen bonds.

References

1) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977); C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, **27**, 153 (1980).

2) S. L. Rose, R. E. Hoskin, J. E. Cavanaugh, C. J. Smith, and E. L. Blinn, *Inorg. Chim. Acta*, **40**, 7 (1980).

3) I. Murase, S. Ueno, and S. Kida, *Bull. Chem. Soc. Jpn.*, **56**, 2748 (1983).

4) S. Kawano, *Rep. Comput. Cent. Kyushu Univ.*, **16**, 113 (1983); T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1979); C. K. Johnson, Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

5) R. C. Elder, L. R. Florian, R. F. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973); H. C. Freeman, C. J. Moore, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.*, **17**, 3513 (1978); M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **19**, 554 (1980).

6) P. Andersen, *Acta Chim. Scand.*, **21**, 243 (1967); G. S. Mandel, N. S. Mandel, R. E. Marsh, and W. P. Schaefer, *Acta Crystallogr., Sect B.*, **33**, 700 (1977); G. H. Searle and T. W. Hambley, *Aust. J. Chem.*, **35**, 1297 (1982).