the ClO_4^- ion. The most satisfactory involved an averaged centrosymmetric structure (see below). Full-matrix least-squares refinement was continued in $R\bar{3}$ with anisotropic thermal parameters for all non-hydrogen atoms, and converged at $R = 0{\cdot}065$ after all H atoms had been located. The positions and thermal parameters ($U = 0{\cdot}05$ Å^2) of the H atoms were not refined. Scattering factors were from *International Tables for X-ray Crystallography* (1974). G. M. Sheldrick's *SHELX* 76 program system was used in all calculations. The final atomic positions are given in Table 1, bond lengths and angles in Table 2.*

Discussion. In the low-temperature form of the *MX*.3dx structure (Fig. 1) the chair-conformation dioxane molecule occupies a fixed position with quite small thermal motion. Its O atoms, O(1), lie 0·27 Å from a cell edge, and the molecule has no crystallographically-imposed symmetry other than an inversion centre. The NaO_6 octahedron is slightly elongated along the crystal threefold axis; the Na–O(1) distance (Table 2) is within the normal range. One O atom, O(3), of the ClO_4^- ion is present as two half-atoms on the threefold axis, but the Cl–O(3) distance is very short and both Cl and O(3) refine with large anisotropic thermal parameters. The remaining O atom, O(2), is on a general sixfold position at a reasonable distance from Cl, but its thermal parameters are also large and the O(2)–Cl–O(2)^{ii} angle is only 103·5°. These observations, and the positions of the stronger peaks (*ca* 0·5 e Å^{-3}) in the final difference map, suggest that the above model is too simple. However, attempts to refine the structure with half Cl atoms at $\pm(x,x,x)$ ($x \simeq 0{\cdot}49$) were unsatisfactory, and other models required an excessive number of parameters.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33406 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Bis(*p*-tolyl isocyanide)octadecacarbonylhexaosmium

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Abstract. $Os_6(CO)_{18}(CNC_6H_4CH_3)_2$, monoclinic, $P2_1/c$, $a = 10{\cdot}570$ (3), $b = 16{\cdot}768$ (5), $c = 23{\cdot}752$ (3) Å, $\beta = 101{\cdot}71$ (7)°, $U = 4122$ Å^3, $D_m = 2{\cdot}96$ (2), $Z = 4$ for $D_x = 2{\cdot}983$ g cm^{-3}, μ(Mo $K\alpha$) = 178·2 cm^{-1}. The structure was refined to an R of 0·064 for 3400 unique diffractometer data. An unusual cluster geometry is found, in which one isocyanide bridges three Os atoms whereas the other acts as a terminal ligand. All carbonyls are terminal, but the pattern of short C···Os interactions and Os–Os lengths can be correlated with the formal oxidation states of the Os atoms.

Introduction. The title compound was isolated as red prismatic crystals (Eady & Malatesta, 1976) from the reaction between $Os_6(CO)_{18}$ and *p*-tolyl isocyanide. Spectroscopic evidence indicated that the two isocyanides were differently coordinated, but full structural elucidation required a crystal structure determination.

7182 reflexions were measured on a Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a crystal 0·10 × 0·20 × 0·13 mm. Lp and numerical absorption corrections

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	*y*	*z*	*U*
Os(1)	8728 (2)	4189 (1)	3817 (1)	*
Os(2)	6714 (1)	4404 (1)	2876 (1)	*
Os(3)	8155 (1)	5686 (1)	3329 (1)	*
Os(4)	9365 (1)	4508 (1)	2740 (1)	*
Os(5)	6301 (1)	5881 (1)	2262 (1)	*
Os(6)	10378 (1)	4702 (1)	1725 (1)	*
C(11)	10341 (43)	4275 (26)	4350 (19)	77 (12)
O(11)	11279 (34)	4317 (20)	4660 (15)	106 (11)
C(12)	7753 (40)	4362 (24)	4380 (18)	70 (11)
O(12)	6982 (29)	4480 (18)	4640 (13)	88 (9)
C(13)	8899 (41)	3088 (28)	3919 (18)	78 (12)
O(13)	8966 (33)	2402 (21)	4010 (14)	105 (10)
C(21)	5954 (37)	4180 (23)	2104 (17)	63 (10)
O(21)	5499 (28)	3937 (17)	1653 (13)	82 (8)
C(22)	6649 (35)	3305 (22)	3092 (15)	59 (10)
O(22)	6425 (25)	2670 (16)	3165 (11)	74 (8)
C(23)	5136 (31)	4646 (20)	3119 (14)	46 (8)
O(23)	4289 (31)	4706 (19)	3347 (13)	95 (9)
C(31)	8606 (44)	6626 (29)	2929 (19)	84 (13)
O(31)	8976 (32)	7213 (21)	2781 (14)	104 (10)
C(32)	7045 (51)	6058 (32)	3741 (23)	103 (16)
O(32)	6400 (43)	6295 (26)	4065 (19)	146 (15)
C(33)	9519 (36)	5898 (22)	3992 (16)	59 (10)
O(33)	10235 (26)	6124 (17)	4382 (12)	76 (8)
C(41)	10622 (41)	3807 (26)	3151 (18)	73 (12)
O(41)	11491 (33)	3415 (20)	3376 (14)	102 (10)
C(42)	10455 (36)	5359 (23)	3056 (16)	61 (10)
O(42)	11419 (26)	5759 (16)	3262 (12)	74 (7)
C(43)	8559 (31)	3517 (21)	2421 (14)	47 (8)
O(43)	8194 (24)	2928 (16)	2227 (11)	69 (7)
C(51)	5113 (53)	6211 (33)	2687 (23)	108 (17)
O(51)	4400 (32)	6498 (19)	2957 (14)	99 (10)
C(52)	6307 (39)	6938 (26)	2028 (17)	68 (11)
O(52)	6376 (28)	7568 (18)	1884 (13)	85 (9)
C(53)	4922 (36)	5671 (22)	1642 (17)	61 (10)
O(53)	4085 (32)	5579 (19)	1275 (14)	96 (9)
C(61)	10527 (40)	5094 (25)	1004 (18)	74 (12)
O(61)	10539 (29)	5398 (19)	555 (13)	88 (9)
C(62)	11886 (39)	4069 (24)	1881 (17)	67 (11)
O(62)	12753 (31)	3629 (19)	2003 (13)	94 (9)
C(63)	11318 (37)	5587 (24)	2027 (16)	66 (10)
O(63)	11818 (37)	6217 (23)	2136 (16)	123 (12)
C(64)	8734 (31)	5104 (19)	1973 (14)	46 (8)
N(64)	7779 (24)	5541 (15)	1802 (11)	43 (6)
C(641)	7520 (36)	5791 (22)	1194 (16)	61 (10)
C(642)	6868 (34)	5355 (22)	745 (15)	56 (9)
C(643)	6721 (34)	5642 (22)	173 (16)	62 (10)
C(644)	7324 (40)	6352 (25)	80 (18)	74 (12)
C(645)	7959 (38)	6770 (23)	495 (17)	66 (11)
C(646)	8166 (38)	6527 (24)	1088 (17)	70 (11)
C(65)	9212 (32)	3858 (21)	1301 (14)	48 (8)
N(65)	8507 (33)	3408 (20)	1032 (14)	71 (9)
C(651)	7578 (38)	2971 (24)	653 (17)	68 (11)
C(652)	7091 (39)	2260 (24)	864 (17)	70 (11)
C(653)	6168 (33)	1807 (21)	530 (15)	52 (9)
C(654)	5571 (41)	2065 (27)	−27 (19)	79 (12)
C(655)	6048 (49)	2783 (31)	−205 (21)	97 (15)
C(656)	6946 (41)	3286 (26)	79 (18)	74 (12)
C(647)	7146 (45)	6616 (28)	−564 (20)	90 (14)
C(657)	4540 (50)	1610 (32)	−403 (22)	105 (17)

* Anisotropic thermal parameters have been deposited.

were applied, and equivalent reflexions averaged to give 3400 unique data with $F > 4\sigma(F)$ based on counting statistics. Os atoms were located by multisolution $\sum_2$ sign expansion, and C, N and O from difference syntheses. The structure was refined by blocked-cascade least squares with anisotropic Os and isotropic C, N and O to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}065$ and $R = 0{\cdot}064$. Complex neutral-atom scattering factors were employed, with the weighting scheme $w = [\sigma^2(F) + 0{\cdot}0019F^2]^{-1}$ for the final stages of refinement. Final atomic coordinates and isotropic thermal parameters are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The structure may be derived from that of $Os_6(CO)_{18}$ by breaking three Os—Os bonds involving Os(6), inserting the triply-bridging isocyanide linking Os(5), Os(4) and Os(6), and adding a terminal isocyanide ligand to Os(6). Os(5), C(641), N(64),

Table 2. *Bond lengths* (Å)

Os(1)—Os(2)	2·779 (5)	Os(2)—Os(5)	2·864 (5)
Os(1)—Os(3)	2·778 (5)	Os(3)—Os(4)	2·868 (5)
Os(1)—Os(4)	2·826 (5)	Os(3)—Os(5)	2·891 (5)
Os(2)—Os(3)	2·727 (5)	Os(4)—Os(6)	2·847 (5)
Os(2)—Os(4)	2·891 (5)	Os(2)—Os(4)	2·891 (5)
Os(1)—C(11)	1·911 (42)	C(11)—O(11)	1·111 (53)
Os(1)—C(12)	1·870 (48)	C(12)—O(12)	1·134 (57)
Os(1)—C(13)	1·866 (48)	C(13)—O(13)	1·171 (59)
Os(2)—C(21)	1·885 (40)	C(21)—O(21)	1·156 (48)
Os(2)—C(22)	1·918 (39)	C(22)—O(22)	1·111 (46)
Os(2)—C(23)	1·915 (37)	C(23)—O(23)	1·140 (51)
Os(3)—C(31)	1·949 (51)	C(31)—O(31)	1·141 (62)
Os(3)—C(32)	1·785 (61)	C(32)—O(32)	1·194 (78)
Os(2)—C(33)	1·940 (36)	C(33)—O(33)	1·135 (44)
Os(4)—C(41)	1·892 (42)	C(41)—O(41)	1·166 (53)
Os(4)—C(42)	1·891 (39)	C(42)—O(42)	1·235 (46)
Os(4)—C(43)	1·949 (36)	C(43)—O(43)	1·125 (44)
Os(5)—C(51)	1·848 (62)	C(51)—O(51)	1·186 (71)
Os(5)—C(52)	1·857 (45)	C(52)—O(52)	1·117 (54)
Os(5)—C(53)	1·884 (37)	C(53)—O(53)	1·118 (47)
Os(6)—C(61)	1·870 (47)	C(61)—O(61)	1·185 (55)
Os(6)—C(62)	1·888 (42)	C(62)—O(62)	1·166 (52)
Os(6)—C(63)	1·848 (41)	C(63)—O(63)	1·186 (57)
Os(4)—C(64)	2·064 (33)	Os(5)—N(64)	2·157 (29)
Os(6)—C(64)	2·058 (37)	Os(6)—C(65)	2·007 (35)
C(64)—N(64)	1·248 (41)	C(65)—N(65)	1·158 (46)
N(64)—C(641)	1·475 (46)	N(65)—C(651)	1·397 (50)
C(641)—C(642)	1·358 (50)	C(651)—C(652)	1·429 (60)
C(642)—C(643)	1·420 (52)	C(652)—C(653)	1·359 (51)
C(643)—C(644)	1·390 (58)	C(653)—C(654)	1·412 (54)
C(644)—C(645)	1·283 (56)	C(654)—C(655)	1·404 (71)
C(645)—C(646)	1·438 (58)	C(655)—C(656)	1·344 (65)
C(646)—C(641)	1·457 (56)	C(656)—C(651)	1·489 (57)
C(644)—C(647)	1·565 (66)	C(654)—C(657)	1·473 (65)

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Table 3. *Bond angles* (°)

Os(2)–Os(1)–Os(3)	58·8 (1)	Os(2)–Os(1)–Os(4)	62·1 (1)	Os(3)–Os(4)–C(41)	120·8 (14)	C(41)–Os(4)–C(42)	87·5 (18)
Os(3)–Os(1)–Os(4)	61·6 (2)	Os(2)–Os(1)–C(11)	163·3 (14)	Os(1)–Os(4)–C(43)	91·4 (11)	Os(2)–Os(4)–C(43)	68·6 (11)
Os(3)–Os(1)–C(11)	107·3 (14)	Os(4)–Os(1)–C(11)	103·9 (16)	Os(3)–Os(4)–C(43)	125·0 (11)	Os(6)–Os(4)–C(43)	88·8 (11)
Os(2)–Os(1)–C(12)	96·4 (12)	Os(3)–Os(1)–C(12)	93·1 (13)	C(41)–Os(4)–C(43)	82·9 (16)	C(42)–Os(4)–C(43)	168·7 (16)
Os(4)–Os(1)–C(12)	152·4 (12)	C(11)–Os(1)–C(12)	93·5 (20)	Os(1)–Os(4)–C(64)	142·8 (10)	Os(2)–Os(4)–C(64)	88·9 (10)
Os(2)–Os(1)–C(13)	105·7 (13)	Os(3)–Os(1)–C(13)	162·7 (13)	Os(3)–Os(4)–C(64)	90·1 (10)	Os(6)–Os(4)–C(64)	46·2 (10)
Os(4)–Os(1)–C(13)	105·6 (15)	C(11)–Os(1)–C(13)	86·5 (19)	C(41)–Os(4)–C(64)	145·5 (17)	C(42)–Os(4)–C(64)	92·7 (15)
C(12)–Os(1)–C(13)	96·5 (20)	Os(1)–Os(2)–Os(4)	59·8 (1)	C(43)–Os(4)–C(64)	91·9 (14)	Os(1)–Os(4)–C(42)	91·2 (13)
Os(1)–Os(2)–Os(3)	60·6 (2)	Os(1)–Os(2)–Os(5)	122·3 (2)	Os(2)–Os(4)–C(42)	121·8 (13)	Os(3)–Os(4)–C(42)	65·3 (13)
Os(3)–Os(2)–Os(4)	61·3 (2)	Os(3)–Os(2)–Os(5)	62·2 (2)	Os(6)–Os(4)–C(42)	87·0 (13)	Os(1)–Os(4)–Os(6)	171·0 (1)
Os(4)–Os(2)–Os(5)	86·6 (2)	Os(1)–Os(2)–C(21)	149·6 (12)	Os(6)–Os(4)–C(41)	99·4 (15)	Os(2)–Os(5)–Os(3)	56·6 (1)
Os(3)–Os(2)–C(21)	129·4 (13)	Os(4)–Os(2)–C(21)	97·7 (13)	Os(2)–Os(5)–C(52)	165·6 (11)	Os(3)–Os(5)–C(53)	160·7 (12)
Os(5)–Os(2)–C(21)	71·7 (13)	Os(1)–Os(2)–C(22)	74·0 (11)	C(52)–Os(5)–C(53)	89·7 (17)	Os(2)–Os(5)–N(64)	88·8 (8)
Os(3)–Os(2)–C(22)	134·4 (10)	Os(4)–Os(2)–C(22)	100·1 (12)	Os(3)–Os(5)–N(64)	89·0 (7)	Os(2)–Os(5)–C(53)	104·5 (12)
Os(5)–Os(2)–C(22)	163·3 (10)	C(21)–Os(2)–C(22)	92·2 (17)	Os(2)–Os(4)–Os(6)	129·9 (2)	Os(3)–Os(4)–Os(6)	128·1 (2)
Os(1)–Os(2)–C(23)	110·9 (10)	Os(3)–Os(2)–C(23)	99·5 (11)	C(52)–Os(5)–N(64)	93·1 (16)	Os(3)–Os(5)–C(52)	109·1 (12)
Os(4)–Os(2)–C(23)	160·7 (9)	Os(5)–Os(2)–C(23)	85·3 (11)	C(53)–Os(5)–N(64)	94·5 (15)	Os(2)–Os(5)–C(51)	91·7 (18)
C(21)–Os(2)–C(23)	96·3 (16)	C(22)–Os(2)–C(23)	92·4 (16)	Os(3)–Os(5)–C(51)	88·3 (16)	C(52)–Os(5)–C(51)	85·5 (23)
Os(1)–Os(2)–C(43)	76·4 (7)	Os(3)–Os(2)–C(43)	101·0 (8)	C(53)–Os(5)–C(51)	88·8 (21)	N(64)–Os(5)–C(51)	176·4 (15)
Os(4)–Os(2)–C(43)	39·8 (7)	Os(5)–Os(2)–C(43)	107·7 (8)	Os(4)–Os(6)–C(61)	158·6 (13)	Os(4)–Os(6)–C(63)	91·6 (14)
C(21)–Os(2)–C(43)	73·4 (14)	C(22)–Os(2)–C(43)	70·3 (15)	C(61)–Os(6)–C(63)	86·2 (19)	Os(4)–Os(6)–C(64)	46·4 (9)
C(23)–Os(2)–C(43)	159·1 (12)	Os(1)–Os(3)–Os(2)	60·6 (2)	C(61)–Os(6)–C(64)	112·3 (17)	C(63)–Os(6)–C(64)	92·6 (17)
Os(1)–Os(3)–Os(4)	60·0 (2)	Os(2)–Os(3)–Os(4)	62·2 (2)	Os(4)–Os(6)–C(65)	92·6 (11)	C(61)–Os(6)–C(65)	86·9 (17)
Os(1)–Os(3)–Os(5)	121·3 (2)	Os(2)–Os(3)–Os(5)	61·2 (1)	C(63)–Os(6)–C(65)	171·0 (15)	C(64)–Os(6)–C(65)	84·7 (14)
Os(4)–Os(3)–Os(5)	86·5 (2)	Os(1)–Os(3)–C(31)	151·6 (14)	Os(4)–Os(6)–C(62)	102·6 (14)	C(61)–Os(6)–C(62)	98·8 (19)
Os(2)–Os(3)–C(31)	128·1 (14)	Os(4)–Os(3)–C(31)	98·1 (16)	C(63)–Os(6)–C(62)	90·5 (18)	C(64)–Os(6)–C(62)	148·9 (16)
Os(5)–Os(3)–C(31)	70·7 (13)	Os(1)–Os(3)–C(32)	101·5 (18)	C(65)–Os(6)–C(62)	96·3 (16)	Os(1)–C(11)–O(11)	179·3 (44)
Os(2)–Os(3)–C(32)	96·6 (18)	Os(4)–Os(3)–C(32)	156·3 (17)	Os(1)–C(12)–O(12)	167·7 (34)	Os(1)–C(13)–O(13)	175·9 (37)
Os(5)–Os(3)–C(32)	92·1 (17)	C(31)–Os(3)–C(32)	103·8 (24)	Os(2)–C(21)–O(21)	170·8 (35)	Os(2)–C(22)–O(22)	169·1 (27)
Os(1)–Os(3)–C(33)	76·4 (12)	Os(2)–Os(3)–C(33)	136·8 (11)	Os(2)–C(23)–O(23)	167·6 (28)	Os(3)–C(31)–O(31)	168·8 (40)
Os(4)–Os(3)–C(33)	101·0 (13)	Os(5)–Os(3)–C(33)	161·9 (11)	Os(3)–C(32)–O(32)	173·3 (45)	Os(3)–C(33)–O(33)	170·3 (33)
C(31)–Os(3)–C(33)	91·9 (18)	C(32)–Os(3)–C(33)	87·4 (21)	Os(4)–C(41)–O(41)	172·7 (40)	Os(4)–C(42)–O(42)	162·7 (32)
Os(1)–Os(3)–C(42)	77·6 (9)	Os(2)–Os(3)–C(42)	101·7 (9)	Os(4)–C(43)–O(43)	174·0 (30)	Os(5)–C(51)–O(51)	173·3 (47)
Os(4)–Os(3)–C(42)	39·6 (8)	Os(5)–Os(3)–C(42)	107·2 (8)	Os(5)–C(52)–O(52)	176·3 (38)	Os(6)–C(63)–O(63)	168·8 (32)
C(31)–Os(3)–C(42)	74·1 (18)	C(32)–Os(3)–C(42)	158·0 (17)	Os(6)–C(62)–O(62)	173·6 (38)	Os(6)–C(61)–O(61)	173·6 (36)
C(33)–Os(3)–C(42)	71·0 (15)	Os(1)–Os(4)–Os(2)	58·1 (1)	Os(5)–C(53)–O(53)	177·0 (36)	Os(4)–C(64)–Os(6)	87·4 (13)
Os(1)–Os(4)–Os(3)	58·4 (2)	Os(2)–Os(4)–Os(3)	56·5 (1)	Os(4)–C(64)–N(64)	131·9 (27)	Os(6)–C(64)–N(64)	140·6 (27)
Os(1)–Os(4)–C(41)	71·7 (15)	Os(2)–Os(4)–C(41)	120·0 (15)				

Os(5)–N(64)–C(64)	127·7 (24)	Os(5)–N(64)–C(641)	114·3 (21)
C(64)–N(64)–C(641)	117·6 (30)	N(64)–C(641)–C(642)	125·4 (34)
N(64)–C(641)–C(646)	114·1 (30)	C(642)–C(641)–C(646)	120·1 (36)
C(641)–C(642)–C(643)	120·5 (35)	C(643)–C(644)–C(647)	115·4 (35)
C(645)–C(644)–C(647)	122·6 (41)	C(643)–C(644)–C(645)	122·0 (41)
C(644)–C(645)–C(646)	123·4 (40)	C(641)–C(646)–C(645)	115·2 (33)
C(642)–C(643)–C(644)	118·6 (34)	Os(6)–C(65)–N(65)	175·6 (28)
C(65)–N(65)–C(651)	170·8 (36)	N(65)–C(651)–C(652)	117·9 (35)
N(65)–C(651)–C(656)	122·0 (36)	C(652)–C(651)–C(656)	119·4 (34)
C(651)–C(652)–C(653)	121·8 (36)	C(652)–C(653)–C(654)	120·5 (37)
C(653)–C(654)–C(655)	115·2 (38)	C(653)–C(654)–C(657)	122·9 (42)
C(655)–C(654)–C(657)	121·9 (41)	C(654)–C(655)–C(656)	130·4 (44)
C(651)–C(656)–C(655)	112·2 (40)		

C(64), Os(4) and Os(6) are approximately coplanar (mean deviation 0·06 Å), and the distances N(64)—Os(5), C(64)—Os(4) and C(64)—Os(6) are consistent with single σ bonds, so we can consider the C and N atoms to be approximately sp^2 hybridized, with a double C—N bond. This plane would also be an approximate molecular mirror plane if the terminal isocyanide were replaced by a carbonyl. The molecular conformation is shown in Fig. 1. Another type of triply-bridging isocyanide (complicated by disorder) has been observed in $(\mathrm{Bu}^t\mathrm{NC})_7\mathrm{Ni}_4$ (Day, Day, Kristoff, Hirsekorn & Muetterties, 1975); a carbonyl group in $[\mathrm{Fe}_4(\mathrm{CO})_{13}\mathrm{H}]^-$ is also analogous, bridging a total of four Fe atoms through C and O (Manassero, Sansoni & Longoni, 1976). The terminal isocyanide in $\mathrm{Os}_6(\mathrm{CO})_{18}(\mathrm{CNC}_6\mathrm{H}_4\mathrm{CH}_3)_2$ is linear at C and almost linear at N [C(65)—N(65)—C(651) 170·8 (36)°] with C—N 1·16 (5) Å, analogous to the terminal [linear, C—N 1·15 (3) Å] but not the bridging [C—N—C 132·7°, N—C 1·21 (3) Å] isocyanides in $(\mathrm{Bu}^t\mathrm{NC})_6\mathrm{Pt}_3$ (Green, Howard, Murray, Spencer & Stone, 1977).

We can calculate formal oxidation states for the Os atoms by adding the number of single bonds made by each to twice the number of terminal carbonyl or isocyanide ligands and subtracting 10 (perhaps electron connectivity would be a better name). If, by a similar

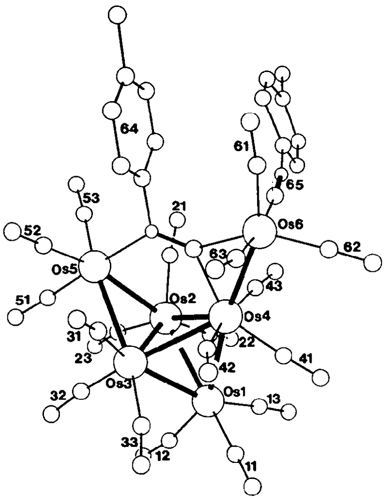

Fig. 1. The molecule of $Os_6(CO)_{18}(CNC_6H_4CH_3)_2$, indicating the labelling scheme.

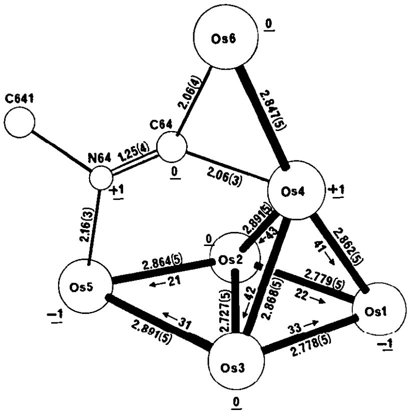

Fig. 2. Bond lengths and mean oxidation states (underlined) in the cluster. Short C···Os interactions (indicated by arrows) are: C(42)···Os(3) 2·70, C(43)···Os(2) 2·84, C(41)···Os(1) 2·87, C(21)···Os(5) 2·89, C(31)···Os(5) 2·90, C(22)···Os(1) 2·91, C(33)···Os(1) 2·99 Å (uncertainties 0·04 Å).

argument, +1 is assigned to N(64), the values (Fig. 2) sum to zero, indicating that an average 18-electron rule is obeyed for a localized bond model. As found by Mason, Thomas & Mingos (1973) for $Os_6(CO)_{18}$, the shortest Os–Os bond links the two Os atoms with the same oxidation state. If we ignore the terminal Os(6), then for every Os–Os bond in which the two oxidation states differ, one carbonyl attached to the Os with higher oxidation state has a short C···Os interaction (in the range 2·70 to 2·99 Å) with the Os atom in the lower oxidation state. On Fig. 2 these interactions are indicated by arrows, with the number of the carbonyl group in question. The interactions are accompanied by small Os–Os–C angles (in the range 65–77°) and, subject to experimental uncertainties, a bend of the Os–C–O angle away from the second Os atom. The effect may be seen as incipient carbonyl bridge bonding, which would serve to equalize the oxidation states and number of bonds made by the Os atoms. A similar effect arises in $Os_5(CO)_{16}$ (Reichert & Sheldrick, 1977) and in Fe carbonyl derivatives (Cotton, 1976).

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