Metal Atom Clusters III. The Acceptor Properties and Bonding of (Mo₆Cl₈)⁴⁺ and (Nb₆Cl₁₂)²⁺ Clusters[1]

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Complexes of the type [(Nb₆Cl₁₂)Cl₂(4-ZC₅H₄NO)₄] and [(Mo₆Cl₈)Cl₄(4-ZC₅H₄NO)₂] with 4-substituted pyridine 1-oxides have been prepared. The dependance of the metal-oxygen stretching frequencies upon the electron withdrawing power of the 4-substituent suggests that cluster-ligand π-bonding is not important. A study of the electronic transitions within the (Nb₆Cl₁₂)²⁺ cluster indicates that the metal-metal bonding becomes stronger as the metal-ligand bond becomes weaker. These two results are correlated with the known chemistry of these clusters. Some compounds with 4-substituted pyridines, and with 2,2'-dipyridyl N,N'-dioxide are also described.

Introduction

It is now firmly established that the halides of niobium, tantalum, molybdenum and tungsten in their low formal oxidation states have structures based on octahedral clusters of metal atoms.[2] There are two distinct types of cluster, (M₆X₈)ˣ⁺ (where M is Nb, Mo or W) which have bridging halogen atoms X above each face of the octahedral core of metal atoms M₆, and (M₆X₁₂)ˣ⁺ (where M is Nb, Ta or W) which have bridging halogen atoms above each edge of the octahedron formed by the six metal atoms. It is also firmly established that in addition to the four adjacent metal atoms and the four bridging halogen atoms, each metal atom can add one additional ligand in a « centrifugal » position such that the metal-ligand bond points radially outward from the centre of the octahedral cluster.[1,2] The bonding within the cluster of metal atoms has been the subject of considerable theoretical interest,[3] although as yet there has been remarkably little experimental evidence concerning this problem.

One approach to this question is to prepare and study compounds where the ligand in the « centrifugal » position is systematically varied. A particularly appropriate series of ligands are the 4-substituted pyridine 1-oxides, where the oxygen pπ electrons are

conjugated with the aromatic ring, and the donor properties of the oxygen atom may be systematically varied by appropriate substitution on the aromatic ring in the 4-position. Electron withdrawing groups decrease the negative charge on the oxygen atom and increase the nitrogen-oxygen double bond character. The most convenient measure of this effect is σ_{pyO} which is directly related to the base strength of the ligand. These ligands have been extensively used over recent years to study the nature of the metal-ligand bonding in a number of transition metal complexes.[4]

The object of this work was to study such complexes with a typical representative of each type of cluster, namely the diamagnetic (Mo₆Cl₈)⁴⁺ and (Nb₆Cl₁₂)²⁺. The former has 24 electrons available for metal-metal bonding with short molybdenum-molybdenum distances of 2.61 Å,[5] whereas the latter has only 16 electrons available for metal-metal bonding with niobium-niobium distances of 2.92 Å.[6,7]

Experimental Section

Pyridine 1-oxide, 4-nitropyridine 1-oxide, 4-chloropyridine 1-oxide, 4-methylpyridine 1-oxide, 4-dimethylaminopyridine 1-oxide,[8] and 2,2'-dipyridyl N,N'-dioxide[9] were prepared by standard methods. Other ligands were obtained commercially. All pyridine 1-oxide ligands were sublimed under vacuum immediately before use. 4-Methylpyridine and pyridine were distilled from calcium hydride. 4-Benzylpyridine was distilled from calcium oxide under reduced pressure. 4-Cyanopyridine was recrystallised from benzene.

Molybdenum dichloride, (Mo₆Cl₈)Cl₄ and [(Nb₆Cl₁₂)Cl₂(H₂O)₄]4H₂O were prepared by literature methods,[10] with the improvement that in the last case after extraction of the reduction mixture the solution

(1) For Part II of this series see R. A. Field and D. L. Kepert, *J. Less-Common Metals*, 13, 378 (1967).
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Table I. Analytical Data

	Found				Calcd.			
	M %	Hal %	C %	H %	M %	Hal %	C %	H %
[(Mo₆Cl₈)Cl₄((CH₃)₂N . C₅H₄NO)₂]	45.5	33.8	12.5	2.1	45.0	33.3	13.2	1.6
[(Mo₆Cl₈)Cl₄(CH₃O . C₅H₄NO)₂]	46.2	34.3	12.0	1.2	46.0	34.0	11.5	1.1
[(Mo₆Cl₈)Cl₄(CH₃ . C₅H₄NO)₂]	47.6	35.1	11.9	1.4	47.2	34.9	11.8	1.1
[(Mo₆Cl₈)Cl₄(C₅H₅NO)₂]	48.0	36.0	11.0	1.1	48.3	35.7	10.1	0.9
[(Mo₆Cl₈)Cl₄(Cl . C₅H₄NO)₂]	45.8	33.4	10.1	1.1	45.7	33.8*	9.5	0.6
[(Nb₆Cl₁₂)Cl₂((CH₃)₂N . C₅H₄NO)₄]	34.6	30.5	—	—	34.7	30.9	20.9	2.5
[(Nb₆Cl₁₂)Cl₂(CH₃O . C₅H₄NO)₄]	35.6	32.1	16.6	2.5	35.8	31.9	18.5	1.8
[(Nb₆Cl₁₂)Cl₂(CH₃ . C₅H₄NO)₄]	37.0	32.9	16.6	2.4	37.4	33.3	19.3	1.9
[(Nb₆Cl₁₂)Cl₂(C₅H₅NO)₄]	37.4	33.9	15.7	1.9	38.8	34.6	16.7	1.4
[(Nb₆Cl₁₂)Cl₂(Cl . C₅H₄NO)₄]	35.0	—	13.4	1.8	35.4	31.6*	15.3	1.0
[(Nb₆Cl₁₂)Cl₂(NO₂ . C₅H₄NO)₄]	33.5	31.6	14.6	1.9	34.5	30.7	14.9	1.0
[(Nb₆Cl₁₂)Cl₂(C₁₀H₈N₂O₂)₂]	38.4	34.7	16.2	2.3	39.0	34.7	16.8	1.1
[(Nb₆Cl₁₂)Cl₂(CH₃ . C₅H₄N)₄]	38.7	33.2	18.1	2.4	39.1	34.8	20.2	2.0
[(Nb₆Cl₁₂)Cl₂(C₆H₅ . CH₂ . C₅H₄N)₄]	31.8	27.9	28.2	2.8	32.2	28.7	33.3	2.5
[(Nb₆Cl₁₂)Cl₂(C₅H₅N)₄]	38.6	35.4	17.2	2.1	40.6	36.2	17.5	1.5

* These figures do not include the chlorine in the ligand, which is not hydrolysed under the basic conditions used for the destruction of the complexes.

was slowly evaporated under nitrogen in a rotary evaporator until precipitation was almost complete. Under atmospheric conditions there was some contamination with $(Nb_6Cl_{12})^{3+}$ species. Since some of the intense bands in the visible and ultra violet spectrum of the analogous tantalum compounds are near some of the weaker bands in the niobium compounds, the niobium pentachloride used was analysed for tantalum, and was found to be less than 0.02% of the metal content.

The molybdenum complexes were prepared by adding excess of an ethanolic solution of the ligand to $(Mo_6Cl_8)Cl_4$ dissolved in a minimum of ethanol. Yellow precipitates formed immediately except with the strongly deactivated ligands 4-nitropyridine 1-oxide and 4-cyanopyridine 1-oxide for which no complexes could be prepared; evaporation yielded the free ligand. The precipitates were washed thoroughly with ethanol and ether and dried under vacuum. The unsubstituted pyridine 1-oxide complex has been described previously.[11] The niobium complexes were prepared by dissolving $[(Nb_6Cl_{12})Cl_2(H_2O)_4]4H_2O$ in ethanol under nitrogen reflux, filtering to remove undissolved halide and hydrolysis products, then reducing the volume to about one third of the original volume. To this solution was added excess ligand (approx. 7 moles per mole of cluster) dissolved in the minimum amount of ethanol. Precipitation was observed within one hour, and was complete after standing overnight. No complex could be obtained with 4-cyanopyridine 1-oxide or with 4-cyanopyridine. The green products were washed thoroughly with ethanol and ether, and dried under vacuum. The 2,2'-dipyridyl N,N'-dioxide complex was prepared by adding the ligand (0.33 g) in aqueous ethanol (2 ml water, 10 ml ethanol) to $Nb_6Cl_{14} . 8H_2O$ (0.3 g) in a minimum amount of ethanol. On standing for one week the excess ligand had precipitated and was filtered from the green solution which was then evaporated to dryness. The dark green compound was washed with water, ethanol and ether, and dried under vacuum. Infra-red spectra showed the absence

(11) J. E. Fergusson, B. H. Robinson, and C. J. Wilkins, *J. Chem. Soc.*, Sect. A, 486 (1967).

of ethanol. The conductivity in dimethylformamide was 25-50 cm² ohm⁻¹ mole⁻¹ at $10^{-3} M$ for all complexes. The compounds were insufficiently soluble to allow n.m.r. measurements. Elemental analyses for all compounds are given in Table I.

Ultra-violet and visible spectra were recorded on a Unicam SP700 spectrophotometer calibrated against 4% holmium oxide in 1.4 M perchloric acid[12] Diffuse reflectance spectra were measured on the same instrument fitted with a Unicam SP735 diffuse reflectance attachment. The samples were diluted with magnesium oxide, which was also used as a reference. The position of the band maxima could be measured to ±50 cm⁻¹. The infrared spectra were measured as Nujol mulls between potassium bromide (4000-400 cm⁻¹) and polythene (450-245 cm⁻¹) plates using a Perkin-Elmer 521 spectrophotometer which was flushed continuously with dry air. Water vapour was used to calibrate the instrument below 450 cm⁻¹.[13]

Molybdenum was determined by the oxinate method.[14] Niobium was determined as the oxide after decomposition of the complex with concentrated nitric acid. Tantalum was determined in niobium pentachloride by X-ray fluorescence (Philips) after hydrolysis and ignition to the oxide. Halogen was determined potentiometrically against silver nitrate after decomposition of the complex with hot alkaline peroxide. Carbon and hydrogen were determined by the C.S.I.R.O. Microanalytical Service, Melbourne.

Results

The analytical results for the molybdenum cluster compounds are satisfactory. However the preparation of analytically pure niobium cluster complexes was found to be extremely difficult, the chloride: ligand ratio being greater than 14:4. The $(Nb_6Cl_{12})^{2+}$ moiety, in the presence of air or oxygen-donor ligands, has a tendency to oxidise to $(Nb_6Cl_{12})^{3+}$ and form

(12) A. McNeirney and W. Slavin, *Applied Optics*, 1, 365 (1962).
(13) K. N. Rao, R. V. de Vore, and E. K. Plyler, *J. Res. Natl. Bur. Std.*, 67A, 351 (1963).
(14) A. I. Vogel, « Quantitative Inorganic Analysis », 3rd Ed., Longmans, London, 1961.

Table II. Infra Red Spectra

	σ_{pyO}	ν_{N-O} (Ligand)	ν_{N-O} (Complex)	ν_{O-M}	ν_{M-Cl}	
[(Mo₆Cl₈)Cl₄((CH₃)₂N.C₅H₄NO)₂]	−1.48	1210	1207	458	327	357
[(Mo₆Cl₈)Cl₄(CH₃O.C₅H₄NO)₂]	−0.603	1208	1191	431	327	355
[(Mo₆Cl₈)Cl₄(CH₃.C₅H₄NO)₂]	−0.240	1224, 1209	1201	418	330	353
[(Mo₆Cl₈)Cl₄(C₅H₅NO)₂]	0	1235	1197	398	331	353
[(Mo₆Cl₈)Cl₄(Cl.C₅H₄NO)₂]	0.206	1243	1196	391	331	353
[(Nb₆Cl₁₂)Cl₂((CH₃)₂N.C₅H₄NO)₄]	−1.48	1210	1211	393, 382	339	292, 276
[(Nb₆Cl₁₂)Cl₂(CH₃O.C₅H₄NO)₄]	−0.603	1208	1196	403-408	341	288
[(Nb₆Cl₁₂)Cl₂(CH₃.C₅H₄NO)₄]	−0.240	1224, 1209	1201	393	342	288
[(Nb₆Cl₁₂)Cl₂(C₅H₅NO)₄]	0	1235	1197	403	340, 336 (sh)	283
[(Nb₆Cl₁₂)Cl₂(Cl.C₅H₄NO)₄]	0.206	1243	1200	387, 383	342, 336	285
[(Nb₆Cl₁₂)Cl₂(NO₂.C₅H₄NO)₄]	1.19	1269	1212	388, 386	346, 343, 341	287
	pK$_a$ (BH⁺)					
[(Nb₆Cl₁₂)Cl₂(CH₃.C₅H₄N)₄]	6.03				340	286, 279 (sh)
[(Nb₆Cl₁₂)Cl₂(C₆H₅.CH₂.C₅H₄N)₄]	5.59				341	283, 279 (sh)
[(Nb₆Cl₁₂)Cl₂(C₅H₅N)₄]	5.21				340	282, 277 (sh)

Table III. Diffuse reflectance (DR) and solution spectra in dimethylformamide (DMF)

[(Nb₆Cl₁₂)Cl₂((CH₃)₂N.C₅H₄NO)₄]	(DMF)	—	9950	23400
[(Nb₆Cl₁₂)Cl₂(CH₃O.C₅H₄NO)₄]	(DR)	(7450)	10050	22750
	(DMF)	—	10100	23500
[(Nb₆Cl₁₂)Cl₂(CH₃.C₅H₄NO)₄]	(DR)	(7550)	10200	22750
	(DMF)	—	10250	23750
[(Nb₆Cl₁₂)Cl₂(C₅H₅NO)₄]	(DR)	(7750)	9600	22400
	(DMF)	—	10400	23800
[(Nb₆Cl₁₂)Cl₂(Cl.C₅H₄NO)₄]	(DR)	(7600)	10250	23950
	(DMF)	—	10450	23850
[(Nb₆Cl₁₂)Cl₂(NO₂.C₅H₄NO)₄]	(DR)	(7450)	9350	23400
	(DMF)	—	10650	24250
[(Nb₆Cl₁₂)Cl₂(C₁₀H₆N₂O₂)₂]	(DMF)	—	10200	23850
[(Nb₆Cl₁₂)Cl₂(CH₃.C₅H₄N)₄]	(DR)	(7550)	9950	23150
	(DMF)	—	10400	23800
[(Nb₆Cl₁₂)Cl₂(C₆H₅.CH₂.C₅H₄N)₄]	(DR)	(7300)	9850	23150
	(DMF)	—	10100	23100
[(Nb₆Cl₁₂)Cl₂(C₅H₅N)₄]	(DR)	(7500)	9800	23450
	(DMF)	—	10250	23800

[(Nb₆Cl₁₂)Cl₃(Ligand)₃] which can be detected by a strong band in the visible region at about 8000 cm⁻¹.

The N—O, O—M and M—Cl vibrations in the infra-red are recorded in Table II. All other bands observed have counterparts in the free ligands. The N—O vibration at 1235 cm⁻¹ for C₅H₅NO is for a mull prepared under nitrogen; this compound is very deliquescent and this frequency is lowered to 1220-1225 cm⁻¹ for a mull prepared in air.

Formation of an oxygen-metal coordinate bond decreases the partial double bond character of the nitrogen-oxygen bond, which is reflected in a decrease in the nitrogen-oxygen stretching frequency upon coordination. The decrease observed for these cluster complexes is typical for these ligands.[4]

The (Nb₆Cl₁₂)²⁺ complexes show bands at 341 and 286 cm⁻¹ which have been previously assigned to niobium-chlorine vibrations.[1,15] Similarly the bands at 350 and 330 cm⁻¹ for the (Mo₆Cl₈)⁴⁺ complexes have been previously assigned to molybdenum-chlorine vibrations.[16]

The diffuse reflectance spectra and solution spectra in nitromethane or ethanol of the niobium compounds in the visible region showed in addition to the strong bands at 24,000 and 10,000 cm⁻¹ due to (Nb₆Cl₁₂)²⁺, a weaker band at about 8,000 cm⁻¹ due to (Nb₆Cl₁₂)³⁺. However this oxidised cluster was not present in solutions to which a reducing agent (for example stannous chloride) had been added, or in dimethylformamide solutions (Table III). Bands above 30,000 cm⁻¹ are obscured by ligand bands. The bands at 10,650 and 24,250 cm⁻¹ for the 4-nitropyridine 1-oxide derivative are higher in energy than for the dimethylformamide derivative[1] (10,180 and 23,800 cm⁻¹) indicating that displacement of ligand by dimethylformamide is not significant, since the 4-nitropyridine 1-oxide would be the most easily displaced ligand. The spectrum of the molybdenum clusters was featureless except for the edge of a continuous absorption above 22,000 cm⁻¹; bands reported by others[11] could not be found in this work.

It is not known whether the compounds prepared in this work are *cis*- or *trans*-isomers. The crystal structures of clusters which have different centrifugal environments have all been found to have the *trans*-structure, namely [(Ta₆Cl₁₂)Cl₂(H₂O)₄]3H₂O,[17] (Nb₆-

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(16) R. J. H. Clark, D. L. Kepert, R. S. Nyholm, and G. A. Rodley, *Spectrochim. Acta,* 22, 1697 (1966). F. A. Cotton, R. M. Wing, and R. A. Zimmerman, *Inorg. Chem.,* 6, 11 (1967). D. Hartley and M. J. Ware, *Chem. Commun.,* 912 (1967). R. Mattes, *Z. Anorg. Allgem. Chem.,* 357, 30 (1968).

(17) R. D. Burbank, *Inorg. Chem.,* 5, 1491 (1966).

$Cl_{12})Cl_2$,[6] $(Ta_6I_{12})I_2$,[18] $(Mo_6Cl_8)Cl_4$,[5] and $(W_6Br_8)^{6+}Br_4$-(Br_4^{2-}).[19] In this work the bidentate 2,2'-dipyridyl N,N'-dioxide was used, which models show is capable of occupying two *cis*-centrifugal positions, forming an eight-membered chelate ring. The distortion of the octahedral cluster of metal atoms (see later) would be different in the *trans*-isomer to that in the *cis*-isomer, which might be expected to be reflected in different splitting of those bands in the visible spectrum originating from within the M_6 cluster, or at least in different half-widths. The visible spectra of the bis 4-substituted pyridine 1-oxide complexes are not noticeably different to that of the 2,2'-dipyridyl N,N'-dioxide complex.

Discussion

Infra Red Spectra. Table II and Figure 1 show that the molybdenum-oxygen stretching frequency decreases as σ_{pyO} increases, that is, as the electron density on the donor oxygen atom decreases. For complexes of the later transition metals and post transition metals such as nickel(II),[20] chromium(III), iron(III), cobalt(II), copper(II)[21] and zinc(II),[22] ν_{M-O} *increases* as the electron withdrawing power of the 4-substituent increases, whereas complexes of titanium tetrafluoride[23] and zirconium tetrafluoride[24] are the only other cases where the expected decrease in
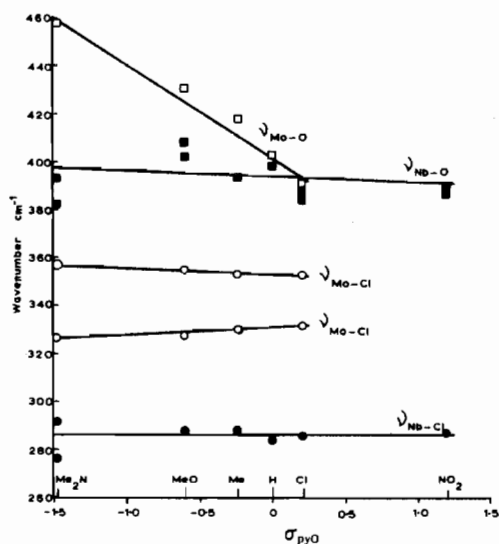

Figure 1. Infrared spectra of $[(Nb_6Cl_{12}(4-Z \cdot C_5H_4NO)_4]$ and $[(Mo_6Cl_8)Cl_4(4-Z \cdot C_5H_4NO)_2]$ as a function of σ_{pyO}.

- ■ ν_{M-O} (Nb-clusters) □ ν_{M-O} (Mo-clusters)
- ● ν_{M-Cl} (Nb-clusters) ○ ν_{M-Cl} (Mo-clusters)

(18) D. Bauer, H. G. v. Schnering, and H. Schafer, *J. Less-Common Metals*, 8, 388 (1965).
(19) R. Siepmann and H. G. v. Schnering, *ibid.*, 357, 289 (1968).
(20) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, 5, 2009 (1966).
(21) R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chim. Acta*, 1, 113 (1967).
(22) G. Schmauss and H. Specker, *Z. Anorg. Allgem. Chem.*, 363, 113 (1968).
(23) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *Inorg. Chem.*, 6, 1099 (1967).
(24) F. E. Dickson, E. W. Baker, and F. F. Bentley, *J. Inorg. Nucl. Chem.*, 31, 559 (1969).

ν_{M-O} occurs as the electron withdrawing power of the 4-substituent increases. This has been attributed to substantial metal-to-oxygen or oxygen-to-metal π-bonding in the case of the later transition metals, but which cannot occur in the TiF_4 and ZrF_4 complexes where the empty *d*-orbitals are used for fluorine-to-metal π-bonding.[4] The behaviour of the $(Mo_6Cl_8)^{4+}$ cluster resembles TiF_4 and ZrF_4 rather than the later transition metals, suggesting that ligand-cluster π-bonding is unimportant. This result is an important verification of one of the assumptions made when discussing the bonding within this cluster.

The metal-chlorine stretching vibrations show little change with varying σ_{pyO}.
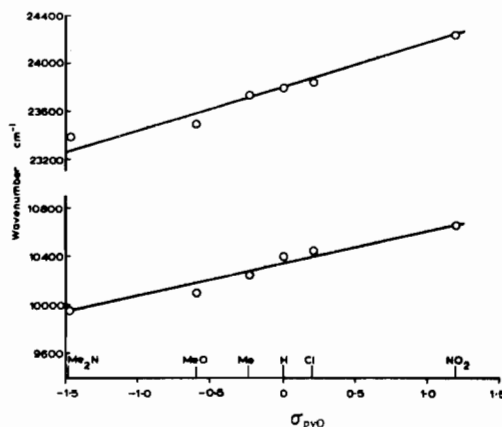

Figure 2. Visible absorption spectra of $[(Nb_6Cl_{12})Cl_2(4-Z \cdot C_5H_4NO)_4]$ as a function of σ_{pyO} in dimethylformamide.

Visible Spectra. Figure 2 shows that as the electron density on the donor atom *decreases* (that is, increasing σ_{pyO}), the two bands of $(Nb_6Cl_{12})^{2+}$ at 10,000 and 24,000 cm^{-1} move significantly to *higher* energy. This is in marked contrast to the spectra of complexes containing a single metal atom, where the *d*–*d* transitions move to lower energy with increasing σ_{pyO} as expected.[20,21] If it is assumed that the transitions in the $(Nb_6Cl_{12})^{2+}$ cluster are due to transitions between metal-metal bonding and metal-metal antibonding molecular orbitals, and that this splitting is a measure of the extent of metal-metal bonding, then these results indicate that the metal-metal bonding increases as σ_{pyO} increases. That is, the metal-metal bonding increases as the metal-ligand bonding decreases. This is in contrast to the metal-chlorine bonding which is insensitive to the nature of the centrifugal ligand, although this bonding also plays an important role in holding the cluster together (and the dominant role in clusters such as (Pt_6Cl_{12})).

This conclusion, that the metal-metal bonding is sensitive to the metal-centrifugal ligand bonding appears important for an understanding of the bonding within these $(Nb_6C_{12})^{2+}$ clusters, and is substantiated by an examination of those clusters with known structures. The structure of the M_6 cluster in $(Nb_6F_{12})F_3$,[25]

(25) H. Schafer, H. G. v. Schnering, K. J. Niehues, and H. G. Neider-Vahrenholz, *J. Less-Common Metals*, 9, 95 (1965).

$(Ta_6Cl_{12})Cl_3$,[26] $K_4[(Nb_6Cl_{12})Cl_6]$,[7] and $(W_6Cl_{12})Cl_6$,[27] is an undistorted octahedron, and in each case the six metal atoms are bonded to six identical centrifugal groups. In complexes where the centrifugal groups are not identical, the difference in the metal-metal bonding resulting from the different metal-ligand bonding produces a distortion in the M_6 octahedron. For example two of the *trans* Ta—I(centrifugal) bonds in $(Ta_6I_{12})I_2$[18] are much longer than the other four coplanar Ta—I(centrifugal) bonds (4.32 and 3.11 Å respectively), and the resulting Ta—Ta bonding flattens the octahedron (distance from centre of octahedron being 1.77 Å for the two *trans*-Ta atoms, compared with 2.18 Å for the other four metal atoms). Similar distortions are observed in Nb_6Cl_{14}.[6] This flattening of the M_6 octahedron is in contrast to the octahedron in $[(Ta_6Cl_{12})Cl_2(H_2O)_4]3H_2O$[17] which is elongated due to stronger metal-metal bonding of the metals attached to the four aquo groups. This is similar to the distortion shown by the Re_3 cluster in $[(Re_3Cl_9)Cl_2]^{2-}$,[28] $[(Re_3Br_9)Br_2]^{2-}$,[29] and ReI_3,[30] where two of the centrifugal sites are different to the third, compared with undistorted Re_3 clusters having three equivalent centrifugal ligands.[31] However in the M_6X_8 clusters $(Nb_6I_8)I_3$,[32] $(Mo_6Cl_8)Cl_4$[5] and $(W_6Br_8)Br_4$ (Br_4),[19] the M_6 octahedra are undistorted, despite different types of centrifugal ligand in the last two cases.

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