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Structure and characterization of tris(4-morpholinedithiocarbamato-*S*,*S*′)cobalt($\cdot$)-acetonitrile solvate complex: $[Co(S_2CNC_4H_8O)_3]\cdot CH_3CN$

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The crystal and molecular structure of the complex $[Co(S_2CNC_4H_8O)_3]\cdot CH_3CN$ has been determined by X-ray crystallography. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a = 10.561(2)$, $b = 11.114(2)$, $c = 13.011(3)$ Å, $\alpha = 103.88(3)$, $\beta = 101.58(3)$, $\gamma = 114.91(1)^\circ$, and $Z = 2$. X-ray analysis reveals that the cobalt(III) atom is located at the apparent intersection of D_3 symmetry. Despite the apparent presence of the rotational axes, all of the atoms in the structure were found to be unique; there are no symmetry-related atoms. The central cobalt atom is octahedrally coordinated by an arrangement of six S atoms. The octahedron is distorted as a result of the forced configuration of the four-membered chelate ring. The average Co–S distance is 2.273 Å. The FT-IR spectra clearly show there are acetonitrile molecules in the crystal lattice.

KEY WORDS: Cobalt complex; dialkyldithiocarbamate; octahedron.

Introduction

The dialkyldithiocarbamate anion, S_2CNR_2 (dtc), and its derivatives are used extensively in inorganic and organic chemistry, and as active agents in pharmacology, medicine, and biochemistry.[1] The ability of dtc to bind to metals has been known for many years.[2] It forms chelate complexes with virtually all transition elements.[3] Water soluble dialkyldithiocarbamate complexes are known to have been tested in various medical applications.[4,5] Their good performance in liquid–liquid extraction and other analytical procedures[6] makes them further attractive for the determination of metals by gas chromatography.[7] Morpholine-*N*-carbodithioate has been suggested as a possible analytical reagent in the spectrophotometric and volumetric determination of some 34 elements.[8] Recently, it has been utilized in the gravimertic determination of tellurium, copper, bismuth, cobalt, palladium, and nickel.[9] The reagent was used in the thin layer and paper chromatographic separation of metal complexes.[10] We also know that the tris-chelated cobalt(III) complexes of N,N-disubstituted dithiocarbamates which are noncharged species and kinetically inert should be resolvable into optical enantiomers.[11] In this paper, we reported the crystal structure of the title compound. Also, IR and TG spectra of the title compound have been determined.

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Experimental

All chemicals were obtained from a commercial source and used without further purification.

Synthesis of the $C_4H_8ONCS_2Na$

To a stirred solution of morpholine (1.00 g, 11.5 mmol) in CH_3CN (100 mL) was added at below 4°C, carbon disulfide (0.874 g, 11.5 mmol) and sodium hydroxide (50% aqueous solution, 11.5 mmol). After stirring for 4–5 h, the solution was left to evaparate at room temperature. The pure $C_4H_8ONCS_2Na$ was obtained by recrystallization from the solution of CH_3CN. Yield: 92%.

Synthesis of the $Co(III)(C_4H_8ONCS_2)_3$

To a heated aqueous solution of $C_4H_8ONCS_2Na$ (0.15 mol) was added an aqueous solution of $Co(CH_3COO)_3$, (0.05 mol) with stirring. A green precipitate was deposited and collected by filtration. The precipitate was washed with water and dried over P_4O_{10}. Single crystals suitable for X-ray analysis were obtained by recrystalization from CH_3CN. The C, H, and N contents were determined by elemental analysis (Found: C, 34.47; H, 4.24; N, 9.42%. Calcd for $C_{17}H_{27}N_4NCoO_3S_6$: C, 34.77; H, 4.60; N, 9.54%).

The IR spectrum (KBr pellets) showed $\nu_{C=N}$ stretching bands at 1483, 2963, and 2849 cm^{-1} for the morpholine ring. The absence of $\nu_{C=S}$ at 1600 cm^{-1} in the IR spectrum of Co(III) complex suggests that the cobalt atom is chelated with both the sulfur atoms of CS_2.[12] The existence of $\nu_{C\equiv N}$ at 2080 cm^{-1} suggests the presence of CH_3CN.

Thermal analysis of the title compound show that the complex first decomposes at a temperature of 144°C. The lost weight is 7.4%, which indicates the evaporation of the CH_3CN solvent (Calcd 7.0%). At 347.8°C, the complex decomposes quickly, until at 395.2°C the weight loss is 82.0%, suggesting that the residue is Co_2S_3 (Calcd 81.8%).

A summary of the key crystallographic information is given in Table 1. The crystal was mounted on a four-circle CAD4 diffractometer. Reflection data and reflections for the unit cell determination were measured at 20°C using Mo Kα radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The technique used was ω-scan with θ limits $1.72° < \theta < 24.98°$. Empirical absorption correction were carried out by using the SADABS[13] program.

The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the *SHELXTL*[14] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional $R(F) = 0.0368$ and $wR(F^2) = 0.1126$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(F^2) + (0.0662P)^2 + 1.4057P]$, where $P = (F^2 + 2Fc^2)/3$. The molecular graphics were plotted using

Table 1. Summary of Crystallographic Results for $[Co(S_2CNC_4H_8O)_3]\cdot CH_3CN$

Empirical formula	$CoC_{17}H_{27}N_4O_3S_6$
Formula weight	586.72
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.561(2)$ Å
	$b = 11.114(2)$ Å
	$c = 13.011(3)$ Å
	$\alpha = 103.88(3)°$
	$\beta = 101.58(3)°$
	$\gamma = 114.91(3)°$
Volume, Å^3	1263.2(4)
Z	2
Density (calculated), Mg/m^3	1.543
Absorption coefficient, mm^{-1}	1.202
$F(000)$	608
Radiation, Å	Mo Kα($\lambda = 0.71073$)
Temperature, K	293(2)
θ range, deg	1.72–24.98
Limiting indices	$0 \le h \le 12, -13 \le k \le 11, -15 \le l \le 15$
Independent reflections	4698/4434 [$R_{int} = 0.0242$]
$R[I > 2\sigma(I)]$	$R1 = 0.0368$, $wR2 = 0.1126$
R(all data)	$R1 = 0.0525$, $wR2 = 0.1291$
Goodness of fit on F^2	1.133
Largest diffraction peak and hole e/Å^{-3}	0.809 and −0.466

SHELXTL.[14] Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*.[15] The final position parameters of non-H atoms are given in Table 2.

Results and discussions

Figure 1 shows a perspective view of the title compound with atomic numbering scheme. Selected bond lengths and angles are presented in Table 3.

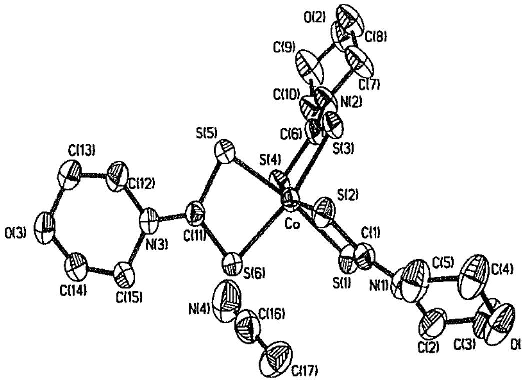

Fig. 1. The molecular structure of $[Co(S_2CNC_4H_8O)_3]\cdot CH_3CN$ showing the atom labeling scheme. Atoms are represented as thermal ellipsoids at 30% level.

The crystal structure contains two tris (4-morpholinedithiocarbamato-*S,S′*) cobalt(III) acetonitrile solvate molecules, $[Co(S_2CNC_4H_8O)_3]\cdot CH_3CN$. X-ray analysis reveals that the cobalt(III) atom is located at the apparent intersection of D_3 symmetry. Despite the apparent presence of the rotational axes, all of the atoms in the structure were found to be unique; there are no symmetry-related

Table 2. Atomic Coordinates(10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2)

	X	*Y*	*Z*	$U_{eq}{}^a$
Co	7293(1)	4756(1)	2313(1)	35(1)
S(1)	5053(1)	4583(1)	1542(1)	46(1)
S(2)	6049(1)	4101(1)	3487(1)	44(1)
S(3)	6620(1)	2480(1)	1340(1)	41(1)
S(4)	7983(1)	4882(1)	768(1)	44(1)
S(5)	9494(1)	5211(1)	3469(1)	41(1)
S(6)	8480(1)	7144(1)	3302(1)	41(1)
O(1)	372(4)	2379(5)	2815(4)	84(1)
O(2)	7426(4)	524(3)	−2436(3)	67(1)
O(3)	14021(3)	10226(3)	6108(3)	59(1)
N(1)	3276(4)	3679(4)	2740(3)	51(1)
N(2)	7261(4)	2256(4)	−567(3)	53(1)
N(3)	11117(3)	7978(3)	4824(3)	41(1)
N(4)	8874(7)	8673(8)	699(6)	120(2)
C(1)	4579(4)	4062(4)	2605(3)	43(1)
C(2)	2090(5)	3807(6)	2055(5)	66(1)
C(3)	607(6)	2566(7)	1817(5)	78(2)
C(4)	1457(6)	2099(7)	3376(5)	77(2)
C(5)	2988(6)	3309(6)	3709(4)	71(2)
C(6)	7296(4)	3085(4)	369(3)	40(1)
C(7)	6485(7)	694(5)	−922(5)	73(2)
C(8)	7204(7)	72(5)	−1506(5)	74(2)
C(9)	8311(8)	2012(6)	−2031(5)	84(2)
C(1)	7684(7)	2767(5)	−1455(5)	73(2)
C(1)	9885(4)	6941(4)	3997(3)	35(1)
C(1)	12203(5)	7727(5)	5495(4)	51(1)
C(1)	13733(5)	8793(5)	5627(5)	60(1)
C(1)	13061(5)	10447(5)	5375(4)	52(1)
C(1)	11425(4)	9451(4)	5233(4)	47(1)
C(1)	7893(7)	8562(6)	968(5)	75(2)
C(1)	6634(8)	8390(9)	1322(5)	96(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of the Compound

Bond lengths	
Co—S(3)	2.257(1)
Co—S(2)	2.263(1)
Co—S(5)	2.273(1)
Co—S(6)	2.277(2)
Co—S(1)	2.282(1)
Co—S(4)	2.287(1)
S(1)—C(1)	1.708(4)
O(1)—C(3)	1.416(7)
N(1)—C(1)	1.321(5)
N(1)—C(2)	1.465(6)
Bond angles	
S(3)—Co—S(6)	167.37(4)
S(5)—Co—S(1)	166.33(5)
S(2)—Co—S(4)	164.42(5)
S(5)—Co—S(6)	76.20(6)
S(2)—Co—S(1)	76.12(5)
S(3)—Co—S(4)	76.41(5)
C(3)—O(1)—C(4)	109.4(4)
C(9)—O(2)—C(8)	109.4(4)
C(14)—O(3)—C(13)	109.2(3)
C(2)—N(1)—C(5)	113.8(4)
C(7)—N(2)—C(10)	113.5(4)
C(15)—N(3)—C(12)	113.7(3)

atoms. The central cobalt atom is octahedrally coordinated by an arrangement of six S atoms. The octahedron is distorted as a result of the forced configuration of the four-membered chelate ring. The average Co–S distance is 2.273Å. The cobalt atom lies on a twofold axis, which bisects one of the two dithiocarbamate ligands. The atoms in a second dithiocarbamate ligand all lie in general positions, but in turn they generate a third dithiocarbamate ligand by the action of the twofold axis. It is easy to see in Fig. 1 that the geometry of the six S atoms surrounding the cobalt are quite distorted from that of a regular octahedron, as demonstrated by the S_1–Co–S_5, S_2–Co–S_4 and S_3–Co–S_6 angles of 166.33(5), 164.42(5), and 167.37(4)°. This distortion from a perfect octahedron is due primarily to the constraint imposed on the geometry of the molecule by the rigid nature of the dithiocarbamate ligands and by the size of the "bite" angles at the metal, which in this case are S_1–Co–S_2= 76.12(5), S_3–Co–S_4 = 76.41(5), and S_5–Co–S_6= 76.20(6)°. The distorted octahedral configuration of the title complex is also seen in other derivatives in this series $[Co(S_2CNR_2)_3]$: [R = Et, i-Pr, CH_2Ph].[16,17] The bond lengths of Co–S are in the range of 2.257(1)–2.287(1) Å. The N_1–C_1 bond distance [1.321(5) Å] is shorter than the other N–C bond distance, which are indicative of considerable double-bond character.

Three morpholine rings all form the chair conformation. The maximum atom deviations from planes of each ring are 2.54, 2.66, 2.68Å, respectively. The chelate rings with the carbon atoms of the conjunct morpholine ring are coplanar. Three planes are mostly perpendicular to one another, with the dihedral angles of 85.53, 84.09, and 81.73°, respectively.

The solvent molecules are orientated to minimize electrostatic repulsions with the complex. However, no strong hydrogen bonding interactions exist.[18]

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