Structures of Nickel(II) Bis- and Tris-phosphine Diisothiocyanate Complexes

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Abstract

The structures of [*P,P*-diethyl-*P′P′*-diphenyl-1,2-ethanediphosphine-*P,P′*)di(thiocyanato-*N*)nickel(II), $Ni(NCS)_2(Et_2PCH_2CH_2PPh_2)$ (1), and {bis[2-(diphenylphosphino)ethyl]ethylphosphine-*P,P′,P″*}di-(thiocyanato-*N*)nickel(II), $Ni(NCS)_2[EtP(CH_2CH_2PPh_2)_2]$ (2), have been determined. Complex (1) has square-planar geometry about Ni defined by the bidentate diphosphine ligand and two N-bonded thiocyanato ions. Thiocyanate coordination is nearly linear, with Ni—N—C angles of 170.2 (2) and 172.4 (2)°. The P—Ni—P bite angle of the chelating $Ph_2P(CH_2)_2PEt_2$ ligand is 87.05 (3)°. Coordination-sphere bond lengths are Ni—N = 1.876 (3), 1.885 (2) Å, Ni—P = 2.1413 (8), 2.145 (1) Å. Complex (2) has distorted square-pyramidal geometry about the Ni center with the tridentate phosphine ligand and one thiocyanato ligand in the basal plane. The axial N-bonded thiocyanato ligand deviates from linear coordination, with an Ni—N—C angle of 158.1 (6)°. The P—Ni—P bite angles are 86.20 (9) and 85.53 (9)°. Coordination-sphere bond lengths are Ni—P = 2.223 (2), 2.150 (2), 2.189 (2) Å, where the shortest distance is to the central P atom, and Ni—N = 1.896 (6) (basal), 2.088 (7) Å (axial).

Comment

Our group has been involved in the synthesis and study of bimetallic complexes in homogeneous catalysis. This has led to successful synthesis of the linear tetratertiary phosphine ligand $(Et_2PCH_2CH_2)(Ph)$-$PCH_2P(Ph)(CH_2CH_2PEt_2)$, eLTTP, designed to bridge and chelate two metal centers (Laneman, Fronczek & Stanley, 1988, 1989). The reaction of eLTTP with two equivalents of $NiCl_2.6H_2O$ in EtOH produces $Ni_4Cl_4(eLTTP)$ in nearly quantitative yield. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of both diastereomers of $Ni_2Cl_4(eLTTP)$ in equal amounts (Laneman *et al.*, 1989). However, the separation of these two diastereomers has proven to be somewhat of a challenge. We decided to use the monometallic complex $Ni(NCS)_2(Et_2PCH_2CH_2PPh_2)$

as a possible model compound to study the chemistry needed to separate the two diastereomers of $Ni_2Cl_4(eLTTP)$. The coordinating properties of the common and similar bisphosphine ligand $Ph_2PCH_2CH_2PPh_2$, dppe, have been investigated by numerous workers (Spek, van Eijck, Jans & van Koten, 1987; Rahn, Delian & Nelson, 1989). The $Et_2PCH_2CH_2PPh_2$ (dedppe, diethyldiphenylbisphosphinoethane) ligand, however, is a better bisphosphine model of our binucleating eLTTP ligand system relative to dppe.

$Et_2PCH_2CH_2PPh_2$ was synthesized by Meek's (Dubois, Hyers & Meek, 1975) free-radical pathway from Ph_2PH and $Et_2PCH=CH_2$, using catalytic amounts of 2,2-azobis(isobutyronitrile) as the free-radical initiator. In our hands, a 41% yield of dedppe was isolated. Characterization of the colorless dedppe was performed by ^{31}P and ^1H NMR spectroscopy, which indicated the presence of an additional phosphine product which could not be readily separated, but the simple ^{31}P NMR doublet-doublet pattern of dedppe clearly identified it as the major phosphine component. The crude dedppe was then allowed to react with one equivalent of $Ni(NCS)_2$ in EtOH under inert atmosphere conditions. A mixture of yellow–brown plates and orange needles was obtained.

(1)   (2)
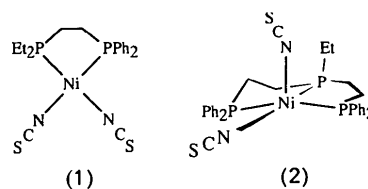
The X-ray structure of the yellow–brown plates revealed the expected $Ni(NCS)_2(dedppe)$ complex (1) (Fig. 1). The coordination geometry around the nickel(II) center is essentially square planar with the Ni and the four coordinated atoms all lying within 0.047 (2) Å of a common plane. The five-membered dedppe chelate ring is puckered with C3 0.406 (3) Å and C4 −0.130 (3) Å out of the coordination plane. The two N-bonded thiocyanate groups are *cis* to each other and form an angle of 93.9 (1)° about Ni. The bite angle of the dedppe ligand is 87.05 (3)°. The short Ni—P [2.1413 (8), 2.145 (1) Å] and Ni—N [1.876 (3), 1.885 (2) Å] bond distances agree reasonably well with corresponding but longer values of Ni—P [2.178 (3), 2.182 (4) Å] and Ni—N [1.864 (12), 1.916 (10) Å] in $Ni(NO_2)_2(dppe)$ (Kriege-Simondsen & Feltham, 1983) and $NiBr_2(dppe)$ (Rahn *et al.*, 1989).

To our surprise, the orange needles were identified by a crystal-structure determination as $Ni(NCS)_2$-$[\eta^3$-$Ph_2PCH_2CH_2P(Et)CH_2CH_2PPh_2]$, (2). The tridentate phosphine ligand $Ph_2PCH_2CH_2P(Et)CH_2$-

CH_2PPh_2 is formed as a rearrangement product in the free-radical ligand synthesis reaction. Unlike $Ni(NCS)_2(dedppe)$, which is soluble in acetone and heptane, the orange $Ni(NCS)_2[Ph_2CH_2CH_2P(Et)-CH_2CH_2PPh_2]$ complex is essentially insoluble in these solvents, but it is soluble in acetonitrile. This allows easy separation of the two compounds.

The structure of (2) is best described as a distorted square pyramid, although it could also be considered to be a distorted trigonal bipyramid with P2 and N1 axial. We favor the distorted square-pyramid descriptor because of the long Ni—N2 bond distance, 2.088 (7) Å, which is 0.192 (9) Å longer than the Ni—N1 distance of 1.896 (6) Å. This fits well

with a square-pyramidal geometry and corresponding electronic structure where the axial ligand has the weakest metal–ligand bonding. The Ni—P bond distances are in the normal bonding range with Ni—P = 2.223 (2), 2.150 (2), 2.189 (2) Å. The axial NCS ligand is bent quite substantially with an Ni—N2—C2 angle of 158.1 (6)°. This bending appears to be caused mainly by crystal packing forces since the only close intramolecular contact is between N2 and the calculated H atom on C26 with a distance of 2.608 Å. This, however, should not cause any bending of the NCS ligand.
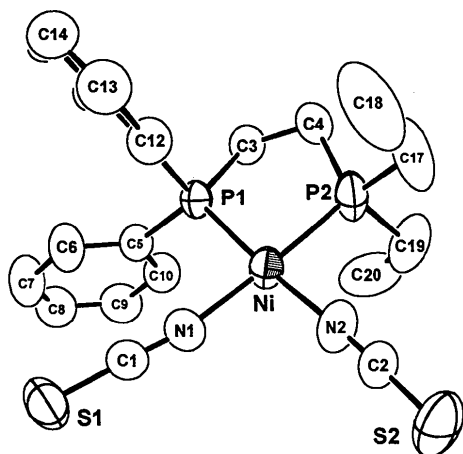

Fig. 1. ORTEP (Johnson, 1965) plot of (1) showing the non-H atoms. Thermal ellipsoids are shown at the 50% probability level.

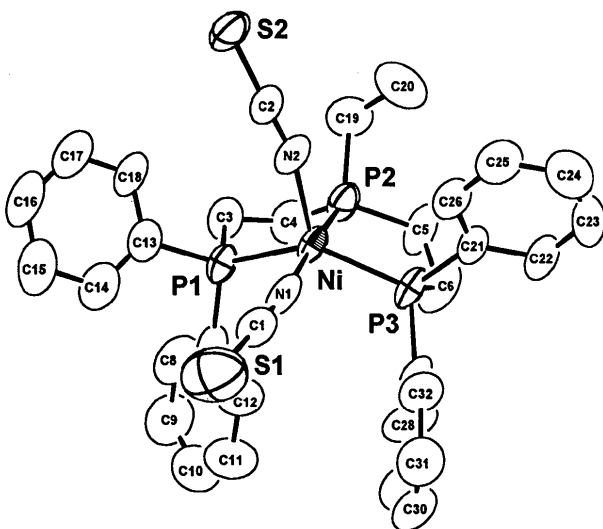Fig. 2. ORTEP (Johnson, 1965) plot of (2) showing the non-H atoms. Thermal ellipsoids are shown at the 50% probability level.

Experimental

Compound (1)

Crystal data

$[Ni(SCN)_2(C_{18}H_{24}P_2)]$	$D_x = 1.372$ Mg m^{-3}
$M_r = 477.2$	Cu $K\alpha$ radiation
Monoclinic	$\lambda = 1.54184$ Å
$P2_1/n$	Cell parameters from 25
$a = 8.4008$ (7) Å	reflections
$b = 18.178$ (2) Å	$\theta = 14$–$25°$
$c = 15.164$ (2) Å	$\mu = 4.3$ mm^{-1}
$\beta = 93.803$ (7)°	$T = 297$ K
$V = 2310.6$ (4) Å^3	Plate
$Z = 4$	$0.30 \times 0.18 \times 0.05$ mm
	Yellow-brown

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.020$
diffractometer	$\theta_{max} = 75°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 10$
Absorption correction:	$k = 0 \rightarrow 22$
empirical	$l = -18 \rightarrow 18$
$T_{min} = 0.671$, $T_{max} =$	3 standard reflections
0.996	frequency: 167 min
5297 measured reflections	intensity variation: -8.2%
4738 independent reflections	
3717 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

Final $R = 0.039$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
$wR = 0.050$	$\Delta\rho_{min} = -0.48$ e Å^{-3}
$S = 2.154$	Extinction correction:
3717 reflections	$(1 + gI_c)^{-1}$ applied to F_c
245 parameters	Extinction coefficient: $g =$
H-atom parameters not re-	4.2 (2) $\times 10^{-7}$
fined	Atomic scattering factors
$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$	from Cromer & Waber
$(\Delta/\sigma)_{max} = 0.06$	(1974)

Compound (2)

Crystal data

$[Ni(SCN)_2(C_{30}H_{33}P_3)]$	Cu $K\alpha$ radiation
$M_r = 661.4$	$\lambda = 1.54184$ Å

Monoclinic
$P2_1/n$
$a = 7.602 (2)$ Å
$b = 20.599 (2)$ Å
$c = 20.712 (4)$ Å
$\beta = 97.98 (2)°$
$V = 3212 (2)$ Å^3
$Z = 4$
$D_x = 1.368$ Mg m^{-3}

Data collection

Enraf-Nonius CAD-4
  diffractometer
$\omega/2\theta$ scans
Absorption correction:
  empirical
  $T_{min} = 0.493$, $T_{max} =$
  0.994
6559 measured reflections
5947 independent reflections
3417 observed reflections
  $[I > 3\sigma(I)]$

Refinement

Final $R = 0.081$
$wR = 0.089$
$S = 3.23$
3417 reflections
362 parameters
H atoms not refined
$w = 4F_o^2[\sigma^2(I)+(0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.01$

Cell parameters from 25
  reflections
$\theta = 14$–$25°$
$\mu = 3.7$ mm^{-1}
$T = 298$ K
Flat needle
$0.32 \times 0.12 \times 0.08$ mm
Orange

$R_{int} = 0.029$
$\theta_{max} = 70°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 25$
$l = -25 \rightarrow 25$
3 standard reflections
  frequency: 167 min
  intensity variation:
  -16.4%

$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}
Extinction correction:
  $(1+gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 4.2 (4) \times 10^{-7}$
Atomic scattering factors
  from Cromer & Waber
  (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$B_{eq} = \tfrac{8\pi^2}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	0.28547 (5)	0.25823 (2)	0.24948 (3)	3.969 (9)
S1	0.3130 (1)	0.42543 (5)	0.47975 (6)	6.43 (2)
S2	0.6906 (1)	0.11116 (5)	0.37181 (8)	7.46 (2)
P1	0.11882 (7)	0.33396 (3)	0.18668 (4)	3.47 (1)
P2	0.2611 (1)	0.19461 (4)	0.13020 (6)	5.30 (2)
N1	0.2976 (3)	0.3185 (1)	0.3508 (2)	4.61 (5)
N2	0.4396 (3)	0.1917 (1)	0.2962 (2)	5.87 (6)
C1	0.3018 (3)	0.3636 (2)	0.4044 (2)	4.08 (5)
C2	0.5446 (3)	0.1577 (2)	0.3267 (2)	4.59 (6)
C3	0.0163 (3)	0.2913 (2)	0.0888 (2)	4.28 (6)
C4	0.1318 (4)	0.2410 (2)	0.0462 (2)	4.73 (6)
C5	-0.0357 (3)	0.3680 (1)	0.2540 (2)	3.67 (5)
C6	-0.0306 (3)	0.4375 (2)	0.2888 (2)	5.25 (6)
C7	-0.1496 (4)	0.4608 (2)	0.3421 (2)	6.25 (7)
C8	-0.2725 (3)	0.4156 (2)	0.3601 (2)	5.39 (7)
C9	-0.2762 (3)	0.3456 (2)	0.3273 (2)	5.29 (7)
C10	-0.1591 (3)	0.3214 (2)	0.2745 (2)	4.77 (6)
C11	0.2250 (3)	0.4131 (1)	0.1480 (2)	3.80 (5)
C12	0.3891 (3)	0.4167 (2)	0.1627 (2)	4.65 (6)
C13	0.4722 (4)	0.4762 (2)	0.1322 (2)	6.04 (8)
C14	0.3929 (4)	0.5326 (2)	0.0890 (2)	6.31 (8)
C15	0.2294 (4)	0.5302 (2)	0.0752 (2)	6.06 (8)
C16	0.1459 (4)	0.4704 (2)	0.1040 (2)	5.18 (7)
C17	0.4445 (5)	0.1744 (2)	0.0786 (3)	9.1 (1)
C18	0.5409 (5)	0.2414 (3)	0.0567 (4)	11.9 (1)
C19	0.1727 (6)	0.1055 (2)	0.1534 (3)	8.8 (1)
C20	0.0140 (7)	0.1124 (2)	0.1959 (3)	10.7 (1)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$B_{eq} = \tfrac{8\pi^2}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	0.1752 (2)	0.08042 (5)	0.26659 (6)	4.11 (3)
S1	-0.3394 (4)	0.0339 (2)	0.1308 (2)	10.7 (1)
S2	-0.0849 (3)	0.2314 (1)	0.4007 (1)	6.24 (6)
P1	0.2063 (3)	0.1588 (1)	0.1952 (1)	4.46 (5)
P2	0.4346 (3)	0.1080 (1)	0.3135 (1)	4.92 (5)
P3	0.2667 (3)	-0.01957 (9)	0.2845 (1)	4.67 (5)
N1	-0.0411 (8)	0.0531 (3)	0.2174 (3)	4.9 (2)
N2	0.0382 (9)	0.1282 (3)	0.3333 (3)	5.5 (2)
C1	-0.166 (1)	0.0441 (4)	0.1821 (4)	4.9 (2)
C2	-0.014 (1)	0.1706 (3)	0.3604 (4)	4.4 (2)
C3	0.399 (1)	0.2077 (4)	0.2284 (4)	5.6 (2)
C4	0.541 (1)	0.1621 (4)	0.2607 (4)	5.9 (2)
C5	0.580 (1)	0.0375 (4)	0.3322 (5)	7.3 (3)
C6	0.507 (1)	-0.0197 (5)	0.2951 (5)	7.8 (3)
C7	0.251 (1)	0.1292 (4)	0.1176 (4)	5.4 (2)
C8	0.343 (2)	0.1674 (5)	0.0774 (5)	9.9 (3)
C9	0.375 (2)	0.1453 (6)	0.0178 (5)	12.0 (4)
C10	0.319 (2)	0.0849 (7)	-0.0033 (5)	10.4 (4)
C11	0.230 (1)	0.0474 (6)	0.0341 (5)	8.3 (3)
C12	0.198 (1)	0.0684 (5)	0.0948 (4)	6.6 (2)
C13	0.026 (1)	0.2169 (4)	0.1771 (4)	5.0 (2)
C14	-0.081 (1)	0.2185 (4)	0.1179 (5)	6.6 (3)
C15	-0.220 (1)	0.2635 (5)	0.1051 (5)	7.4 (3)
C16	-0.252 (1)	0.3043 (4)	0.1549 (5)	7.0 (3)
C17	-0.150 (1)	0.3017 (4)	0.2143 (5)	6.6 (2)
C18	-0.011 (1)	0.2597 (4)	0.2256 (4)	5.6 (2)
C19	0.442 (1)	0.1510 (5)	0.3913 (4)	6.7 (2)
C20	0.383 (1)	0.1125 (6)	0.4477 (5)	9.1 (3)
C21	0.196 (1)	-0.0589 (3)	0.3559 (4)	4.7 (2)
C22	0.275 (1)	-0.1165 (4)	0.3822 (4)	6.4 (2)
C23	0.215 (1)	-0.1424 (5)	0.4368 (4)	8.0 (3)
C24	0.083 (1)	-0.1149 (5)	0.4640 (5)	8.3 (3)
C25	0.005 (1)	-0.0586 (5)	0.4380 (5)	7.7 (3)
C26	0.061 (1)	-0.0315 (4)	0.3836 (4)	5.6 (2)
C27	0.201 (1)	-0.0763 (4)	0.2182 (4)	4.9 (2)
C28	0.305 (2)	-0.0867 (5)	0.1707 (5)	9.0 (3)
C29	0.248 (2)	-0.1255 (7)	0.1191 (6)	11.0 (4)
C30	0.087 (2)	-0.1559 (5)	0.1144 (5)	9.5 (3)
C31	-0.018 (1)	-0.1465 (5)	0.1612 (5)	8.3 (3)
C32	0.041 (1)	-0.1061 (4)	0.2136 (4)	6.5 (2)

Table 3. *Selected geometric parameters* (Å, °) *for* (1)

Ni—P1	2.1413 (8)	P1—C11	1.810 (3)
Ni—P2	2.145 (1)	P2—C4	1.826 (3)
Ni—N1	1.885 (2)	P2—C17	1.811 (4)
Ni—N2	1.876 (3)	P2—C19	1.826 (4)
S1—C1	1.601 (3)	N1—C1	1.153 (4)
S2—C2	1.605 (3)	N2—C2	1.149 (4)
P1—C3	1.837 (3)	C3—C4	1.509 (4)
P1—C5	1.813 (3)		
P1—Ni—P2	87.05 (3)	Ni—P2—C17	115.9 (1)
P1—Ni—N1	89.27 (7)	Ni—P2—C19	109.4 (1)
P1—Ni—N2	175.49 (9)	C4—P2—C17	106.0 (2)
P2—Ni—N1	176.32 (8)	C4—P2—C19	108.3 (2)
P2—Ni—N2	89.75 (9)	C17—P2—C19	105.8 (2)
N1—Ni—N2	93.9 (1)	Ni—N1—C1	170.2 (2)
Ni—P1—C3	110.23 (9)	Ni—N2—C2	172.4 (2)
Ni—P1—C5	116.14 (9)	S1—C1—N1	178.3 (2)
Ni—P1—C11	109.45 (8)	S2—C2—N2	178.5 (3)
C3—P1—C5	106.5 (1)	P1—C3—C4	108.8 (2)
C3—P1—C11	106.7 (1)	P2—C4—C3	110.5 (2)
C5—P1—C11	107.3 (1)	P1—C5—C6	121.8 (2)
Ni—P2—C4	111.0 (1)	P1—C5—C10	119.3 (2)
Ni—P1—C3—C4	-34.7 (2)	P1—Ni—P2—C4	3.6 (1)
Ni—P2—C4—C3	-26.0 (2)	P2—Ni—P1—C3	15.2 (1)
P1—C3—C4—P2	37.1 (2)		

Table 4. *Selected geometric parameters (Å, °) for* (2)

Ni—P1	2.223 (2)	P2—C4	1.826 (9)
Ni—P2	2.150 (2)	P2—C5	1.834 (9)
Ni—P3	2.189 (2)	P2—C19	1.83 (1)
Ni—N1	1.896 (6)	P3—C6	1.81 (1)
Ni—N2	2.088 (7)	P3—C21	1.829 (8)
S1—C1	1.587 (8)	P3—C27	1.821 (8)
S2—C2	1.635 (8)	N1—C1	1.131 (9)
P1—C3	1.832 (8)	N2—C2	1.14 (1)
P1—C7	1.795 (9)	C3—C4	1.51 (1)
P1—C13	1.820 (8)	C5—C6	1.47 (1)
P1—Ni—P2	86.20 (9)	Ni—P2—C5	112.0 (2)
P1—Ni—P3	137.3 (1)	Ni—P2—C19	116.1 (3)
P1—Ni—N1	91.2 (2)	C4—P2—C5	107.8 (4)
P1—Ni—N2	101.9 (2)	C4—P2—C19	105.6 (4)
P2—Ni—P3	85.53 (9)	C5—P2—C19	104.7 (4)
P2—Ni—N1	173.7 (2)	Ni—P3—C6	108.2 (3)
P2—Ni—N2	95.0 (2)	C6—P3—C21	107.7 (4)
P3—Ni—N1	92.5 (2)	C6—P3—C27	105.0 (4)
P3—Ni—N2	120.5 (2)	C21—P3—C27	104.2 (3)
N1—Ni—N2	91.2 (3)	Ni—N1—C1	169.9 (6)
Ni—P1—C3	107.6 (3)	Ni—N2—C2	158.1 (6)
Ni—P1—C7	113.6 (3)	S1—C1—N1	177.6 (8)
Ni—P1—C13	117.9 (3)	S2—C2—N2	178.5 (6)
C3—P1—C7	106.3 (4)	P1—C3—C4	107.9 (6)
C3—P1—C13	104.9 (4)	P2—C4—C3	107.3 (6)
C7—P1—C13	105.7 (4)	P2—C19—C20	116.4 (7)
Ni—P2—C4	110.1 (2)		
P2—Ni—P1—C3	−12.0 (3)	Ni—P1—C3—C4	39.2 (6)
P3—Ni—P1—C3	−91.1 (3)	Ni—P2—C4—C3	39.7 (6)
P1—Ni—P2—C4	−12.4 (3)	C5—P2—C4—C3	162.2 (6)
P1—Ni—P2—C5	−132.4 (4)	Ni—P2—C5—C6	16.0 (8)
P3—Ni—P2—C4	125.7 (3)	C4—P2—C5—C6	−105.3 (7)
P3—Ni—P2—C5	5.7 (4)	Ni—P3—C6—C5	38.7 (8)
P1—Ni—P3—C6	57.3 (4)	P1—C3—C4—P2	−48.7 (7)
P2—Ni—P3—C6	−22.1 (4)	P2—C5—C6—P3	−34.0 (9)

Programs used include the Enraf–Nonius *SDP* (Frenz, 1978), *ORTEP* (Johnson, 1965) and *MULTAN78* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). For (2), the crystal was of relatively poor quality giving rise to higher than expected *R* values and residual densities.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71031 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1033]

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Structure of Bis(diethyldithiocarbamato)-diiodotellurium(IV)

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Abstract

Centrosymmetric dimers are formed in the structure through two I atoms bridging two Te atoms. Te is seven-coordinated, bound to four S atoms, two intramolecular axial I atoms and one intermolecular planar bridging I atom, in a distorted pentagonal bipyramidal geometry. The non-bridging I atoms in the dimer have a secondary interaction with similar I atoms of other dimers.

Comment

The dithiocarbamate group $R_2NCS_2^-$ (*L*) is a strong chelating ligand for Te^{IV}. As a result, mixed-ligand complexes of Te^{IV} with dithiocarbamates and halides, such as TeL_3X and TeL_2X_2 (X = halides) were considered difficult to prepare. It was reasoned that by suitably substituting electron-withdrawing groups on the N atom of the dithiocarbamate group, the ligand could be made to bond weakly and