

Crystal and molecular structure of pyrrolidine dithio carbamate cobalt(III) chelate

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Abstract. Pyrrolidine dithio carbamate (PDTC) cobalt(III) chelate has been used as a coprecipitation matrix for obtaining preconcentration factors of 100 or more for analytical estimation of trace metals in natural waters. This chelate, suitable for bivalent and trivalent ions, crystallizes as dark green crystals in monoclinic space group $C2/c$ with unit cell parameters $a = 28.89 \text{ \AA}$, $b = 14.39 \text{ \AA}$, $c = 16.17 \text{ \AA}$ and $\beta = 104.2^\circ$. X-ray crystallographic analysis of these crystals reveals that three PDTC are coordinated to a Co_0^{3+} atom through their sulphur atoms, the six sulphur atoms forming a distorted octahedra around the metal atom at an average distance of 2.26 \AA . The thiocarbamate part of the ligands is nearly planar but the pyrrolidine rings are puckered.

Keywords. Pyrrolidine dithio carbamate; cobalt-chelate; crystal structure.

1. Introduction

The occurrence of heavy metals, especially lead and cadmium in the environment is now recognized as a major health problem. The abundance of these heavy metals in natural waters has been directly linked to the extent of their low level toxic interaction with tissues such as kidney. With the low ambient level of Cd ($< 1 \text{ ppb}$) in public waters, available analytical methods are inadequate and the method of coprecipitation for preconcentrations of trace metals prior to their analytical determination by atomic absorption spectroscopy has special advantage in reducing large volumes of the sample to a few milligrams of the material. Coprecipitation of trace heavy metals on trispyrrolidine dithio carbamate cobalt (III) has been developed earlier for the study of sea water by Boyle and Edmond (1975). Krishnamurthy and Reddy (1977) extended the procedure to include other natural waters, soil extracts and sediment digestates. Concentration factors ranging from 40 to 400 are obtained in this method and it is particularly useful for preconcentration of Pb, Cd, Ni and Cu. In this study the coprecipitation matrix has been the subject of investigation in view of its extraordinary thermal and photochemical stability under ambient conditions as also its versatility to retain several trace metals such as Cu, Cd, Pb, Ni, Fe and Cr but not Mn and Zn. The dithio carbamate ligand is also of great biological interest due to its action on the growth and viability of sarcoma cells and fibrocytes, use in the treatment of alcoholism and its function as a protectant against lethal effects of radiation (Powell 1954; Cohen *et al* 1957). The structural studies of these ligand metal complexes provides much needed information on the metal-sulphur distances for characterizing the heavy metal sulphur binding in the tissue. In this paper we report the results of our study on the crystal structure of the matrix cobalt (III)-(pyrrolidine dithio carbamate)₃.

2. Experimental

Several batch samples of the cobalt-chelate are prepared under the coprecipitation conditions used in the analysis of natural waters. The procedure is as follows: to one litre of di-ionized distilled water are added 5 ml of 6 M HNO_3 and 2.5 ml of $\text{Co}(\text{NO}_3)_2$ stock solution ($\approx 2000 \mu\text{g Co (II)}$ per 10 ml) followed by 10 ml of NH_4OAc buffer solution (170 g NH_4OAc in 5000 ml of water purified by ADPC-CCl_4 extraction 3 times). The pH of the mixture should be ≈ 4 . A 2% solution of the precipitant, ammonium pyrrolidine dithio carbamate (APDC) in the meanwhile is purified by repeated CCl_4 extractions and 5 ml of this reagent are added to the cobalt mixture. The contents of the beaker are allowed to stand for 30 minutes with intermittent stirring when a yellowish green opalescence develops due to the formation of cobalt (II) pyrrolidine dithio carbamate chelate. The yellowish green colour gradually changes to green on standing due to ready oxidation of the chelate to a +3 cobalt state (Gleu and Schwab 1950; Malissa and Schöffmann 1955). The cobalt (III) chelate thus obtained is filtered through a 0.45 millipore filter and air dried at room temperature to yield a green flaky material exhibiting creep properties. Several one liter batch precipitations are filtered through the same filter paper to increase yield and facilitate sample handling. Microanalytical results using Perkin-Elmer 240 elemental analyzer gave molecular formula $\text{CON}_3\text{S}_6\text{C}_{15}\text{H}_{24}$ (M.W. 497) corresponding to 1 : 3 chelation between cobalt and the ligand.

The $\text{Co}(\text{PDTC})_3$ is dissolved in methyl isobutyl ketone and recrystallized to yield dark green shining crystals. The crystals are monoclinic, C centered with $a = 28.89 \text{ \AA}$, $b = 14.39 \text{ \AA}$, $c = 16.17 \text{ \AA}$ and $\beta = 104.2^\circ$. The x-ray diffraction intensities were measured to a Bragg angle of 60° using nickel filtered Cu radiation ($\lambda = 1.542 \text{ \AA}$) on a General Electric 490 automatic diffractometer by stationary crystal stationary counter method (Furnas and Harker, 1955). The crystals were very small and poor scatterers and so 7116 diffraction data from two equivalent sets were measured and averaged to give 3506 unique reflections. Only about 2100 of these (60%) had intensities greater than $3\sigma(I)$ and were considered observed and used in structure refinement. The intensities were corrected for geometrical factors in the usual way. No absorption corrections were applied.

3. Structure determination

Systematic absence hkl for $h + k$ odd and hol for l odd revealed C centering and a glide plane parallel to c axis. The intensity statistics favoured a centrosymmetric space group. Hence the structure analysis and refinements were carried out in space group $\text{C}2/c$. The measured density and volume of the unit cell indicated 12 molecules of $\text{Co}(\text{PDTC})_3$ in the unit cell. In space group $\text{C}2/c$ this implies one molecule in the general position and another in a special position on the two-fold axis. The location of the cobalt atoms were found from a sharpened Patterson map and all the remaining 37 atoms were found and refined by Fourier and least squares methods. Positional and anisotropic thermal parameters of all but the three atoms on the two fold axes were refined by block diagonal least squares and the usual R factors for 2105 reflections used in the structure determination and refinement is 12%. Fractional atomic coordinates and equivalent thermal parameters are given in table 1. Lists of observed and calculated structure factors are also included as supplementary material.

Table 1. Fractional coordinates and equivalent B values of atoms.

Atom	X/a	Y/b	Z/c	B _{eq}	Atom	X/a	Y/b	Z/c	B _{eq}
COA	0.1673	0.4609	0.5303	5.6	C5A	0.2134	0.7214	0.3607	4.5
COB	0.0000	0.0408	0.7500	5.4	C1B	0.2419	0.3775	0.6477	3.9
S1A	0.1366	0.6072	0.5153	5.1	C2B	0.3080	0.3839	0.7745	4.8
S2A	0.2108	0.5308	0.4498	4.4	C3B	0.3402	0.3083	0.8206	6.1
S3A	0.2117	0.3299	0.5519	4.1	C4B	0.3402	0.2324	0.7521	5.3
S4A	0.2220	0.4870	0.6574	4.7	C5B	0.2959	0.2415	0.6860	4.2
S5A	0.1093	0.4033	0.5862	5.3	C1C	0.0796	0.3665	0.4856	5.1
S6A	0.1144	0.4004	0.4158	3.9	C2C	0.0180	0.2929	0.3713	3.4
S1B	0.0627	-0.0586	0.7785	4.8	C3C	-0.0323	0.2784	0.3786	5.4
S2B	0.0153	0.0258	0.8918	5.2	C4C	-0.0277	0.2435	0.4681	5.3
S3B	0.0487	0.1651	0.7510	5.3	C5C	0.0106	0.2993	0.5292	5.3
NA	0.1813	0.7098	0.4158	5.5	C1D	0.0649	-0.0430	0.8852	3.9
NB	0.2790	0.3369	0.6987	5.6	C2D	0.1430	-0.1155	0.9459	5.6
NC	0.0374	0.3198	0.4642	4.9	C3D	0.1734	-0.0942	1.0322	5.9
ND	0.0953	-0.0684	0.9527	5.1	C4D	0.1409	-0.0954	1.0951	6.1
NE	0.0000	0.3216	0.7500	6.8	C5D	0.0927	-0.0459	1.0421	6.0
C1A	0.1772	0.6288	0.4549	4.6	C1E	0.0000	0.2336	0.7500	5.4
C2A	0.1539	0.7942	0.4283	4.4	C2E	-0.0441	0.3785	0.7419	6.2
C3A	0.1710	0.8666	0.3728	5.7	C3E	0.2250	0.4799	0.7292	6.4
C4A	0.1873	0.8082	0.3051	6.0					

4. Discussion

The coordination geometry of the chelate complex and the atom numbering scheme are shown in figure 1. A stereoscopic drawing of the molecule in the general position is given in figure 2. There is another molecule in the asymmetric part of the unit cell which

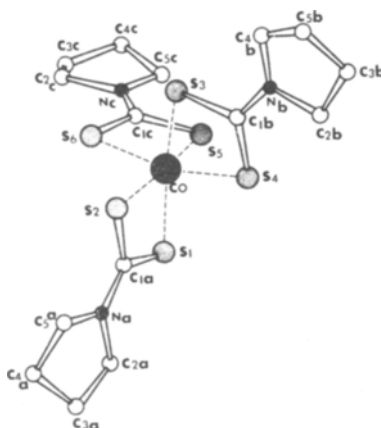


Figure 1. The coordination of the bidentate ligand around the cobalt atom is shown. The six sulphur atoms form a distorted octahedron around the cobalt atom with an average Co-S distance of 2.26 Å. There is another similar molecule in the asymmetric unit sitting with the cobalt atom and C₁ and N atoms of one of the ligand molecules on a crystallographic two fold axis. These molecules are also repeated by the glide and inversion symmetries of the space group.

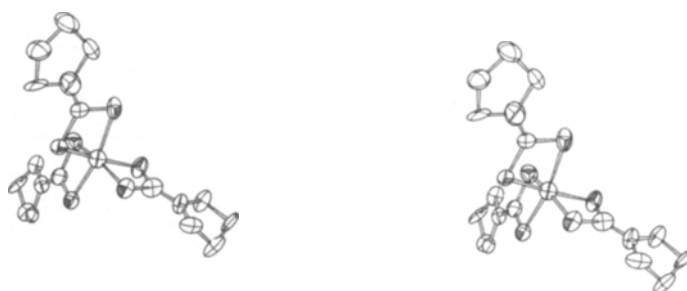


Figure 2. The stereo view of the $\text{Co}(\text{PDTC})_3$ molecule. This stereo pair may be conveniently viewed to see three dimensional arrangement with some practice or using simple hand held stereo viewers.



Figure 3. Average dimensions of a pyrrolidine dithio carbamate ligand. The carbamate part is planar but the pyrrolidine rings are puckerred.

is very similar but sitting with the crystallographic two fold axis passing through cobalt, C1E and NE atoms.

Each molecule is formed by three PDTC ligands coordinated to the Co atoms through their sulphur atoms. The six sulphur atoms form a distorted octahedron around the Co atom with an average Co–O distance of 2.26 Å. The distortion from regular octahedron is imposed by the molecular geometry resulting in $\text{S}_1\text{–Co–S}_2$ angle of 77° while $\text{S}_1\text{–Co–S}_3$ and $\text{S}_1\text{–Co–S}_4$ are 169 and 96 degrees respectively.

All atoms in the PDTC ligand lie very nearly in a plane with the cobalt atom. The dithio carbamate part is mostly planar, but the pyrrolidine part is puckerred. The C–N and S–C bonds are appreciably shortened and show partial double bond character. The bond lengths and angles in the five independent ligands are very similar and figure 3 shows the average dimensions for these. These bond lengths and angles do not show significant deviations from other similar complexes (Merlino 1968; Brennen and Bernal 1969; Healy and White 1972) involving both divalent and trivalent metals. This seems to indicate that for dithio carbamate ligand, the contributions of various resonance structures are not much affected by the nature of the central atoms or the crystal geometry. These resonance stabilized hybrids presumably readily react with radiation induced radicals giving the dithio carbamate the ability to protect the sensitive biological targets from effect of radiations.

The pyrrolidine ring shows some interesting variations for the different PDTC ligand molecules in the asymmetric unit. The intra ring torsion angles for the five different pyrrolidine rings are given in table 2 as well as their pseudo rotation amplitude and phase angle (Altona and Sundaralingam 1972) parameters. It must be remembered that because of the space group symmetry of the crystal there are also an equal number of

Table 2. Torsion angles of pyrrolidine rings.

	1	2	3	4	5
χ_0 (C ^d -N-C ^a -C ^b)	-1	-8	16	-16	-16
χ_1 (N-C ^a -C ^b -C ^c)	25	22	-32	34	40
χ_2 (C ^a -C ^b -C ^c -C ^d)	-39	-30	43	-41	-48
χ_3 (C ^b -C ^c -C ^d -N)	37	24	-29	28	40
χ_4 (C ^c -C ^d -N-C ^a)	-23	-9	7	-7	-16
Pseudo rotation amplitude	40	29	40	40	49
Pseudo rotation phase	268	254	66	244	252

rings for which the torsion angles of each ring are reversed in sign and hence have a pseudo rotation-phase angle which is 180 degrees in advance. Except for the ring 1 which has an envelope conformation with the C^c atom out of the plane formed by the other four atoms (Kartha *et al* 1974), all other pyrrolidine rings are significantly twisted and have conformations similar to those observed in other studies (Druyan *et al* 1976; Kartha *et al* 1982) also.

The sulphur atoms of the different ligands around the cobalt atom show contacts of 3.27 to 3.33 Å and correspond to some of the shortest S-S contacts reported in the literature.

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