

bond angles for the N—H...Cl hydrogen bond are 171 (2) and 177 (2)°, respectively. Both bonds are close to the expected 180° for hydrogen bonding of this type. The amine H atom that exhibits the more linear and shorter hydrogen bond is on the ligand which is more distorted from planarity, suggesting that this may be the origin of the distortion.

References

- 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.)
- 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. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64-71. Delft Univ. Press.
- JACOBSON, R. A. & JENSEN, W. P. (1986). *Inorg. Chim. Acta*, **114**, L9-L10.
- JENSEN, W. P. & JACOBSON, R. A. (1981). *Inorg. Chim. Acta*, **49**, 199-204.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- JOHNSON, J. E., BEINEKE, T. A. & JACOBSON, R. A. (1971). *J. Chem. Soc. A*, pp. 1372-1374.
- JOHNSON, J. E. & JACOBSON, R. A. (1973a). *J. Chem. Soc. Dalton Trans.* pp. 580-584.
- JOHNSON, J. E. & JACOBSON, R. A. (1973b). *Acta Cryst.* **B29**, 1669-1674.
- THOMPSON, J. S. & WHITNEY, J. F. (1984). *Inorg. Chem.* **23**, 2813-2819.

Acta Cryst. (1991). **C47**, 513-516

Structure of [PhCH₂NMe₃]₂[B₁₀H₁₂]₂Pd] Acetonitrile Solvate

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Abstract. [PhCH₂NMe₃]₂²⁺[Pd(B₁₀H₁₂)₂]²⁻·2CH₃CN, $M_r = 729.39$, triclinic, $P\bar{1}$, $a = 9.2094$ (18), $b = 10.772$ (3), $c = 11.3707$ (23) Å, $\alpha = 67.721$ (21), $\beta = 83.394$ (16), $\gamma = 78.801$ (21)°, $V = 1022.8$ Å³, $Z = 1$, $D_x = 1.184$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.470$ mm⁻¹, $F(000) = 380$, $T = 291$ (1) K, $R = 0.0265$ for 5850 independent observed reflections. The palladaborane anion has effective C_{2h} molecular symmetry (C_i imposed). The {B₁₀} fragment has a geometry close to intermediate between that of *nido*-{B₁₀H₁₂}²⁻ and *arachno*-{B₁₀H₁₂}⁴⁻, and the verticity of the Pd atom is 39.4%.

Introduction. We are involved in a major research programme which critically examines the structures of metallaboranes and metallaheteroboranes. The aims of the work are firstly to measure the extent to which the metal atom present can be regarded as a true cluster vertex, and then to determine the factors responsible for the 'verticity' of the metal. The family of metallaboranes represented by $MB_{10}H_{12}$ is particularly useful in this respect, since the {B₁₀H₁₂} ligand appears able to accommodate both metal vertices and (non-vertex) metal bridges with only subtle, but nevertheless measureable, structural change. In brief, if the metal is formally present as a polyhedral vertex the {B₁₀H₁₂} ligand is formally the

arachno fragment {B₁₀H₁₂}⁴⁻, whereas for a bridging metal atom the polyhedral unit is merely the *nido* species {B₁₀H₁₂}²⁻.

We have previously shown that clear examples of both types of metallaborane exist. Thus, in [7,7,7-(CO)₃-*nido*-7-CoB₁₀H₁₂]⁻ (Macgregor, Yellowlees & Welch, 1990a) the Co atom, formally Co³⁺, is a true polyhedral vertex (high verticity), whereas in (the superficially structurally similar) [5,6,9,10- μ_4 -{AuP(C₆H₁₁)₃}-*nido*-B₁₀H₁₂]⁻ (Wynd, Welch & Parish, 1990), the Au atom, formally Au⁺, is not (low verticity).

We recently showed (Macgregor, Yellowlees & Welch, 1990b) that metallaboranes of the type [(B₁₀H₁₂)₂M]ⁿ⁻ [$M = Ni$, $n = 2$ (Guggenberger, 1972); $M = Pt$, $n = 2$ (Macgregor, Yellowlees & Welch, 1990b); $M = Au$, $n = 1$ (Wynd & Welch, 1987)] are particularly interesting in that they show intermediate behaviour, *i.e.* the {B₁₀H₁₂} fragments of the molecules have structures that lie between those expected for {B₁₀H₁₂}²⁻ and {B₁₀H₁₂}⁴⁻, resulting in metal verticities that are neither high nor low. The situation was further complicated by the fact that the platinaborane structure appeared to suffer from an unusual asymmetry which we were forced to conclude was the result of crystal packing effects. Seeking further data on the [(B₁₀H₁₂)₂M]ⁿ⁻

metallaboranes, we have resynthesized the palladium derivative ($n = 2$) for the purposes of the structural study reported here. This will furnish precise stereochemical information on a complete group of analogous metallaboranes from the first, the second, and the third transition series. Fortuitously, [PhCH₂NMe₃]₂[(B₁₀H₁₂)₂Pd] crystallizes from acetonitrile/diethyl ether with two molecules of acetonitrile solvate whereas the platinum analogue is solvate free, allowing additional comment on the possible influence of packing forces on the structure of the latter.

Experimental. The salt [PhCH₂NMe₃]₂[(B₁₀H₁₂)₂Pd] was prepared by a modified version of a published procedure (Klanberg, Wegner, Parshall & Muetterties, 1968), and wine-red crystals grown by the slow diffusion of diethyl ether into an acetonitrile solution at 243 K; single crystal, 0.3 × 0.3 × 0.2 mm, removed from solvent mixture and quickly covered with silicone grease, then sealed inside a Lindemann capillary; mounted on an Enraf-Nonius CAD-4 diffractometer (Mo K α radiation, graphite monochromator); cell parameters and orientation matrix from least-squares refinement of the setting angles ($13 < \theta < 15^\circ$) of 25 centred reflections; data collection by ω - 2θ scans in 96 steps with ω scan width ($0.8 + 0.34 \tan \theta$); data (h : 0 to 12, k : -15 to 15, l : -16 to 16. h : -12 to 0, k : -15 to 15, l : -16 to -2) measured for $1 \leq \theta \leq 30^\circ$ over 202 X-ray hours; corrections for Lorentz and polarization effects applied (Gould & Smith, 1986); 7835 reflections measured; structure solution *via* iterative full-matrix least-squares refinement (on F)/ ΔF syntheses (Pd atom at origin) (Sheldrick, 1976); empirical absorption correction (Walker & Stuart, 1983) applied after isotropic convergence (correction factors 0.793–1.313); data merged ($R_{\text{merge}} = 0.0142$) to give 5864 independent reflections of which 5850 [$F \geq 2.0\sigma(F)$] retained; all non-H atoms refined with anisotropic thermal parameters; borane, phenyl and methylene H atoms freely refined (including individual isotropic thermal parameters), and CH₃ moieties treated as rigid groups, with separate group thermal parameters for H atoms of the benzyltrimethylammonium cation and the acetonitrile solvate; weighting scheme $w^{-1} = \sigma^2(F) + 0.000700F^2$; 313 variables, data:variable ratio > 18:1; max. shift/e.s.d. in final cycle < 0.13 (H atom); $R = 0.0265$, $wR = 0.0352$, $S = 1.128$; max. and min. residues in final ΔF synthesis 0.52 and -1.05 e \AA^{-3} , respectively; scattering factors for C, H, B and N inlaid in *SHELX76*. Those for Pd from *International Tables for X-ray Crystallography* (1974, Vol. IV); Fig. 1 drawn using *EASYORTEP* (Mallinson & Muir, 1985); molecular geometry calculations *via* *CALC* (Gould & Taylor, 1986).

Table 1. Fractional coordinates of non-H atoms and equivalent isotropic thermal parameters

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Pd	0.00000	0.00000	0.00000	0.0318 (1)
B(a)	0.05941 (14)	-0.22922 (12)	0.11364 (12)	0.0379 (3)
B(b)	0.22174 (13)	0.01148 (12)	-0.11556 (11)	0.0373 (3)
B(c)	0.00450 (14)	-0.18732 (13)	-0.04241 (12)	0.0380 (3)
B(d)	0.09237 (13)	-0.05590 (13)	-0.16722 (11)	0.0367 (3)
B(j)	0.31487 (14)	-0.27865 (13)	-0.04638 (12)	0.0404 (3)
B(g)	0.28606 (14)	-0.11884 (13)	-0.17461 (11)	0.0393 (3)
B(i)	0.35679 (14)	-0.13439 (13)	-0.02919 (12)	0.0398 (3)
B(e)	0.15571 (14)	-0.23081 (13)	-0.13862 (12)	0.0405 (3)
B(f)	0.14379 (15)	-0.33020 (12)	0.02590 (13)	0.0406 (3)
B(h)	0.26101 (14)	-0.27731 (13)	0.10615 (12)	0.0393 (3)
C(1)	0.22667 (13)	0.06314 (14)	0.36903 (12)	0.0469 (3)
C(2)	0.20236 (15)	-0.04673 (14)	0.48024 (13)	0.0531 (3)
C(3)	0.31791 (15)	0.03825 (16)	0.27166 (12)	0.0559 (3)
C(4)	0.26626 (17)	-0.17689 (15)	0.49152 (15)	0.0614 (3)
C(5)	0.35606 (17)	-0.20146 (16)	0.39376 (16)	0.0673 (3)
C(6)	0.38256 (16)	-0.09320 (17)	0.28410 (14)	0.0667 (3)
C(7)	0.14763 (14)	0.20338 (15)	0.35198 (13)	0.0532 (3)
N(1)	0.22615 (14)	0.28558 (12)	0.40039 (11)	0.0495 (3)
C(8)	0.12703 (20)	0.41814 (16)	0.38372 (18)	0.0735 (3)
C(9)	0.25637 (22)	0.21256 (16)	0.53771 (15)	0.0835 (3)
C(10)	0.36641 (18)	0.31553 (18)	0.32580 (19)	0.0820 (3)
C(A1)	0.70103 (20)	-0.40641 (17)	0.13582 (17)	0.0735 (3)
C(A2)	0.69530 (21)	-0.44438 (16)	0.27029 (18)	0.0758 (3)
N(A1)	0.69141 (25)	-0.47402 (19)	0.37764 (19)	0.1333 (3)

Discussion. Table 1* lists coordinates of refined non-H atoms and equivalent isotropic thermal parameters, and Table 2 details internuclear distances and selected interbond angles. The palladaborane anion is viewed in perspective in Fig. 1. Cage atoms are labelled B(a) to B(j), as in the platinum analogue, to reflect the ambiguity in formal classification (*nido* or *arachno*) of the B₁₀ residue. The compound crystallizes with no unusually short contacts between ions.

Although this structural study was performed at room temperature, the high quality of the crystal, the relatively high θ_{max} , and the measurement of more than one asymmetric fraction of data combine to afford a result that is highly accurate, as evidenced by the low e.s.d.'s on the molecular parameters. Although the anion has crystallographically required C_i symmetry, the *effective* point group is C_{2h} . Thus, in the present compound there is no evidence of the small but real distortion of the MB₈ coordination sphere that is observed in [(B₁₀H₁₂)₂Pt]²⁻ (Macgregor, Yellowlees & Welch, 1990b). The fact that the palladium species reported here has a totally different *crystal* structure to its platinum analogue is wholly consistent with our previous suggestion (Macgregor, Yellowlees & Welch, 1990b) that the

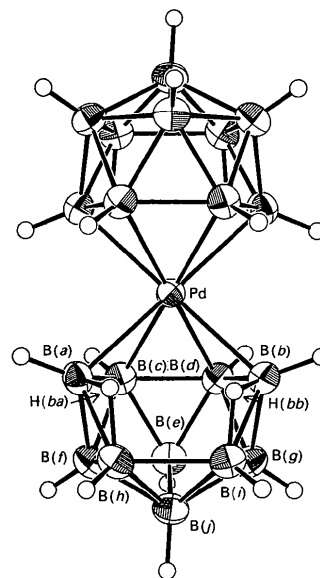
* Lists of structure factors, H-atom positions and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53524 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and interbond angles (°)*

Pd—B(a)	2.2988 (13)	B(i)—B(h)	1.9837 (19)
Pd—B(b)	2.2955 (12)	B(j)—H(i)	1.050 (3)
Pd—B(c)	2.2375 (14)	B(i)—H(bb)	1.252 (3)
Pd—B(d)	2.2357 (13)	B(e)—B(f)	1.7713 (19)
B(a)—B(c)	1.7659 (19)	B(e)—H(e)	1.029 (3)
B(a)—B(f)	1.7603 (19)	B(f)—B(h)	1.7839 (19)
B(a)—B(h)	1.8292 (19)	B(f)—H(f)	0.984 (3)
B(a)—H(a)	1.131 (3)	B(h)—H(ba)	1.302 (3)
B(a)—H(ba)	1.214 (3)	B(h)—H(h)	1.053 (3)
B(b)—B(d)	1.7639 (18)	C(1)—C(2)	1.3974 (20)
B(b)—B(g)	1.7528 (18)	C(1)—C(3)	1.3883 (20)
B(b)—B(i)	1.8254 (18)	C(1)—C(7)	1.4942 (20)
B(b)—H(bb)	1.283 (3)	C(2)—C(4)	1.3744 (22)
B(b)—H(b)	1.101 (3)	C(2)—H(2C)	1.007 (3)
B(c)—B(d)	1.8249 (19)	C(3)—C(6)	1.3854 (22)
B(c)—B(e)	1.7720 (19)	C(3)—H(3C)	0.938 (3)
B(c)—B(f)	1.7814 (19)	C(4)—C(5)	1.3843 (24)
B(c)—H(c)	1.158 (3)	C(4)—H(4C)	0.731 (4)
B(d)—B(g)	1.7854 (18)	C(5)—C(6)	1.3828 (24)
B(d)—B(e)	1.7743 (19)	C(5)—H(5C)	0.926 (4)
B(d)—H(d)	1.096 (3)	C(6)—H(6C)	0.904 (4)
B(f)—B(g)	1.7799 (19)	C(7)—H(1C7)	0.897 (3)
B(f)—B(i)	1.7558 (19)	C(7)—H(2C7)	0.991 (3)
B(f)—B(e)	1.7789 (19)	C(7)—N(1)	1.5231 (19)
B(f)—B(f)	1.7782 (19)	N(1)—C(8)	1.4955 (23)
B(f)—B(h)	1.7529 (19)	N(1)—C(9)	1.4893 (22)
B(f)—H(j)	1.114 (3)	N(1)—C(10)	1.4813 (23)
B(g)—B(i)	1.7838 (19)	C(A1)—C(A2)	1.422 (3)
B(g)—B(e)	1.7716 (19)	C(A2)—N(A1)	1.137 (3)
B(g)—H(g)	1.009 (3)		
B(a)—Pd—B(c)	45.80 (5)	B(g)—B(d)—H(d)	121.59 (19)
B(b)—Pd—B(d)	45.80 (5)	B(e)—B(d)—H(d)	121.22 (19)
B(c)—Pd—B(d)	48.15 (5)	B(g)—B(j)—B(i)	60.59 (7)
B(a)—Pd—B(b')	86.30 (5)	B(g)—B(j)—B(e)	59.71 (7)
B(a)—Pd—B(d')	95.75 (5)	B(g)—B(j)—H(j)	122.99 (19)
B(c)—Pd—B(b')	95.95 (5)	B(i)—B(j)—B(h)	68.86 (8)
Pd—B(a)—B(c)	65.27 (6)	B(e)—B(j)—B(f)	59.73 (8)
Pd—B(a)—H(a)	117.15 (18)	B(f)—B(j)—B(h)	60.68 (8)
B(c)—B(a)—B(f)	60.69 (8)	B(f)—B(j)—H(j)	115.84 (19)
B(c)—B(a)—H(a)	131.05 (19)	B(h)—B(j)—H(j)	113.71 (19)
B(f)—B(a)—B(h)	59.56 (7)	B(b)—B(g)—B(d)	59.80 (7)
B(f)—B(a)—H(a)	123.05 (19)	B(b)—B(g)—B(i)	62.14 (7)
B(h)—B(a)—H(a)	117.61 (19)	B(b)—B(g)—B(e)	110.86 (9)
B(h)—B(a)—H(ba)	45.27 (16)	B(b)—B(g)—H(g)	119.52 (20)
Pd—B(b)—B(d)	65.31 (6)	B(d)—B(g)—B(e)	59.84 (7)
Pd—B(b)—H(b)	117.12 (18)	B(d)—B(g)—H(g)	126.27 (21)
B(d)—B(b)—B(g)	61.02 (7)	B(j)—B(g)—B(i)	59.03 (7)
B(d)—B(b)—H(b)	129.55 (19)	B(j)—B(g)—B(e)	60.12 (7)
B(g)—B(b)—B(i)	59.76 (7)	B(j)—B(g)—H(g)	120.51 (21)
B(g)—B(b)—H(b)	122.30 (19)	B(i)—B(g)—H(g)	119.54 (20)
B(i)—B(b)—H(bb)	43.29 (15)	B(e)—B(g)—H(g)	121.75 (21)
B(i)—B(b)—H(b)	118.39 (19)	B(b)—B(i)—B(g)	58.10 (7)
Pd—B(c)—B(a)	68.93 (6)	B(b)—B(i)—H(i)	119.73 (20)
Pd—B(c)—B(d)	65.87 (6)	B(b)—B(i)—H(bb)	44.62 (15)
Pd—B(c)—H(c)	114.22 (17)	B(j)—B(i)—B(g)	60.37 (7)
B(a)—B(c)—B(f)	59.50 (7)	B(j)—B(i)—B(h)	55.50 (7)
B(a)—B(c)—H(c)	120.93 (18)	B(j)—B(i)—H(i)	123.94 (20)
B(d)—B(c)—B(e)	59.09 (7)	B(g)—B(i)—H(i)	123.63 (20)
B(d)—B(c)—H(c)	118.11 (18)	B(h)—B(i)—H(i)	121.46 (20)
B(e)—B(c)—B(f)	59.80 (8)	B(h)—B(i)—H(bb)	94.73 (16)
B(e)—B(c)—H(c)	116.44 (18)	B(c)—B(e)—B(d)	61.94 (7)
B(f)—B(c)—H(c)	120.04 (18)	B(c)—B(e)—B(f)	60.36 (8)
Pd—B(d)—B(b)	68.89 (6)	B(c)—B(e)—H(e)	121.49 (20)
Pd—B(d)—B(c)	65.97 (6)	B(d)—B(e)—B(g)	60.46 (7)
Pd—B(d)—H(d)	110.70 (18)	B(d)—B(e)—H(e)	122.84 (20)
B(b)—B(d)—B(g)	59.18 (7)	B(j)—B(e)—B(g)	60.17 (7)
B(b)—B(d)—H(d)	117.43 (19)	B(j)—B(e)—B(f)	60.11 (8)
B(c)—B(d)—B(e)	58.97 (7)	B(j)—B(e)—H(e)	122.64 (20)
B(c)—B(d)—H(d)	120.28 (19)	B(g)—B(e)—H(e)	119.99 (20)
B(g)—B(d)—B(e)	59.69 (7)	B(f)—B(e)—H(e)	117.66 (20)

Table 3. *Root-mean-square misfit values (Å), and percentage verticities, for the series [(B₁₀H₁₂)₂M]²⁻ (M = Ni, Pd, Pt)*

Compound	Misfit vs B ₁₀ H ₁₄	Misfit vs [B ₁₁ H ₁₃] ²⁻	% Verticity	Reference
[(B ₁₀ H ₁₂) ₂ Ni] ²⁻	0.080	0.136	36.1	Guggenberger (1972)
[(B ₁₀ H ₁₂) ₂ Pd] ²⁻	0.084	0.127	39.4	This work
[(B ₁₀ H ₁₂) ₂ Pt] ²⁻	0.085	0.125	42.6	Macgregor, Yellowlees & Welch (1990b)
Mutual misfits (Å)				
[(B ₁₀ H ₁₂) ₂ Ni] ²⁻ vs [(B ₁₀ H ₁₂) ₂ Pd] ²⁻			0.030	
[(B ₁₀ H ₁₂) ₂ Ni] ²⁻ vs [(B ₁₀ H ₁₂) ₂ Pt] ²⁻			0.029	
[(B ₁₀ H ₁₂) ₂ Pd] ²⁻ vs [(B ₁₀ H ₁₂) ₂ Pt] ²⁻			0.011	

Fig. 1. Perspective view of, and atom-labelling scheme for, the [Pd(B₁₀H₁₂)₂]²⁻ anion (30% thermal ellipsoids, except for H atoms which have an artificial radius of 0.1 Å for clarity).

structural distortion in the platinaborane is due to crystal packing effects.

Root-mean-square misfit calculations (Wynd, Macgregor, Gould, Taylor, Yellowlees & Welch, 1990) on the {B₁₀} fragment of the palladaborane afford (mis)fits of 0.084 Å *versus* B₁₀H₁₄ (Brill, Dietrich & Dierks, 1971) and 0.127 Å *versus* [B₁₁H₁₃]²⁻ (Fritchie, 1967). The verticity of the Pd atom is calculated to be 39.4%. These data position [(B₁₀H₁₂)₂Pd]²⁻ nicely between [(B₁₀H₁₂)₂Ni]²⁻ (Guggenberger, 1972) and [(B₁₀H₁₂)₂Pt]²⁻ (Macgregor, Yellowlees & Welch, 1990b) (Table 3), but clearly show that the greatest similarity is between the palladium and platinum analogues. Other key molecular parameters that may ultimately be useful in formal classification of the {B₁₀H₁₂}

ligand in the present compound are as follows: B(c)—B(d) 1.8249 (19), B(h)—B(i) 1.9837 (19), B(a)···B(b) 3.352 (2) Å; height of Pd above the B(a)B(h)B(i)B(b) plane 0.5693 (22) Å.

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References

BRILL, R., DIETRICH, H. & DIERKS, H. (1971). *Acta Cryst.* B27, 2003–2018.
FRITCHIE, C. J. (1967). *Inorg. Chem.* 6, 1199–1203.
GOULD, R. O. & SMITH, D. E. (1986). *CADABS*. Program for data reduction. Univ. of Edinburgh, Scotland.

GOULD, R. O. & TAYLOR, P. (1986). *CALC*. Program for molecular geometry calculations. Univ. of Edinburgh, Scotland.
GUGGENBERGER, L. J. (1972). *J. Am. Chem. Soc.* 94, 114–119.
KLANBERG, F., WEGNER, P. A., PARSHALL, G. W. & MUETTERTIES, E. L. (1968). *Inorg. Chem.* 7, 2072–2077.
MACGREGOR, S. A., YELLOWLEES, L. J. & WELCH, A. J. (1990a). *Acta Cryst.* C46, 551–554.
MACGREGOR, S. A., YELLOWLEES, L. J. & WELCH, A. J. (1990b). *Acta Cryst.* C46, 1399–1402.
MALLINSON, P. & MUIR, K. W. (1985). *J. Appl. Cryst.* 18, 51–53.
SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
WALKER, N. G. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.
WYND, A. J., MACGREGOR, S. A., GOULD, R. O., TAYLOR, P., YELLOWLEES, L. J. & WELCH, A. J. (1990). Work in progress.
WYND, A. J. & WELCH, A. J. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1174–1176.
WYND, A. J., WELCH, A. J. & PARISH, R. V. (1990). *J. Chem. Soc. Dalton Trans.* pp. 2185–2193.

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Structure of Di- μ -bromo-(tetrabromo-1 κ^4 Br)bis(*N,N*-dimethylselenourea-2 κ^2 Se)-ditellurium(II,IV)—Acetonitrile—Methanol (2/3/1)

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Abstract. 2[Te₂Br₆(C₃H₈N₂Se)₂].3C₂H₃N.CH₃OH, *M_r* = 2228.7, monoclinic, *P*2₁, *a* = 9.973 (3), *b* = 16.659 (6), *c* = 16.930 (6) Å, β = 101.03°, *V* = 2760.8 (16) Å³, *Z* = 2, *D_x* = 2.681 Mg m⁻³, Mo *K*α, λ = 0.71073 Å, μ = 13.11 mm⁻¹, *F*(000) = 2016, *T* = 193 K, *R* = 0.053 for 3379 reflections and 305 parameters. The structure consists of two crystallographically distinct units. In each of them, a Te^{IV} species has a sixfold, nearly octahedral configuration of Br atoms around it. Two of these Br atoms are shared (*cis*) with a Te^{II} atom to which are also attached two molecules of *N,N*-dimethylselenourea, producing a distorted square-planar configuration of ligands around Te^{II}. The two crystallographically distinct units are similar, but one of them is coordinated by two CH₃CN moieties and the other by one CH₃CN and one CH₃OH moiety.

Introduction. During the preparation of thin films of Te–Se alloys, a number of products of the reactions between Te^{IV} halides and substituted selenoureas have been isolated. One of these, the title compound, is unusual in that both Te^{IV} and Te^{II} are present in the same molecule and share two Br atoms. There

appear to be no previously reported cases of such structures involving tellurium, although the compound [(C₂H₅)₂N]₂Se₂Br₈ contains an anion with Se^{II} and Se^{IV} sharing two Br atoms, which is remarkably similar to the uncharged species found here (Hauge, Maroy & Odegard, 1988). The purpose of the present study is to compare the structure of this mixed valence compound with those that contain Te^{II} and Te^{IV} in more conventional materials and also to compare the structure with that of the analogous selenium compound mentioned above.

Experimental. When TeBr₄ was reacted with *N,N*-dimethylselenourea (DMSeU) in C₂H₅OH, an insoluble product was formed. After separating the solid, refluxing in CH₃OH and filtering, a few orange crystals of the title compound grew from solution upon standing. A single crystal was selected, attached with Dow stopcock grease to a glass fiber, mounted on a Nicolet R3m/V diffractometer and cooled to *T* = 193 K with a stream of N₂ gas. Unit-cell dimensions were obtained from measurements of 2θ for 25 reflections, 8 ≤ 2θ ≤ 30°, using graphite-monochromatized Mo *K*α radiation. Intensities were measured for reflections in the range 4.0 ≤ 2θ ≤ 50°, –11 ≤ *h* ≤ 9, –19 ≤ *k* ≤ 0, –20 ≤ *l* ≤ 0, using a

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