

STRUCTURE OF THE TRIS(DIALLYLDITHIOCARBAMATE)COBALT(III) COMPLEX

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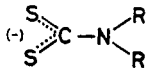
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The structure of $[\text{Co}\{\text{S}_2\text{CN}(\text{CH}_2\text{—CH}=\text{CH}_2)_2\}_3]$ was determined by the heavy atom method, all nonhydrogen atoms being refined by anisotropic diagonal approximation using the least squares method to the value of $R = 0.067$ for 1 024 reflections with $I \geq 1.96\sigma(I)$. The substance is isostructural with $[\text{Fe}\{\text{S}_2\text{CN}(\text{CH}_2\text{—CH}=\text{CH}_2)_2\}_3]$, crystallizes in the monoclinic system, space group C2/c, lattice parameters $a = 1.8763(9)$, $b = 1.0209(5)$, $c = 1.5402(7)$ nm, $\beta = 106.18(4)^\circ$, $Z = 4$. Cobalt is coordinated by 3 dithiocarbamate ligands in the bidentate way, the average Co—S length is 0.2267(2) nm. The metal atom and two ligand atoms are located on the twofold axis. The CoS_6 polyhedron is a trigonally distorted octahedron.

It is well known that tris-dithiocarbamate (henceforth tris-dtc) complexes of Fe(III), Co(III), In(III) and Ni(IV) (refs¹⁻⁸) exhibit octahedral coordination of the central atom, which is distorted appreciably from octahedral symmetry to trigonal prismatic symmetry. The coordination polyhedra of these compounds can be best described as transition states between two limiting forms, the octahedron and the trigonal prism (TP), the D_3 symmetry remaining preserved. The distortion of the coordination polyhedron of the central atom is also affected by the kind of substituent at the nitrogen atom. The distortion of the coordination polyhedron is due to the electronic effect, the participation of steric effects of the substituents being also feasible. The effect of phenyl substituents on the ligand field strength in $[\text{Co}(\text{dtc})_3]$ complexes was the concern of Healy and coworkers⁹, who observed a correlation between the ligand field strength and the number of phenyl groups at the nitrogen atom. This effect manifests itself in the C—N bond length and in the occurrence

of the dtc-ligand in the  form, where complete delocalization

of the π -electrons at the C=S bond into a four-membered chelate ring takes place, as is the case with the majority of transition metal dtc-complexes.

Determination of the crystal structure of the title compound contributes to the theory of the stereochemistry of $[\text{M}(\text{dtc})_3]$ complexes ($\text{M} = \text{Fe}, \text{Co}, \text{In}, \text{Ni}$) where the dtc-ligand involves the unconventional allyl substituent.

EXPERIMENTAL

The dark-green precipitate of $[\text{Co}(\text{allyl}_2\text{dtc})_3]$ separated from a mixture of aqueous solutions of sodium diallyldithiocarbamate and CoSO_4 combined in the ratio of 3 : 1. After filtering out and drying, the substance was dissolved in boiling hexane; by free evaporation of the solvent at -10°C , dark-green platelets of the $[\text{Co}(\text{allyl}_2\text{dtc})_3]$ crystals, stable in air, separated from the solution. The purity of the substance was confirmed by elemental analysis and by chelatometric determination of cobalt. For $\text{C}_{21}\text{H}_{30}\text{CoN}_3\text{S}_6$ (575.8) calculated: 43.80% C, 5.25% H, 10.23% Co, 7.30% N; found: 43.90% C, 5.33% H, 9.97% Co, 7.33% N. The measurements were performed on a crystal $0.35 \times 0.15 \times 0.20$ mm in size using a Syntex P2₁ four-circle diffractometer working with MoK_α radiation ($\lambda = 71.069$ pm) filtered by a graphite monochromator. Weissenberg photographs revealed that the substance crystallizes in the monoclinic system. The systematic extinction of the $h + k = 2n + 1$ and $h0l$ type for $l = 2n + 1$ suggested two space groups, $C2/c$ or Cc . The lattice parameters were refined based on 15 centered reflections ($15^\circ < 2\theta < 28^\circ$). The crystal density was measured by the flotation method in ZnSO_4 solution.

The intensities were measured by using the $\omega/2\theta$ scan technique and recorded in the range $2\theta \leq 50^\circ$. Out of the 2 431 independent reflections ($h = 0 \rightarrow 19$, $k = 0 \rightarrow 12$, $l = -18 \leftrightarrow 18$), 1 024 with $I \geq 1.96\sigma(I)$ were classified as observed, employed for the structure solution and refining. The crystal was recentered after each 100 measured reflections. The intensities of two standard reflections, (1 - 1 0, 2 0 - 2), did not reveal significant fluctuations. All intensities were corrected for the Lorentz and polarization factors. Correction for absorption was not accomplished. The structure was solved by the heavy atom method. The position of the Co atom, $x = 0.00$, $y = 0.08$ and $z = 0.25$, indicated that cobalt lies in a special position on the twofold axis. From the symmetry of the molecule it follows that this position should also suit to the C1 and N1 atoms. For this reason, the structure was solved in the space group $C2/c$. The correctness of the space group choice ($C2/c$ or Cc) was confirmed by the successful refinement of the structure, i.e. of the position parameters and thermal parameters of the atoms. The terminal C4, C8 and C11 carbon atoms possess high values of the thermal parameters B_{eq} , which are due to the appreciable flexibility of these atoms along the carbon chain. Disorder of these atoms was not confirmed by the performed detailed analysis of the ΔF maps. This fact may also be responsible for the anomaly in the C=C bond length in the allyl chain and for the associated increase in the bond angle. The structure was refined by the diagonal approximation using the least squares method for the minimization function $\sum w(|F_o| - |F_c|)^2$, where $w = 1$ for $|F_o| < 45$ and $w = 45/|F_o|$ for $|F_o| < 45$; the values obtained are $R = 0.067$ and $R_w = 0.069$. The shift of all parameters in the last refining cycle was $(\Delta/\sigma)_{\text{max}} = 0.2$. The differential Fourier synthesis of the residual electron density had the maximum and minimum of $8.7 \cdot 10^2$ and $-5.7 \cdot 10^2$ e . nm^{-3} , respectively. The scattering factors of the neutral atoms were taken from International Tables¹⁰. The calculations were performed on an M40-30 computer using crystallographic programs of NRC¹¹ and the PARST program¹². The basic crystallographic data are given in Table I, the refined position parameters, in Table II. The interatomic distances and bond angles are given in Table III. Figure 1 shows the projection of the molecule into the (100) plane with the labelling of the atoms. The IR spectra were measured by the KBr technique on a Perkin-Elmer 225 instrument, the ¹³C NMR spectra were measured on an NMR-FX 100 spectrometer (JEOL, Japan) at 15 GHz in deuteriochloroform.

DISCUSSION

The structure of the complex compound consists of discrete $[\text{Co}(\text{allyl}_2\text{dtc})_3]$ molecules located in a special position on the twofold axis. Intermolecular interactions

TABLE I
Basic crystallographic data of $[\text{Co}\{\text{S}_2\text{CN}(\text{CH}_2-\text{CH}=\text{CH}_2)_2\}_3]$

Crystallographic system	monoclinic
Space group	$C2/c$
Unit cell dimensions, nm	$a = 1.8763(9)$ $b = 1.0209(5)$ $c = 1.5402(7)$ $\beta = 106.18(4)^\circ$
Unit cell volume, nm^3	$V = 2.833$
Number of formula units per unit cell	$Z = 4$
Number of electrons per unit cell	$F(000) = 1\ 200$
Crystal density ($1\ 000$) kg m^{-3}):	
measured	$D_m = 1.33(2)$
calculated	$D_c = 1.35$
Linear absorption coefficient, mm^{-1}	$\mu(\text{MoK}\alpha) = 1.07$

TABLE II
Position parameters ($\cdot 10^4$) and isotropic thermal parameters $B_{\text{eq}} = (4/3) \sum \sum \beta_{ij} a_i a_j$. Standard deviations are given in parentheses

Atom	x	y	z	B_{eq} 10^{-2}nm^2
Co	0	864(1)	2500	4.35(7)
S(1)	351(1)	683(2)	1216(1)	5.60(7)
S(2)	736(1)	2606(2)	3050(1)	5.31(6)
S(3)	948(1)	-612(2)	2858(1)	5.30(6)
C(1)	0	3539(9)	2500	6.5(4)
C(2)	635(4)	5591(6)	3095(5)	5.7(2)
C(3)	540(4)	5710(8)	4052(6)	7.9(3)
C(4)	507(6)	6768(9)	4437(7)	10.9(6)
C(5)	1026(4)	-354(6)	1750(4)	5.7(3)
C(6)	1535(5)	-650(10)	512(5)	8.6(4)
C(7)	2063(5)	450(12)	452(6)	11.3(5)
C(8)	2377(7)	1267(15)	878(10)	18.4(9)
C(9)	2130(5)	-1750(9)	1967(6)	9.1(4)
C(10)	1810(8)	-3289(12)	1601(9)	15.1(9)
C(11)	2063(9)	-3921(19)	1381(10)	21.4(14)
N(1)	0	4885(7)	2500	5.4(4)
N(2)	1525(3)	-938(7)	1433(4)	7.5(3)

lower than 0.38 nm were not observed in the structure. All the three dtc ligands are coordinated to the Co atom in the bidentate way; the average Co—S bond length, 0.2267(2) nm, bears out the fact that the M—S bond lengths in the transition series increase with the number of unpaired electrons, the Fe—S bond length in the isostructural $[\text{Fe}(\text{allyl}_2\text{dtc})_3]$ complex being 0.2343(6) nm (ref.¹³). Due to the d^6 configuration, the Co—S bonds in $[\text{Co}(\text{dtc})_3]$ complexes are shorter and the S—Co—S chelate angle is larger. The chelate angle α in $[\text{Co}(\text{allyl}_2\text{dtc})_3]$ has the values of

TABLE III

Interatomic distances (pm) and bond angles (deg) in $[\text{Co}\{\text{S}_2\text{CN}(\text{CH}_2-\text{CH}=\text{CH}_2)_2\}_3]$. Standard deviations are given in parentheses

Atoms	Distance	Atoms	Distance
Co—S(1)	225.9(2)	N(1)—C(1)	137.4(11)
Co—S(2)	226.5(2)	N(2)—C(5)	131.4(9)
Co—S(3)	227.8(2)	N(1)—C(2)	147.3(7)
S(1)—S(3)	279.6(10)	N(2)—C(6)	145.3(10)
S(1)—S(2)	334.8(12)	N(2)—C(9)	146.0(10)
S(1)—S(1')	450.2(10)	C(2)—C(3)	153.7(11)
S(2)—S(2')	280.8(4)	C(6)—C(7)	151.8(11)
S(1)—S(3')	341.4(8)	C(3)—C(4)	124.2(12)
S(1)—C(5)	167.9(6)	C(7)—C(8)	112.1(18)
S(2)—C(1)	169.7(5)	C(9)—C(10)	162.0(10)
S(3)—C(5)	177.3(7)	C(10)—C(11)	110.4(19)
Atoms	Angle	Atoms	Angle
S(1)—Co—S(3)	76.1(1)	S(1)—C(5)—N(2)	128.5(5)
S(2)—Co—S(2')	76.6(1)	S(3)—C(5)—N(2)	123.3(5)
S(1)—Co—S(2)	95.5(1)	S(2)—C(1)—N(1)	124.1(1)
S(2)—Co—S(3)	94.3(1)	C(5)—N(2)—C(6)	118.3(6)
S(1)—Co—S(3')	97.6(4)	C(5)—N(2)—C(9)	124.8(6)
S(3)—Co—S(3')	97.2(1)	C(1)—N(1)—C(2)	119.3(3)
S(1)—Co—S(2')	91.9(4)	C(6)—N(2)—C(9)	116.5(6)
S(1)—Co—S(1')	170.6(10)	C(2)—N(1)—C(2')	121.4(7)
S(3)—Co—S(2')	164.3(1)	N(2)—C(6)—C(7)	113.2(7)
Co—S(1)—C(5)	89.3(2)	N(2)—C(9)—C(10)	110.9(7)
Co—S(3)—C(5)	86.4(2)	N(1)—C(2)—C(3)	110.3(5)
Co—S(2)—C(1)	85.8(1)	C(2)—C(3)—C(4)	124.2(8)
S(1)—C(5)—S(3)	108.2(4)	C(6)—C(7)—C(8)	129.5(9)
S(2)—C(1)—S(2')	111.7(5)	C(9)—C(10)—C(11)	124.2(8)

76.1(3)° and 76.6(1)°, while in [Fe(allyl₂dte)₃] the values are lower, 75.0(2)° and 74.4(2)°. The coordination polyhedron is trigonally distorted and is formed by two triangular walls which are nearly perpendicular to the pseudo-C₃ crystallographic axis (the walls form an angle of 1.7°). The mutual tilting of the S1S2'S3' and S1'S2S3 walls is characterized by the angle $\bar{\varphi} = 44.0^\circ$ (refs^{13,14}). The extent of distortion of the coordination polyhedron can also be described in terms of the S—Co—S angles, which can be divided¹⁴ into : (i) the chelate angle α (e.g. S1—Co—S3, $\bar{\alpha} = 76.3(2)^\circ$); (ii) angle between the Co atom and sulfur atoms of the same triangle

TABLE IV

Optimum planes constructed through selected atoms of the [Co{S₂CN(CH₂—CH=CH₂)₃}] molecule by using the least squares method. Each plane is defined as $AX + BY + CZ = D$. Standard deviations are given in parentheses

Co—S1—S3—C5—N2—C6—C9 plane		S1—S3—C5—N2 plane	
<i>A</i>	−0.5759(7)		−0.551(2)
<i>B</i>	−0.7560(7)		−0.769(1)
<i>C</i>	−0.3110(10)		−0.324(1)
<i>D</i>	−1.190(3)		−1.195(4)
χ^2	9.49		3.84
Atom deviation from plane, pm			
Co	−0.9(1)	S1	0.05(2)
S1	2.4(2)	S3	0.04(2)
S3	2.9(2)	C5	−1.3(7)
C5	−1.8(7)	N2	0.6(7)
N2	−3.9(7)	Co	−9.1(1)
C6	−7.6(10)	C6	−0.7(9)
C9	−17.9(9)	C9	−11.2(9)

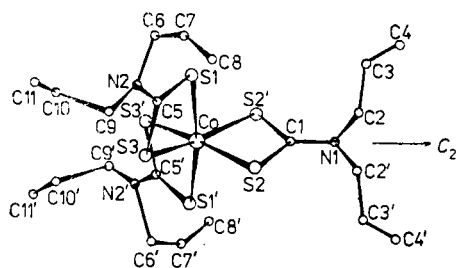


FIG. 1
Projection of the [Co{S₂CN(CH₂—CH=CH₂)₂}₃] molecule into the (100) plane

(e.g. S1—Co—S2', $\zeta = 94.6(4)^\circ$); (iii) angle between the Co atom and sulfur atoms of different triangles (e.g. S3—Co—S3', $\zeta' = 96.3(2)^\circ$); (iv) angle between the Co atom and sulfur atoms in the trans position belonging to different triangles (e.g. S1—Co—S1', $\gamma = 167.5(5)^\circ$). In the ideal octahedron, the angles $\alpha = \zeta = \zeta' = 90^\circ$, $\gamma = 180^\circ$.

In the dtc ligand, the S—C bond lengths lie within the range of 167.9(6) to 177.3(7) pm. The S3—C5 bond length, 177.3(7) pm, is significantly higher than the

average values found in the $\text{Co}(\text{S}_2\text{CN} \begin{array}{l} \text{R} \\ \diagup \quad \diagdown \\ \text{R} \end{array})_3$ complexes with $\text{R} = (\text{CH}_2)_4$, Me_2 ,

Et_2 , $i\text{-Pr}_2$, Ph_2 (ref.⁹) and H_2 (ref.⁴). The average C—N bond length, 134(1) pm, indicates a high double bond character. This was also confirmed by the occurrence of the $\tilde{\nu}(\text{C—N})$ band at 1480 cm^{-1} in the IR spectrum of this compound¹⁵. In the allyl part of the dtc ligand the average $\text{C}(sp^3)\text{—C}(sp^2)$ bond length, 155(1) pm, and $\text{C}(sp^2)=\text{C}(sp^2)$ bond length, 119(1) pm, differ from the values given by Allen and coworkers¹⁶, which are 150.2(13) and 130.0(27) pm, respectively. The shortening of the C=C double bond brings about extension of the C—C single bond. The existence of the double bond has been confirmed for the compounds $[\text{M}(\text{allyl}_2\text{dtc})_2]$ and $[\text{M}(\text{allyl}_2\text{dtc})_3]$ with $\text{M} = \text{Ni}, \text{Cu}, \text{Zn}, \text{Fe}$ and Co by the presence of a sharp $\tilde{\nu}(\text{C=C})$ band at 1640 cm^{-1} and by the chemical shifts in the ^{13}C NMR spectrum, $\sigma(\text{—CH=}) = 130.1$ and $\sigma(\text{CH}_2=) = 119.3$ (for $[\text{Zn}(\text{allyl}_2\text{dtc})_2]$, the two values are 130.9 and 119.3, respectively). Similar anomalies in the C—C bond lengths also appeared in the crystal structure determination of $[\text{Fe}(\text{Et}_2\text{dtc})_3]$ at 6°C (ref.¹⁴), of $[\text{Fe}(\text{Et}_2\text{dtc})_3\text{I}_5]$ (ref.¹⁷) and of $[\text{Ru}(\text{Et}_2\text{dtc})_3]$ (ref.¹⁸). As mentioned above, the cause of this is the high values of thermal parameters of the terminal carbon atoms, which are due to the flexibility of the carbon chain in the crystal structure. The parts of the ligand fragments were tested for planarity (Table IV). The metal atom is only slightly displaced from the two planes constructed. The high degree of π -conjugation in the ligand fragment is confirmed by the high planarity of the S_2CN fragment ($\chi^2 = 3.84$).

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