five-membered rings exhibit both half-chair (Davis, Einstein & Willis, 1982*b*) and approximate envelope (Davis, Einstein & Willis, 1982*a*) conformations.

The structure of the cation (Fig. 1) indicates that the chiralities of N(6), N(9) and N(12) are *R*, *R* and *S*, respectively. Since the space group is centrosymmetric, the crystal must contain a racemic mixture of both *RRS* and *SSR* enantiomers.

The bond parameters of the perchlorate anions are in keeping with those found in other structures (Davis, Einstein & Willis, 1982*a,b*). Both perchlorate anions are hydrogen-bonded to the cation, *viz.* N(9)—H(9*A*)···O(13) = 2·01 (3) Å with N—H···O = 173 (3)° and N(12)—H(12*A*)···O(21) = 2·16 (3) Å with N—H···O = 162 (3)°.

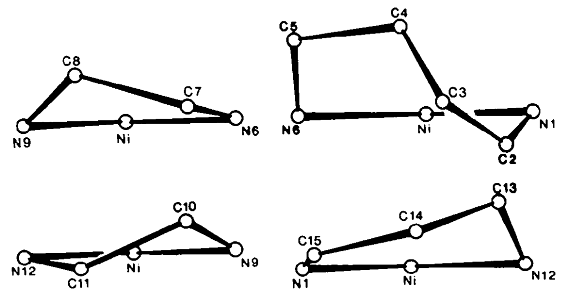

Fig. 2. The conformations of the chelate rings in $[Ni(L)](ClO_4)_2$ described, in each case, by the deviations of remaining ring atoms from the 'NiN₂' plane. Mean-plane equations have been deposited.

We acknowledge the support of NSERC of Canada and thank Dr N. F. Curtis for his gift of the crystals.

References

Cromer, D. T. & Waber, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

Curtis, N. F. (1979). *Coordination Chemistry of Macrocyclic Compounds*, edited by G. A. Melson, pp. 219–344. New York: Plenum Press.

Curtis, N. F. (1982). Private communication.

Curtis, N. F., de Courcey, J. S. & Waters, T. N. (1979). Private communication.

Davis, A. R., Einstein, F. W. B. & Willis, A. C. (1982*a*). *Acta Cryst.* B**38**, 437–442.

Davis, A. R., Einstein, F. W. B. & Willis, A. C. (1982*b*). *Acta Cryst.* B**38**, 443–448.

Gabe, E. J., Larsen, A. C., Lee, F. L. & Wang, Y. (1979). *The NRC PDP-8e Crystal Structure System.* Ottawa: NRC.

Grant, D. F. & Gabe, E. J. (1977). *J. Appl. Cryst.* **11**, 114–120.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Acta Cryst. (1983). C**39**, 874–877

Structure of Sodium Diisopropyldithiocarbamate Pentahydrate, $Na[C_7H_{14}NS_2].5H_2O$

By Ingvar Ymén

Inorganic Chemistry 1, Chemical Center, University of Lund, POB 740, S-220 07 Lund 7, Sweden

(*Received* 31 *January* 1983; *accepted* 28 *March* 1983)

Abstract. $M_r = 289{\cdot}4$, triclinic, $P\bar{1}$, $a = 5{\cdot}983\ (1)$, $b = 7{\cdot}741\ (2)$, $c = 17{\cdot}545\ (1)$ Å, $\alpha = 92{\cdot}02\ (1)$, $\beta = 94{\cdot}73\ (1)$, $\gamma = 106{\cdot}97\ (3)^\circ$, $V = 773\ (6)$ Å^3, $Z = 2$, $D_m = 1{\cdot}234\ (6)$, $D_x = 1{\cdot}243\ (9)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}37$ mm^{-1}, $F(000) = 312$, $T = 295$ K, $R = 0{\cdot}053$ for 1187 reflections. The structure is based on single-crystal diffractometer X-ray data. Pairs of distorted octahedra $[Na(H_2O)_6^+]$ are formed by edge sharing and these polyhedra are connected to form layers parallel to the *ab* plane by O—H···O and O—H···S hydrogen bonds. Along **c** the structure is kept together by van der Waals forces. The S(1)—C(1)—S(2) angle, 118·3 (3)°, in the organic ligand is the smallest so far observed in a Na dithiocarbamate.

Introduction. For Fe^{III} dithiocarbamates there is a strong correlation between the effective magnetic moment and the size of the ligand bite angle (Ståhl & Ymén, 1983). This angle is affected by the substituents R_2 in $^-S_2CNR_2$ as well as by the nature of the coordinating metal ion (Ymén, 1983*a*). In order to elucidate the influence of the R_2 groups a systematic study of compounds with weak metal—ligand interactions has been commenced. In $NaS_2CN(CH_3)_2.2H_2O$ (Oskarsson & Ymén, 1983) the ligand bite angle is smaller than in $NaS_2CN(CH_2)_4.2H_2O$ (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980; Ymén, 1982) as a result of a larger intramolecular steric interference, C—H···S, in the former compound. This paper reports the crystal structure of $NaS_2CN[CH(CH_3)_2]_2.5H_2O$ where an even larger steric interference is expected.

Experimental. Stoichiometric amounts of CS_2, $HN[CH(CH_3)_2]_2$ and NaOH in H_2O, efflorescent plate-like single crystals on evaporation under reduced

0108-2701/83/070874-04$01.50

(*ca* 1000 Pa) pressure at 277K, crystal 0·24 × 0·19 × 0·04 mm in a sealed capillary, Enraf–Nonius CAD-4, Laue class $\bar{1}$; $P1$ or $P\bar{1}$, $P\bar{1}$ was assumed in the calculations; D_m by flotation, cell dimensions obtained by least squares from 25 θ values; 4584 independent reflections with $3 < \theta \leq 30°$, 1187 with $I \geq 3\sigma_{\text{count}}(I)$ used in the calculations [$\sigma_{\text{count}}(I)$ is based on counting statistics]; graphite (002)-monochromatized Mo $K\alpha$, ω–2θ scan, scan width = $(0{\cdot}70 + 0{\cdot}5\tan\theta)°$, $\sigma_{\text{count}}(I)/I$ requested in a scan 0·030, maximum recording time 120s; five standard reflections, intensity decreased 18% as a linear function of the exposure time (corrected); I and $\sigma_{\text{count}}(I)$ corrected for Lorentz, polarization and absorption effects, range of transmission factors 0·94 – 0·98. Direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and subsequent ρ_{Diff}, $\sum w\Delta F^2$ minimized with weights $w = [\sigma_{\text{count}}(I)^2/4|F_o|^2 + (0{\cdot}07|F_o|)^2]^{-1}$, number of reflections in final least-squares cycle $m = 1187$, number of parameters $n = 218$, $R = 0{\cdot}053$, $wR = 0{\cdot}064$, $S = 0{\cdot}961$, max. height in final ρ_{Diff} less than 0·57 e Å^{-3}, max. shift to error 0·89, mean shift to error 0·084, scattering factors with corrections for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974), no secondary extinction (Zachariasen, 1967); a full normal δR plot comparing observed and calculated structure amplitudes (Abrahams & Keve, 1971) resulted in an approximately straight line with slope 0·868 (2), intercept 0·054 (2), correlation coefficient 0·996; computer programs used are given by Svensson (1978).

Discussion. Final atomic parameters are given in Table 1* and distances and angles in Table 2. The structure is depicted in Fig. 1. Na coordinates six water O atoms forming a distorted octahedron. Pairs of such octahedra are formed by sharing the edge O(1)···O(1$^{\text{i}}$) (Table 2). These pairs are connected by four O–H···O hydrogen bonds (Hamilton & Ibers, 1968) to form layers parallel to the *ab* plane. No Na–S bonds are formed but instead S(1) accepts four and S(2) two hydrogen bonds from the water molecules. The S···O distances are in the range given by Mereiter, Preisinger & Guth (1979). Along **c** the structure is kept together by van der Waals forces between the non-polar ends of the dithiocarbamate ions. The shortest intermolecular van der Waals distancc, 2·45 (12) Å, is between the atoms HC(7) and HC(4).

Table 1. *Positional and isotropic thermal parameters, with estimated standard deviations for the nonhydrogen atoms*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B(Å^2)
S(1)	0·7329 (3)	0·4163 (2)	0·8147 (1)	2·6 (1)
S(2)	0·4932 (3)	0·0936 (2)	0·7110 (1)	3·2 (1)
N	0·8212 (9)	0·3789 (6)	0·6683 (3)	1·9 (1)
C(1)	0·6945 (10)	0·3019 (8)	0·7249 (3)	1·9 (2)
C(2)	0·8012 (12)	0·2941 (8)	0·5898 (4)	2·5 (2)
C(3)	0·9948 (12)	0·5614 (8)	0·6800 (4)	2·5 (2)
C(4)	0·8817 (17)	0·1242 (11)	0·5888 (6)	3·6 (3)
C(5)	0·5660 (16)	0·2677 (14)	0·5447 (5)	3·5 (3)
C(6)	1·2467 (13)	0·5501 (12)	0·6706 (5)	3·4 (2)
C(7)	0·9279 (18)	0·6950 (11)	0·6294 (6)	3·7 (3)
Na	0·5033 (4)	0·1634 (3)	0·0717 (1)	2·6 (1)
O(1)	0·7191 (10)	0·1525 (7)	−0·0372 (4)	2·8 (2)
O(2)	0·7087 (12)	0·4703 (8)	0·1170 (4)	3·6 (2)
O(3)	0·7657 (12)	0·0137 (9)	0·1352 (3)	3·6 (2)
O(4)	0·2534 (11)	0·1498 (10)	0·1768 (4)	3·3 (2)
O(5)	0·2210 (10)	0·2319 (10)	0·9826 (4)	3·6 (2)

Table 2. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s*

Symmetry code: (i) $1-x, -y, -z$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $2-x, 1-y, 1-z$; (v) $1-x, y, 1-z$; (vi) $1+x, y, z$; (vii) $x-1, y, 1+z$.

(*a*) The dithiocarbamate ligand

S(1)···S(2)	2·961 (3)	N–C(3)	1·485 (8)
S(1)–C(1)	1·745 (6)	C(2)–C(4)	1·527 (11)
S(2)–C(1)	1·703 (6)	C(2)–C(5)	1·511 (11)
C(1)–N	1·347 (7)	C(3)–C(6)	1·556 (10)
N–C(2)	1·486 (8)	C(3)–C(7)	1·506 (11)

C–H: 0·85 (9)–1·16 (9)

S(1)–C(1)–S(2)	118·3 (3)	S(1)–C(1)–N–C(2)	−179·5 (5)
S(1)–C(1)–N	120·1 (4)	S(1)–C(1)–N–C(3)	−0·3 (8)
S(2)–C(1)–N	121·6 (4)	S(2)–C(1)–N–C(2)	0·0 (9)
C(1)–N–C(2)	124·5 (5)	S(2)–C(1)–N–C(3)	179·2 (5)
C(1)–N–C(3)	121·7 (5)	C(1)–N–C(2)–C(4)	−65·8 (8)
N–C(2)–C(4)	112·4 (6)	C(1)–N–C(2)–C(5)	65·2 (9)
N–C(2)–C(5)	114·1 (6)	C(1)–N–C(3)–C(6)	117·2 (7)
N–C(3)–C(6)	110·6 (5)	C(1)–N–C(3)–C(7)	−116·7 (7)
N–C(3)–C(7)	111·9 (6)	C(6)–C(3)–N–C(2)	−63·6 (7)
C(4)–C(2)–C(5)	113·5 (7)	C(7)–C(3)–N–C(2)	62·6 (8)
C(6)–C(3)–C(7)	112·3 (7)	C(4)–C(2)–N–C(3)	115·0 (7)
C(2)–N–C(3)	113·8 (5)	C(5)–C(2)–N–C(3)	−114·0 (7)

(*b*) The coordination polyhedron

Na–O(1)	2·405 (7)	Na–O(3)	2·432 (7)
Na–O(1$^{\text{i}}$)	2·445 (6)	Na–O(4)	2·454 (7)
Na–O(2)	2·405 (7)	Na–O(5)	2·392 (6)

(*c*) The hydrogen bonds

S(1)···O(1$^{\text{i}}$)	3·352 (6)	S(2)···O(4$^{\text{v}}$)	3·340 (7)
S(1)···O(2$^{\text{iii}}$)	3·305 (7)	O(3)···O(4$^{\text{vi}}$)	2·821 (9)
S(1)···O(2$^{\text{iv}}$)	3·315 (7)	O(5)···O(1$^{\text{vii}}$)	2·873 (8)
S(1)···O(4$^{\text{iii}}$)	3·334 (7)	O(5)···O(2$^{\text{iii}}$)	2·895 (9)
S(2)···O(3$^{\text{v}}$)	3·235 (7)	O(5)···O(3$^{\text{v}}$)	2·780 (9)

O···H: 1·74 (11) – 2·21 (9) S···H: 1·94 (12) – 2·79 (6)

The observed conformation of the dithiocarbamate ion (Fig. 2) is the same as predicted from NMR measurements and molecular-mechanics calculations on the related methyl *N*,*N*-diisopropyldithiocarbamate molecule (Lidén, Roussel, Liljefors, Chanon, Carter,

---

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38479 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

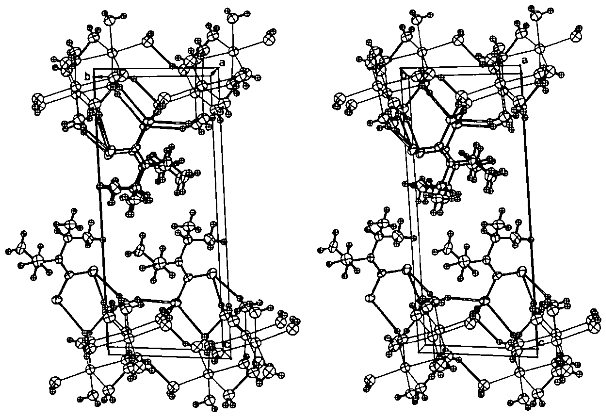

Fig. 1. A stereoscopic view of the structure.

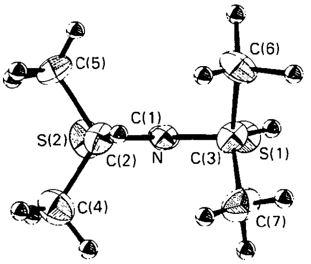

Fig. 2. The diisopropyldithiocarbamate ion viewed along the N—C(1) bond. C(1) is hidden by N.

Metzger & Sandström, 1976). The deviations for C(2) and C(3) from the plane S_2CN are only 0·009 (7) and 0·016 (7) Å, respectively, in contrast to $[H_2N\{CH(CH_3)_2\}_2][S_2CN\{CH(CH_3)_2\}_2]$ (Wahlberg, 1978) where the corresponding deviations from the plane S_2CNC_2 are −0·103 (4) and −0·084 (3) Å. The twist around the C(1)—N bond in the latter compound has no detectable effect on bond distances and angles since they are not significantly different in the two compounds.

The geometry of the S_2CNC_2 moiety in the title compound may be compared to the corresponding parts in $NaS_2CN(CH_2)_4.2H_2O$ (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980; Ymén, 1982) and $NaS_2CN(CH_3)_2.2H_2O$ (Oskarsson & Ymén, 1983). In all these compounds the two S—C(1) distances are different but the average values are all equal to 1·723 Å. The C(1)—N distances show a small increase from 1·326 (3) to 1·347 (7) Å in the series $R_2 = (CH_2)_4$, $(CH_3)_2$, $[CH(CH_3)_2]_2$. For the same series the ligand bite angle S(1)—C(1)—S(2) decreases very significantly, 122·3 (1), 120·9 (1), 118·3 (3)°. The observed variation of the C(1)—N distance and the S(1)—C(1)—S(2) angle may be described as the result of an increasing intramolecular steric interaction C—H···S, when the substituents R_2 become bulkier. This is reflected in the shortest intramolecular H···S distances, 2·77 (4) [2·85 (2) neutron diffraction], 2·56 (5) and 2·48 (6) Å for $R_2 = (CH_2)_4$, $(CH_3)_2$ and $[CH(CH_3)_2]_2$, respectively.

For a given dithiocarbamate ion the S(1)—C(1)—S(2) angle is dependent on the nature of the acceptor atom(s) (Ymén, 1983*a*). Weakly interacting acceptor atoms (*e.g.* Na^+, Li^+ and $NH_2R_2^+$) produce large angles whereas strong interaction with the acceptor (*d*-block metals) results in smaller angles. If the model of steric interference is correct there should be a strong correlation between the C(2)—N—C(3) and S(1)—C(1)—S(2) angles, since the steric strain can be increased or decreased through the influence of the coordinating metal ion. For diisopropyldithiocarbamates such a correlation is actually found (Fig. 3).

I would like to express my special gratitude to Dr Åke Oskarsson for all his help and to the Swedish Natural Science Research Council for financial support.

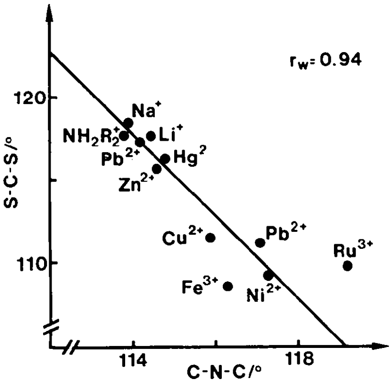

Fig. 3. The angle S—C—S (°) as a function of the angle C—N—C (°). The weighted correlation coefficient is 0·94. References: (Na^+) this work; (Li^+) Ymén (1983*b*); ($NH_2R_2^+$) Wahlberg (1978); (Pb^{2+}) Ito & Iwasaki (1980); (Hg^{2+}) Ito & Iwasaki (1979); (Zn^{2+}) Miyamae, Ito & Iwasaki (1979); (Cu^{2+}) Iwasaki & Kobayashi (1980); (Pd^{2+}) Bailey, Taylor & Maitlis (1978); (Ru^{3+}) Raston & White (1975); (Ni^{2+}) Newman & White (1972); (Fe^{3+}) Mitra, Figgis, Raston, Skelton & White (1979).

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.

Albertsson, J., Oskarsson, Å., Ståhl, K., Svensson, C. & Ymén, I. (1980). *Acta Cryst.* **B36**, 3072–3078.

Bailey, P. M., Taylor, S. H. & Maitlis, P. M. (1978). *J. Am. Chem. Soc.* **100**, 4711–4716.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

Hamilton, W. C. & Ibers, J. A. (1968). In *Hydrogen Bonding in Solids*. New York: Benjamin.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Ito, M. & Iwasaki, H. (1979). *Acta Cryst.* **B35**, 2720–2721.

ITO, M. & IWASAKI, H. (1980). *Acta Cryst.* B**36**, 443–444.
IWASAKI, H. & KOBAYASHI, K. (1980). *Acta Cryst.* B**36**, 1655–1657.
LIDÉN, A., ROUSSEL, C., LILJEFORS, T., CHANON, M., CARTER, R. E., METZGER, J. & SANDSTRÖM, J. (1976). *J. Am. Chem. Soc.* **98**, 2853–2860.
MEREITER, K., PREISINGER, A. & GUTH, H. (1979). *Acta Cryst.* B**35**, 19–25.
MITRA, S., FIGGIS, B. N., RASTON, C. L., SKELTON, B. W. & WHITE, A. H. (1979). *J. Chem. Soc. Dalton Trans.* pp. 753–757.
MIYAMAE, H., ITO, M. & IWASAKI, H. (1979). *Acta Cryst.* B**35**, 1480–1482.
NEWMAN, P. W. G. & WHITE, A. H. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2239–2243.
OSKARSSON, Å. & YMÉN, I. (1983). *Acta Cryst.* C**39**, 66–68.
RASTON, C. L. & WHITE, A. H. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2410–2418.
STÅHL, K. & YMÉN, I. (1983). To be published.
SVENSSON, C. (1978). Thesis, Univ. of Lund.
WAHLBERG, A. (1978). *Acta Cryst.* B**34**, 3479–3481.
YMÉN, I. (1982). *Acta Cryst.* B**38**, 2671–2674.
YMÉN, I. (1983*a*). *Acta Cryst.* C**39**, 570–572.
YMÉN, I. (1983*b*). To be published.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1983). C**39**, 877–879

Structure of Diiodo[1,2-bis(phenylthio)benzene]palladium(II) Diiodine (1/1), $[Pd(C_{18}H_{14}S_2)I_2]I_2$

BY L. R. GRAY, D. J. GULLIVER, W. LEVASON AND M. WEBSTER*

Department of Chemistry, The University, Southampton SO9 5NH, England

(*Received* 13 *January* 1983; *accepted* 14 *April* 1983)

Abstract. $M_r = 908\cdot43$, monoclinic, $C2/c$, $a = 16\cdot551\ (9)$, $b = 11\cdot588\ (2)$, $c = 12\cdot521\ (5)$ Å, $\beta = 99\cdot12\ (4)^\circ$, $V = 2371\cdot1$ Å^3, $Z = 4$, $D_m = 2\cdot56\ (2)$, $D_x = 2\cdot544$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu(\text{Mo } K\alpha) = 6\cdot08$ mm^{-1}, $F(000) = 1648$, room temperature, $R = 0\cdot0668$ for 2218 observed reflections. The palladium atom, which lies on the twofold axis, is planar four-coordinate (S_2I_2 donor set) Pd—S = 2·293 (2), Pd—I = 2·606 (1) Å, with adjacent molecules linked by diiodine (I···I—I···I) producing essentially linear I_4 groups I···I = 3·563 (2), I—I = 2·733 (2) Å. The chelating dithioether has an *anti* conformation of the phenyl groups.

Introduction. Palladium(IV) complexes of types $[R_4N][PdLX_5]$ and $[Pd(L{-}L)X_4]$ (L, $L{-}L$ respectively mono- and bidentate amine, phosphine or arsine, X = Cl, Br) have recently been obtained by halogen oxidation of the palladium(II) analogues (Gulliver & Levason, 1982*a*; Gray, Gulliver, Levason & Webster, 1983*a*). The corresponding reactions of $[Pd(L'{-}L')I_2]$ [$L'{-}L'$ = *cis*-$Ph_2PCH{=}CHPPh_2$, $Me_2As(CH_2)_3AsMe_2$] with molecular iodine gave black materials of empirical formula $Pd(L'{-}L')I_4$, and the X-ray structure determination of Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_4 revealed a planar (P_2I_2) arrangement about the palladium(II) with iodine molecules linking the Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_2 units (Gray, Gulliver, Levason & Webster, 1983*b*). The reaction of $[Pd\{o\text{-}C_6H_4(SPh)_2\}I_2]$ with iodine gave a black material of composition $Pd\{o\text{-}C_6H_4(SPh)_2\}I_3$, and a crystal structure analysis of this was undertaken to establish the nature of the (presumed) palladium(II) polyiodide. It should be noted that one genuine palladium(IV) iodocomplex is known, Cs_2PdI_6 (Sinram, Brendel & Krebs, 1982).

Experimental. Air-stable black crystals prepared (Gray *et al.*, 1983*b*) by recrystallization from $C_2H_4Cl_2$, D_m by flotation, preliminary data obtained from Weissenberg photographs, data collection on Enraf–Nonius CAD-4 diffractometer, cell dimensions from 25 accurately centred reflections, systematic absences hkl, $h + k \neq 2n$; $h0l$, $(h \neq 2n)$, $l \neq 2n$; $0k0$, $(k \neq 2n)$ indicated Cc (No. 9) or $C2/c$ (No. 15), the latter established by structure determination; 3881 reflections (3540 not including systematic absences), crystal 0·20 × 0·10 × 0·05 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation ($1\cdot5 \leq \theta \leq 30\cdot0^\circ$); three check reflections showed no deterioration; $R_{\text{int}} = 0\cdot0041$, 2221 reflections [$F > 2\sigma(F)$] used in refinement, index range h −23–22, k 0–16, l 0–17, empirical absorption correction based on a φ scan applied [transmission: 99·9 (max.), 75·5 (min)] plus usual Lorentz and polarization factors; distribution of E's (normalized structure factors) favoured a centrosymmetric space group.

Structure solved by Patterson methods; initial attempts in $C2/c$ by both direct methods and inspection of the Patterson function failed to yield a solution. An electron density synthesis phased on Pd and two I atoms in Cc gave a recognizable ligand fragment and the remaining I atoms and the model was developed by conventional structure factor and electron density

---

* To whom correspondence should be addressed.

0108-2701/83/070877-03$01.50