

Thus there is no apparent relationship between the two structure types, although the higher pressure phases have much lower molar volumes as expected.

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## Bis[2,2'-biphenyldiyl(dimethylarsine)]diiodonickel(II)

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**Abstract.**  $[\text{Ni}\{\text{As}_2(\text{CH}_3)_4(\text{C}_{12}\text{H}_8)\}_2\text{I}_2]$ ,  $M_r = 1036.83$ , triclinic,  $P\bar{1}$ ,  $a = 10.074$  (3),  $b = 11.562$  (4),  $c = 18.372$  (5) Å,  $\alpha = 111.96$  (2),  $\beta = 116.07$  (3),  $\gamma = 90.95$  (2)°,  $U = 1740$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_m(\text{floatation}) = 1.92$ ,  $D_x = 1.98$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 6.01$  mm<sup>-1</sup>,  $F(000) = 996$ ,  $T = 125$  K, final  $R = 0.0371$  for 3479 independent reflections [ $I > 2.5\sigma(I)$ ]. The Ni<sup>II</sup> atom has a tetragonally distorted octahedral configuration with the I<sup>-</sup> ligands occupying the axial positions. The diarsine ligands and the Ni atom form two seven-membered chelate rings. The average Ni–I and Ni–As bond lengths are 2.751 and 2.515 Å, respectively. There are no significant intermolecular interactions.

**Introduction.** The diarsine 2,2'-bis(dimethylarsino)biphenyl (dmab) has been used to prepare a series of compounds of the type  $\text{Ni}(\text{dmab})_2\text{X}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ ) (Allen, Ashford, Hogarth & Mann, 1977). These compounds are unusual in that they are Ni–diarsine complexes which are not only pseudo-octahedral but also paramagnetic and they contain a seven-membered chelate ring. The structure of the chloro derivative has already been reported (Allen, Kennedy & Nowell, 1980). However, of greater interest is the iodo derivative because for many years the structure of the diamagnetic compound diiodo[*o*-phenylenebis(dimethylarsine)]nickel(II),  $[\text{Ni}(\text{diars})\text{I}_2]$  (Stephenson, 1964), has been used as a paradigm despite the long Ni–I bond distance of 3.215 (2) Å. The present study was undertaken as the necessary first step in a detailed analysis of the metal–ligand interactions in these iodo–diarsine complexes using the bonding-orientated angular-overlap model.

**Experimental.** Crystals grown from butanol as yellow-green rhombs, dimensions 0.30 × 0.18 × 0.08 mm. Preliminary oscillation and Weissenberg photography ( $\text{Cu } K\alpha$ ) indicated triclinic system. Space group  $P\bar{1}$  chosen and confirmed by success of refinement. Data collected on Nicolet  $P\bar{3}$  diffractometer,  $\text{Mo } K\alpha$  radiation (graphite monochromator) at 125 K; cell dimensions from angular measurement of 25 strong reflections in range  $20 < 2\theta < 30^\circ$ . 4711 reflections in range  $h, k, l: \pm 10, \pm 12, 19$  ( $2\theta_{\text{max}} = 47^\circ$ ) collected using  $\theta/2\theta$  scans. 3 standard reflections (700, 080, 009) showed <4% intensity variation. Lp corrections and analytical absorption correction applied; transmission factors 0.621–0.323. Data averaged to give 4566 unique reflections ( $R_{\text{int}} = 0.021$ ) of which 3479 considered observed [ $I > 2.5\sigma(I)$ ]. Surprisingly, the chloro and iodo derivatives are isomorphous. The cell given for the iodo derivative conforms to a type II reduced cell and is related to that reported by Allen *et al.* by the transformation matrix  $s_{ij} = \bar{1}\bar{1}\bar{1}/010/100$  (*International Tables for X-ray Crystallography*, 1969). Starting coordinates taken from chloro derivative and refined, with all non-H atoms anisotropic, by full-matrix least squares, minimizing  $\sum w(|F_o| - |F_c|)^2$ , using *SHELX76* (Sheldrick, 1976). H atoms included in calculated positions (C–H = 1.08 Å) with fixed isotropic temperature factors. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974), weighting scheme  $w = 0.9854/[\sigma^2(F_o) + 0.0017|F_o|^2]$ . Final  $R = 0.0371$ ,  $wR = 0.0402$ .  $(\Delta/\sigma)_{\text{max}} = 0.024$ . Final difference map showed a number of residual peaks around heavy atoms (all peaks <1.2 e Å<sup>-3</sup> and <1.2 Å from heavy atoms); peak heights no higher than those earlier

Table 1. Final positional and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|       | x           | y            | z            | $U_{eq}(\text{\AA}^2)$ |
|-------|-------------|--------------|--------------|------------------------|
| Ni(1) | 0.4904 (1)  | -0.01662 (9) | -0.24192 (7) | 0.017                  |
| As(1) | 0.5233 (1)  | -0.20967 (8) | -0.20793 (6) | 0.018                  |
| As(2) | 0.2334 (1)  | -0.14594 (8) | -0.36339 (6) | 0.023                  |
| As(3) | 0.7329 (1)  | 0.12483 (8)  | -0.10585 (5) | 0.020                  |
| As(4) | 0.4787 (1)  | 0.15881 (8)  | -0.29366 (6) | 0.021                  |
| I(1)  | 0.34862 (7) | 0.08372 (5)  | -0.14118 (4) | 0.027                  |
| I(2)  | 0.62720 (7) | -0.11855 (5) | -0.34487 (4) | 0.025                  |
| C(1)  | 0.733 (1)   | -0.2234 (9)  | -0.1465 (6)  | 0.028                  |
| C(2)  | 0.451 (1)   | -0.242 (1)   | -0.1320 (6)  | 0.034                  |
| C(3)  | 0.204 (1)   | -0.260 (1)   | -0.4807 (6)  | 0.041                  |
| C(4)  | 0.074 (1)   | -0.053 (1)   | -0.3991 (8)  | 0.045                  |
| C(5)  | 0.928 (1)   | 0.1295 (9)   | -0.1060 (7)  | 0.031                  |
| C(6)  | 0.795 (1)   | 0.1042 (9)   | 0.0049 (6)   | 0.035                  |
| C(7)  | 0.385 (1)   | 0.3032 (9)   | -0.2616 (7)  | 0.040                  |
| C(8)  | 0.375 (1)   | 0.1045 (9)   | -0.4230 (6)  | 0.033                  |
| C(11) | 0.439 (1)   | -0.3736 (8)  | -0.3148 (6)  | 0.023                  |
| C(12) | 0.536 (1)   | -0.4339 (8)  | -0.3449 (6)  | 0.025                  |
| C(13) | 0.478 (1)   | -0.5485 (8)  | -0.4234 (6)  | 0.033                  |
| C(14) | 0.325 (1)   | -0.6030 (9)  | -0.4709 (6)  | 0.034                  |
| C(15) | 0.228 (1)   | -0.5437 (8)  | -0.4421 (6)  | 0.031                  |
| C(16) | 0.285 (1)   | -0.4289 (8)  | -0.3635 (6)  | 0.024                  |
| C(26) | 0.172 (1)   | -0.3733 (8)  | -0.3351 (6)  | 0.023                  |
| C(25) | 0.098 (1)   | -0.4440 (8)  | -0.3119 (6)  | 0.030                  |
| C(24) | -0.006 (1)  | -0.4007 (9)  | -0.2845 (6)  | 0.032                  |
| C(23) | -0.036 (1)  | -0.2834 (9)  | -0.2791 (7)  | 0.037                  |
| C(22) | 0.0336 (9)  | -0.2113 (8)  | -0.3039 (6)  | 0.027                  |
| C(21) | 0.1395 (9)  | -0.2544 (8)  | -0.3316 (6)  | 0.023                  |
| C(31) | 0.7212 (9)  | 0.3048 (8)   | -0.0638 (5)  | 0.021                  |
| C(32) | 0.688 (1)   | 0.3567 (9)   | 0.0068 (6)   | 0.033                  |
| C(33) | 0.676 (1)   | 0.4839 (9)   | 0.0385 (7)   | 0.038                  |
| C(34) | 0.700 (1)   | 0.560 (1)    | 0.0031 (7)   | 0.047                  |
| C(35) | 0.731 (1)   | 0.5103 (9)   | -0.0685 (7)  | 0.038                  |
| C(36) | 0.743 (1)   | 0.3848 (8)   | -0.1014 (6)  | 0.025                  |
| C(46) | 0.779 (1)   | 0.3363 (8)   | -0.1779 (6)  | 0.026                  |
| C(45) | 0.923 (1)   | 0.3879 (9)   | -0.1597 (7)  | 0.036                  |
| C(44) | 0.970 (1)   | 0.343 (1)    | -0.2227 (6)  | 0.037                  |
| C(43) | 0.871 (1)   | 0.249 (1)    | -0.3074 (7)  | 0.037                  |
| C(42) | 0.728 (1)   | 0.1982 (9)   | -0.3279 (6)  | 0.030                  |
| C(41) | 0.6790 (9)  | 0.2409 (8)   | -0.2624 (6)  | 0.024                  |

Table 2. Selected bond lengths (Å) and angles (°)

|                   |            |                   |           |
|-------------------|------------|-------------------|-----------|
| Ni(1)—As(1)       | 2.523 (1)  | As(2)—C(4)        | 1.955 (9) |
| Ni(1)—As(2)       | 2.493 (1)  | As(2)—C(21)       | 1.950 (9) |
| Ni(1)—As(3)       | 2.517 (1)  | As(3)—C(5)        | 1.967 (8) |
| Ni(1)—As(4)       | 2.527 (1)  | As(3)—C(6)        | 1.960 (8) |
| Ni(1)—I(1)        | 2.754 (1)  | As(3)—C(31)       | 1.957 (8) |
| Ni(1)—I(2)        | 2.747 (1)  | As(4)—C(7)        | 1.957 (9) |
| As(1)—C(1)        | 1.954 (8)  | As(4)—C(8)        | 1.953 (9) |
| As(1)—C(2)        | 1.969 (8)  | As(4)—C(41)       | 1.953 (8) |
| As(1)—C(11)       | 1.966 (8)  | C(16)—C(26)       | 1.50 (1)  |
| As(2)—C(3)        | 1.940 (9)  | C(36)—C(46)       | 1.51 (1)  |
| As(1)—Ni(1)—As(2) | 85.27 (4)  | Ni(1)—As(3)—C(5)  | 122.0 (3) |
| As(1)—Ni(1)—As(3) | 94.76 (4)  | Ni(1)—As(3)—C(6)  | 118.0 (3) |
| As(1)—Ni(1)—As(4) | 169.7 (1)  | Ni(1)—As(3)—C(31) | 112.0 (2) |
| As(1)—Ni(1)—I(1)  | 94.71 (3)  | C(5)—As(3)—C(6)   | 98.8 (4)  |
| As(1)—Ni(1)—I(2)  | 85.38 (3)  | C(5)—As(3)—C(31)  | 103.1 (3) |
| As(2)—Ni(1)—As(3) | 172.1 (1)  | C(6)—As(3)—C(31)  | 99.6 (4)  |
| As(2)—Ni(1)—As(4) | 95.08 (4)  | Ni(1)—As(4)—C(7)  | 123.9 (3) |
| As(2)—Ni(1)—I(1)  | 85.37 (3)  | Ni(1)—As(4)—C(8)  | 116.0 (3) |
| As(2)—Ni(1)—I(2)  | 93.70 (3)  | Ni(1)—As(4)—C(41) | 112.0 (2) |
| As(3)—Ni(1)—As(4) | 86.32 (4)  | C(7)—As(4)—C(8)   | 98.1 (4)  |
| As(3)—Ni(1)—I(1)  | 86.76 (3)  | C(7)—As(4)—C(41)  | 103.2 (4) |
| As(3)—Ni(1)—I(2)  | 94.17 (3)  | C(8)—As(4)—C(41)  | 100.2 (4) |
| As(4)—Ni(1)—I(1)  | 95.61 (3)  | As(1)—C(11)—C(12) | 119.0 (7) |
| As(4)—Ni(1)—I(2)  | 84.30 (3)  | As(1)—C(11)—C(16) | 121.8 (6) |
| I(1)—Ni(1)—I(2)   | 179.05 (2) | C(11)—C(16)—C(26) | 123.0 (7) |
| Ni(1)—As(1)—C(1)  | 114.9 (3)  | C(15)—C(16)—C(26) | 117.1 (8) |
| Ni(1)—As(1)—C(2)  | 122.6 (3)  | C(16)—C(26)—C(25) | 117.9 (8) |
| Ni(1)—As(1)—C(11) | 114.1 (2)  | C(16)—C(26)—C(21) | 122.9 (7) |
| C(1)—As(1)—C(2)   | 98.8 (4)   | As(2)—C(21)—C(26) | 123.6 (6) |
| C(1)—As(1)—C(11)  | 100.7 (4)  | As(2)—C(21)—C(22) | 118.1 (6) |
| C(2)—As(1)—C(11)  | 102.6 (4)  | As(3)—C(31)—C(32) | 118.3 (6) |
| Ni(1)—As(2)—C(3)  | 120.3 (3)  | As(3)—C(31)—C(36) | 123.4 (6) |
| Ni(1)—As(2)—C(4)  | 117.2 (3)  | C(31)—C(36)—C(46) | 121.6 (7) |
| Ni(1)—As(2)—C(21) | 113.8 (2)  | C(35)—C(36)—C(46) | 118.7 (8) |
| C(3)—As(2)—C(4)   | 99.3 (5)   | C(36)—C(46)—C(45) | 116.7 (8) |
| C(3)—As(2)—C(21)  | 103.6 (4)  | C(36)—C(46)—C(41) | 123.4 (8) |
| C(4)—As(2)—C(21)  | 99.5 (4)   | As(4)—C(41)—C(46) | 123.2 (6) |
|                   |            | As(4)—C(41)—C(42) | 118.3 (7) |

assigned to H atoms. Such residual peaks are a common feature of Ni–As structure determinations (Cunningham & Hanton, 1986).

**Discussion.** Atomic coordinates are given in Table 1\* with selected bond lengths and angles in Table 2. The monomeric complex and atom labelling are illustrated in Fig. 1. The structure is isomorphous with the chloro derivative (Allen *et al.*, 1980) indicating that packing is dominated by the biphenyl rings. The Ni–I bond distances are longer than the calculated sum of the covalent radii for octahedral Ni<sup>II</sup> complexes (2.67 Å) (Lalancette, Macchia & Furey, 1976). As expected, the values are very much smaller than the Ni–I distance in Ni(diars)<sub>2</sub>I<sub>2</sub> (Stephenson, 1964). They are also considerably smaller than values found in the *trans* macrocyclic complexes Ni(C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>)I<sub>2</sub> (2.880 Å) (Johnston & Horrocks, 1971), [Ni(C<sub>28</sub>H<sub>20</sub>N<sub>4</sub>)IH<sub>2</sub>O]I (2.903 Å) (Hawkinson & Fleischer, 1969) and in *trans*-Ni(pyridine)<sub>4</sub>I<sub>2</sub> (2.886 Å) (Hamm, Bordner & Schreiner, 1973); only the *cis* macrocyclic complex Ni(C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>)I<sub>2</sub> has comparable values (2.711, 2.757 Å) (Lalancette *et al.*, 1976).

The Ni–As bond lengths are shorter than the value (2.57 Å) derived from the respective covalent radii but are longer than values found in other octahedral nickel–arsine complexes (Allen *et al.*, 1980; Cunningham & Hanton, 1986). Allen *et al.* suggest that this elongation could be due to steric constraints arising from the necessity to minimize interactions between groups *ortho* to the phenylene link while at the same time maintaining an optimum chelate bite of about 86°. However, the recent structure of  $\mu$ -(2,2'-biphenylato)-bis[(N,N,N',N'-tetramethylethylenediamine)-

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42969 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

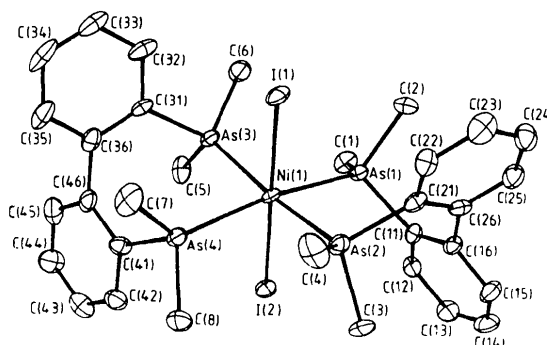


Fig. 1. An ORTEP plot (Johnson, 1965) of the complex; thermal ellipsoids are drawn at the 50% probability level.

lithium(II)] (Schubert, Neugebauer & von Rague Schleyer, 1982) in which the biphenyl unit is perfectly planar suggests that the H atoms *ortho* to the phenylene link are sterically not very demanding. Further, comparison of the non-bonding interactions between the I<sup>-</sup> ligands and the respective phenyl and methyl carbons (mean distance 3.835 Å) indicates the distances are very similar to the non-bonding contacts which cushion the I<sup>-</sup> ligands in Ni(diars)<sub>2</sub>I<sub>2</sub> (Stephenson, 1964). In both complexes it is the non-bonding contacts which determine how close the I<sup>-</sup> ligands can approach the central Ni atom. In Ni(diars)<sub>2</sub>I<sub>2</sub> the I<sup>-</sup> ligands cannot approach very closely and so interaction between the Ni and As ligands must be strong in order for the Ni to achieve electrical neutrality. Conversely, in Ni(dmab)<sub>2</sub>I<sub>2</sub> where the I<sup>-</sup> ligands approach more closely the Ni-As interaction must be reduced and this is reflected in the long Ni-As bond lengths. The variation in bond lengths in the two structures is a direct result of the operation of the electroneutrality principle.

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## Structure of Dibromiodobis(triphenylphosphine oxide)thallium(III)

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**Abstract.** [TlBr<sub>2</sub>I{OP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]<sub>2</sub>, *M*<sub>r</sub> = 1047.68, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 14.954 (3), *b* = 14.605 (4), *c* = 17.489 (2) Å, β = 107.84 (4)°, *V* = 3635.9 Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.91 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 76.2 cm<sup>-1</sup>, *F*(000) = 1984, *T* = 293 K, *R* = 0.049 for 3158 significant reflections. The coordination around the Tl atom is distorted trigonal bipyramidal with the halide atoms in equatorial sites and the triphenylphosphine oxide (tppo) ligands in axial positions. The metal atom is only 0.019 (1) Å out of the plane of the halide atoms. The crystal structure is isotypic with that of [TlBr<sub>3</sub>(tppo)<sub>2</sub>].

**Introduction.** Thallium(III) halides react with triphenylphosphine oxide to form [TLX<sub>3</sub>(tppo)<sub>2</sub>] complexes (*X* = halide, tppo = triphenylphosphine oxide), in which the Tl atom exhibits a distorted trigonal-bipyramidal coordination sphere. In order to gain more insight into the relation between spectroscopic and structural properties of the TLX<sub>3</sub> compounds, we prepared the mixed halocompounds [TlBrClI(tppo)<sub>2</sub>] (Castineiras, Hiller, Strähle, Bermejo & Gayoso, 1986) and [TlBrI<sub>2</sub>(tppo)<sub>2</sub>] (Castineiras, Hiller, Strähle, Bermejo & Gayoso, 1985). Here we report the crystal structure of [TlBr<sub>2</sub>I(tppo)<sub>2</sub>].