The Crystal and Molecular Structure of Dinitratobis(tetramethylthiourea)cobalt(II)

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The crystal structure of dinitratobis(tetramethylthiourea)cobalt(II) has been determined by three-dimensional Patterson and Fourier syntheses and refined by least-squares methods (2516 reflexions collected with a four-circle diffractometer) including anisotropic temperature factors for non-hydrogen and isotropic temperature factors for H atoms to a final $R = 0.035$. The crystals are triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 10.983$ (1), $b = 10.025$ (2), $c = 9.850$ (1) Å, $\alpha = 110.42$ (1), $\beta = 77.43$ (1), $\gamma = 100.27$ (1)°, $Z = 2$. The Co atom is bonded to two S atoms (2.337, 2.379 Å) and to four O atoms of the chelating NO_3^- groups, each of them forming a short (2.025, 2.043 Å) and a long (2.383, 2.496 Å) Co–O bond, with a coordination symmetry intermediate between octahedral and tetrahedral. The NO_3^- groups are planar within 0.001–0.003 Å but have unequal N–O distances and O–N–O angles.

Introduction

The Co^{II} halide CoL_2X_2 complexes of thiourea and substituted thioureas generally have a more or less distorted tetrahedral coordination, as shown by the crystal structure determinations of Cotu$_2$Cl$_2$ (tu = thiourea) (Hall & Horrocks, 1969; Domiano & Tiripicchio, 1972), Co[N,N'-(C$_2$H$_5$)$_2$tu]$_2$Cl$_2$ (Bonamico, Dessy, Fares & Scaramuzza, 1973) and Co[N,N'-(phenyl)$_2$tu]$_2$Br$_2$ (Corradi Bonamartini, Mangia & Pellizzi, 1973). As shown by their electronic and infrared spectra (Devore & Holt, 1972), the complexes [CoL$_4$]A_2 (L = ethylenethiourea, tetramethylthiourea; A = NO$_3$, ClO$_4$) also have tetrahedral or slightly distorted tetrahedral geometry whilst a distorted six-coordinate (effectively pseudotetrahedral based upon physical properties) structure was assigned to the complexes [CoL$_2$(NO$_3$)$_2$] (L = ethylenethiourea, tetramethylthiourea) with both nitrate ions coordinated in a bidentate fashion. Their electronic spectra are highly reminiscent of that observed for bis(acetato)-bis(ethylenethiourea)cobalt(II) which has been shown by X-ray methods to contain coordinated bidentate acetates bonded to the NH groups by intramolecular hydrogen bonds (Holt, Holt & Watson, 1970).

Tetramethylthiourea is a more bulky ligand than ethylenethiourea and cannot form intramolecular hydrogen bonds with the nitrato groups; it is, therefore, more free than the acetato groups to orient itself with respect to the Co atom. The crystal structure of dinitratobis(tetramethylthiourea)cobalt(II) has therefore been determined for a comparison with that of the bis(acetato)bis(ethylenethiourea)cobalt(II) complex.

Experimental

The compound was prepared from the reagents and slowly crystallized in 2-propanol (Devore & Holt,

1972). As the crystals became opaque in moist air in a rather short time they were protected for the X-ray experiments with a thin layer of Sicomet 85. The cell parameters were determined at 18 °C and the intensities were recorded for sin $\theta/\lambda \leq 0.57$ Å^{-1} from a crystal approximately $0.4 \times 0.5 \times 0.7$ mm. A Philips PW 1100 automatic four-circle diffractometer connected on-line with a computer was used with monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The cell parameters were refined by least-squares methods from the 2 sin θ values, each determined twice with independent measurements on 35 reflexions of medium–strong intensities using the *LSRET* program of A. Immirzi (private communication), which also gives their standard deviations.

Crystal data

Dinitratobis(tetramethylthiourea)cobalt(II), Co(tmtu)$_2$(NO$_3$)$_2$, CoS$_2$O$_6$N$_6$C$_{10}$H$_{24}$; triclinic pinacoidal, space group $P\bar{1}$ (C_i^1, No. 2), $a = 10.983$ (1), $b = 10.025$ (2), $c = 9.850$ (1) Å, $\alpha = 110.42$ (1), $\beta = 77.43$ (1), $\gamma = 100.27$ (1)°, $V = 985.82$ Å^3; $F(000) = 466$, FW 447.4, $Z = 2$, $d_c = 1.51$ g cm^{-3}.

The number of molecules per cell was also calculated ($Z = 2.08$) from the molecular volume (Immirzi, 1976) by assuming a covalent radius of 1.32 Å (Pauling, 1960) for the Co^{II} ion.

The measured intensities were corrected for Lorentz and polarization factors and 2516 reflexions with $F_o > 1.5\sigma(F_o)$ were used for the calculations. The atomic scattering factors (Hanson, Herman, Lea & Skillman, 1964) of the Co and S atoms were corrected for the real part of the anomalous dispersion (*International Tables for X-ray Crystallography*, 1962).

The structure was solved by three-dimensional Patterson and Fourier syntheses and difference Fourier syntheses for some N or C atoms and for the H atoms

using the *FOUR3D* program of Immirzi (1967*a*); the H atoms were located after the isotropic and some aniso- tropic refinements of all the non-hydrogen atoms. The structure was then refined, anisotropically for the non- hydrogen and isotropically for the H atoms, by the block-diagonal least-squares method with the program *MIQUAD* of Immirzi (1967*b*) to a final $R = \Sigma \|F_o\| - |F_c\|/\Sigma |F_o| = 0.035$ and a fitting value of 1.01 using the weighting formula $1/w = \sigma^2(F_o) + 0.002F_o^2$ (Gilmore & Woodward, 1971). The final positional

Table 1. *Fractional coordinates for non-hydrogen* ($\times 10^5$) *and for hydrogen atoms* ($\times 10^4$)

Thermal parameters for hydrogen atoms are defined by $\exp|-B(\sin \theta/\lambda)^2|$. Standard deviations are in parentheses.

	x	y	z		x	y	z	B (Å^2 4π^2)
Co	78365 (3)	72063 (4)	68579 (4)	H(1111)	4758 (36)	1968 (41)	7161 (41)	3.7 (0.9)
S(1)	73916 (7)	55866 (8)	81641 (8)	H(1112)	3930 (39)	2740 (44)	6608 (47)	4.7 (1.0)
S(2)	94713 (7)	87312 (8)	80550 (9)	H(1113)	3692 (37)	2978 (41)	8369 (44)	4.3 (1.0)
C(1)	64141 (26)	41926 (28)	71724 (30)	H(1121)	3789 (35)	5379 (39)	8201 (41)	3.5 (0.9)
C(2)	89633 (27)	104008 (30)	88110 (30)	H(1122)	4342 (45)	5408 (49)	9326 (53)	6.1 (1.2)
N(11)	51741 (23)	41673 (25)	75594 (29)	H(1123)	4988 (36)	6306 (39)	8120 (41)	3.8 (0.9)
N(12)	68986 (24)	31429 (25)	60449 (29)	H(1211)	8754 (54)	3593 (58)	6714 (65)	9.9 (1.7)
N(21)	79098 (25)	106325 (27)	98024 (28)	H(1212)	8610 (50)	3226 (53)	5039 (57)	8.0 (1.5)
N(22)	96413 (26)	114938 (26)	84055 (29)	H(1213)	8326 (43)	1956 (46)	5541 (50)	5.6 (1.1)
C(111)	43039 (32)	28454 (36)	73815 (46)	H(1221)	6916 (36)	2334 (39)	3923 (43)	3.6 (0.9)
C(112)	45745 (32)	54698 (37)	84162 (45)	H(1222)	6105 (43)	1278 (48)	4748 (51)	6.7 (1.3)
C(121)	81991 (37)	28875 (42)	58097 (50)	H(1223)	5497 (40)	2942 (44)	4871 (48)	4.9 (1.0)
C(122)	62476 (42)	23464 (40)	47994 (42)	H(2111)	8106 (44)	9047 (47)	10757 (51)	6.5 (1.3)
C(211)	73687 (37)	96425 (43)	106178 (39)	H(2112)	6773 (42)	8984 (42)	10129 (46)	5.3 (1.1)
C(212)	71625 (39)	117563 (42)	99940 (49)	H(2113)	7186 (42)	10018 (47)	11540 (51)	5.8 (1.2)
C(221)	97547 (41)	129652 (36)	94416 (46)	H(2121)	6424 (37)	11406 (41)	10103 (44)	4.2 (0.9)
C(222)	105250 (36)	112413 (42)	70396 (42)	H(2122)	7211 (41)	12531 (46)	10943 (51)	5.4 (1.1)
N(3)	79748 (28)	55805 (29)	41525 (29)	H(2123)	7451 (34)	12180 (39)	9192 (44)	3.7 (0.9)
O(31)	88401 (20)	63043 (24)	48624 (23)	H(2211)	9367 (33)	12971 (38)	10471 (40)	3.1 (0.8)
O(32)	82278 (33)	48561 (35)	28735 (29)	H(2212)	9298 (36)	13629 (40)	9120 (42)	4.1 (0.9)
O(33)	68743 (22)	56701 (26)	48357 (26)	H(2213)	10677 (41)	13288 (45)	9290 (48)	5.4 (1.1)
N(4)	65450 (26)	91865 (27)	67827 (31)	H(2221)	10549 (43)	11973 (46)	6771 (49)	5.8 (1.2)
O(41)	63119 (21)	83115 (24)	74924 (27)	H(2222)	11323 (35)	11196 (38)	7272 (41)	3.7 (0.9)
O(42)	58019 (29)	100268 (29)	69647 (38)	H(2223)	10269 (31)	10318 (35)	6331 (37)	2.7 (0.8)
O(43)	75520 (26)	91160 (29)	59174 (30)					

Table 2. *Interatomic distances* (Å) *and their e.s.d.'s*

The values corrected for rigid-body libration are shown in square brackets.

Co–S(1)	2.331 (1) [2.337]	Co–S(2)	2.374 (1) [2.379]
S(1)–C(1)	1.740 (3) [1.744]	S(2)–C(2)	1.718 (4) [1.723]
C(1)–N(11)	1.330 (5) [1.334]	C(2)–N(21)	1.339 (6) [1.344]
C(1)–N(12)	1.323 (6) [1.328]	C(2)–N(22)	1.342 (4) [1.344]
N(11)–C(111)	1.470 (5) [1.472]	N(21)–C(211)	1.457 (4) [1.460]
N(11)–C(112)	1.465 (7) [1.470]	N(21)–C(212)	1.447 (6) [1.451]
N(12)–C(121)	1.451 (6) [1.455]	N(22)–C(221)	1.474 (6) [1.477]
N(12)–C(122)	1.466 (5) [1.470]	N(22)–C(222)	1.448 (7) [1.454]
C(111)–H(1111)	1.02 (5)	C(211)–H(2111)	1.14 (5)
C(111)–H(1112)	0.91 (4)	C(211)–H(2112)	0.92 (5)
C(111)–H(1113)	1.04 (6)	C(211)–H(2113)	0.85 (7)
C(112)–H(1121)	0.91 (4)	C(212)–H(2121)	0.82 (4)
C(112)–H(1122)	0.90 (6)	C(212)–H(2122)	0.99 (7)
C(112)–H(1123)	0.99 (4)	C(212)–H(2123)	0.99 (4)
C(121)–H(1211)	1.14 (7)	C(221)–H(2211)	1.01 (5)
C(121)–H(1212)	0.93 (6)	C(221)–H(2212)	1.06 (3)
C(121)–H(1213)	0.91 (6)	C(221)–H(2213)	1.00 (5)
C(122)–H(1221)	1.00 (6)	C(222)–H(2221)	0.86 (4)
C(122)–H(1222)	1.04 (5)	C(222)–H(2222)	0.96 (4)
C(122)–H(1223)	1.08 (5)	C(222)–H(2223)	0.98 (4)
N(3)–O(31)	1.268 (4) [1.271]	N(4)–O(41)	1.262 (3) [1.266]
N(3)–O(32)	1.214 (6) [1.218]	N(4)–O(42)	1.218 (5) [1.222]
N(3)–O(33)	1.251 (5) [1.255]	N(4)–O(43)	1.237 (6) [1.241]
Co—O(31)	2.017 (3) [2.025]	Co—O(41)	2.036 (3) [2.043]
Co—O(33)	2.377 (3) [2.383]	Co—O(43)	2.490 (2) [2.497]

parameters for the non-hydrogen atoms and positional and thermal parameters for the H atoms are given in Table 1.*

The interatomic distances and angles with their e.s.d.'s (Tables 2 and 3, Fig. 3) were calculated with the program *MIQUAD* of Immirzi (1967*b*); the least-squares planes (Table 4) and the atom deviations from them were calculated with *PIAMED* (Immirzi, 1967*b*). The orthographic projections on the *ab* plane of the unit cell (Fig. 1) and of the thermal ellipsoids of the asymmetric unit (Fig. 2) were drawn with *ORTEP* (Johnson,

1965). A composite drawing of the difference Fourier given in Fig. 4 and an *ORTEP* projection on the *ac* plane of the CoS_2O_4 polyhedron is given in Fig. 5.

Results and discussion

The asymmetric unit of the crystal coincides with the stoichiometric unit of the complex. There are some non-equivalences in the bond lengths and angles between the two tetramethylthiourea molecules S-bonded to the Co ion (Tables 2 and 3). The C—H bonds have normal distances and form normal angles with the other bonds. C(1) and C(2) have trigonal sp^2 hybridization with the three bonds 120° apart and coplanar within 0·006–0·003 Å. The amide N atoms form very flat pyramidal non-equivalent N—C bonds, the distances of the N

Table 3. *Interatomic angles (°) and their e.s.d.'s*

S(1)—Co—S(2)	98·63 (1)		
S(1)—Co—O(31)	109·24 (6)	S(2)—Co—O(41)	107·44 (5)
S(1)—Co—O(33)	95·25 (3)	S(2)—Co—O(43)	89·90 (3)
S(1)—Co—O(41)	105·19 (5)	S(2)—Co—O(31)	99·58 (6)
S(1)—Co—O(43)	159·78 (15)	S(2)—Co—O(33)	156·43 (16)
O(31)—Co—O(33)	57·66 (9)	O(41)—Co—O(43)	54·63 (8)
O(31)—Co—O(43)	87·13 (5)	O(33)—Co—O(41)	86·98 (7)
O(31)—Co—O(41)	131·87 (11)	O(33)—Co—O(43)	83·37 (4)
Co—S(1)—C(1)	104·00 (8)	Co—S(2)—C(2)	105·85 (10)
S(1)—C(1)—N(11)	120·04 (16)	S(2)—C(2)—N(21)	121·26 (19)
S(1)—C(1)—N(12)	120·29 (18)	S(2)—C(2)—N(22)	119·24 (16)
C(1)—N(11)—C(111)	123·89 (16)	C(2)—N(21)—C(211)	121·06 (17)
C(1)—N(11)—C(112)	121·86 (20)	C(2)—N(21)—C(212)	122·52 (21)
C(1)—N(12)—C(121)	122·20 (21)	C(2)—N(22)—C(221)	122·11 (17)
C(1)—N(12)—C(122)	122·24 (19)	C(2)—N(22)—C(222)	121·10 (19)
N(11)—C(1)—N(12)	119·66 (17)	N(21)—C(2)—N(22)	119·50 (16)
C(111)—N(11)—C(112)	113·61 (18)	C(211)—N(21)—C(212)	115·97 (17)
C(121)—N(12)—C(122)	114·48 (18)	C(221)—N(22)—C(222)	115·34 (22)
N(11)—C(111)—H(1111)	112·1 (2·4)	N(21)—C(211)—H(2111)	112·6 (1·7)
N(11)—C(111)—H(1112)	106·0 (2·5)	N(21)—C(211)—H(2112)	108·9 (2·5)
N(11)—C(111)—H(1113)	106·8 (2·2)	N(21)—C(211)—H(2113)	115·8 (4·1)
N(11)—C(112)—H(1121)	109·9 (2·6)	N(21)—C(212)—H(2121)	106·1 (2·9)
N(11)—C(112)—H(1122)	104·6 (4·1)	N(21)—C(212)—H(2122)	111·6 (3·6)
N(11)—C(112)—H(1123)	112·5 (2·3)	N(21)—C(212)—H(2123)	110·6 (1·6)
N(12)—C(121)—H(1211)	115·5 (2·6)	N(22)—C(221)—H(2211)	110·1 (2·8)
N(12)—C(121)—H(1212)	105·8 (3·7)	N(22)—C(221)—H(2212)	109·3 (2·1)
N(12)—C(121)—H(1213)	115·0 (3·6)	N(22)—C(221)—H(2213)	104·1 (2·3)
N(12)—C(122)—H(1221)	103·4 (2·5)	N(22)—C(222)—H(2221)	105·3 (2·8)
N(12)—C(122)—H(1222)	107·1 (2·7)	N(22)—C(222)—H(2222)	106·3 (2·5)
N(12)—C(122)—H(1223)	107·3 (1·6)	N(22)—C(222)—H(2223)	110·0 (2·7)
H(1111)—C(111)—H(1112)	109·3 (2·1)	H(2111)—C(211)—H(2112)	109·3 (2·4)
H(1111)—C(111)—H(1113)	108·4 (2·5)	H(2111)—C(211)—H(2113)	90·8 (3·2)
H(1112)—C(111)—H(1113)	114·2 (2·3)	H(2112)—C(211)—H(2113)	118·2 (4·0)
H(1121)—C(112)—H(1122)	97·8 (2·2)	H(2121)—C(212)—H(2122)	102·6 (2·2)
H(1121)—C(112)—H(1123)	101·7 (1·6)	H(2121)—C(212)—H(2123)	117·4 (2·0)
H(1122)—C(112)—H(1123)	128·4 (2·4)	H(2122)—C(212)—H(2123)	108·4 (2·3)
H(1211)—C(121)—H(1212)	100·0 (3·1)	H(2211)—C(221)—H(2212)	110·1 (1·6)
H(1211)—C(121)—H(1213)	111·5 (3·4)	H(2211)—C(221)—H(2213)	115·4 (2·7)
H(1212)—C(121)—H(1213)	107·3 (2·7)	H(2212)—C(221)—H(2213)	107·5 (2·1)
H(1221)—C(122)—H(1222)	102·2 (2·1)	H(2221)—C(222)—H(2222)	111·1 (1·7)
H(1221)—C(122)—H(1223)	112·2 (2·3)	H(2221)—C(222)—H(2223)	115·0 (2·1)
H(1222)—C(122)—H(1223)	123·1 (2·4)	H(2222)—C(222)—H(2223)	108·8 (1·9)
O(31)—N(3)—O(32)	120·40 (21)	O(41)—N(4)—O(42)	120·41 (16)
O(31)—N(3)—O(33)	116·54 (15)	O(41)—N(4)—O(43)	115·62 (16)
O(32)—N(3)—O(33)	123·05 (18)	O(42)—N(4)—O(43)	123·96 (19)

Table 4. *Least-squares planes and acute angles between planes*

The equation in the form $Ax + By + Cz + D = 0$ is referred to the crystallographic axes a, b and c [plane coefficients A, B, C, D are $(\times 10^4)$]. Deviations of the atoms from the planes and their r.m.s. deviations are in Å $(\times 10^3)$; the deviations of the atoms not included in the mean plane are indicated with an asterisk.

Co	40*	63*							270	353
S(1)			2		749*	−665*			50	2685*
S(2)				1			−642*	770*	2680*	16
C(1)			−5		19	−24				
C(2)				−2			−15	27		
N(11)			2		−49	400*				
N(12)			2		−455*	64				
N(21)				1			42	−448*		
N(22)				1			434*	−72		
C(111)		645*			15					
C(112)		−458*			15					
C(121)		355*				−20				
C(122)		−592*				−20				
C(211)				418			−13			
C(212)				−558			−13			
C(221)				712				23		
C(222)				−430				23		
N(3)	3									
O(31)	−1								−213	−273
O(32)	−1									
O(33)	−1								−2015*	134
N(4)		1								
O(41)		0							−287	−229
O(42)		0								
O(43)		0							179	−2006*
r.m.s.	3	1	6	3	57	74	48	83	343	367
A	2695	5222	2456	6675	3319	−1016	5865	8484	7346	0560
B	−9403	3662	−7744	−1483	−4177	−8619	2628	−4392	3196	−8619
C	6043	6488	8449	8294	9809	6887	6906	6240	5107	7464
D	−4302	114600	44496	122251	74938	5515	145227	91624	118105	−10553

N(11)C(1)C(111)C(112) ∧ N(12)C(1)C(121)C(122)   45·2°
N(21)C(2)C(211)C(212) ∧ N(22)C(2)C(221)C(222)   47·2
C(1)S(1)N(11)N(12) ∧ N(11)C(1)C(111)C(112)   26·2
C(2)S(2)N(21)N(22) ∧ N(22)C(2)C(221)C(222)   27·3
C(1)S(1)N(11)N(12) ∧ N(12)C(1)C(121)C(122)   22·9
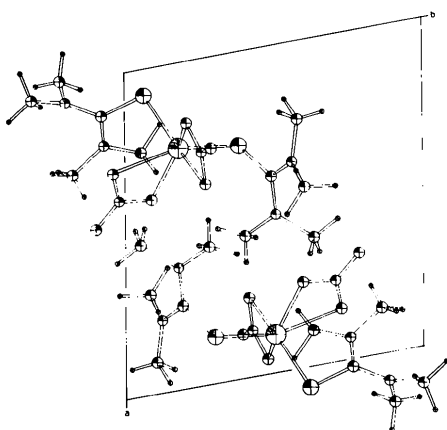C(2)S(2)N(21)N(22) ∧ N(21)C(2)C(211)C(212)   23·8

Fig. 1. Orthographic projection on the ab plane of the asymmetric units x,y,z and $1 - x$, $1 - y$, $-z$.

Fig. 2. *ORTEP* plot of the thermal ellipsoids scaled to include 40% probability (asymmetric unit x,y,z).

atoms from their CCC plane being: N(11) −0·066, N(12) 0·084, N(21) 0·055, and N(22) −0·099 Å.

The NO_3^- groups are planar within 0·001–0·003 Å,

but the angle of the chelating ONO groups coordinated to the Co ion is reduced to about 116°. The bond lengths between the N and the uncoordinated O atoms (1·214, 1·218 Å) are very close to the mean value of the N–O distance in the NO_3^- ion in $NaNO_3$ and

$Pb(NO_3)_2$ (1.220 ± 0.005 Å) (Sutton, 1965), while the other two N—O distances are significantly longer.

The Co is coordinated to two S atoms (2·331, 2·374 Å) and four O atoms of the chelating nitrato groups: two at short distances (2·017, 2·036 Å) and two at long distances (2·377, 2·490 Å). This coordination is very similar to that of bis(acetato)bis(ethylenethiourea)-cobalt(II) (Holt, Holt & Watson, 1970) having a Co—S distance (2·328 Å) close to the shorter bond length of the tmtu complex, but with a much greater difference between the short (1·957 Å) and long (2·928 Å) Co—O bond distances, the last corresponding to a weak interaction. The bond angles at the Co atom are rather irregular, although there is some correspondence between the values in the left and right halves of the *ac* projection of Fig. 5. The CoS(1)O(31)O(41)O(43) and CoS(2)O(31)O(33)O(41) atoms are roughly coplanar within about 0·34–0·37 Å (Table 4). The geometry of

Fig. 3. Interatomic distances (Å) and angles (°) for the asymmetric unit.

the coordination polyhedron cannot be reduced either to octahedral or to tetrahedral symmetry.

Bond valences (S) were calculated for the Co ion in the CoS_2O_4 group from the bond lengths (R) by the expression $S = S_0(R/R_0)^{-N}$, where the values of S_0 (0·333) and R_0 (2·087 Å) for the Co—O bond were taken from Brown & Shannon (1973), and R_0 (2·4975 Å) for the Co—S bond was assumed to be the sum of the effective ionic radius of S^{2-} (1·84 Å) (Shannon & Prewitt, 1969) and the averaged effective ionic radius (0·6575 Å) of the high-spin tetrahedral (0·57 Å) and octahedral (0·745 Å) Co^{2+} ion (Shannon & Prewitt, 1970); a value of $N = 5·2$ was used, very close to that (5·0) given by Brown & Shannon (1973) for Co—O bonds. The following bond valences were obtained: Co—S(1) = 0·48, Co—S(2) = 0·43, Co—O(31) = 0·40, Co—O(33)=0·17, Co—O(41)=0·38, Co—O(43)= 0·13, their sum being 1·99. The bond valences calculated by the same procedure from the bond lengths (R) given by Holt, Holt & Watson (1970) for Co(ethylenethiourea)$_2$(OOCCH$_3$)$_2$ are: Co—S = 0·48, Co—O$_A$ = 0·466, Co—O$_B$ = 0·057 (sum = 1·003 × 2 = 2·006), the strength of this last 'long' Co—O bond being about $\frac{1}{2}$ and $\frac{1}{3}$ of those of the 'long' Co—O bonds of the Co(tetramethylthiourea)$_2$(NO$_3$)$_2$ complex.

An attempt was made to correct the bond distances for rigid-body motion assuming the entire asymmetric unit to be a rigid body, both the nitrate groups being chelated to the central Co atom. The calculation was performed using the program *ESA* of Trueblood & Gantzel (1966), based on the method of Schomaker & Trueblood (1966, 1968). The rigid-body tensors are reported in Table 5. Most of the differences between the corrected and uncorrected bond distances (Table 2) are of the order of their standard deviations, the greatest differences being for the Co—S and Co—O bonds.
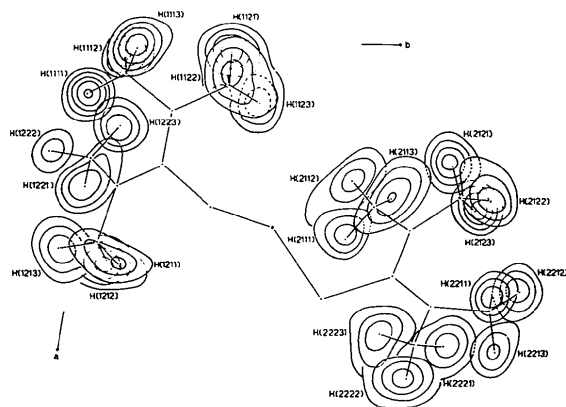
Fig. 4. Sections of the difference electron density map, projected on the *ab* plane, corresponding to the *z* refined positions for hydrogen atoms, calculated using the reflexions with sin $\theta/\lambda <$ 0·5 Å^{-1}. Contours are at 0·1 e Å^{-3} intervals, beginning with 0·6 e Å^{-3}.
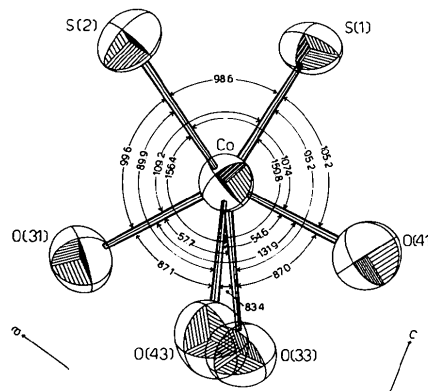

Fig. 5. *ORTEP* plot of the thermal ellipsoids, scaled to include 40% probability, of the coordination polyhedron CoS_2O_4 projected on the *ac* plane.

Table 5. *Rigid-body tensors* **T**, **L** *and* **S** (*ESA program, Trueblood & Gantzel,* 1966)

The tensors are referred to a Cartesian coordinate system defined by unit vectors **a**, $c^* \times a$, c^*. The values have been multiplied by 10^4 for **T** and **L** and by 10^5 for **S**; e.s.d.'s are in parentheses.

T $(Å^2)$	416 (34)	−26 (23)	−16 (28)
		483 (24)	−15 (23)
			359 (30)
L (rad^2)	27 (3)	17 (2)	7 (2)
		47 (6)	5 (3)
			13 (3)
S $(Å\ rad)$	−122 (76)	143 (49)	102 (40)
	−271 (65)	6 (110)	262 (71)
	−139 (41)	9 (56)	116 (1057)

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Structure Cristalline du Bis-thioacétate de Nickel γ Picoline (1:2) Forme *a*

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Ni(CH$_3$COS)$_2$.2(γ-picoline) (*a* phase) is orthorhombic, space group $P2_12_12_1$, with eight molecules in a unit cell of dimensions $a = 14{\cdot}590$ (8), $b = 19{\cdot}053$ (6), $c = 13{\cdot}655$ (4) Å. The structure was solved by the direct method from 2578 intensities collected with an automatic diffractometer. The final R is 0·048. The coordination of the Ni^{2+} ion is six. The O and N atoms are *cis*. The S atoms are *trans*. The *cis* arrangement of the N atoms occurs in five nickel thioacetate solvates.

Ce travail entre dans le cadre d'une étude structurale systématique des thioacétates de nickel solvatés par la pyridine et les picolines β et γ. Il concerne la forme *a* du bis-thioacétate de nickel γ picoline (1:2) (CH$_3$COS)$_2$-Ni(γC$_6$H$_7$N)$_2$

Partie expérimentale

Les paramètres de la forme *a* ont été précisés à l'aide d'un diffractomètre automatique. Les données cristallographiques sont rassemblées dans le Tableau 1.