Instrumental Achievements

Crystal Structure of an Oxygen Carrier, [N,N'-Bis(3-aminopropyl)-1,3-propanediamine-N,N',N'',N''']-bis(thiocyanato-N)cobalt(III)

Yasuko T. OSANO, Kaoru HORIUCHI, Jun-ichi MATSUURA and Takao MATSUZAKI

Research Center, Mitsubishi Kasei Corporation, Kamoshida, Yokohama 227, Japan

The process of selective transport across membranes is often facilitated by carriers; such a process is called facilitated transport. Several cobalt complexes are known as oxygen carriers which are of interest as biological models¹ or as practical means to produce pure

oxygen from the air.^{2,3} The title complex is obtained from a solution used for a facilitated oxygen transport membrane. The penta-coordination complex is formed when the complex dissolved in a nonaqueous solvent with or without a suitable base. Since it binds a molecular oxygen reversibly, it is able to act as an oxygen carrier for facilitated transport.⁴ An X-ray crystallographic analysis of this complex was performed in order to elucidate the coordination mode of the chain ligand, bis(3-aminopropyl)-1,3-propanediamine.

Crystals suitable for the X-ray analysis were obtained by recrystallization from ethanol under a nitrogen atmosphere. Crystal data and experimental details are listed in Table 1. Hydrogen atoms were identified on a difference-Fourier map and refined with isotropic temperature factors, except for those attached to C6, C11 and C13, the positions of which were calculated geometrically. Atomic parameters for non-hydrogen atoms are listed in Table 2.

Bond distances are listed in Table 1. ORTEP drawing is shown in Fig. 1. The complex has a typical octahedral structure, with four N atoms of 3-amino-propyl-1,3-propanediamine at equatorial positions and two thiocyanate N atoms at axial positions. One of the thiocyanate ligands, (N31-C32-S33) exists in disordered structures which are characterized by a slight variation in the Co-N=C angle. The Co atom is shifted from the equatorial plane formed with four N atoms toward the N21 atom of thiocyanate by 0.1 Å. The Co-N21 bond distance is the shortest among all the Co-N bonds. The structural feature indicated that the coordination strengths between Co and the two thiocyanate with longer Co-N bond distance (and thus weaker

Table 1 Crystal and experimental data

Formula: C ₁₁ H ₂₆ N ₆ S ₂ Co
Formula weight=365.4
Crystal system: monoclinic
Space group: C2/c Z=8
a=25.457(4) Å α=—
b=7.728(1) β=93.46(1)°
c=17.464(1) γ=—
V=3429(2) Å ³
D _x =1.416 g/cm ³
R=0.084
No. of reflections used=3529
Measurement: Enraf-Nonius CAD4
Structure determination: SHELXS86
Refinement: SHELX76

Table 2 Final coordinates of non-hydrogen atoms (×10⁵ for Co atom, ×10⁴ for other atoms)

Atom	x	y	z	B or B _{eq}
CO	36973(3)	29312(12)	12940(5)	2.7
N1	3720(2)	3411(8)	2524(3)	2.9
C2	3839(3)	1970(11)	3089(4)	3.5
C3	4324(3)	994(11)	2894(4)	3.4
C4	4242(3)	-208(10)	2204(4)	3.3
N5	4236(2)	695(7)	1456(3)	2.3
C6	4209(3)	-627(9)	836(4)	3.5
C7	4238(3)	93(10)	45(4)	3.5
C8	3757(3)	1032(10)	-279(4)	3.1
N9	3704(2)	2775(7)	42(3)	2.3
C10	3279(3)	3708(10)	-406(4)	3.3
C11	2914(3)	5831(11)	538(4)	4.2
C12	3218(3)	5576(11)	-172(4)	3.8
N13	3217(3)	5258(8)	1241(3)	3.7
N21	3050(2)	1253(8)	1359(3)	3.1
C22	2870(2)	197(9)	1721(4)	2.8
S23	2624(1)	-1317(3)	2253(1)	4.1
N31	4412(2)	4461(8)	1257(3)	3.4
C32	4821(3)	5092(8)	1270(4)	2.7
S33A	5359(3)	6215(12)	1223(5)	2.7(2)
S33B	5422(3)	5706(10)	1232(5)	2.5(1)
S33C	5389(2)	6165(8)	1435(3)	2.3(1)

Occupancy factors of S33A, S33B and S33C are 0.3, 0.3 and 0.4, respectively.

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j)$$

Fig. 1 Chemical structure.

Table 3 Bond distances (Å)

N1	---C0	2.177(5)
N5	---C0	2.213(5)
N9	---C0	2.191(5)
N13	---C0	2.173(6)
N21	---C0	2.104(6)
N31	---C0	2.173(6)
C2	---N1	1.507(9)
C3	---C2	1.504(10)
C4	---C3	1.522(10)
N5	---C4	1.484(8)
C6	---N5	1.487(8)
C7	---C6	1.496(9)
C8	---C7	1.504(10)
N9	---C8	1.468(9)
C10	---N9	1.484(8)
C12	---C10	1.510(11)
C12	---C11	1.515(10)
N13	---C11	1.479(8)
C22	---N21	1.145(8)
S23	---C22	1.642(7)
C32	---N31	1.149(8)
S33A	---C32	1.629(10)
S33B	---C32	1.608(9)
S33C	---C32	1.678(8)

Fig. 2 ORTEP drawing (Hydrogen atoms are omitted for clarity).

coordination strength) is released and replaced by a molecular oxygen.

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