$C_{22}H_{36}BMoN_7OS_2$

require that it occupy a facial stereochemical position of an octahedron. This in turn requires the oxo group and each S atom of the dithiocarbamato ligand to be mutually *cis* to each other. The molecule has approximate C_s symmetry with the plane of symmetry containing the pyrazole ring possessing N11 of *L*, Mo, O, and C41, N41 of the dithiocarbamate. Overall C_s symmetry is broken by the two different conformations of the propyl groups of the dithiocarbamate.

The Mo—O distance [1·676 (4) Å] is equal to the average reported for a large number of oxo-molybdenum(IV) complexes (1·678 Å) and is also essentially the same as the Mo—O distance for the analogous diethyldithiocarbamato complex [1·669 (3) Å] (Young *et al.*, 1987). In a statistical treatment of the structural data on 122 molybdenum monooxo complexes (Mayer, 1988), it was found that mean Mo—O distances for Mo^{VI}, Mo^V, and Mo^{IV} complexes are 1·674, 1·677 and 1·678 Å, respectively. Further, the narrow range of Mo—O values was found to be insensitive to coordination number as well as to oxidation state. This phenomenon has been explained in terms of the high Mo—O bond strength (Mayer, 1988). Comparison of the Mo—O bond distance of the title complex with that of the closely related Mo^V complex, $LMoO(SPh)_2$ (Cleland *et al.*, 1987), shows that they are identical [1·676 (4) Å], in agreement with the findings mentioned above.

The Mo—N11 bond distance is elongated by 0·28 Å relative to Mo—N21 and Mo—N31, owing to the *trans*-labilizing effect of the oxo group. A lengthening of the Mo—N11 bond in $LMoO(S_2CNEt_2)$ is also observed and is of identical magnitude. The Mo atom is displaced 0·267 Å

toward the O atom above the plane defined by S1,S2,N21,N31 and is 0·32 Å above the plane containing S1,S2,C41,N41. Analogous displacements for the Mo atom in $LMoO(S_2CNEt_2)$ are 0·276 Å and 0·33 Å, respectively (Young *et al.*, 1987). Bond distances and angles within the S_2CNC_2 portions of —S_2CNPr_2 are very similar to those of the analogous —S_2CNEt_2 complex (Young *et al.*, 1987). The bond distances and angles in the hydrotrispyrazolylborate ligand, *L*, are normal (Cleland *et al.*, 1987).

References

BRAY, R. C. (1980). *Adv. Enzymol. Relat. Areas Mol. Biol.* **51**, 107–165.
CLELAND, W. E. JR, BARNHART, K. M., YAMANOUCHI, K., COLLISON, D., MABBS, F. E., ORTEGA, R. B. & ENEMARK, J. H. (1987). *Inorg. Chem.* **26**, 1017–1025.
CRAMER, S. P. (1983). *Adv. Inorg. Bioinorg. Mech.* **2**, 273–281.
CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distrubutor Kluwer Academic Publishers, Dordrecht.)
FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP. A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONIGSVELD & G. C. BASSI. Delft Univ. Press.
MAYER, J. M. (1988). *Inorg. Chem.* **27**, 3899–3903.
NUGENT, W. A. & MAYER, J. M. (1988). *Metal-Ligand Multiple Bonds*. New York: Wiley–Interscience.
SIT, F., COLLISON, D., MABBS, F. E. & CLELAND, W. E. JR (1989). In preparation.
SPENCE, J. T. (1983). *Coord. Chem. Rev.* **48**, 59–82.
SPIRO, T. G. (1985). *Molybdenum Enzymes*. New York: Wiley-Interscience.
YOUNG, C. G., ROBERTS, S. A., ORTEGA, R. B. & ENEMARK, J. H. (1987). *J. Am. Chem. Soc.* **109**, 2938–2946.

Structures of Trichlorobis(*N,N,N′,N′*-tetramethylurea)indium(III) and Trichlorobis(*N,N,N′,N′*-tetramethylthiourea)indium(III)

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Abstract. (1) Trichlorobis(*N,N,N′,N′*-tetramethylurea)indium(III), [InCl$_3$(C$_{10}$H$_{24}$N$_4$O$_2$)], $M_r = 453\cdot3$, monoclinic, $C2/c$, $a = 18\cdot687$ (3), $b = 8\cdot112$ (2), $c = 17\cdot929$ (2) Å, $\beta = 134\cdot91$ (2)°, $V = 1924\cdot8$ Å^3, $Z = 4$, $D_x = 1\cdot56$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 17\cdot5$ cm^{-1}, $F(000) = 912$, $R = 4\cdot1\%$ for 1595 reflec-

tions. (2) Trichlorobis(N,N,N',N'-tetramethyl-thiourea)indium(III), [InCl$_3$(C$_{10}$H$_{24}$N$_4$S$_2$)], M_r = 485·3, monoclinic, $P2/c$, a = 15·182 (9), b = 8·469 (1), c = 20·519 (4) Å, β = 131·66 (4)°, V = 1971·0 Å^3, Z = 4, D_x = 1·64 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 19·1 cm^{-1}, $F(000)$ = 976, R = 4·32% for 2705 reflections. In each compound the structures consist of discrete five coordinate molecules, with each molecule having a twofold axis coincident with an In—Cl bond. The first coordination sphere about the In atom in each molecule may be regarded as distorted trigonal bipyramidal. For (1) the 'axial' direction is O(1)—In—O(1A) (171·0°) whereas for (2) the 'axial' direction is Cl—In—Cl (average 169·7° for the two crystallographically independent molecules).

Introduction. We are currently interested in the chemical, structural and electronic properties of compounds of the early d-transition elements. Of particular interest to us are those compounds containing the [VO]$^{2+}$ moiety. One particular technique for probing the electronic structure is electron paramagnetic resonance (EPR) spectroscopy. In order to maximize the information available from single-crystal EPR studies it is usually necessary to dilute the paramagnetic compound in a diamagnetic isostructural host. We are currently exploring the use of compounds containing the [MCl]$^{2+}$ moiety, where M = Ga, In, for this purpose and have already reported the results of a single-crystal EPR study on one such pair of compounds, namely [VO(mquin)$_2$] and [GaCl(mquin)$_2$], where mquin is 2-methylquinolin-8-olate (Collison, Gahan & Mabbs, 1987). As part of an extension of this work we now wish to report the single-crystal X-ray structures of InCl$_3$L$_2$, where L = tmu = N,N,N',N'-tetramethylurea (1) or L = tmtu = N,N,N',N'-tetramethylthiourea (2). The single-crystal EPR spectra of the corresponding VOCl$_2$L$_2$ compounds diluted in these hosts will be published elsewhere.

Experimental. InCl$_3$L$_2$ compounds were prepared from stoichiometric amounts of InCl$_3$ (Fluka) and the substituted urea (Aldrich), all used as received, according to the method of Sinha & Irving (1970). Crystals suitable for X-ray structure determination were grown directly from the reaction solution under an atmosphere of dinitrogen. For (1) the solvent was a 1:1 mixture of dried chloroform and dried acetone, whilst for (2) the solvent was dried dichloromethane.

Compound (1). Preliminary investigations on four separate crystals (coated in grease to protect them from the atmosphere) gave the unit-cell dimensions and indicated the space group Cc or $C2/c$. A crystal was chosen for data collection on a CAD-4 diffractometer system using graphite-monochromated Mo $K\alpha$ radiation. Data collection parameters are

Table 1. *Crystallographic data*

	(1)	(2)
Empirical formula	C$_{10}$H$_{24}$Cl$_3$InN$_4$O$_2$	C$_{10}$H$_{24}$Cl$_3$InN$_4$S$_2$
Crystal system	Monoclinic	Monoclinic
Crystal dimensions, mm	0·26 × 0·26 × 0·40	0·10 × 0·21 × 0·23
Space group	$C2/c$ (No. 15)	$P2/c$ (No. 13)
Range h:	0–21	0–18
k:	0–9	0–90
l:	−21–14	−21–14
Reflections and range of θ for defining unit cell,°	25, 9·3 to 12·4	25, 11·5 to 12·8
Max. counting time, s	120	120
Scan width,°	0·6 + 0·35tanθ	0·7 + 0·35tanθ
Scan range,°	1 ≤ 2θ ≤ 50	1 ≤ 2θ ≤ 50
Unique intensities	1833	3501
Observed intensities	1595 [$F > 3\sigma(F)$]	2705 [$F > 3\sigma(F)$]
R, %	4·1	4·32
wR, %	5·8	5·1
Max. shift/e.s.d in the refinement	0·71	0·47
Max. and min. $\Delta\rho$ in the last difference map, e Å^{-3}	+0·6 and −0·5	+0·7 and −0·9

summarized in Table 1. The monitoring of standard reflections revealed a smooth fall of intensity of 41·5% during the data collection, and hence a linear drift correction was applied. Although $\mu R \sim 0·7$ for the maximum crystal dimension, no absorption correction was attempted in view of both the uncertainty in the orientation of the crystal inside the protective coating and the deterioration of the crystal. A Patterson synthesis yielded the positions of the In and Cl atoms for either the general case, Cc, or for the special case of twofold molecular symmetry. The structure was initially refined for the general case by difference Fourier techniques to R = 3·5%. Approximate twofold molecular symmetry was noted. This twofold molecular symmetry was also required by the single-crystal EPR spectroscopy on the doped InCl{VO}Cl$_2$(tmu)$_2$ system. Refinement in $C2/c$ was then initiated after averaging and constraining appropriate atomic positions. Further refinement using Fourier techniques enabled least-squares convergence of all light-atom positions at R = 4·1%. The In and Cl atoms were permitted anisotropic thermal motion consistent with the symmetry. This refinement resulted in a more satisfactory molecular geometry. During the final refinement cycles a weighting scheme $w = (2·64 + 0·038F + 0·00086F^2)^{-1/2}$ was adopted to give a uniform ($w \times \Delta f)^2$ distribution over the F range. A final difference Fourier map showed no peak > 0·6 e Å^{-3} and gave no reliable indication of methyl H-atom positions.

Compound (2). Preliminary investigations of two different crystals gave the cell dimensions and indicated the space group Pc or $P2/c$. A crystal was chosen for data collection. Data parameters are given in Table 1. Standard reflections were monitored throughout the data collection and no drift correction was necessary. $\mu R < 0·5$ and no absorption correction was made. A Patterson synthesis

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *for* InCl$_3$(tmu)$_2$ (1) *and for* InCl$_3$(tmtu)$_2$ (2)

	x	y	z
(1)			
In(1)	0	390 (1)	2500
Cl(1)	0	3298 (3)	2500
Cl(2)	987 (1)	−675 (2)	2225 (1)
O(1)	1351 (3)	180 (5)	4186 (3)
N(2)	1380 (4)	−2033 (6)	4991 (4)
N(3)	1921 (4)	545 (6)	5778 (4)
C(4)	1530 (4)	−424 (6)	4952 (4)
C(5)	1092 (6)	−2619 (11)	5526 (7)
C(6)	1209 (6)	−3198 (9)	4251 (6)
C(7)	1875 (6)	2335 (11)	5641 (6)
C(8)	2683 (6)	−61 (9)	6872 (6)
(2)			
In(1)	0	551 (1)	2500
Cl(2)	0	3364 (3)	2500
Cl(3)	2152 (1)	272 (2)	3751 (1)
S(4)	572 (2)	−698 (2)	1705 (1)
C(5)	−715 (6)	−1018 (8)	621 (4)
N(6)	−968 (5)	−2506 (7)	332 (4)
C(7)	−1594 (8)	−2882 (11)	−592 (6)
C(8)	−504 (8)	−3863 (12)	911 (6)
N(9)	−1380 (5)	161 (7)	97 (4)
C(12)	−1012 (8)	1815 (11)	295 (6)
C(11)	−2673 (8)	−19 (11)	−640 (6)
In(12)	5000	5301 (1)	2500
Cl(13)	5000	2455 (3)	2500
Cl(14)	6157 (2)	5550 (3)	4090 (1)
S(15)	3153 (1)	6414 (2)	2096 (1)
C(16)	3461 (5)	6581 (6)	3082 (4)
N(17)	3981 (5)	7863 (7)	3568 (3)
C(18)	4707 (7)	7836 (10)	4517 (5)
C(19)	4075 (8)	9320 (10)	3237 (6)
N(20)	3107 (5)	5448 (6)	3312 (4)
C(21)	2860 (7)	3830 (10)	2964 (5)
C(22)	2691 (7)	5795 (10)	3775 (5)

Table 3. *Selected bond distances* (Å) *and angles* (°)

InCl$_3$(tmu)$_2$, (1)

In(1)—Cl(1)	2·359 (2)	O(1)—C(4)	1·261 (6)
In(1)—Cl(2)	2·382 (2)	C(4)—N(2)	1·347 (7)
In(1)—O(1)	2·183 (4)	C(4)—N(3)	1·348 (7)

Cl(1)—In(1)—Cl(2)	111·3 (1)	O(1)—In(1)—O(1A)	171·0 (1)
Cl(1)—In(1)—O(1)	94·5 (1)	In(1)—O(1)—C(4)	134·2 (4)
Cl(2)—In(1)—O(1)	87·2 (1)	O(1)—C(4)—N(2)	121·9 (3)
Cl(2)—In(1)—Cl(2A)	137·5 (1)	O(1)—C(4)—N(3)	119·4 (3)

InCl$_3$(tmtu)$_2$, (2)

In(1)—Cl(2)	2·383 (3)	In(12)—Cl(13)	2·410 (3)
In(1)—Cl(3)	2·484 (2)	In(12)—Cl(14)	2·481 (2)
In(1)—S(4)	2·531 (2)	In(12)—S(15)	2·521 (2)
S(4)—C(5)	1·750 (7)	S(15)—C(16)	1·752 (6)
C(5)—N(6)	1·338 (9)	C(16)—N(17)	1·325 (8)
C(5)—N(9)	1·313 (9)	C(16)—N(20)	1·330 (8)

Cl(2)—In(1)—Cl(3)	95·5 (1)	Cl(13)—In(12)—Cl(14)	94·9 (1)
Cl(2)—In(1)—S(4)	114·7 (1)	Cl(13)—In(12)—S(15)	112·0 (1)
Cl(3)—In(1)—S(4)	81·2 (1)	Cl(14)—In(12)—S(15A)	82·8 (1)
Cl(3)—In(1)—S(4A)	94·2 (1)	Cl(14)—In(12)—S(15)	93·5 (1)
Cl(3)—In(1)—Cl(3A)	169·1 (1)	Cl(14)—In(12)—Cl(14A)	170·2 (1)
S(4)—In(1)—S(4A)	130·7 (1)	S(15)—In(12)—S(15A)	136·1(1)
In(1)—S(4)—C(5)	108·2 (2)	In(12)—S(15)—C(16)	105·4 (1)
S(4)—C(5)—N(6)	117·3 (3)	S(15)—C(16)—N(17)	120·2 (3)
S(4)—C(5)—N(9)	121·6 (3)	S(15)—C(16)—N(20)	119·4 (3)

The fractional atomic coordinates of (1) and (2) are in Table 2* whilst selected bond distances are in Table 3.

Discussion. Both InCl$_3$(tmu)$_2$ (1) and InCl$_3$(tmtu)$_2$ (2) occur in the crystals as discrete five-coordinate molecules, see Figs. 1 and 2 which also show the atomic numbering. Each molecule has twofold molecular symmetry with the twofold axis coincident with an In—Cl bond. The first coordination sphere about the In atom in each molecule may be regarded as distorted trigonal bipyramidal. However, for (1) the 'axial' direction is O(1)—In—O(1A) (171·0°), whereas for each molecule in (2) the 'axial' direction is Cl—In—Cl (average 169·7°). In both (1) and (2) those In—Cl bonds which may be approximated to be in the trigonal plane have lengths which compare favourably with the corresponding In—Cl bond lengths reported for the approximately trigonal bipyramidal molecules InCl$_3$(Ph$_3$P)$_2$ (2·383 Å, Veidis & Palenik, 1969), InCl$_3$(hmpa)$_2$ (2·359 Å, Sinha, Pakkanen, Pakkanen & Niinisto, 1982) and Me[2,6-(Et$_2$NCH)$_2$C$_6$H$_3$]InCl (2·377 Å, Schumann, Wassermann & Dietrich, 1989). In contrast the 'axial' In—Cl bonds [Cl(3) and Cl(14)] in InCl$_3$(tmtu)$_2$ are slightly but significantly longer. The In—O(1) bond length in (1) is similar to those found in InCl$_3$(hmpa)$_2$. The two crystallographically

indicated that the two In atoms in the asymmetric unit had an approximate C-centred relationship. However, each In atom had a different Cl and S atom environment. The {InCl$_3$S$_2$} groups were fixed by cautious difference Fourier methods, starting with the In atoms and working in the lower symmetry space group Pc. The structure was refined to R = 4·17% in this space group. At this stage it was noted that both molecules had approximate twofold symmetry. Further refinement in the space group P2/c was carried out with In—Cl in each half-molecule on a twofold axis with half occupancy. The resulting molecular geometry was more satisfactory than in the non-centrosymmetric case. In the refinement In, Cl and S atoms were allowed anisotropic thermal motion consistent with the symmetry. During the final cycles of least-squares refinement a weighting scheme, $w = (7 \cdot 0 - 0 \cdot 21F + 0 \cdot 003F^2)^{-1/2}$, was adopted to give a uniform ($w \times \Delta f)^2$ distribution over the F range. A final difference Fourier map showed no peaks > 0·8 e Å^{-3} and again gave no reliable indications of methyl H-atom positions.

Atomic scattering factors from Cromer & Waber (1974) and anomalous-dispersion factors from Cromer (1974) were used.
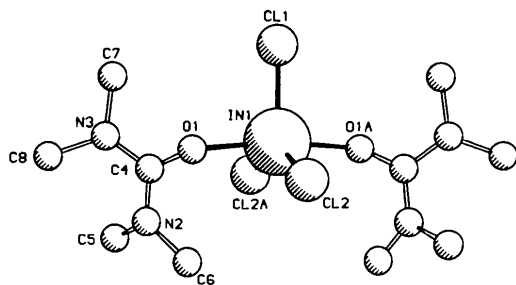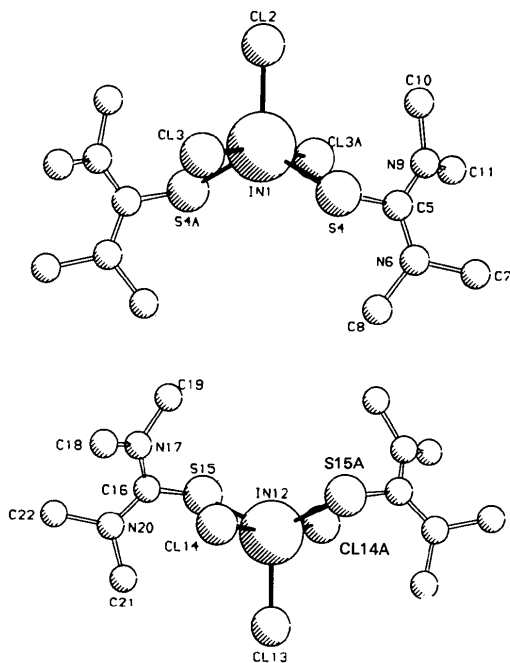
Fig. 1. Molecular structure and atomic numbering of InCl₃(tmu)₂.

Fig. 2. Molecular structures and atomic numbering of the two independent molecules in InCl₃(tmtu)₂.

independent molecules in (2) show small but significant differences in the detailed coordination geometry about the In atoms. The In—Cl lengths involving the unique Cl atoms show a difference of *ca* 0·027 Å. There are also significant differences in interatomic angles between otherwise equivalent atoms. Thus the S—In—S angles differ significantly, S(4)—In(1)—S(4A) = 130·7 (1) whilst S(15)—In(12)—S(15A) = 136·1 (1)°. Similar but smaller differences occur for other bond angles, for example Cl(3)—In(1)—S(4) = 81·2 (1) compared with Cl(14)—In(12)—S(15A) = 82·8 (1)°, whilst Cl(3)—In(1)—S(4A) = 94·2 (1) compared with Cl(14)—In(12)—S(5) = 93·5 (1)°. Similarly Cl(2)—In(1)—S(4) = 114·7 (1) compared with Cl(3)—In(12)—S(15) = 112·0 (1)°.

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References

COLLISON, D., GAHAN, B. & MABBS, F. E. (1987). *J. Chem. Soc. Dalton Trans.* pp. 111–117.
CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
SCHUMANN, H., WASSERMANN, W. & DIETRICH, A. (1989). *J. Organomet. Chem.* 365, 11–18.
SINHA, S. P. & IRVING, H. (1970). *Anal. Chim. Acta*, 52, 193–205.
SINHA, S. P., PAKKANEN, T. T., PAKKANEN, T. A. & NIINISTO, L. (1982). *Polyhedron*, 1, 355–359.
VEIDIS, M. V. & PALENIK, G. J. (1969). *J. Chem. Soc. Chem. Commun.* pp. 586–587.

Structure of Bis(tetraphenylphosphonium) Decaarseniotriselenate: an Example of a Two-Site-Disordered Globular Anion

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Abstract. [P(C₆H₅)₄]₂[As₁₀Se₃], [P(Ph)₄]₂ [As₁₀Se₃], M_r = 1664·5, triclinic, $P\bar{1}$, a = 9·291 (3), b = 10·554 (5), c = 27·038 (6) Å, α = 90·10 (3), β = 95·64 (2), γ = 91·33 (4)°, V = 2637 (4) Å³, Z = 2, D_x = 2·095 Mg m⁻³, Mo $K\alpha$, λ = 0·71069 Å, μ = 8·1 mm⁻¹, T = 293 K, $F(000)$ = 1580, final R =