

Fig. 1. Anion und Kation im Na(15-Krone-5)₂[NbOCl₄(CH₃CN)], Anion mit Ellipsoiden der thermischen Schwingung 50% Aufenthaltswahrscheinlichkeit.

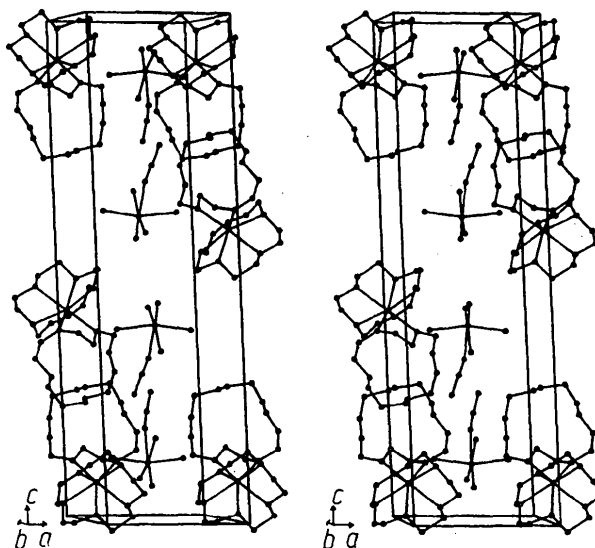


Fig. 2. Stereoansicht der Elementarzelle.

Keine Extinktionskorrektur. $R = 0,076$, $wR = 0,047$. Atomformfaktoren: Cromer & Mann (1968). f' , f'' : Cromer & Liberman (1970). Rechenprogramme: Sheldrick (1976, 1986), Johnson (1965). Die Atomparameter sind in Tabelle 1, die Bindungsabstände und -winkel in Tabelle 2 aufgeführt.* Fig. 1 zeigt Kation und Anion, Fig. 2 die Kristallpackung.

Verwandte Literatur. PMePh₃[NbOCl₄(CH₃CN)]: Hiller, Strähle, Prinz & Dehnicke (1984). PPh₄[NbOCl₄(OH₂)]: Klingelhöfer & Müller (1984).

* Die H-Atomkoordinaten, die Parameter für den anisotropen Temperaturfaktor und die Liste der beobachteten und berechneten Strukturparameter sind beim British Library Document Supply Centre (Supplementary Publication No. SUP 53193: 15 pp.) hinterlegt. Kopien sind erhältlich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexacarbonylbis(pentamethylcyclopentadienyl)ditungsten(W–W), [W₂{η⁵-C₅(CH₃)₅}₂(CO)₆]

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Abstract. C₂₆H₃₀O₆W₂, $M_r = 806.19$, monoclinic, $P2_1/n$, $a = 9.411(3)$, $b = 9.119(3)$, $c = 15.608(5)$ Å,

$\beta = 97.20(2)^\circ$, $V = 1328.9(7)$ Å³, $Z = 2$, $\frac{1}{2}$ independent molecule per asymmetric unit, $D_x = 2.015$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 91.8$ cm⁻¹, $F(000) = 764$, $T = 294$ K, $R_F = 2.43\%$ for

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Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U^*
W	4664.2 (2)	4991.4 (5)	1008.4 (1)	28.0 (1)
O(1)	7986 (6)	4609 (7)	1044 (4)	53 (3)
O(2)	5373 (7)	2342 (7)	2248 (4)	64 (3)
O(3)	2696 (7)	2465 (7)	158 (4)	62 (3)
C(1)	6760 (10)	4735 (8)	951 (5)	43 (3)
C(2)	5131 (9)	3324 (11)	1778 (6)	41 (3)
C(3)	3474 (10)	3397 (11)	404 (5)	46 (3)
C(4)	4935 (8)	7429 (10)	1580 (5)	35 (3)
C(5)	4625 (9)	6417 (10)	2238 (5)	40 (3)
C(6)	3215 (9)	5816 (10)	1995 (5)	37 (3)
C(7)	2637 (8)	6481 (9)	1203 (5)	35 (3)
C(8)	3690 (7)	7451 (8)	936 (4)	28 (2)
C(9)	6204 (8)	8453 (10)	1638 (6)	51 (3)
C(10)	5556 (11)	6188 (11)	3096 (5)	58 (4)
C(11)	2415 (10)	4867 (11)	2556 (6)	55 (3)
C(12)	1113 (9)	6340 (12)	793 (6)	56 (4)
C(13)	3467 (10)	8531 (9)	195 (5)	43 (3)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

W—C(1)	2.000 (10)	W—C(2)	1.953 (10)
W—C(3)	1.999 (9)	W—C(4)	2.397 (9)
W—C(5)	2.323 (8)	W—C(6)	2.308 (9)
W—C(7)	2.392 (8)	W—C(8)	2.421 (8)
W—W _a	3.288 (1)	O(1)—C(1)	1.150 (11)
O(2)—C(2)	1.162 (12)	O(3)—C(3)	1.155 (11)
C(4)—C(5)	1.439 (12)	C(4)—C(8)	1.445 (10)
C(4)—C(9)	1.510 (12)	C(5)—C(6)	1.442 (12)
C(5)—C(10)	1.520 (11)	C(6)—C(7)	1.423 (11)
C(6)—C(11)	1.499 (13)	C(7)—C(8)	1.428 (11)
C(7)—C(12)	1.501 (11)	C(8)—C(13)	1.514 (11)
C(1)—W—C(2)	77.8 (3)	C(1)—W—C(3)	113.1 (4)
C(2)—W—C(3)	78.1 (4)	W—C(2)—O(2)	177.9 (8)
W—C(1)—O(1)	170.3 (7)	C(5)—C(6)—C(11)	125.4 (7)
W—C(3)—O(3)	170.5 (8)	C(7)—C(6)—C(11)	126.0 (7)
C(5)—C(4)—C(8)	106.7 (7)	C(6)—C(7)—C(8)	108.3 (6)
C(5)—C(4)—C(9)	125.7 (7)	C(6)—C(7)—C(12)	125.1 (8)
C(8)—C(4)—C(9)	126.9 (8)	C(4)—C(8)—C(7)	108.7 (6)
C(4)—C(5)—C(6)	108.5 (7)	C(4)—C(8)—C(13)	124.3 (7)
C(4)—C(5)—C(10)	124.9 (8)	C(8)—C(7)—C(12)	126.1 (7)
C(6)—C(5)—C(10)	126.1 (8)	C(7)—C(8)—C(13)	126.2 (6)
C(5)—C(6)—C(7)	107.8 (7)		

1488 observed data and 155 parameters. The structure contains an *anti* arrangement of η^5 -pentamethylcyclopentadienyl ligands, and two distinct sets of carbonyl groups: essentially linear C(2) [W—C(2)—O(2) = 177.9 (8) $^\circ$] and slightly bent C(1) and C(3) [av. W—C(1,3)—O(1,3) = 170.4 (7) $^\circ$] correctly positioned for semi-bridging of the very long [3.288 (1) \AA], otherwise unsupported, W—W bond.

Experimental. Orange crystals from toluene (0.20 \times 0.22 \times 0.28 mm); Nicolet R3m diffractometer with graphite monochromator; ω scans; lattice parameters from least-squares fit of 25 reflections ($25 \leq 2\theta \leq 30^\circ$); empirical absorption correction, ψ scans, 216 data, $T_{\max}/T_{\min} = 1.73$, reduction in $R(\text{merge})$ from 4.23 to 1.95%; $2\theta_{\max} = 52^\circ$ ($h = \pm 12, k = +12, l = +20$); standard reflections $\bar{5}14, 2\bar{5}1$ and $22\bar{8}$, < 1%

variation. 2986 reflections collected, 2612 independent and symmetry allowed ($R_{\text{int}} = 2.32\%$). 1488 observed with $F_o \geq 5\sigma(F_o)$, 1124 unobserved reflections. Heavy-atom structure solution; least-squares refinement on 155 parameters; all non-H atoms anisotropic, all H atoms found, but in final refinement idealized and updated (C—H = 0.96 \AA , $U = 1.2U$ of attached C); $R_F = 2.43\%$, $wR_F = 2.63\%$ (all data, $R_F = 5.52\%$, $wR_F = 4.27\%$), $S = 1.033$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0.0005$; $(\Delta/\sigma)_{\max} = 0.012$, $\Delta\rho_{\max} = 1.14$, $\Delta\rho_{\min} = -0.85 \text{ e } \text{\AA}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149); *SHELXTL* computer programs (Sheldrick, 1985).

Atomic and equivalent isotropic thermal parameters are given in Table 1 and bond lengths and angles in Table 2. Fig. 1 shows the labeled molecular

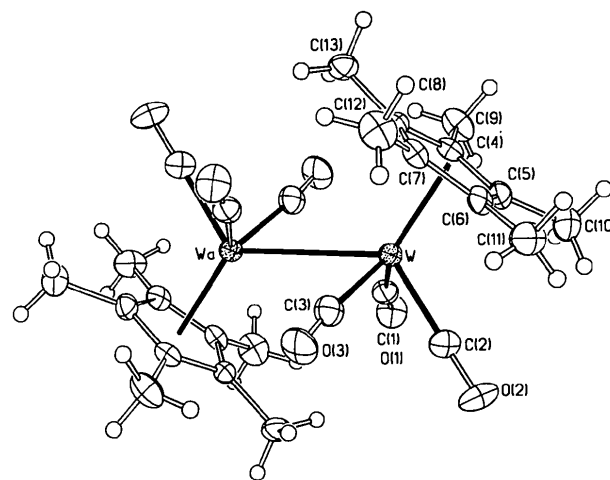


Fig. 1. Molecular structure of $[\text{Cp}^*\text{W}(\text{CO})_3]_2$ (Cp^* = pentamethylcyclopentadienyl) drawn with 40% thermal ellipsoids. The H atoms are shown with an arbitrary radius.

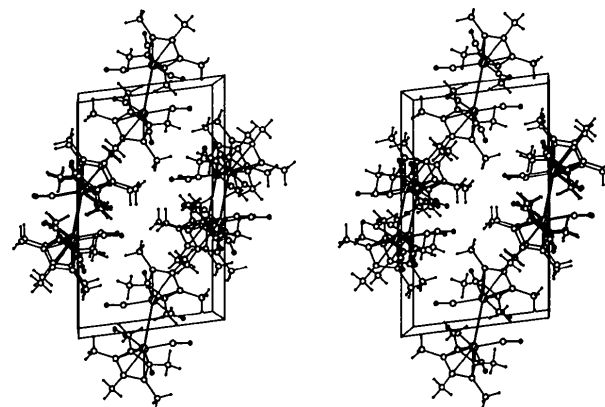


Fig. 2. Stereoview of the unit cell for $[\text{Cp}^*\text{W}(\text{CO})_3]_2$ as viewed down the a axis (c axis vertical).

structure of the compound and Fig. 2 a stereo-diagram of the unit-cell packing.*

Related literature. The title compound is obtained as a ubiquitous, low-yield product in oxidation reactions of W₂{η⁵-C₅(CH₃)₅}₂(CO)₄ with methylarsaoxane, *cyclo*-(CH₃AsO)₄, in sealed tubes in which the CO eliminated produces autoprressurizations of 2.5–5 MPa; under these conditions a portion of the W

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and further bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53240 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Di-μ-bromo-(4-thia-1,7-diazoniaheptane)bis[bromocopper(I)] and Bromo(1,4,7-triazaheptane)copper(II) Bromide

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Abstract. (I) [Cu₂Br₄(C₄H₁₄N₂S)], *M_r* = 568.94, monoclinic, *C*2/*c*, *a* = 14.104 (2), *b* = 7.414 (1), *c* = 13.025 (4) Å, β = 93.54 (2)°, *V* = 1359.5 Å³, *Z* = 4, *D_x* = 2.780 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 149.0 cm⁻¹, *F*(000) = 1064, room temperature, final *R* = 0.0393 for 1377 unique reflections. (II) [CuBr(C₄H₁₃N₃)]Br, *M_r* = 326.52, orthorhombic, *Pmn*2₁, *a* = 8.716 (1), *b* = 8.588 (1), *c* = 6.337 (1) Å, *V* = 474.33 Å³, *Z* = 2, *D_x* = 2.286 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 106.0 cm⁻¹, *F*(000) = 314, room temperature, final *R* = 0.0394 for 1271 unique reflections. In (I) the S atom lies on a twofold axis and is coordinated to two Cu atoms. Each Cu atom is tetrahedrally coordinated with one S and three Br atoms in its coordination sphere. Two Br atoms are bridging, giving rise to a polymeric structure. In (II) the Cu atom, both Br atoms and one N atom lie in a mirror plane and the geometry around the Cu atom is best described as square planar with one Br and three N donor atoms in the plane. The Br ion lies above and below the plane of the complex with a Cu...Br distance of 3.12 Å.

Experimental. Crystals of (I) were obtained as follows. Methanol solutions of 4-thia-1,7-diazaheptane (daes) and copper dibromide were reacted according to the method of Taylor & Barefield (1969) and the

starting material is carbonylated (Harper & Rheingold, 1990). The title compound is isomorphous with its Mo analogue (Clegg, Compton, Ewington & Norman, 1988).

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expected yellow-green precipitate of Cu(daes)Br₂ was obtained. The precipitate was redissolved in water and drops of dilute HBr acid were added to prevent copper hydroxide precipitation. The solution was evaporated partially, filtered and then evaporated further until a solid started to appear. On standing, olive-green crystals formed in the brown-green solution, these were decanted and washed with ethanol. Crystals of (II) were grown by slow diffusion in a U-tube. Methanol was placed in the U-tube and on either side, separated by glass frits, were placed equimolar solutions of copper dibromide and 1,4,7-triazaheptane (dien). The system was stoppered and allowed to stand. The two solutions diffused to give a green mother liquor and from this dark-blue crystals of Cu(dien)Br₂ were obtained.

Intensities measured at room temperature on an Enraf-Nonius CAD-4 diffractometer (graphite-monochromated Mo *K*α radiation). Cell dimensions determined from least-squares refinement of 25 reflections (14 ≤ θ ≤ 21°). Reflections measured in the ω:2θ scan mode [scan width (0.6 + 0.35tanθ)° and variable scan speed]. Three standard reflections showed no significant variation over the data collection. Lp and absorption corrections (North, Phillips & Mathews, 1968) applied to the data. Additional experimental details are given in Table 1.