Inorganica Chimica Acta, *86* (1984) L35–L36 L35

Preparation and Structure of the Hexaiodobis(μ-iodo)(μ-hydrido)dimolybdenum(II) Ion, $[Mo_2I_8H]^{3-}$

AVI BINO and SHALOM LUSKI

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Received February 20, 1984

The dinuclear molybdenum(III) complex $[Mo_2X_8H]^{3-}$ (X = Cl, Br) is a product of oxidative addition of HX to the quadruply-bonded Mo_2^{4+} unit (eqn. 1):

$$8HX + Mo_2^{II\,4+} \longrightarrow [Mo_2^{III}X_8H]^{3-} + 7H^+ \qquad (1)$$

These complexes were the subject of numerous structural, spectroscopic and theoretical studies in recent years [1–6]. An SCF-Xα-SW study of the chloride ion, $[Mo_2Cl_8H]^{3-}$ [6] suggested that the Mo–H–Mo unit is essentially a three-center 4-electron system with a strong interaction. The structural data in Table I indicate that this interaction causes a considerable shortening of the Mo–Mo distance in $[Mo_2X_8]^{3-}$ (X = Cl, Br) compared with the corresponding distances in $[Mo_2X_9]^{3-}$.

This work reports the preparation and structural characterization of the iodo analogue of the μ-hydrido dinuclear Mo(III) complex $[Mo_2X_8H]^{3-}$, namely, $[Mo_2I_8H]^{3-}$.

Experimental

Crystals of the tetraethylammonium salt of $[Mo_2I_8H]^{3-}$ were obtained by dissolving $Mo_2(O_2CCH_3)_4$ (0.25 g) and Et_4NI (0.5 g) in 6 ml of HI 55% at 70 °C followed by slow evaporation of the solution under a stream of argon. Dark yellow-brown crystals were deposited after 24 h.

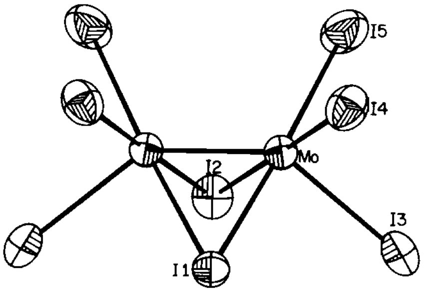

Fig. 1. The structure of $[Mo_2I_8H]^{3-}$. The μ-H atom was not located.

The crystals were found to belong to the orthorhombic space group *Pnma* with *a* = 32.683(4) Å, *b* = 11.384(1) Å, *c* = 10.868(1) Å and *Z* = 4.

A total of 2747 reflections were collected in the range of 3° < 2θ < 45°, of which 1755 were found to have $I > 3\sigma(I)$ and were therefore used in refining of the structural parameters. The structure was refined by least-squares methods to a conventional R factor of 4.4%. Details on data collection and processing have been described elsewhere [7].

Results and Discussion

The formula of the compound was shown to be $(H_7O_3)[(C_2H_5)_4N]_2[Mo_2I_8H]$. The dinuclear anion has the structure shown in Fig. 1. The positional parameters are listed in Table II, and Table III presents some important bond distances and angles.

The overall symmetry of the $[Mo_2I_8H]^{3-}$ unit is very nearly C_{2v} (mm) and one of the two mirror planes is a rigorous, crystallographic one, containing I(1), I(2) and the H atom.

The data listed in Table I show that the iodo complex preserves the same structural features found in the chloro and bromo analogues. The Mo–X distances in all three complexes are in the order $Mo{-}X_{t,H} > Mo{-}X_b > Mo{-}X_{t,X}$. The difference

TABLE I. Structural Data for $Mo_2X_8H^{3-}$ and $Mo_2X_9^{3-}$.

	Bond distances, A				Bond angles, deg.
	Mo–Mo	$Mo{-}X_b$	$Mo{-}X_{t,X}$	$Mo{-}X_{t,H}$	$M{-}X_b{-}M$
$[Mo_2Cl_8H]^{3-}$ [a]	2.377	2.477	2.394	2.502	57.6
$[Mo_2Br_8H]^{3-}$ [b]	2.384	2.630	2.550	2.635	54.0
$[Mo_2I_8H]^{3-}$ [c]	2.408	2.813	2.758	2.869	50.67
$[Mo_2Cl_9]^{3-}$ [d]	2.655	2.487	2.384	–	64.5
$[Mo_2Br_9]^{3-}$ [d]	2.816	2.624	2.544	–	64.9

[a] Ref. 6. [b] As found in $(H_7O_3)[(CH_3)_4N]_2[Mo_2Br_8H]$, A. Bino, unpublished results. [c] This work. [d] Ref. 8.

0020-1693/84/$3.00

TABLE II. Positional Parameters and Estimated Standard Deviations for $(H_7O_3)(Et_4N)_2[Mo_2I_8H]$.[a]

Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
I(1)	0.10540(6)	0.25	0.1124(1)	C(16)	0.4290(8)	0.474(2)	0.420(2)
I(2)	0.18948(6)	0.25	0.3826(2)	N(2)	0.2391(8)	0.25	0.947(2)
I(3)	0.15516(4)	0.5463(1)	0.2290(1)	C(21)	0.247(2)	0.25	0.813(5)
I(4)	0.3682(4)	0.4576(1)	0.3100(1)	C(22)	0.212(4)	0.25	0.78(1)
I(5)	0.11636(5)	0.4502(1)	0.5783(1)	C(23)	0.289(2)	0.25	0.978(7)
Mo	0.11254(5)	0.3558(1)	0.3449(1)	C(24)	0.289(4)	0.25	1.11(1)
N(1)	0.4251(7)	0.25	0.432(2)	C(25)	0.216(1)	0.353(3)	0.999(3)
C(11)	0.379(1)	0.25	0.454(3)	C(26)	0.246(2)	0.460(7)	0.997(7)
C(12)	0.353(1)	0.25	0.345(4)	O(1)	0.5254(9)	0.25	0.880(3)
C(13)	0.446(1)	0.25	0.562(3)	O(2)	0.3955(9)	0.25	0.923(3)
C(14)	0.492(1)	0.25	0.553(4)	O(3)	0.464(1)	0.25	1.008(3)
C(15)	0.4386(6)	0.355(2)	0.356(2)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

TABLE III. Important Bond Lengths (Å) and Important Angles (degrees) for $(H_7O_3)(Et_4N)_2[Mo_2I_8H]$.

Mo–Mo′	2.408(2)	I(4)–Mo	2.759(2)
I(1)–Mo	2.809(2)	I(5)–Mo	2.758(2)
I(2)–Mo	2.818(2)	O(2)–O(3)	2.41(4)
I(3)–Mo	2.869(2)	O(1)–O(3)	2.45(4)
I(1)–Mo–I(2)	91.25(7)	I(3)–Mo–I(4)	93.30(6)
I(1)–Mo–I(3)	88.25(6)	I(3)–Mo–I(5)	94.99(6)
I(1)–Mo–I(4)	88.97(7)	I(4)–Mo–I(5)	90.18(6)
I(1)–Mo–I(5)	176.69(8)	Mo–I(1)–Mo′	50.76(5)
I(2)–Mo–I(3)	87.34(6)	Mo–I(2)–Mo′	50.58(6)
I(2)–Mo–I(4)	179.34(8)	O(1)–O(3)–O(2)	123(2)
I(2)–Mo–I(5)	89.57(7)		

between the Mo–$I_{t,H}$ and Mo–$I_{t,X}$ is *ca.* 0.11 Å due to the greater *trans* effect of the *μ*-H than that of the *μ*-I. The corresponding differences between Mo–$X_{t,H}$ and Mo–$X_{t,X}$ (X = Cl, Br) are 0.11 Å and 0.09 Å, respectively.

The drastic change in the size of the bridging halide in the three complexes hardly affects the Mo–Mo distance (2.377 Å when X = Cl to 2.408 Å when X = I). This feature points clearly to the conclusion that the Mo–Mo separation is determined almost exclusively by the strong Mo–H–Mo interaction. Since the Mo–X_b bond length increases markedly from 2.477 Å (Mo–Cl_b) to 2.813 Å (Mo–I_b) the Mo–X–Mo angle decreases in that order from 57.6° in the chloro complex to the very acute and quite unusual value of 50.65° in the iodo complex.

References

1 M. J. Bennett, J. V. Brencic and F. A. Cotton, *Inorg. Chem., 8,* 1060 (1968).
2 F. A. Cotton, B. A. Frenz and Z. C. Mester, *Acta Crystallogr., Sect. B, B29,* 1515 (1973).
3 F. A. Cotton and B. J. Kalbacher, *Inorg. Chem., 15,* 522 (1976).
4 A. Bino and F. A. Cotton, *Angew. Chem., Int. Ed. Engl., 18,* 322 (1979).
5 A. Bino and F. A. Cotton, *J. Am. Chem. Soc., 101,* 4150 (1979).
6 A. Bino, B. E. Bursten, F. A. Cotton and A. Fang, *Inorg. Chem., 21,* 3755 (1982).
7 A. Bino, *Inorg. Chem., 21,* 1917 (1982).
8 R. Saillant, R. B. Jackson, W. E. Streib, K. Folting and R. A. D. Wentworth, *Inorg. Chem., 10,* 1453 (1971).