V(1)—O(4)	1.970 (1)	C(4)—C(5)	1.486 (3)
V(1)—O(5)	1.584 (2)	C(6)—C(7)	1.497 (3)
O(1)—C(2)	1.280 (2)	C(7)—C(8)	1.386 (3)
O(2)—C(4)	1.279 (2)	C(8)—C(9)	1.392 (3)
O(3)—C(7)	1.285 (2)	C(9)—C(10)	1.492 (3)
O(4)—C(9)	1.280 (2)		
O(1)—V(1)—O(2)	87.59 (5)	O(1)—C(2)—C(1)	114.9 (2)
O(1)—V(1)—O(3)	150.13 (6)	O(1)—C(2)—C(3)	124.2 (2)
O(1)—V(1)—O(4)	83.80 (6)	C(1)—C(2)—C(3)	120.9 (2)
O(1)—V(1)—O(5)	104.87 (7)	C(2)—C(3)—C(4)	124.0 (2)
O(2)—V(1)—O(3)	83.84 (6)	O(2)—C(4)—C(3)	123.8 (2)
O(2)—V(1)—O(4)	145.63 (6)	O(2)—C(4)—C(5)	116.2 (2)
O(2)—V(1)—O(5)	107.15 (7)	C(3)—C(4)—C(5)	119.9 (2)
O(3)—V(1)—O(4)	87.29 (6)	O(3)—C(7)—C(6)	115.1 (2)
O(3)—V(1)—O(5)	105.00 (7)	O(3)—C(7)—C(8)	123.9 (2)
O(4)—V(1)—O(5)	107.22 (7)	C(6)—C(7)—C(8)	121.0 (2)
V(1)—O(1)—C(2)	129.0 (1)	C(7)—C(8)—C(9)	124.0 (2)
V(1)—O(2)—C(4)	129.3 (1)	O(4)—C(9)—C(8)	123.8 (2)
V(1)—O(3)—C(7)	128.0 (1)	O(4)—C(9)—C(10)	116.0 (2)
V(1)—O(4)—C(9)	128.8 (1)	C(8)—C(9)—C(10)	120.1 (2)

The unit-cell can be transformed to that used by Dodge, Templeton & Zalkin (1961) by using the matrix: (0 0 1, -1 0 0, 0 -1 0). The scan width was $(1.21 + 0.35\tan\theta)^\circ$ with a θ scan rate of 32° min^{-1} (up to nine scans). Stationary background counts were made at each end of the scan; scan/background time ratio 2:1. All H atoms were visible in a difference map and refined isotropically; the C—H distances are in the range 0.77 (4)–1.01 (4) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: FG1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Tetranuclear Butterfly Cluster of Molybdenum, $[PPh_4]_2[Mo_4I_{11}]$

John C. Gordon and Rinaldo Poli*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA

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Abstract

Bis(tetraphenylphosphonium) undecaiodotetramolybdate, $2[PPh_4]^+[Mo_4I_{11}]^{2-}$, was obtained by treating $[Mo_2(MeCN)_8]^{4+}$ with PPN^+I^- in dichloromethane. The four Mo atoms of the anion adopt a 'butterfly' arrangement which can be viewed as a portion of an octahedron with two missing mutually *cis* vertices. Ten of the eleven I atoms are located at the vertices of a cube in which the ideal octahedron would be inscribed; two of them cap the two triangular faces of the Mo_4 buttefly, four bridge the edges and four are terminally coordinated to the metal atoms. The eleventh I atom bridges the two 'wing-tip' metal atoms. The metal–metal distances for four edges of the butterfly wings are in the range 2.533 (3)–2.547 (3) Å, whereas the 'hinge' edge is slightly longer [2.688 (3) Å] and the separation between the two wing tips is 3.051 (3) Å.

Comment

Octahalodimolybdate tetraanions, $[Mo_2X_8]^{4-}$, are known for $X = Cl$ (Brencic & Cotton, 1969) and Br (Brencic, Dobcnik & Segedin, 1974) but have never been reported for $X = I$. The above complexes were prepared by interaction of the acetate complex $Mo_2(OOCCH_3)_4$ or the sulfate complex $(NH_4)_4Mo_2(SO_4)_4.2H_2O$ with aqueous HX solutions. On the other hand, the analogous interaction between $Mo_2(OOCCH_3)_4$ and HI affords, after treatment with $[{}^nBu_4N]I$, the salt $[{}^nBu_4N]_2[Mo_4I_{11}]$ (Glicksman & Walton, 1978). There are, however, numerous dimeric complexes of the $Mo_2X_4L_4$ type where $X = I$ (Cotton & Walton, 1982) and the hexaiodo complexes $[Cat]_2[Mo_2I_6(H_2O)_2]$ (Cat = pyH^+, $picH^+$) are also known (Brencic & Segedin, 1978; Brencic & Golic, 1977). We attempted the synthesis of the octaiododimolybdate tetraanion by a new route, *i.e.* the interaction of the trifluoromethylsulfonate (triflate) salt of the acetonitrile complex $[Mo_2(MeCN)_8]$ (Mayer & Abbott, 1983) with tetraphenylphosphonium iodide. The product of the reaction was not a salt of the $[Mo_2I_8]^{4-}$ anion as expected, but a new salt of the previously reported $[Mo_4I_{11}]^{2-}$ anion. It seems therefore that the hypothetical $[Mo_2I_8]^{4-}$ ion might be unstable since all the reactions that are expected to produce it {thermal decomposition of $[\mathrm{MoI_3(CO)_4}]^-$ (Stensvad, Helland, Babich, Jacobson & McCarley, 1978), treatment of $\mathrm{Mo_2(OOCCH_3)_4}$ with HI (Glicksman & Walton, 1978), and now reaction of $[\mathrm{Mo_2(MeCN)_8}]^{4+}$ with I^-} invariably generate the same $[\mathrm{Mo_4I_{11}}]^{2-}$ cluster instead.

There have been two structure determinations of this anion, one with the $[^n\mathrm{Bu_4N}]^+$ counterion (Stensvad, Helland, Babich, Jacobson & McCarley, 1978) and another with the $[\mathrm{AsPh_4}]^+$ counterion (Cotton & Poli, 1988), but neither was reported in full. We report here the full details of the structure of the tetraphenylphosphonium salt, $[\mathrm{PPh_4}]_2[\mathrm{Mo_4I_{11}}]$, which is not isomorphous with the previously described $[\mathrm{AsPh_4}]^+$ salt and does not have the twinning problems encountered in that case.

The compound crystallizes in the centrosymmetric space group $P\overline{1}$ with both cations and the dianion in general positions. The two independent tetraphenylphosphonium cations are similar to each other. The average P—C bond lengths for the two ions are 1.78 (2) and 1.82 (3) Å. The values of the C—P—C angles are all very close to the expected tetrahedral value, being in the range 107–112° with averages of 109.7 (10) and 109.5 (20)° for the two ions. Other features of these cations are normal and do not merit further discussion.

A view of the $[\mathrm{Mo_4I_{11}}]^{2-}$ anion is shown in Fig. 1. The I atoms have been labeled according to the number of the Mo atom(s) to which they are bonded. For instance, I(23) is bonded to atoms Mo(2) and Mo(3), *etc.* I atoms with one-digit numbers are thus terminal ligands, those with two-digit numbers are doubly bridging and those with three-digit numbers are triply bridging. The best geometical description of this ion is based on the geometry of the well known family of octahedral clusters $[\mathrm{Mo_6}X_8]^{4+}$, as described for the tetra-*n*-butylammonium salt of this ion (Stensvad, Helland, Babich, Jacobson & McCarley, 1978). The most relevant example to the present discussion is α-$\mathrm{MoI_2}$, which can be described as $[(\mathrm{Mo_6I_8})\mathrm{I_2I_{4/2}}]_\infty$ (Aliev, Klinkova, Dubrovin & Atovmyan, 1981). Two adjacent Mo atoms of the octahedral core are removed leaving a 'butterfly' arrangement of the remaining four Mo atoms, Mo(3) and Mo(4) being located on the 'wing tips'. One I atom is also removed from the $[\mathrm{Mo_6I_8}]^{4+}$ core and a second I atom, *i.e.* I(34), is shifted to the middle of the cube edge to adopt a bridging position between the wing-tip atoms (Fig. 2). In this way, an $[\mathrm{Mo_4I_7}]^+$ fragment is obtained. Of the other six I atoms present in the parent $[\mathrm{Mo_6I_8}]^{4+}$ structure [all of which cap (triply bridge) a triangular face of the $\mathrm{Mo_6}$ octahedron] only two [*i.e.* I(123) and I(124)] remain in capping positions after this ideal transformation, the other four [I(13), I(14), I(23) and I(24)] becoming bridging atoms bonded to only two Mo atoms. The final structure is formally obtained by completing the coordination geometry around the four Mo atoms with terminal I atoms that are located radially outward from the center of the parent $\mathrm{Mo_6}$ octahedron and by removing one electron from the cluster.

The Mo(3) and Mo(4) atoms move toward each other as a result of the presence of the I(34) atom in a bridging position and thus distort the ideal arrangement shown in Fig. 2; the most evident result is that the Mo(3)—I(3) and Mo(4)—I(4) bonds are not collinear. Also, the Mo(4)—Mo(3)—I(3) and Mo(3)—Mo(4)—I(4) angles are 162.34 (9) and 157.75 (8)°, respectively, rather than 180°. The variations of the metal–metal distances are also a consequence of the distortion on going from the ideal O_h $[\mathrm{Mo_6I_8}]^{4+}$ cluster (where, by symmetry, all distances between adjacent Mo atoms are equivalent) to the butterfly fragment. The Mo(1)—Mo(3), Mo(1)—Mo(4), Mo(2)—Mo(3) and Mo(2)—Mo(4) bonds remain chemically, although not crystallographically, equivalent (they are all bridged by one μ_2-I and one μ_3-I atom) and their distances

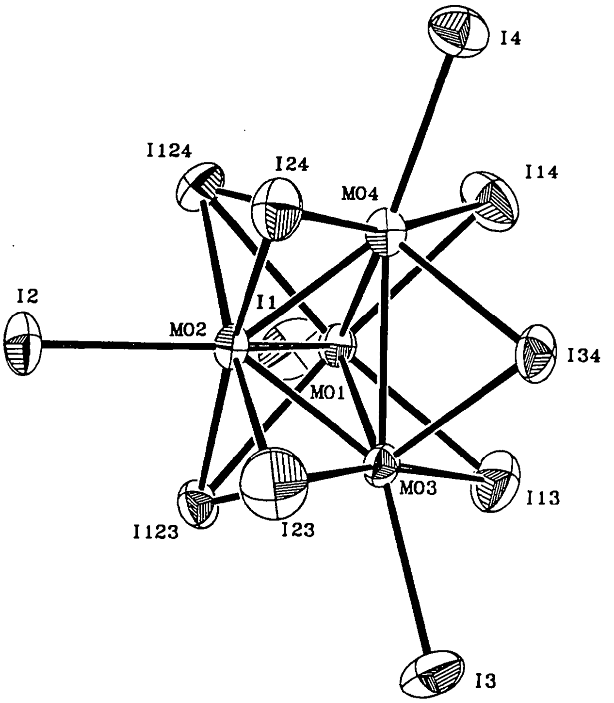

Fig. 1. Molecular configuration and atomic labelling scheme for the $[\mathrm{Mo_4I_{11}}]^{2-}$ ion. Ellipsoids are drawn at the 40% probability level.

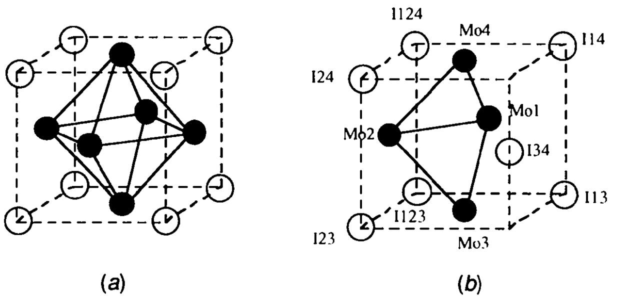

Fig. 2. Structures of (*a*) the $[\mathrm{Mo_4I_8}]^{4+}$ core and (*b*) the derived $[\mathrm{Mo_2I_7}]^+$ core.

are rather similar, *i.e.* in the range 2.533–2.547 Å with an average of 2.541 Å and a standard deviation of 0.006 Å. However, the Mo(1)—Mo(2) bond is different since it is bridged by two μ_3-I atoms and its distance is slightly longer [2.688 (3) Å]. This latter distance is close to that reported for α-MoI_2 (2.672 Å; Aliev, Klinkova, Dubrovin & Atovmyan, 1981) which exhibits a similar coordination environment for the Mo—Mo bonds. The Mo(3)—Mo(4) distance [3.051 (3) Å] is much shorter than the non-bonding interaction (3.779 Å) between two opposite Mo atoms in the $[Mo_6I_8]^{4+}$ cluster (Aliev, Klinkova, Dubrovin & Atovmyan, 1981). The effect of the distortion induced by the presence of the I(34) bridging atom is therefore quite substantial. Although Mo(3)—Mo(4) is considerably longer than the other Mo—Mo distances in the $[Mo_4I_{11}]^{2-}$ cluster, it can still be considered to represent a bonding interaction; for example, the $[Mo_2I_7(PMe_3)_2]^-$ anion has a well established Mo—Mo bonding interaction of 3.022 (1) Å (Cotton & Poli, 1987).

The Mo—I distances within sets of chemically equivalent bonds are quite similar with averages of 2.838 (9) for terminal bonds, 2.744 (29) for bridging bonds and 2.821 (46) Å for capping bonds. The Mo—(μ_2-I) bonds do not show particular trends for chemically non-equivalent distances [*i.e.* Mo(wedge)—I—Mo(wing tip), Mo(wedge)—I—Mo(wing tip) and Mo(wing tip)—I—Mo(wing tip) bonds], whereas the Mo—(μ_3-I) bonds involving the Mo(1) and Mo(2) 'wedge' atoms [average 2.793 (13) Å] are significantly shorter than those involving the Mo(3) and Mo(4) wing-tip atoms [average 2.877 (18) Å]. As expected, longer bonds are observed for the triply-bridging atoms compared to the doubly bridging atoms. However, the terminal Mo—I bonds would be expected to be shorter than the Mo—(μ-I) bonds which is contrary to what is found. The same phenomenon was observed for α-MoI_2 and was attributed to the compression of the Mo_6 octahedron inside the I_8 cube because of strong Mo—Mo bonding (Aliev, Klinkova, Dubrovin & Atovmyan, 1981). A similar rationalization can be invoked here since Mo(1) is displaced from the least-square plane through I(13), I(14), I(123) and I(124), and Mo(2) is displaced from that through I(23), I(24), I(123) and I(124) both towards the center of the Mo_4 core, and a similar distortion has occurred for Mo(3) and Mo(4) (as discussed earlier). Evidence for this is provided by the *trans* angles at the Mo atoms which deviate significantly from 180° [I(13)—Mo(1)—I(124) 171.8 (1), I(14)—Mo(1)—I(123) 174.92 (9), I(23)—Mo(2)—I(124) 173.0 (1), I(24)—Mo(2)—I(123) 172.58 (8), I(13)—Mo(3)—I(23) 170.6 (1) and I(14)—Mo(4)—I(24) 165.5 (1)°]. This is consistent with the observation that in the family of compounds $Mo_3HI_7L_3$, (L = thf, MeCN, PhCN) which can also be viewed as derived from a fragment of $[Mo_6I_8]^{4+}$ and where the terminal Mo—I bonds are no longer subject to Mo displacement effects, the Mo—I distances are in the expected order (capping > bridging > terminal) (Cotton & Poli, 1988).

Experimental

Crystal data

$(C_{24}H_{20}P)_2[Mo_4I_{11}]$
M_r = 2458.5
Triclinic
$P\bar{1}$
a = 10.474 (6) Å
b = 12.862 (5) Å
c = 23.882 (8) Å
α = 94.72 (3)°
β = 91.80 (5)°
γ = 107.98 (5)°
V = 3044 (5) Å^3
Z = 2
D_x = 2.68 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.5–13.5°
μ = 6.391 mm^{-1}
T = 293 K
Plate
0.5 × 0.4 × 0.1 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.262, $T_{\max}$ = 1.000
8368 measured reflections
7938 independent reflections
5900 observed reflections
[$F_o > 6\sigma(F_o)$]

$R_{\rm int}$ = 0.003
$\theta_{\max}$ = 22.5°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -25 \rightarrow 25$
3 standard reflections
monitored every 97 reflections
intensity variation: −0.2%

Refinement

Refinement on F
R = 0.060
wR = 0.078
S = 2.97
5900 reflections
586 parameters
H-atom parameters not refined

$w = 1/\sigma^2(|F_o|)$
$(\Delta/\sigma)_{\max}$ = 0.47
$\Delta\rho_{\max}$ = 1.91 e Å^{-3}
$\Delta\rho_{\min}$ = −2.45 e Å^{-3}
Atomic scattering factors from *TEXSAN* (Molecular Structure Corporation, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
I(1)	0.0085 (2)	−0.0171 (1)	0.71882 (8)	6.01 (8)
I(2)	0.6323 (1)	0.3583 (1)	0.75412 (8)	5.50 (7)
I(3)	0.1386 (2)	0.4661 (2)	0.59111 (8)	6.77 (9)
I(4)	0.1514 (2)	0.4197 (1)	0.93927 (7)	5.62 (8)
I(13)	−0.0786 (2)	0.2459 (1)	0.67591 (8)	5.81 (8)
I(14)	−0.0635 (2)	0.2088 (1)	0.82592 (8)	6.34 (8)
I(23)	0.4226 (2)	0.5420 (2)	0.7001 (1)	8.6 (1)
I(24)	0.4364 (2)	0.5199 (1)	0.84860 (8)	5.64 (7)
I(34)	0.0843 (2)	0.5189 (1)	0.77417 (8)	5.08 (7)
I(123)	0.2888 (1)	0.2269 (1)	0.65588 (6)	4.01 (6)
I(124)	0.3027 (1)	0.1958 (1)	0.82728 (7)	4.37 (6)
Mo(1)	0.1183 (2)	0.2145 (1)	0.74476 (8)	3.23 (7)
Mo(2)	0.3646 (2)	0.3636 (1)	0.75694 (8)	3.23 (7)
Mo(3)	0.1751 (2)	0.3918 (1)	0.69709 (8)	3.27 (7)
Mo(4)	0.1827 (2)	0.3701 (1)	0.82332 (9)	3.73 (7)
P(1)	0.7544 (5)	0.1533 (4)	0.0669 (3)	3.7 (2)
P(2)	0.3888 (6)	0.1828 (4)	0.4381 (3)	4.0 (2)
C(10)	0.698 (2)	0.229 (1)	0.0177 (9)	3.3 (8)

C(11)	0.580 (2)	0.251 (2)	0.023 (1)	5 (1)
C(12)	0.533 (2)	0.305 (2)	−0.018 (1)	6 (1)
C(13)	0.611 (3)	0.339 (2)	−0.062 (1)	6 (1)
C(14)	0.731 (3)	0.318 (2)	−0.066 (1)	5 (1)
C(15)	0.772 (2)	0.261 (2)	−0.028 (1)	5 (1)
C(20)	0.629 (2)	0.112 (2)	0.116 (1)	4 (1)
C(21)	0.543 (2)	−0.001 (1)	0.117 (1)	4 (1)
C(22)	0.441 (2)	−0.026 (2)	0.153 (1)	6 (1)
C(23)	0.422 (2)	0.054 (2)	0.191 (1)	5 (1)
C(24)	0.499 (2)	0.156 (2)	0.193 (1)	5 (1)
C(25)	0.608 (2)	0.189 (2)	0.156 (1)	5 (1)
C(30)	0.904 (2)	0.238 (1)	0.105 (1)	3.8 (9)
C(31)	0.952 (2)	0.199 (2)	0.152 (1)	5 (1)
C(32)	1.080 (2)	0.254 (2)	0.178 (1)	5 (1)
C(33)	1.156 (2)	0.343 (2)	0.160 (1)	5 (1)
C(34)	1.116 (2)	0.388 (2)	0.114 (1)	5 (1)
C(35)	0.989 (2)	0.333 (2)	0.088 (1)	5 (1)
C(40)	0.784 (2)	0.037 (1)	0.031 (1)	3.7 (9)
C(41)	0.738 (2)	0.005 (2)	−0.022 (1)	5 (1)
C(42)	0.759 (3)	−0.090 (2)	−0.050 (1)	7 (1)
C(43)	0.827 (2)	−0.149 (2)	−0.022 (1)	5 (1)
C(44)	0.875 (2)	−0.115 (2)	0.031 (1)	5 (1)
C(45)	0.853 (2)	−0.023 (2)	0.058 (1)	5 (1)
C(50)	0.504 (2)	0.269 (2)	0.491 (1)	5 (1)
C(51)	0.484 (2)	0.359 (2)	0.520 (1)	5 (1)
C(52)	0.569 (3)	0.410 (2)	0.566 (1)	7 (1)
C(53)	0.674 (3)	0.376 (2)	0.581 (1)	7 (1)
C(54)	0.700 (3)	0.292 (3)	0.552 (2)	9 (2)
C(55)	0.614 (3)	0.237 (2)	0.506 (1)	7 (1)
C(60)	0.477 (2)	0.131 (2)	0.384 (1)	4 (1)
C(61)	0.438 (2)	0.023 (2)	0.364 (1)	5 (1)
C(62)	0.508 (3)	−0.016 (2)	0.325 (1)	7 (1)
C(63)	0.619 (4)	0.051 (3)	0.306 (1)	8 (2)
C(64)	0.664 (3)	0.166 (3)	0.329 (2)	8 (2)
C(65)	0.589 (3)	0.198 (2)	0.368 (1)	6 (1)
C(70)	0.277 (2)	0.071 (1)	0.4719 (9)	3.1 (8)
C(71)	0.308 (2)	0.051 (2)	0.521 (1)	4 (1)
C(72)	0.218 (3)	−0.038 (2)	0.547 (1)	7 (2)
C(73)	0.106 (3)	−0.108 (2)	0.514 (2)	7 (2)
C(74)	0.080 (2)	−0.085 (2)	0.466 (1)	6 (1)
C(75)	0.162 (2)	0.006 (2)	0.442 (1)	5 (1)
C(80)	0.287 (2)	0.256 (2)	0.403 (1)	5 (1)
C(81)	0.293 (3)	0.277 (2)	0.352 (1)	6 (1)
C(82)	0.218 (3)	0.330 (2)	0.327 (1)	8 (2)
C(83)	0.130 (4)	0.362 (2)	0.357 (2)	8 (2)
C(84)	0.114 (3)	0.345 (2)	0.412 (2)	8 (2)
C(85)	0.196 (2)	0.288 (2)	0.437 (1)	6 (1)

Table 2. *Selected geometric parameters* (Å, °)

I(1)—Mo(1)	2.848 (3)	I(124)—Mo(1)	2.793 (3)
I(2)—Mo(2)	2.829 (3)	I(124)—Mo(2)	2.775 (2)
I(3)—Mo(3)	2.833 (3)	I(124)—Mo(4)	2.895 (3)
I(4)—Mo(4)	2.843 (3)	Mo(1)—Mo(2)	2.688 (3)
I(13)—Mo(1)	2.744 (3)	Mo(1)—Mo(3)	2.547 (3)
I(13)—Mo(3)	2.743 (3)	Mo(1)—Mo(4)	2.540 (3)
I(14)—Mo(1)	2.749 (3)	Mo(2)—Mo(3)	2.543 (3)
I(14)—Mo(4)	2.773 (3)	Mo(2)—Mo(4)	2.533 (3)
I(23)—Mo(2)	2.681 (3)	Mo(3)—Mo(4)	3.051 (3)
I(23)—Mo(3)	2.707 (3)	P(1)—C(10)	1.78 (2)
I(24)—Mo(2)	2.764 (3)	P(1)—C(20)	1.78 (2)
I(24)—Mo(4)	2.772 (3)	P(1)—C(30)	1.78 (2)
I(34)—Mo(3)	2.745 (3)	P(1)—C(40)	1.78 (2)
I(34)—Mo(4)	2.760 (3)	P(2)—C(50)	1.78 (2)
I(123)—Mo(1)	2.800 (3)	P(2)—C(60)	1.81 (2)
I(123)—Mo(2)	2.804 (3)	P(2)—C(70)	1.82 (2)
I(123)—Mo(3)	2.859 (2)	P(2)—C(80)	1.86 (2)

Mo(1)—I(13)—Mo(3)	55.31 (7)	I(23)—Mo(2)—I(124)	173.0 (1)
Mo(1)—I(14)—Mo(4)	54.76 (7)	I(23)—Mo(2)—I(123)	90.6 (1)
Mo(2)—I(23)—Mo(3)	56.31 (8)	I(24)—Mo(2)—I(123)	172.58 (8)
Mo(2)—I(24)—Mo(4)	54.45 (7)	I(24)—Mo(2)—I(124)	90.97 (8)
Mo(3)—I(34)—Mo(4)	67.31 (7)	I(124)—Mo(2)—I(123)	96.05 (7)
Mo(1)—I(123)—Mo(2)	57.33 (7)	Mo(1)—Mo(3)—Mo(2)	63.76 (8)
Mo(1)—I(123)—Mo(3)	53.48 (6)	Mo(1)—Mo(3)—Mo(4)	53.03 (7)
Mo(2)—I(123)—Mo(3)	53.35 (6)	Mo(1)—Mo(3)—I(3)	140.0 (1)
Mo(1)—I(124)—Mo(2)	57.73 (7)	Mo(1)—Mo(3)—I(13)	62.37 (8)
Mo(1)—I(124)—Mo(4)	53.00 (6)	Mo(1)—Mo(3)—I(23)	124.9 (1)
Mo(2)—I(124)—Mo(4)	53.02 (6)	Mo(1)—Mo(3)—I(34)	99.67 (9)
Mo(2)—Mo(1)—Mo(3)	58.05 (8)	Mo(1)—Mo(3)—I(123)	62.06 (7)
Mo(2)—Mo(1)—Mo(4)	57.87 (8)	Mo(2)—Mo(3)—Mo(4)	52.89 (7)
Mo(2)—Mo(1)—I(1)	136.75 (9)	Mo(2)—Mo(3)—I(3)	138.1 (1)
Mo(2)—Mo(1)—I(13)	120.32 (9)	Mo(2)—Mo(3)—I(13)	126.07 (9)
Mo(2)—Mo(1)—I(14)	120.5 (1)	Mo(2)—Mo(3)—I(23)	61.32 (8)
Mo(2)—Mo(1)—I(123)	61.42 (7)	Mo(2)—Mo(3)—I(34)	99.63 (9)
Mo(2)—Mo(1)—I(124)	60.80 (7)	Mo(2)—Mo(3)—I(123)	62.22 (7)
Mo(3)—Mo(1)—Mo(4)	73.72 (8)	Mo(4)—Mo(3)—I(3)	162.34 (9)
Mo(3)—Mo(1)—I(1)	140.6 (1)	Mo(4)—Mo(3)—I(13)	94.71 (9)
Mo(3)—Mo(1)—I(13)	62.32 (8)	Mo(4)—Mo(3)—I(23)	94.6 (1)
Mo(3)—Mo(1)—I(14)	112.0 (1)	Mo(4)—Mo(3)—I(34)	56.57 (6)
Mo(3)—Mo(1)—I(123)	64.45 (7)	Mo(4)—Mo(3)—I(123)	101.43 (7)
Mo(3)—Mo(1)—I(124)	117.80 (9)	I(3)—Mo(3)—I(13)	86.34 (9)
Mo(4)—Mo(1)—I(1)	145.0 (1)	I(3)—Mo(3)—I(23)	84.4 (1)
Mo(4)—Mo(1)—I(13)	107.7 (1)	I(3)—Mo(3)—I(34)	105.81 (8)
Mo(4)—Mo(1)—I(14)	63.10 (8)	I(3)—Mo(3)—I(123)	96.18 (8)
Mo(4)—Mo(1)—I(123)	117.91 (9)	I(13)—Mo(3)—I(23)	170.6 (1)
Mo(4)—Mo(1)—I(124)	65.55 (8)	I(13)—Mo(3)—I(34)	91.45 (9)
I(1)—Mo(1)—I(13)	90.35 (9)	I(13)—Mo(3)—I(123)	90.28 (8)
I(1)—Mo(1)—I(14)	90.47 (8)	I(23)—Mo(3)—I(34)	92.8 (1)
I(1)—Mo(1)—I(123)	90.52 (8)	I(23)—Mo(3)—I(123)	88.88 (9)
I(1)—Mo(1)—I(124)	93.29 (8)	I(34)—Mo(3)—I(123)	158.00 (8)
I(13)—Mo(1)—I(14)	83.50 (8)	Mo(1)—Mo(4)—Mo(2)	64.00 (8)
I(13)—Mo(1)—I(124)	171.8 (1)	Mo(1)—Mo(4)—Mo(3)	53.25 (7)
I(13)—Mo(1)—I(123)	91.51 (9)	Mo(1)—Mo(4)—I(4)	142.51 (9)
I(14)—Mo(1)—I(124)	89.17 (9)	Mo(1)—Mo(4)—I(14)	62.15 (8)
I(14)—Mo(1)—I(123)	174.92 (9)	Mo(1)—Mo(4)—I(24)	126.4 (1)
I(123)—Mo(1)—I(124)	95.75 (8)	Mo(1)—Mo(4)—I(34)	99.47 (9)
Mo(1)—Mo(2)—Mo(4)	58.12 (8)	Mo(1)—Mo(4)—I(124)	61.44 (7)
Mo(1)—Mo(2)—Mo(3)	58.20 (7)	Mo(2)—Mo(4)—Mo(3)	53.20 (7)
Mo(1)—Mo(2)—I(2)	136.02 (8)	Mo(2)—Mo(4)—I(4)	140.2 (1)
Mo(1)—Mo(2)—I(23)	120.4 (1)	Mo(2)—Mo(4)—I(14)	125.6 (1)
Mo(1)—Mo(2)—I(24)	120.8 (1)	Mo(2)—Mo(4)—I(24)	62.61 (8)
Mo(1)—Mo(2)—I(124)	61.47 (7)	Mo(2)—Mo(4)—I(34)	99.50 (9)
Mo(1)—Mo(2)—I(123)	61.25 (8)	Mo(2)—Mo(4)—I(124)	61.07 (7)
Mo(3)—Mo(2)—Mo(4)	73.91 (8)	Mo(3)—Mo(4)—I(4)	157.75 (8)
Mo(3)—Mo(2)—I(2)	142.9 (1)	Mo(3)—Mo(4)—I(14)	97.82 (9)
Mo(3)—Mo(2)—I(23)	62.36 (9)	Mo(3)—Mo(4)—I(24)	96.49 (9)
Mo(3)—Mo(2)—I(24)	109.99 (9)	Mo(3)—Mo(4)—I(34)	56.12 (6)
Mo(3)—Mo(2)—I(124)	118.6 (9)	Mo(3)—Mo(4)—I(124)	100.54 (8)
Mo(3)—Mo(2)—I(123)	64.43 (8)	I(4)—Mo(4)—I(14)	85.00 (9)
Mo(4)—Mo(2)—I(2)	142.7 (1)	I(4)—Mo(4)—I(24)	82.67 (9)
Mo(4)—Mo(2)—I(23)	108.8 (1)	I(4)—Mo(4)—I(34)	101.67 (8)
Mo(4)—Mo(2)—I(24)	62.95 (8)	I(4)—Mo(4)—I(124)	101.65 (8)
Mo(4)—Mo(2)—I(123)	117.98 (9)	I(14)—Mo(4)—I(24)	165.5 (1)
Mo(4)—Mo(2)—I(124)	65.92 (7)	I(14)—Mo(4)—I(34)	96.18 (9)
I(2)—Mo(2)—I(23)	91.6 (1)	I(14)—Mo(4)—I(124)	86.67 (8)
I(2)—Mo(2)—I(24)	90.48 (9)	I(24)—Mo(4)—I(34)	93.80 (8)
I(2)—Mo(2)—I(123)	91.82 (9)	I(24)—Mo(4)—I(124)	88.34 (8)
I(2)—Mo(2)—I(124)	90.59 (8)	I(34)—Mo(4)—I(124)	156.7 (1)
I(23)—Mo(2)—I(24)	82.31 (9)		

The largest peak and deepest hole in the final difference Fourier map and all other peaks of > 1.0 e Å^{-3} were closer than 1.5 Å to heavy atoms (Mo or I).

Crystallographic computing was performed with *TEXSAN* (Molecular Structure Corporation, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: GR1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichloro(1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane-*N*,*N*′,*N*″)chromium

FENG-JUNG WU AND G. PATRICK STAHLY*

Albemarle Technical Center, Box 14799, Baton Rouge, LA 70898, USA

FRANK R. FRONCZEK AND STEVEN F. WATKINS

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

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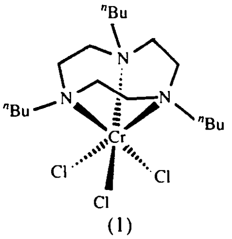
Abstract

The facially coordinated macrocyclic ligand 1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane (^{n}Bu$_3$tacn) plus three Cl ligands assume a distorted octahedral geometry around the Cr atom in the title compound, $[CrCl_3(C_{18}H_{39}N_3)]$. The average Cr—N distance of 2.149 (5) Å is slightly longer than the distance of 2.090 (8) Å found in *fac*-(diethylenetriamine)$CrCl_3$ [Fowlie, House, Robinson & Rumball (1970). *J. Chem. Soc. A*, pp. 803–806] and that of 2.089 (4) Å found in $[(Me_3tacn)_2Cr_2(OH)_3]I_3$ [Wieghardt, Chaudhuri, Nuber & Weiss (1982). *Inorg. Chem.* **21**, 3086–3090], indicating some repulsion between ^{n}Bu$_3$tacn and the Cl atoms. The Cr—Cl distances average 2.324 (5) Å.

Comment

An important method for controlling the course of olefin chain-growth reactions involves ligand-based catalyst design. In particular, transition metal catalyst activities can be tuned by complexation of the metals with various multidentate ligands. Commercially significant procedures based on such an approach include metallocene-catalyzed polyolefin production (Kaminsky, Engehausen, Zoumis, Spaleck & Rohrmann, 1992) and the Ni-catalyzed olefin chain-growth process (Keim, 1990).

Our efforts to develop new Cr-based ethylene oligomerization catalysts led to the synthesis of trichloro(1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane)-chromium, (^{n}Bu$_3$tacn)$CrCl_3$ (1). This new complex was made by procedures analogous to those reported for the preparation of the 1,4,7-triisopropyl derivative, (^{i}Pr$_3$tacn)$CrCl_3$, which has been characterized by spectroscopic means only (Haselhorst, Stoetzel, Strassburger, Walz, Wieghardt & Nuber, 1993).



(1)

The ability of 1,4,7-triazacyclononane and its derivatives to form stable complexes with a wide variety of metals is well known (Chaudhuri & Wieghardt, 1987). These ligands proved to be superior for our Cr-based ethylene oligomerization/trimerization catalysts because variation of the alkyl groups bound to the N atoms allowed selection between two reaction pathways. Smaller groups, like methyl, gave catalysts favoring oligomerization, while larger groups, like butyl, gave catalysts favoring trimerization to hexene.

An *ORTEP* (Johnson, 1965) drawing of (1) is shown in Fig. 1. The macrocyclic ligand coordinates facially. The distance between Cr and the ring centroid (defined by the three N atoms) is 1.395 Å. The ligand plus three Cl atoms assume a distorted octahedral geometry around the Cr atom. The molecule possesses approximate C_3 symmetry along the Cr–ring-centroid axis. The average of the three N—Cr—N bite angles is 82.4 (3) , a deviation of 7.6 (3) from an ideal octahedral value. By comparison, in the closely related complex *fac*-(diethylenetriamine)$CrCl_3$ (Fowlie, House, Robinson & Rumball, 1970), the three N—Cr—N angles are 89.7 (6) for the unconnected pair of N atoms and 82.8 (6) and 83.7 (5) for the connected pairs. The average Cr—N distance of 2.149 (5) Å is slightly longer than the value of 2.090 (8) Å found in *fac*-(diethylenetriamine)$CrCl_3$ (Fowlie, House, Robinson & Rumball, 1970) and that of 2.089 (4) Å in

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