

Table 2 (cont.)

X—H...Y	X—H	X...Y	H...Y	X—H...Y	Symmetry	Translation		
OW1—H1W1...O7	0.76	2.750 (5)	2.01	165	1	0	0	-1
OW1—H2W1...OW3	0.99	2.822 (5)	1.84	168	1	0	0	-1
O2—HO2...O7	0.82	2.658 (3)	1.97	142	1	1	0	0
O6—HO6...O4	0.78	2.745 (5)	1.97	175	1	-1	0	0.
O3...OW4		2.935 (5)			1	0	0	0
O7...OW4		2.855 (5)			1	-1	0	1

a direct interaction between the phosphate group and the K^+ ion (Fig. 2), a feature also observed in the crystal structures of *G-1-P* K_2 (Narendra, Seshadri & Viswamitra, 1984), ADP K_2 (Katti & Viswamitra, 1979) and PEP K (Katti & Viswamitra, 1981). Interestingly, the O5, O6 and O9 atoms of the same molecule bind to the K^+ ion while in *G-1-P* K_2 , O9 belongs to another molecule related by space-group symmetry. In *G-1-P* Na_2 the O5 and O6 atoms of the same molecule also bind to the Na^+ ion. However, the additional link with the phosphate O atom of the same molecule does not exist because of the smaller ionic radius of Na^+ (0.98 Å) compared to K^+ (1.33 Å). The two coordination polyhedra share a face formed by OW5, O6 and O3 atoms and their arrangement in the monoclinic lattice is shown in Fig. 2.

There is extensive hydrogen bonding summarized in Table 2. All the hydroxyl O atoms except O4—H are involved in hydrogen bonding with the water O atoms. The *G-1-P** molecules are linked to form an infinite chain along the *a* axis through the intermolecular hydrogen bond between O2 and O7 atoms.

We thank Professor Viswamitra for his interest and encouragement.

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Structure of Poly[- μ -(2,2'-dithiodibenzoato- $O^1, O^2:O^3:O^4$)-hexamethylenetetraminiocobalt(II)]*

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Abstract. $[Co(C_6H_{13}N_4)(C_{14}H_8O_4S_2)]$, $M_r = 504.46$, triclinic, $P\bar{1}$, $a = 11.074$ (3), $b = 12.000$ (4), $c = 9.585$ (3) Å, $\alpha = 117.40$ (2), $\beta = 70.41$ (2), $\gamma =$

116.65 (2)°, $V = 997.3$ (6) Å³, $Z = 2$, $D_x = 1.68$, $D_m = 1.68$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.09$ mm⁻¹, $F(000) = 520$, $T = 296$ K. The structure was solved by the heavy-atom method and refined to $R = 0.067$ and $wR = 0.063$ for 3632 unique observed reflections. The single Co in the unit cell occupies

* Hexamethylenetetramine is 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]-decane.

two positions with fractional occupancy of 0.5. The structure is polymeric in nature with Co surrounded by four O atoms and one N showing a distorted trigonal bipyramidal stereochemistry. Two O atoms belonging to one carboxylate group of the dithiodibenzoate ion chelate to a Co atom and the two O atoms of the other carboxylate group of the dithiodibenzoate ion are singly bonded to two other neighbouring Co atoms. Interestingly, a short Co—O distance of 1.796 (3) Å is observed.

Introduction. Electronic spectral and magnetic investigations of the title compound (Subrahmanian, 1982) indicated a five-coordinate cobalt(II) complex. The single-crystal structure work was undertaken and has led to very interesting observations such as fractional occupancy of coordination sites of cobalt and a very short Co—O bond.

Experimental. The title compound was synthesized as follows: 20 ml 0.5 M hydrochloric acid were added to 100 ml of 1 M hexamethylenetetramine solution. 2 mmol of 2,2'-dithiodibenzoic acid were dissolved in that solution by heating. After cooling to 298 K, 4.5 ml of 1 M cobalt chloride solution were added and the contents set aside. After 15 d, transparent deep-pink needles of the title compound separated. They were washed with methanol and air dried. The yield was nearly quantitative. Seeding with earlier preparations enabled proper crystal growth to occur in fewer days. The slow rate of formation of crystals of this metal complex is suggestive of its unusual structural features. Elemental analysis: found (calculated): Co 6.1 (6.2), C 49.8 (50.6), H 4.3 (4.4), N 11.4 (11.8), S 14.0 (13.5)%.

A single crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was used for intensity-data collection; a diffraction photograph of the crystal showed absence of twinning and there were no superlattice reflections observed in the diffraction pattern; density measured by flotation; data collection using an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo $K\alpha$ radiation; accurate lattice parameters from least-squares refinement of 20 reflections with $30 < 2\theta < 40^\circ$. Integrated intensities were measured by $\omega/2\theta$ -scan technique; 3632 unique reflections in the range $2 < 2\theta < 60^\circ$ with $I \geq 3\sigma(I)$; $h - 13 \rightarrow 12$, $k - 14 \rightarrow 13$, $l 0 \rightarrow 12$; three standard reflections measured every hour showed no significant change. The data were corrected for Lorentz and polarization effects; no absorption correction was made. The structure was solved by the heavy-atom method. The single Co atom in the unit cell, when placed at the centre of inversion in $P\bar{1}$, did not develop the structure; the alternative of placing it in a general position in $P1$ also failed to produce the structure. One of the general positions in $P\bar{1}$

obtained from the Patterson map alone developed the structure. Hence the Co atom was given an occupancy factor of 0.5 in this position and the structure was obtained from subsequent difference Fourier maps. The occupancy of Co was refined, but remained close to 0.50 and hence the occupancy of Co was fixed at 0.50 in later refinement cycles. H-atom positions from difference Fourier maps; refinement using full-matrix least-squares procedure using *SHELX76* (Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms and isotropic thermal parameter for H atoms. Refinement converged to $R = 0.067$ and $wR = 0.063$ for 3632 unique reflections; the weighting scheme used was $w = 1.000/[\sigma^2(F_o) + 0.0011|F_o|^2]$; $\sum w(F_o - F_c)^2$ minimized; reflection-to-parameter ratio was 10.4; (shift/e.s.d.)_{max} in the final cycle of refinement of non-H atoms was 0.117; the maximum height in the final difference Fourier map was 0.50 e Å⁻³. Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion-correction factors from Cromer & Liberman (1970).

Discussion. Fig. 1 shows the molecular plot and atom-numbering scheme (Motherwell & Clegg, 1978). Table 1 lists the fractional atomic coordinates along with the equivalent isotropic thermal parameter of non-H atoms. Table 2 gives the bond parameters involving non-H atoms.*

* Lists of calculated and observed structure factors, anisotropic thermal parameters of non-H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52640 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

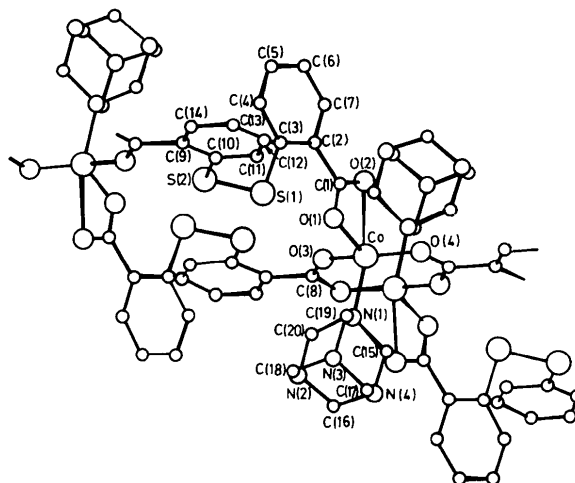


Fig. 1. Molecular plot and atom-numbering scheme.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2 , $\times 10^4$ for Co and S; $\times 10^3$ for other non-H atoms)

$$U_{eq} = (1/3\sin\alpha\sin\beta\sin\gamma)[(U_{11}\sin\alpha/\sin\beta\sin\gamma) + (U_{22}\sin\beta/\sin\alpha\sin\gamma) + (U_{33}\sin\gamma/\sin\alpha\sin\beta) + (U_{23}\sin 2\alpha/\sin^2\alpha) + (U_{13}\sin 2\beta/\sin^2\beta) + (U_{12}\sin 2\gamma/\sin^2\gamma)].$$

	x	y	z	U_{eq}
Co	0.4522 (1)	0.0289 (1)	0.6893 (1)	274 (4)
S(1)	0.1260 (1)	0.0911 (1)	1.1440 (1)	467 (4)
S(2)	-0.0632 (1)	0.0638 (1)	1.2834 (1)	448 (4)
O(1)	0.3480 (3)	0.1014 (3)	0.9196 (3)	61 (1)
O(2)	0.4478 (3)	0.2386 (3)	0.7894 (4)	89 (2)
O(3)	0.3147 (3)	-0.0283 (3)	0.5457 (4)	77 (2)
O(4)	0.6279 (3)	0.1041 (3)	0.7172 (4)	97 (2)
C(1)	0.3632 (3)	0.2040 (4)	0.9042 (4)	61 (2)
C(2)	0.2839 (3)	0.2921 (3)	1.0201 (4)	44 (1)
C(3)	0.1750 (3)	0.2522 (3)	1.1352 (4)	41 (1)
C(4)	0.1073 (3)	0.3417 (3)	1.2418 (4)	48 (2)
C(5)	0.1432 (4)	0.4642 (4)	1.2319 (5)	57 (2)
C(6)	0.2487 (4)	0.5017 (4)	1.1172 (5)	62 (2)
C(7)	0.3178 (4)	0.4154 (4)	1.0123 (4)	55 (2)
C(8)	0.2860 (8)	-0.0886 (3)	0.4072 (5)	56 (2)
C(9)	-0.1377 (3)	0.1438 (3)	1.6133 (4)	41 (1)
C(10)	-0.0298 (3)	0.1384 (3)	1.4846 (4)	35 (1)
C(11)	0.1037 (3)	0.1910 (3)	1.5153 (4)	46 (2)
C(12)	0.1295 (4)	0.2451 (4)	1.6686 (4)	55 (2)
C(13)	0.0235 (4)	0.2511 (4)	1.7954 (4)	63 (2)
C(14)	-0.1074 (4)	0.2018 (4)	1.7665 (4)	59 (2)
N(1)	0.4115 (3)	-0.1610 (3)	0.6941 (4)	63 (2)
N(2)	0.2437 (3)	-0.3867 (3)	0.6192 (4)	68 (2)
N(3)	0.3520 (4)	-0.3002 (3)	0.8460 (4)	68 (2)
N(4)	0.4837 (3)	-0.3537 (3)	0.5802 (3)	51 (1)
C(15)	0.5217 (4)	-0.2197 (4)	0.5887 (5)	66 (2)
C(16)	0.3549 (4)	-0.4370 (4)	0.5174 (4)	64 (2)
C(17)	0.4616 (4)	-0.3525 (4)	0.7403 (5)	62 (2)
C(18)	0.2268 (4)	-0.3824 (4)	0.7770 (5)	71 (2)
C(19)	0.3924 (5)	-0.1639 (4)	0.8561 (5)	80 (2)
C(20)	0.2816 (4)	-0.2540 (5)	0.6264 (6)	77 (2)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) involving non-H atoms

Co—O(1)	2.094 (2)	Co—O(2)	2.260 (4)
Co—O(3)	2.068 (4)	Co—O(4)	1.796 (3)
Co—N(1)	2.136 (4)	S(1)—S(2)	2.048 (1)
S(1)—C(3)	1.794 (4)	S(2)—C(10)	1.803 (4)
O(1)—C(1)	1.238 (7)	O(2)—C(11)	1.280 (5)
O(3)—C(8)	1.257 (6)	C(1)—C(2)	1.490 (5)
C(2)—C(3)	1.406 (4)	C(2)—C(7)	1.385 (6)
C(3)—C(4)	1.400 (5)	C(4)—C(5)	1.380 (7)
C(5)—C(6)	1.378 (6)	C(6)—C(7)	1.381 (6)
C(9)—C(10)	1.400 (4)	C(9)—C(14)	1.390 (6)
C(10)—C(11)	1.398 (5)	C(11)—C(12)	1.378 (6)
C(13)—C(14)	1.370 (7)	N(1)—C(15)	1.515 (6)
N(1)—C(19)	1.511 (7)	N(1)—C(20)	1.502 (6)
N(2)—C(16)	1.467 (6)	N(2)—C(18)	1.439 (7)
N(2)—C(20)	1.428 (8)	N(3)—C(17)	1.472 (6)
N(3)—C(18)	1.456 (6)	N(3)—C(19)	1.452 (7)
N(4)—C(15)	1.438 (6)	N(4)—C(16)	1.462 (5)
N(4)—C(17)	1.464 (6)		
O(1)—Co—O(2)	60.4 (1)	O(1)—Co—O(3)	103.2 (1)
O(1)—Co—O(4)	103.0 (1)	O(1)—Co—N(1)	95.4 (1)
O(2)—Co—O(3)	88.1 (1)	O(2)—Co—O(4)	87.6 (1)
O(2)—Co—N(1)	155.7 (1)	O(3)—Co—O(4)	146.9 (2)
O(3)—Co—N(1)	99.8 (1)	O(4)—Co—N(1)	97.4 (2)
S(2)—S(1)—C(3)	104.0 (1)	S(1)—S(2)—C(10)	105.0 (1)
Co—O(1)—C(1)	92.5 (2)	Co—O(2)—C(1)	84.0 (3)
Co—O(3)—C(8)	146.3 (3)	O(1)—C(1)—O(2)	121.4 (4)
O(1)—C(1)—C(2)	120.8 (3)	O(2)—C(1)—C(2)	117.9 (5)
C(1)—C(2)—C(3)	121.5 (4)	C(1)—C(2)—C(7)	118.9 (3)
C(3)—C(2)—C(7)	119.6 (3)	S(1)—C(3)—C(2)	120.4 (3)
S(1)—C(3)—C(4)	121.5 (3)	C(2)—C(3)—C(4)	118.1 (4)
C(3)—C(4)—C(5)	121.2 (3)	C(4)—C(5)—C(6)	120.3 (4)
C(5)—C(6)—C(7)	119.3 (5)	C(2)—C(7)—C(6)	121.5 (3)
C(10)—C(9)—C(14)	118.5 (3)	S(2)—C(10)—C(9)	120.4 (3)
S(2)—C(10)—C(11)	120.8 (2)	C(9)—C(10)—C(11)	118.8 (3)
C(10)—C(11)—C(12)	121.1 (3)	C(11)—C(12)—C(13)	120.2 (4)
C(9)—C(14)—C(13)	122.4 (3)	Co—N(1)—C(15)	112.6 (3)
Co—N(1)—C(19)	116.0 (2)	Co—N(1)—C(20)	106.0 (4)
C(15)—N(1)—C(19)	106.6 (4)	C(15)—N(1)—C(20)	107.0 (3)
C(19)—N(1)—C(20)	108.2 (3)	C(16)—N(2)—C(18)	109.0 (5)
C(16)—N(2)—C(20)	108.2 (3)	C(18)—N(2)—C(20)	109.0 (3)
C(17)—N(3)—C(18)	108.9 (3)	C(17)—N(3)—C(19)	108.2 (3)
C(18)—N(3)—C(19)	108.9 (5)	C(15)—N(4)—C(16)	108.9 (4)
C(15)—N(4)—C(17)	109.6 (3)	C(16)—N(4)—C(17)	108.1 (3)
N(1)—C(15)—N(4)	111.1 (3)	N(2)—C(16)—N(4)	111.8 (3)
N(3)—C(17)—N(4)	111.2 (5)	N(2)—C(18)—N(3)	112.5 (3)
N(1)—C(19)—N(3)	110.8 (3)	N(1)—C(20)—N(2)	111.9 (5)
C(12)—C(13)—C(14)	119.0 (4)		

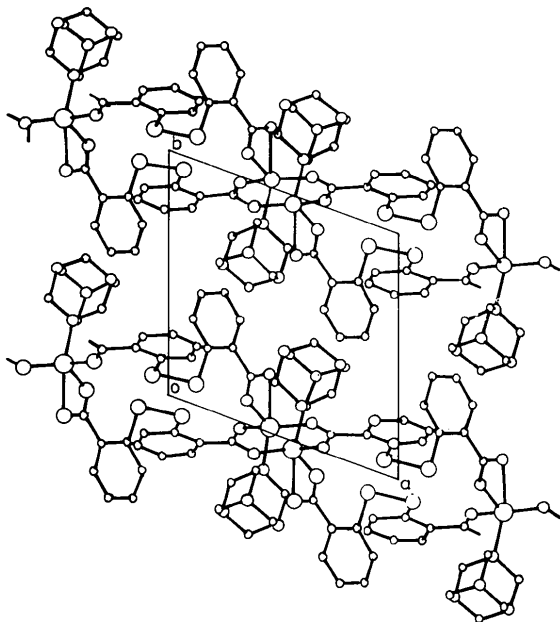


Fig. 2. Packing of the molecules in the unit cell.

The highlight of the structure is the partial occupancy observed for cobalt. We are unable to explain why a single Co in the unit cell sits in the two general positions in $P\bar{1}$. The two centrosymmetrically related disordered Co positions are 3.245 \AA apart.

The cobalt position is disordered in the molecule. Co is coordinated to four O atoms and one N. O(1) and O(2) from the same carboxylate ion are of chelating type whereas O(3) and O(4) from two other carboxylate ions are of bridging type. The geometry around Co is approximately trigonal bipyramidal with O(1), O(3) and O(4) forming the equatorial plane and O(2) and N(1) occupying the apical positions. The O(2)—Co—N(1) angle [$155.7(1)^\circ$] deviates considerably from linearity. Similar coordination geometry was observed around Co in chloro-(nitrilotriethanolato)cobalt(II) (Radha, Seshasayee, Kumar & Aravamudan, 1989). In that structure the angle formed at Co by the apical atoms was $177.9(3)^\circ$.

The Co—O(3) equatorial bonds are normal when compared with the sum of their corresponding ionic radii, 2.1 \AA . Similar Co—O bond lengths are observed in $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$ (Viostat, Khodadad & Rodier, 1981) and $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$ (Ganesh, Seshasayee,

Aravamudan, Heijdenrijk & Schenk, 1990). The short Co—O(4) equatorial bond is probably due to steric reasons since the two inversion-related planes CoO(1)O(3)O(4) and Co'O(1')O(3')O(4') are nearly planar and bring about a crowding in the equatorial region. The Co—O(2) and Co—N(1) bonds are of covalent nature. That the Co—O(2) bond is longer may be attributed to the fact that O(1) and O(2) are bonded to C(1) with O(1) lying in the equatorial plane and O(2) in the apical position.

Each dithiodibenzoate ion links three Co atoms through its carboxylate O atoms making the structure polymeric. The polymerization is chain-like and extends along the *a* axis. The polymeric nature of the compound is depicted in Fig. 2. The chains are packed in layers nearly parallel to the *ac* plane. The bond parameters in the dithiodibenzoate group are normal when compared with those observed in bis(triethanolamine)nickel(II) dithiodibenzoate (Ramalingam, Aravamudan & Seshasayee, 1987).

The hexamethylenetetramine moiety is linked to Co through N(1) and occupies the apical position. The bond parameters in hexamethylenetetramine are normal and compare well with those observed by

Becka & Cruickshank (1963). Each hexamethylenetetramine moiety has a proton attached to it as confirmed by X-ray analysis.

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Structure of $(\text{Cl})(\text{NO})_2\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$

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Abstract. Friedel–Crafts acylation of dicarbonyl[η^5 -(ferrocenylcarbonylcyclopentadienyl)]nitrosylchromium (3) (hereafter called cynichrodenyl ferrocenyl ketone) with dicarbonyl[η^5 -(chloroformyl)cyclopentadienyl]nitrosylchromium (5) led unexpectedly to chloro[η^5 -(ferrocenylcarbonylcyclopentadienyl)]dinitrosylchromium (6), $[\text{CrFe}(\text{C}_5\text{H}_5)(\text{C}_{11}\text{H}_8\text{O})\text{Cl}(\text{NO})_2]$. The structure of (6) has been determined by an X-ray diffraction study: space group $P2_1/c$, $a = 10.938$ (2), $b = 12.487$ (2), $c = 12.460$ (2) Å, $\beta = 111.43$ (1)°, and $Z = 4$. Compound (6) adopts a *transoid* conformation at the organic carbonyl carbon. The Cl atom of the $(\eta^5\text{-C}_5\text{H}_4)\text{Cr}(\text{NO})_2\text{Cl}$ moiety is located at the site away from the exocyclic organic carbonyl carbon

with a twist angle of 137.9°. The organic carbonyl plane is turned away from the corresponding ring planes Cp¹(Fe) and Cp(Cr) by 14.7 and 14.3°, respectively.

Introduction. Several metallocenyl ketones which contain two metalloaromatic substituents are known, for example, diferrocenyl ketone (1), ferrocenyl ruthenocenyl ketone (2) (Rausch, Fischer & Grubert, 1960), dicymantrenyl ketone, cymantrenyl ferrocenyl ketone (Cais & Feldkimmel, 1961) and cynichrodenyl ferrocenyl ketone (3) (Wang, Hwu & Wang, 1989). Compounds such as (1) and (3) have served as important precursors for the synthesis and structural elucidation of metallocenyl-stabilized carbonium ions (Cais, Dani, Herstein & Kapon, 1978; Cais &

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