P—C bond lengths range from 1·824 (6) through 1·838 (6) Å, averaging 1·829 ± 0·006 Å. The tetrahedral environment about the P atoms is distorted from T_d toward C_{3v}, with Ir—P—C(*ipso*) angles of 108·8 (2)–118·9 (2)° (average = 114·8°) and C(*ipso*)—P—C(*ipso'*) angles of 102·1 (3)–106·3 (3)° (average = 103·7°). Internal angles at the *ipso* C atoms [C(n1), n = 1–6] range from 117·1 (6) through 118·4 (6)° [average = 117·9 (5)°]. The six-membered carbocyclic rings are all distorted from D_{6h} to C_{2v} symmetry owing to the electronegative P atoms on the *ipso* C atoms (*cf.* Churchill & De Boer, 1975; Domenicano, Vaciago & Coulson, 1975).*

The current structural study is of additional interest insofar as the complex studied represents an analogue of Vaska's compound, *trans*-[$Ir(PPh_3)_2(CO)Cl$] (Vaska & Di Luzio, 1961; Vaska, 1968), a complex of pivotal importance in the discovery of oxidative addition reactions of transition-metal complexes. To the best of our knowledge, no structural study of Vaska's compound has appeared in the primary literature. An account of the analogous Rh^I species, *trans*-[$Rh(PPh_3)_2(CO)Cl$], has appeared (Del Pra, Zanotti & Segala, 1979); this study was beset with difficulties and the structure is probably disordered. An account of the crystal structure of the tri-*o*-tolylphosphine derivative, *trans*-[$Ir\{P(C_6H_4\text{-}o\text{-}CH_3)_3\}_2(CO)Cl$], has appeared (Brady, DeCamp, Flynn, Schneider, Scott, Vaska & Werneke, 1975); this also exhibits CO/Cl disorder. Bond lengths are similar to those in the current study [Ir—P = 2·338 (5) Å, Ir—Cl = 2·43 (1) Å, Ir—CO = 1·67 (4) Å] but are of intrinsically lower precision and accuracy.

---

* Lists of structure factors, anisotropic thermal parameters, C—C distances, C—C—C angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44006 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

BRADY, R., DECAMP, W. H., FLYNN, B. R., SCHNEIDER, M. L., SCOTT, J. D., VASKA, L. & WERNEKE, M. F. (1975). *Inorg. Chem.* **14**, 2669–2675.

CHURCHILL, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.

CHURCHILL, M. R. & DE BOER, B. G. (1975). *Inorg. Chem.* **14**, 2630–2639.

CHURCHILL, M. R., FETTINGER, J. C., REES, W. M. & ATWOOD, J. D. (1986*a*). *J. Organomet. Chem.* **301**, 99–108.

CHURCHILL, M. R., FETTINGER, J. C., REES, W. M. & ATWOOD, J. D. (1986*b*). *J. Organomet. Chem.* **304**, 227–238.

CHURCHILL, M. R., FETTINGER, J. C., REES, W. M. & ATWOOD, J. D. (1986*c*). *J. Organomet. Chem.* **308**, 361–371.

CHURCHILL, M. R., LASHEWYCZ, R. A. & ROTELLA, F. J. (1977). *Inorg. Chem.* **16**, 265–271.

CLEARFIELD, A., GOPAL, R., BERNAL, I., MOSER, G. A. & RAUSCH, M. D. (1975). *Inorg. Chem.* **14**, 2727–2733.

DEL PRA, A., ZANOTTI, G. & SEGALA, P. (1979). *Cryst. Struct. Commun.* **8**, 959–964.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B**31**, 1630–1641.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101, 149–150. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht, The Netherlands.)

RAPPOLI, B. J., CHURCHILL, M. R., JANIK, T. S., REES, W. M. & ATWOOD, J. D. (1987). *J. Am. Chem. Soc.* In the press.

REES, W. M., CHURCHILL, M. R., FETTINGER, J. C. & ATWOOD, J. D. (1985). *Organometallics*, **4**, 2179–2185.

REES, W. M., CHURCHILL, M. R., FETTINGER, J. C. & ATWOOD, J. D. (1987). *J. Organomet. Chem.* **319**, 411–412.

REES, W. M., CHURCHILL, M. R., LI, Y. J. & ATWOOD, J. D. (1985). *Organometallics*, **4**, 1162–1167.

VASKA, L. (1968). *Acc. Chem. Res.* **1**, 335–344.

VASKA, L. & DI LUZIO, J. W. (1961). *J. Am. Chem. Soc.* **83**, 2784–2785.

Acta Cryst. (1987). C**43**, 1699–1704

The Structures of $Bi_2(CH_3COO)_6.3SC(NH_2)_2.H_2O$ and $Bi(CH_3COO)_3.3SC(NH_2)_2$

BY WOLFGANG BENSCH, EVA BLAZSÓ, ERICH DUBLER AND HANS R. OSWALD

Institute for Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, *CH*-8057 *Zürich, Switzerland*

(*Received* 30 *September* 1986; *accepted* 28 *April* 1987)

Abstract. Compound A: $Bi_2(CH_3COO)_6.3SC(NH_2)_2.H_2O$, M_r = 1018·61, triclinic, $P\bar{1}$, a = 11·450 (7), b = 11·553 (5), c = 11·885 (4) Å, α = 95·44 (4), β = 91·45 (4), γ = 85·05 (4)°, V = 1559 (2) Å^3, Z = 2, D_m = 2·154, D_x = 2·170 (3) Mg m^{-3}, Mo $K\alpha$ radiation, λ = 0·7107 Å, μ = 11·08 mm^{-1}, T = 295 K, $F(000)$ = 964, $R(F)$ = 0·041 for 2549 unique reflections. Compound B: $Bi(CH_3COO)_3.3SC(NH_2)_2$, M_r = 614·48, monoclinic, $P2_1/n$, a = 8·437 (1), b = 15·065 (2), c = 15·843 (2) Å, β = 94·00 (1)°, V = 2008·8 (8) Å^3, Z = 4, D_m = 2·04, D_x = 2·033 (1) Mg m^{-3}, Mo $K\alpha$ radiation, λ = 0·7107 Å, μ = 9·1 mm^{-1}, T = 295 K, $F(000)$ = 1184, $R(F)$ = 0·029 for 3525 unique reflections. The structure of compound A is built from two different dimeric ionic groups: $[Bi_2(CH_3COO)_8]^{2-}$ and [$Bi_2(CH_3COO)_4${SC-

0108-2701/87/091699-06$01.50 © 1987 International Union of Crystallography

$(NH_2)_2\}_6]^{2+}$. The Bi atoms in the anionic group are connected by two O atoms of bridging acetate groups, whereas the Bi atoms within the cationic group are linked by two S atoms of the thiourea molecules. Bi(12)—S distances range from 2·677 (5) to 3·152 (6) Å, Bi(12)—O from 2·31 (1) to 2·71 (2) Å, and Bi(11)—O bonds from 2·26 (2) to 2·78 (1) Å. Compound *B* contains neutral isolated $[Bi(CH_3COO)_3\{SC(NH_2)_2\}_3]$ units; the Bi atom is ninefold coordinated by three S and six O atoms of the bidentate CH_3COO^- groups. The Bi—S distances range from 3·020 (2) to 3·124 (2) Å, and Bi—O from 2·337 (4) to 2·777 (4) Å.

Introduction. In the course of systematic investigations of Bi^{III} thiourea salts the title compounds were isolated. In order to investigate the solid-state thermal decomposition of several Bi^{III} thiourea compounds it became necessary to determine the crystal structures of two nitrates (Jameson, Blazsó & Oswald, 1984), whereas the present work deals with acetates. Preparation of the yellow compound: 5·7 g bismuth acetate and 2·3 g thiourea were dissolved in 50 ml acetic acid at 363 K. After concentration of the solution to one half by evaporation, filtration and subsequent cooling to room temperature, yellow crystals of compound *A* in the form of prisms were deposited at the bottom of the beaker. The complex *B* was prepared by grinding 2·8 g solid bismuth acetate, 2·3 g thiourea and 1·2 g glacial acetic acid. After one day the mixture was dissolved in ethanol and afterwards filtered. The yellow solution was held at 278–283 K. After a few days colourless prismatic crystals were formed.

Experimental. Compound *A*: Precession and Weissenberg photographs showed extended twinning of the yellow crystals with triclinic symmetry. A small fragment (approx. 0·1 × 0·1 × 0·05 mm) cut from a twinned species was mounted on a CAD-4 single-crystal diffractometer. Lattice parameters and crystal orientation determined by least-squares refinement of the θ values of 25 reflections with $6{\cdot}2 < \theta < 10{\cdot}3°$. Six intensity control reflections every 10 000 s; max. isotropic decrease 4%. The orientation was checked by six reflections remeasured every 200 reflections. In the range $\theta < 25°$ a total of 5996 reflections (including standards) were collected using the ω–2θ scan technique; h: 0→13, k: −13→13, l: −14→14. $R_{\rm int} = 0{\cdot}018$ based on F_o, 338 data averaged. Lorentz–polarization and decay corrections were applied. The data reduction procedure led to 4505 unique observations. Owing to the irregular shape of the crystal fragment, a numerical absorption correction could not be applied. An empirical absorption correction with the ψ scan data gave no better results in the final refinement stages. All calculations based on $|F|$ using *SHELX*76 (Sheldrick, 1976). The bond distances, angles and least-squares planes were calculated using *PARST*7 (Nardelli, 1981). The structure was solved with conventional Patterson methods, and full-matrix refinements assuming space group $P\bar{1}$. The H atoms were not located and therefore not included as a fixed contribution in the refinement. All atoms were refined with anisotropic thermal parameters using 2549 unique data for which $I > 2\sigma(I)$; NP = 347. $(\Delta/\sigma)_{\max} < 0{\cdot}05$ in final refinement cycle. Final R and wR are 0·041 and 0·040, respectively. Owing to the lack of a good absorption correction, no extinction correction was applied. The weighting scheme $w = k/[\sigma^2(F) + 0{\cdot}0074F^2]$ based on intensity statistics; the variable k was refined to 0·4. The final difference electron density map showed a maximum of 2·4 e Å^{-3} near Bi atoms and a minimum of 2·6 e Å^{-3}.

Compound *B*: Preliminary single-crystal photographs (Weissenberg and precession technique) revealed monoclinic symmetry, space group $P2_1/n$. The data acquisition was performed on a CAD-4 single-crystal diffractometer with a crystal of dimensions 0·35 × 0·3 × 0·45 mm. The lattice parameters were refined from the θ values of 25 reflections $(8{\cdot}9 \leq \theta \leq 17{\cdot}3°)$. In the range $\theta < 30°$ a total of 6633 data (including standards) were collected using the ω–2θ scan technique; h: 0→12, k: 0→22, l: −25→25. $R_{\rm int} = 0{\cdot}017$ based on F_o, 476 reflections averaged. Six intensity reflections remeasured at regular intervals gave no evidence for significant decay (< 1%). The orientation was checked by six reflections remeasured every 250 data. Lorentz–polarization, empirical absorption and isotropic extinction corrections were applied. The data reduction procedure led to 5473 unique data. The structure was solved using conventional Patterson methods and subsequent difference electron density maps assuming space group $P2_1/n$. All calculations based on $|F|$ using the *SDP* package (Frenz, 1982). Refinement with anisotropically vibrating atoms on 3525 unique data for which $I > 3\sigma(I)$; NP = 227. $(\Delta/\sigma)_{\max} < 0{\cdot}001$ in final refinement cycle; $R = 0{\cdot}029$, $wR = 0{\cdot}035$. The weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}001F^2]$ based on intensity statistics and showed no dependence upon the function minimized or on $(\sin\theta)/\lambda$. The last $\Delta\rho$ map showed no peak higher than 1 e Å^{-3} near the Bi atom. For both structures neutral-atom scattering factors and anomalous-dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1965).

Discussion. Compound *A*: Final positional coordinates and thermal parameters are listed in Table 1.* Selected bond distances and angles are presented in Table 2. The

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44013 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional coordinates and thermal parameters for compound A*

Standard deviations are given in parentheses. The equivalent temperature factor U_{eq} is defined as one third of the trace of the orthogonalized **U** tensor.

	x	y	z	U_{eq}(Å^2)
Bi(11)	0·4957 (1)	0·6439 (1)	0·3895 (1)	0·037
Bi(12)	0·0100 (1)	0·1490 (1)	0·1582 (1)	0·039
S(1)	−0·0001 (4)	0·8819 (4)	0·0876 (4)	0·043
S(2)	0·2143 (4)	0·8984 (4)	0·8350 (4)	0·050
S(3)	0·7263 (5)	0·9353 (6)	0·8952 (4)	0·066
C(1)	0·127 (2)	0·815 (1)	0·147 (1)	0·040
C(2)	0·296 (2)	0·771 (2)	0·779 (2)	0·048
C(3)	0·663 (2)	0·890 (2)	0·770 (2)	0·051
C(4)	0·402 (2)	0·511 (2)	0·191 (2)	0·051
C(5)	0·640 (2)	0·730 (2)	0·244 (2)	0·060
C(6)	0·375 (2)	0·852 (2)	0·491 (2)	0·048
C(7)	0·295 (2)	0·458 (2)	0·492 (1)	0·042
C(8)	0·969 (2)	0·839 (2)	0·598 (2)	0·046
C(9)	0·005 (2)	0·397 (2)	0·152 (2)	0·067
C(41)	0·365 (2)	0·451 (2)	0·077 (2)	0·071
C(51)	0·723 (2)	0·784 (2)	0·171 (2)	0·098
C(61)	0·304 (2)	0·966 (2)	0·537 (2)	0·067
C(71)	0·177 (2)	0·497 (2)	0·439 (2)	0·079
C(81)	0·945 (3)	0·812 (2)	0·470 (2)	0·073
C(91)	−0·030 (3)	0·529 (2)	0·164 (3)	0·109
N(11)	0·192 (2)	0·730 (1)	0·088 (1)	0·053
N(12)	0·155 (2)	0·847 (2)	0·255 (1)	0·063
N(21)	0·256 (2)	0·710 (2)	0·687 (2)	0·064
N(22)	0·400 (2)	0·751 (2)	0·826 (2)	0·071
N(31)	0·579 (2)	0·953 (2)	0·723 (2)	0·062
N(32)	0·699 (2)	0·782 (2)	0·717 (2)	0·075
O(41)	0·380 (1)	0·619 (1)	0·212 (1)	0·057
O(42)	0·456 (1)	0·451 (1)	0·261 (1)	0·057
O(51)	0·565 (1)	0·790 (1)	0·304 (1)	0·058
O(52)	0·647 (1)	0·619 (1)	0·248 (1)	0·053
O(61)	0·470 (1)	0·821 (1)	0·535 (1)	0·052
O(62)	0·332 (1)	0·791 (1)	0·409 (1)	0·053
O(71)	0·317 (1)	0·349 (1)	0·502 (1)	0·055
O(72)	0·363 (1)	0·531 (1)	0·531 (1)	0·045
O(81)	1·009 (1)	0·760 (1)	0·654 (1)	0·063
O(82)	0·941 (2)	0·936 (1)	0·646 (1)	0·066
O(91)	−0·079 (1)	0·330 (1)	0·128 (1)	0·050
O(92)	0·107 (2)	0·356 (2)	0·169 (2)	0·080
O*	0·471 (3)	0·866 (3)	0·029 (3)	0·160

* Isotropically refined atom.

structure exhibits $[Bi_2(CH_3COO)_8]^{2-}$ anions and $[Bi_2(CH_3COO)_4\{SC(NH_2)_2\}_6]^{2+}$ cations. Fig. 1(*a*) depicts the cation of compound *A*. The Bi(12) atom is eightfold coordinated. Within the group the Bi atoms are bonded *via* bridging S(1) atoms with Bi(12)—S(1) 2·909 (5) Å and Bi(12)—S(1′) 3·132 (5) Å. Three of the Bi(12)—S distances are notably longer than those observed in other Bi^{III} thiourea complexes (typically 2·71 Å) and are of the order of the Bi—S bonds in compound *B*. The mean distance for Bi(12)—O of 2·51 (1) Å is within the range found in other Bi^{III} complexes.

The thiourea molecules (1) and (2) are nearly parallel, with a dihedral angle of 19·5°. The stereochemistry of the thiourea is similar to previous observations (Battaglia & Corradi, 1981; Battaglia, Corradi, Nardelli & Tani, 1978). The Bi—S—C angles are in the range 99·5 (7)–113·9 (6)°. The S(1)—C(1) and S(2)—C(2) distances of 1·75 (2) and 1·76 (2) Å respectively are clearly elongated compared with the S—C bond length in the pure thiourea [1·708 (9) Å; Mullen, Heger & Treutmann (1978)], whereas S(3)—C(3) seems to be unaffected [1·70 (2) Å].

Table 2. *Selected bond distances* (Å) *and angles* (°) *in compound A*

Standard deviations are given in parentheses.

Bi(11)–O(41)	2·47 (1)	Bi(11)–O(42)	2·65 (1)
Bi(11)–O(51)	2·26 (1)	Bi(11)–O(52)	2·43 (1)
Bi(11)–O(61)	2·55 (1)	Bi(11)–O(62)	2·42 (1)
Bi(11)–O(71)	2·48 (1)	Bi(11)–O(72)	2·78 (1)
Bi(11)–O(72)′	2·71 (1)		
Bi(12)–S(1)	3·132 (5)	Bi(12)–S(1)′	2·909 (5)
Bi(12)–S(2)	2·677 (5)	Bi(12)–S(3)	3·152 (6)
Bi(12)–O(81)	2·39 (1)	Bi(12)–O(82)	2·65 (1)
Bi(12)–O(91)	2·31 (1)	Bi(12)–O(92)	2·71 (2)
C(1)–S(1)	1·75 (2)	C(1)–N(11)	1·33 (2)
C(1)–N(12)	1·34 (2)		
C(2)–S(2)	1·76 (2)	C(2)–N(21)	1·33 (3)
C(2)–N(22)	1·31 (3)		
C(3)–S(3)	1·70 (2)	C(3)–N(31)	1·29 (3)
C(3)–N(32)	1·39 (3)		
C(4)–C(41)	1·53 (3)	C(4)–O(41)	1·25 (2)
C(4)–O(42)	1·25 (2)		
C(5)–C(51)	1·52 (3)	C(5)–O(51)	1·25 (3)
C(5)–O(52)	1·28 (2)		
C(6)–C(61)	1·54 (3)	C(6)–O(61)	1·24 (2)
C(6)–O(62)	1·26 (2)		
C(7)–C(71)	1·52 (3)	C(7)–O(71)	1·28 (2)
C(7)–O(72)	1·24 (2)		
C(8)–C(81)	1·55 (3)	C(8)–O(81)	1·23 (2)
C(8)–O(82)	1·23 (2)		
C(9)–C(91)	1·54 (3)	C(9)–O(91)	1·29 (3)
C(9)–O(92)	1·25 (3)		

O(72)–Bi(11)–O(72)′	72·6 (4)		
O(71)–Bi(11)–O(72)	50·1 (4)	O(71)–Bi(11)–O(72)′	101·5 (4)
O(71)–Bi(11)–O(42)	119·0 (4)		
O(62)–Bi(11)–O(71)	124·9 (4)	O(62)–Bi(11)–O(72)′	151·7 (4)
O(62)–Bi(11)–O(72)	82·9 (4)	O(62)–Bi(11)–O(42)	115·6 (4)
O(61)–Bi(11)–O(42)	161·9 (5)	O(61)–Bi(11)–O(72)′	111·6 (5)
O(61)–Bi(11)–O(71)	73·5 (4)	O(61)–Bi(11)–O(72)	86·7 (4)
O(61)–Bi(11)–O(62)	51·8 (4)		
O(51)–Bi(11)–O(71)	82·9 (5)	O(51)–Bi(11)–O(62)	78·5 (5)
O(51)–Bi(11)–O(61)	75·5 (5)	O(51)–Bi(11)–O(52)	55·1 (5)
O(51)–Bi(11)–O(72)	122·8 (5)	O(51)–Bi(11)–O(72)′	159·7 (5)
O(51)–Bi(11)–O(42)	117·4 (4)		
O(52)–Bi(11)–O(61)	123·5 (4)	O(52)–Bi(11)–O(42)	74·1 (4)
O(52)–Bi(11)–O(71)	74·9 (5)	O(52)–Bi(11)–O(62)	128·2 (4)
O(52)–Bi(11)–O(72)	79·6 (4)	O(52)–Bi(11)–O(72)′	145·2 (4)
O(41)–Bi(11)–O(71)	152·8 (5)	O(41)–Bi(11)–O(62)	74·3 (4)
O(41)–Bi(11)–O(61)	124·5 (4)	O(41)–Bi(11)–O(51)	82·9 (5)
O(41)–Bi(11)–O(52)	78·0 (5)	O(41)–Bi(11)–O(42)	50·2 (4)
O(41) Bi(11)–O(72)	99·9 (4)	O(41)–Bi(11)–O(72)′	123·0 (4)
O(42)–Bi(11)–O(72)	73·4 (4)	O(42)–Bi(11)–O(72)′	78·1 (4)
O(81)–Bi(12)–O(91)	78·1 (5)	O(81)–Bi(12)–O(82)	49·8 (5)
O(81)–Bi(12)–O(92)	71·8 (5)	O(82)–Bi(12)–O(92)	106·2 (5)
O(82)–Bi(12)–O(91)	127·7 (4)	O(92)–Bi(12)–O(91)	51·7 (5)
S(1)–Bi(12)–S(1)′	72·7 (2)	S(1)–Bi(12)–S(3)	77·1 (1)
S(1)–Bi(12)–S(2)	72·4 (1)		
S(1)′–Bi(12)–S(2)	90·0 (1)	S(1)′–Bi(12)–S(3)	79·3 (1)
S(2)–Bi(12)–S(3)	149·4 (1)		
S(1)–Bi(12)–O(81)	125·4 (3)	S(1)–Bi(12)–O(82)	79·6 (3)
S(1)–Bi(12)–O(91)	142·7 (3)	S(1)–Bi(12)–O(92)	154·6 (4)
S(1)′–Bi(12)–O(81)	160·0 (3)	S(1)′–Bi(12)–O(82)	150·2 (3)
S(1)′–Bi(12)–O(91)	82·0 (3)	S(1)′–Bi(12)–O(92)	94·7 (4)
S(2)–Bi(12)–O(81)	88·0 (4)	S(2)–Bi(12)–O(82)	92·0 (4)
S(2)–Bi(12)–O(91)	80·8 (4)	S(2)–Bi(12)–O(92)	130·8 (4)
S(3)–Bi(12)–O(81)	111·6 (4)	S(3)–Bi(12)–O(82)	84·1 (4)
S(3)–Bi(12)–O(91)	125·0 (4)	S(3)–Bi(12)–O(92)	78·9 (4)
S(1)–C(1)–N(11)	121 (1)	S(1)–C(1)–N(12)	119 (1)
N(11)–C(1)–N(12)	120 (2)		
S(2)–C(2)–N(21)	119 (1)	S(2)–C(2)–N(22)	115 (2)
N(21)–C(2)–N(22)	125 (2)		
S(3)–C(3)–N(31)	122 (2)	S(3)–C(3)–N(32)	119 (2)
N(31)–C(3)–N(32)	119 (2)		
O(41)–C(4)–O(42)	121 (2)		
C(41)–C(4)–O(41)	120 (2)	C(41)–C(4)–O(42)	118 (2)
O(51)–C(5)–O(52)	118 (2)		
C(51)–C(5)–O(51)	122 (2)	C(51)–C(5)–O(52)	120 (2)
O(61)–C(6)–O(62)	121 (2)		
C(61)–C(6)–O(61)	121 (2)	C(61)–C(6)–O(62)	118 (2)
O(71)–C(7)–O(72)	122 (2)		
C(71)–C(7)–O(71)	118 (2)	C(71)–C(7)–O(72)	121 (2)
O(81)–C(8)–O(82)	120 (2)		
C(81)–C(8)–O(81)	119 (2)	C(81)–C(8)–O(82)	120 (2)
O(91)–C(9)–O(92)	122 (2)		
C(91)–C(9)–O(91)	116 (2)	C(91)–C(9)–O(92)	122 (2)

The packing of the cations is illustrated in Fig. 2(*a*). The intramolecular N—C/S—C separation is too long for π-donor–π-acceptor interactions as observed in other Bi^{III} thiourea compounds (Jameson *et al.*, 1984). The environment of the anionic $[Bi_2(CH_3COO)_8]^{2-}$ group is displayed in Fig. 1(*b*). The coordination of the Bi(11) atom is ninefold with a mean Bi(11)—O distance of 2·53 (1) Å. The individual Bi(11)—O bonds range from 2·26 (2) to 2·78 (1) Å. Within the anionic group the Bi(11) atoms are connected by two O atoms of acetate groups with distances Bi(11)—O(72) 2·78 (1) and Bi(11)—O(72′) 2·71 (1) Å. The stereochemistry of the acetate is quite normal with O—C—O angles in the range 118 (2)–122 (2)°, C—C distances from 1·52 (3) to 1·55 (3) Å and C—O bond lengths in the range 1·223 (2)–1·29 (3) Å. The difference between the two Bi—O bond distances to the bidentate acetate groups is more pronounced in the cationic part than in the anionic group. The arrangement of the anionic group within the unit cell is displayed in Fig. 2(*b*). A stereoview of the whole complex is illustrated in Fig. 2(*c*). There are 14 N···O separations in the range 2·77 (2)–3·39 (3) Å which may be indicative of a hydrogen-bonding network between the two ionic groups.

As expected from thermogravimetric measurements and chemical analysis, two molecules of water should be present per cell. A high isotropic temperature factor for the designed water-oxygen atom suggests either that less than two water molecules are in the unit cell or that the water is highly disordered.

Compound *B*: The positional coordinates and thermal parameters, and the bond distances and angles are listed in Tables 3 and 4, respectively.* The structure exhibits neutral isolated $[Bi(CH_3COO)_3\{SC(NH_2)_2\}_3]$ units. Fig. 3 shows the environment of the Bi atom. The three acetate groups are bidentate. A nearly octahedral

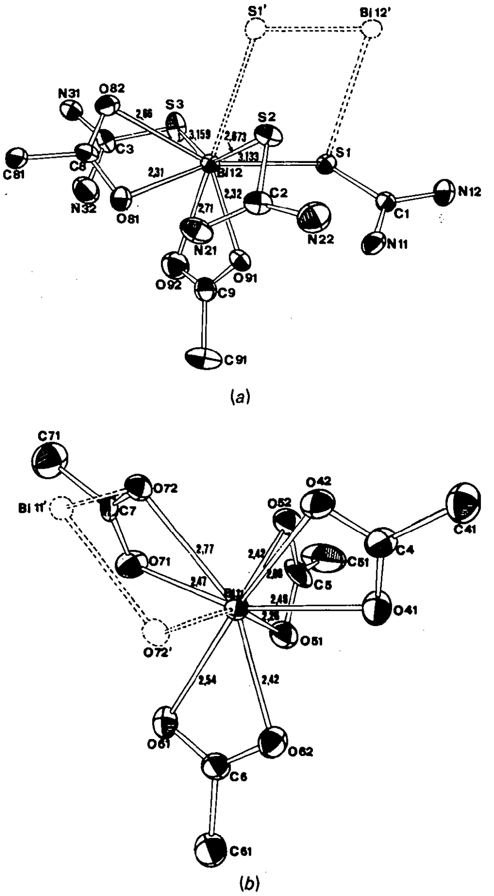

Fig. 1. (*a*) The Bi(12) coordination in *A*. Thermal ellipsoids are drawn at the 50% probability level. The dotted lines indicate the Bi(12)—S(1)—Bi(12′) connection within the dimeric cation. (*b*) The Bi(11) coordination in *A*. Thermal ellipsoids are drawn at the 50% probability level. The dotted lines indicate the Bi(11)—O(72)—Bi(11′) connection within the dimeric anion.

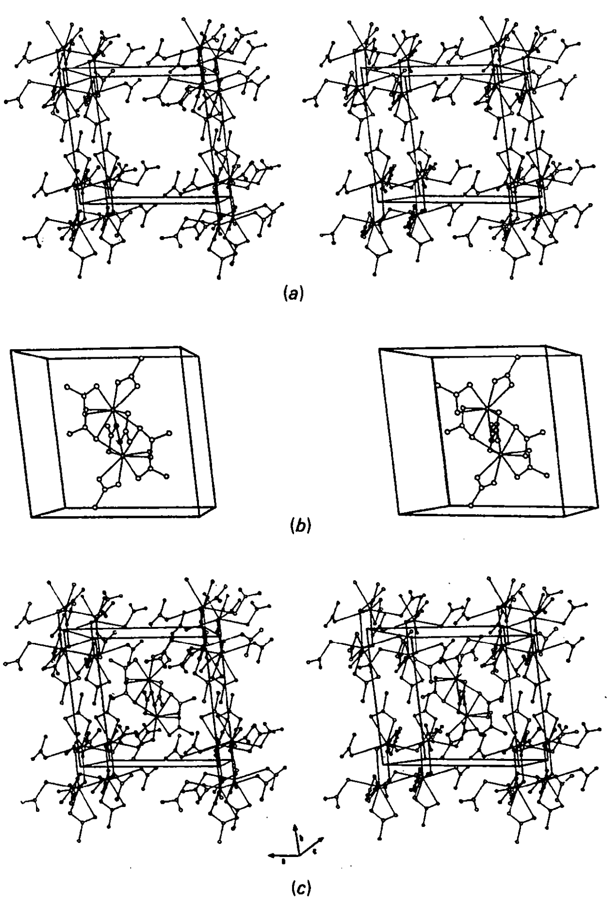

Fig. 2. (*a*) Stereoscopic diagram of the packing of dimeric $[Bi_2(CH_3COO)_4\{SC(NH_2)_2\}_6]^{2+}$ cations in the unit cell of *A*. (*b*) Stereoscopic diagram of the packing of dimeric $[Bi_2(CH_3COO)_8]^{2-}$ anions in the unit cell of *A*. (*c*) Stereoscopic diagram of the contents of the unit cell of *A*. The H_2O molecules are omitted for clarity.

---

* See deposition footnote.

coordination follows if the bidentate acetate coordination is considered as one coordination site. Furthermore, the acetate groups are located on one side of the Bi atom, whereas the thiourea groups are situated on the other side. The Bi—O distances to each individual oxygen of one acetate group are distinctly different. As is usual the longer Bi—O bond causes a shorter C—O distance within the acetate group, and *vice versa.* The largest difference between the two C—O bonds in one acetate is found to be 0·060 (8) Å. The largest Bi—O bond difference is observed between Bi—O(61) and Bi—O(62) [0·44 (5) Å].

The O—C—O angles in the acetate groups range from 118·0 (6) to 120·6 (6)°, the C—C distances are between 1·489 (9) and 1·508 (9) Å and the C—O bond distances are situated between 1·232 (8) and 1·292 (8) Å. The mean Bi—O bond length is 2·509 (4) Å, which is nearly the same value obtained for compound *A*. In contrast, the mean Bi—S distance [3·061 (2) Å] is clearly longer than in the yellow compound.

The stereochemistry in the thiourea molecules is normal. The C—S bond distances are in the region observed in pure thiourea (Mullen *et al.*, 1978). This is expected from the long Bi—S bond distances. The short

Table 3. *Positional coordinates and thermal parameters for compound B*

Standard deviations are given in parentheses. The equivalent temperature factor B_{eq} (Å^2) is defined as $\frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Bi	0·98614 (3)	0·76142 (1)	0·23537 (1)	1·853 (3)
S(1)	1·3406 (2)	0·7669 (1)	0·2775 (1)	3·41 (3)
S(2)	0·9547 (2)	0·8925 (1)	0·3862 (1)	3·68 (4)
S(3)	1·0431 (2)	0·9020 (1)	0·1032 (1)	3·72 (4)
O(41)	0·7788 (5)	0·7299 (3)	0·1290 (3)	2·76 (8)
O(42)	0·7173 (6)	0·8425 (3)	0·2076 (3)	3·3 (1)
O(51)	0·8021 (5)	0·6755 (3)	0·3046 (3)	2·79 (9)
O(52)	1·0325 (5)	0·6734 (3)	0·3771 (3)	2·64 (9)
O(61)	1·0493 (6)	0·6152 (3)	0·2012 (3)	3·1 (1)
O(62)	1·1039 (7)	0·6923 (3)	0·0898 (3)	4·4 (1)
N(11)	1·3139 (7)	0·7796 (4)	0·4442 (4)	3·9 (1)
N(12)	1·5600 (8)	0·7945 (5)	0·4001 (5)	5·2 (2)
N(21)	0·878 (1)	1·0607 (4)	0·4101 (4)	5·3 (2)
N(22)	0·811 (1)	1·0062 (5)	0·2826 (5)	9·8 (2)
N(31)	1·1723 (8)	1·0600 (4)	0·0882 (4)	4·0 (1)
N(32)	1·2710 (8)	0·9782 (4)	0·2023 (4)	4·4 (1)
C(1)	1·4059 (7)	0·7810 (4)	0·3810 (4)	2·4 (1)
C(2)	0·8742 (9)	0·9918 (4)	0·3558 (5)	3·6 (2)
C(3)	1·1697 (8)	0·9853 (4)	0·1356 (4)	3·1 (1)
C(4)	0·6834 (7)	0·7915 (4)	0·1465 (4)	2·5 (1)
C(5)	0·8942 (8)	0·6446 (4)	0·3663 (4)	2·5 (1)
C(6)	1·1015 (8)	0·6202 (4)	0·1266 (4)	3·0 (1)
C(41)	0·5313 (9)	0·8046 (6)	0·0920 (5)	4·5 (2)
C(51)	0·828 (1)	0·5764 (5)	0·4222 (5)	4·8 (2)
C(61)	1·155 (1)	0·5350 (5)	0·0875 (6)	5·5 (2)

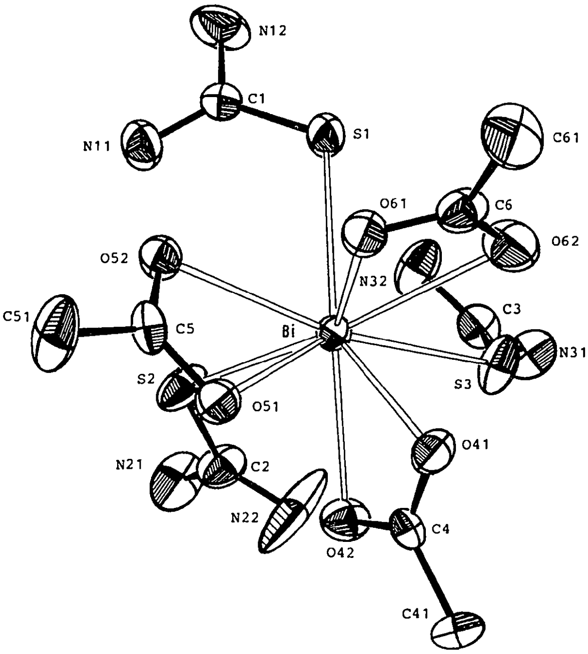

Fig. 3. *ORTEP* diagram (Johnson, 1976) of the [Bi(CH$_3$COO)$_3$-{SC(NH$_2$)$_2$}$_3$] unit in *B*. Thermal ellipsoids are drawn at the 75% probability level.

Table 4. *Bond distances* (Å) *and angles* (°) *in compound B*

Standard deviations are given in parentheses.

Bi–S(1)	3·020 (2)	Bi–S(2)	3·124 (2)
Bi–S(3)	3·038 (2)		
Bi–O(41)	2·390 (4)	Bi–O(42)	2·586 (4)
Bi–O(51)	2·350 (4)	Bi–O(52)	2·613 (4)
Bi–O(61)	2·337 (4)	Bi–O(62)	2·777 (6)
C(1)–S(1)	1·706 (6)	C(1)–N(11)	1·309 (9)
C(1)–N(12)	1·330 (9)		
C(2)–S(2)	1·698 (6)	C(2)–N(21)	1·347 (9)
C(2)–N(22)	1·260 (10)		
C(3)–S(3)	1·703 (6)	C(3)–N(31)	1·353 (9)
C(3)–N(32)	1·316 (9)		
C(4)–C(41)	1·508 (9)	C(4)–O(41)	1·271 (7)
C(4)–O(42)	1·253 (8)		
C(5)–C(51)	1·489 (9)	C(5)–O(51)	1·292 (8)
C(5)–O(52)	1·245 (7)		
C(6)–C(61)	1·508 (9)	C(6)–O(61)	1·292 (8)
C(6)–O(62)	1·232 (8)		
O(61)–Bi–O(62)	49·7 (2)		
O(52)–Bi–O(61)	72·5 (1)	O(52)–Bi–O(62)	118·9 (1)
O(51)–Bi–O(52)	52·0 (1)		
O(51)–Bi–O(61)	76·0 (2)	O(51)–Bi–O(62)	117·9 (2)
O(42)–Bi–O(62)	113·3 (2)	O(42)–Bi–O(61)	128·1 (2)
O(42)–Bi–O(51)	74·8 (2)	O(42)–Bi–O(52)	117·5 (2)
O(41)–Bi–O(62)	68·1 (2)	O(41)–Bi–O(61)	79·5 (2)
O(41)–Bi–O(52)	124·3 (1)	O(41)–Bi–O(51)	75·2 (2)
O(41)–Bi–O(42)	52·0 (1)		
S(1)–Bi–S(2)	87·10 (5)	S(1)–Bi–S(3)	86·06 (5)
S(2)–Bi–S(3)	96·49 (5)		
S(1)–Bi–O(41)	145·7 (1)	S(1)–Bi–O(42)	150·2 (1)
S(1)–Bi–O(51)	126·1 (1)	S(1)–Bi–O(52)	74·8 (1)
S(1)–Bi–O(61)	80·7 (1)	S(1)–Bi–O(62)	77·7 (1)
S(2)–Bi–O(41)	124·6 (1)	S(2)–Bi–O(42)	73·2 (1)
S(2)–Bi–O(51)	84·1 (1)	S(2)–Bi–O(52)	71·3 (1)
S(2)–Bi–O(61)	143·6 (1)	S(2)–Bi–O(62)	157·9 (1)
S(3)–Bi–O(41)	78·2 (1)	S(3)–Bi–O(42)	74·5 (1)
S(3)–Bi–O(51)	147·8 (1)	S(3)–Bi–O(52)	157·5 (1)
S(3)–Bi–O(61)	116·5 (1)	S(3)–Bi–O(62)	66·8 (1)
S(1)–C(1)–N(11)	124·4 (5)	S(1)–C(1)–N(12)	118·9 (6)
N(11)–C(1)–N(12)	116·7 (6)		
S(2)–C(2)–N(21)	120·4 (6)	S(2)–C(2)–N(22)	123·2 (6)
N(21)–C(2)–N(22)	116·4 (6)		
S(3)–C(3)–N(31)	118·6 (5)	S(3)–C(3)–N(32)	122·7 (5)
N(31)–C(3)–N(32)	118·6 (6)		
O(41)–C(4)–O(42)	120·0 (6)		
C(41)–C(4)–O(41)	119·8 (6)	C(41)–C(4)–O(42)	120·1 (6)
O(51)–C(5)–O(52)	119·2 (6)		
C(51)–C(5)–O(51)	118·0 (6)	C(51)–C(5)–O(52)	122·8 (6)
O(61)–C(6)–O(62)	120·2 (6)		
C(61)–C(6)–O(61)	117·2 (6)	C(61)–C(6)–O(62)	122·6 (7)

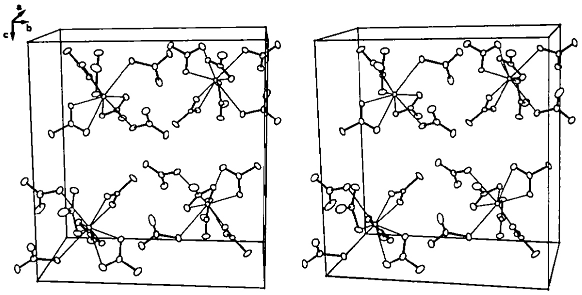

Fig. 4. Stereoscopic diagram of the contents of the unit cell of *B*.

C(2)—N(22) distance [1·260 (10) Å] may be due to strong anisotropic thermal motion or slight disorder within the group. A stereo diagram of the packing of compound *B* within the unit cell is displayed in Fig. 4.

Financial support from the Schweizerischer Nationalfonds zur Unterstützung der wissenschaftlichen Forschung (project No. 2.023-0.83) is gratefully acknowledged.

References

Battaglia, L. P. & Corradi, A. B. (1981). *J. Chem. Soc. Dalton Trans.* pp. 23–26.

Battaglia, L. P., Corradi, A. B., Nardelli, M. & Tani, M. E. V. (1978). *J. Chem. Soc. Dalton Trans.* pp. 583–587.

Frenz, B. (1982). *SDP Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1965). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Jameson, G. B., Blazsó, E. & Oswald, H. R. (1984). *Acta Cryst.* C**40**, 350–354.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mullen, D., Heger, G. & Treutmann, W. (1978). *Z. Kristallogr.* **148**, 95–100.

Nardelli, M. (1981). *PARST*7. Programs for crystallographic calculations. Univ. of Parma, Italy.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). C**43**, 1704–1706

trans-Tétrachlorobis(diméthylsulfure)platine(IV)

Par P. Toffoli, P. Khodadad et N. Rodier

Laboratoire de Chimie minérale, Faculté des Sciences pharmaceutiques et biologiques, rue J.-B. Clément,
92296 Châtenay-Malabry CEDEX, France

(*Reçu le 2 février* 1987, *accepté le* 9 *mai* 1987)

Abstract. $[\mathrm{PtCl_4(C_2H_6S)_2}]$, $M_r = 461{\cdot}2$, monoclinic, $P2_1/c$, $a = 6{\cdot}915\ (2)$, $b = 11{\cdot}454\ (3)$, $c = 9{\cdot}309\ (4)$ Å, $\beta = 124{\cdot}50\ (3)^\circ$, $V = 607{\cdot}6\ (4)$ Å^3, $Z = 2$, $D_x = 2{\cdot}520$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 12{\cdot}84$ mm^{-1}, $F(000) = 428$, $T = 295\ (1)$ K, $R = 0{\cdot}021$ for 1266 independent reflections. The Pt atom is at a centre of symmetry; it is six coordinate with octahedral geometry with Pt—Cl 2·314 (1)–2·319 (1) Å and Pt—S 2·363 (1) Å. The structure can be regarded as constituted of layers of molecules which spread out along the $x = \frac{1}{2}$ planes.

Introduction. Plusieurs composés de coordination du Pt$^{\mathrm{II}}$ ont été obtenus à partir du *cis*-dichlorobis(diméthylsulfoxyde)platine(II). C'est le cas, par exemple, de $[\mathrm{Pt\{(CH_3)_2SO\}_4](ClO_4)_2}$ (Price, Williamson, Schramm & Wayland, 1972), des *cis*- et *trans*-$[\mathrm{Pt\{(CH_3)_2SO\}(picoline\text{-}2)Cl_2}]$ (Melanson & Rochon, 1977, 1978*b*) et du *cis*-$[\mathrm{Pt\{(CH_3)_2SO\}(cyclobutylamine)_2Cl}]$ (Braddock, Romeo & Tobe, 1974). Par analogie, on peut envisager la préparation de composés du Pt$^{\mathrm{IV}}$ en utilisant comme réactif $[\mathrm{PtCl_4\{(CH_3)_2S\}_2}]$. C'est dans cette perspective qu'ont été entreprises la préparation et l'étude cristallographique de la variété *trans* de ce composé. Celui-ci a déjà fait l'objet de plusieurs études spectroscopiques (Adams & Chandler, 1967; Goggin, Goodfellow, Haddock, Knight, Reed & Taylor, 1974). Les derniers auteurs cités l'ont obtenu par action du chlore sur $[\mathrm{PtCl_2\{(CH_3)_2S\}_2}]$ en solution dans le benzène. La méthode de préparation que nous avons utilisée consiste à faire réagir le diméthylsulfure sur le tétrachlorure de platine à l'état solide. Il se forme immédiatement un produit jaune que l'on peut faire recristalliser dans le diméthylformamide.

Partie expérimentale. Cristal en forme de plaquette: 0,04 × 0,10 × 0,45 mm. Dimensions de la maille déterminées avec 25 réflexions telles que $7{,}74 \leq \theta \leq 18{,}36^\circ$. Diffractomètre Enraf–Nonius CAD-4. Scan $\theta/2\theta$ d'amplitude $s = (1{,}30 + 0{,}35\,\mathrm{tg}\,\theta)^\circ$. $0{,}049 \leq (\sin\theta)/\lambda \leq 0{,}704$ Å^{-1}, $0 \leq h \leq 9$, $0 \leq k \leq 16$ et $-13 \leq l \leq 10$. Réflexions de contrôle: $33\bar{1}$, $0\bar{1}\bar{3}$ et $\bar{3}31$. $\sigma(I)/I$ moyen (réflexions de contrôle): 0,0027. 1763 réflexions indépendantes mesurées, 497 réflexions inobservées

0108-2701/87/091704-03\$01.50 © 1987 International Union of Crystallography