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The Nonexistence of $MoCl_4[(C_6H_5)_3AsO]_4$ and Its Relevance to Coordination Theory

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The report of $MoCl_4[(C_6H_5)_3AsO]_4$ (I) and its claim to be a unique eight-coordinate and neutral molybdenum(IV) complex has been examined. It is now established that the method of preparation rarely gives a material resembling I and certainly not one of reproducible composition. The reported material is not a molybdenum(IV) adduct at all, since it is apparent that the "molybdenum tetrachloride" used in the preparation was largely molybdenum(V) chlorides. Attempts to synthesize I by more reliable means have failed; the product appears to be a bis adduct. The nonexistance of I has been predicted in advance of the present work by a new theory of coordination number based on interatomic-core repulsion. The theory is briefly discussed by pointing out the physical significance of Pauling electronegativity as a measure of such repulsion and its quantitative relationship to coordination number.

Introduction

One of us has formulated a theory of interatomic-core repulsion which estimates the coordination number (CN) in a variety of crystals and molecules. We are committed to the test of this theory by searching for proposed or authentic structures displaying CN markedly different from the predictions of the theory. In this manner it will be found whether the theory can be easily disproved. The object of this paper is to report our study of a material formulated as $MoCl_4[(C_6H_5)_3AsO]_4$ (I) by Horner and Tyree[1] (HT) and claimed by them to be the only example of a *neutral* eight-coordinate complex of molybdenum(IV). Our theory predicts that molybdenum(IV) cannot be so surrounded by eight highly electronegative ligands.

HT state[1] that a red carbon tetrachloride solution of "molybdenum tetrachloride," referred to as such for the present, is decolorized when poured into a six- to eightfold *excess* of triphenylarsine oxide in carbon tetrachloride. A flocculent white precipitate immediately forms (mp 161–163°) but on the addition of further "molybdenum tetrachloride" solution, the precipitate is *green*. The white precipitate is diamagnetic and resistant to oxidation so that no molybdenum oxidation state was reported. The erratic analytical figures given by HT do not suggest, however, that they obtained materials of reproducible composition, and moreover the figures give a $(C_6H_5)_3AsO/Mo$ ratio of 3.6, rather than 4.0 as required by I.

It is of interest that HT find[1,2] *excess* triphenylphosphine oxide, triphenylarsine oxide, and dimethyl sulfoxide all *oxidize* molybdenum(V) chloride (*i.e.*, the first gives a complex of MoO_2Cl_2, and the second and third give complexes of $MoOCl_3$) and that *excess* triphenylphosphine oxide and dimethyl sulfoxide *oxidize* their "molybdenum tetrachloride." They report no attempt to show that excess arsine oxide does not oxidize the tetrachloride although the appearance of green precipitates indicates the appearance of molybdenum(V).

Accordingly, our experimental study has taken the form of: (1) establishing the nature of the "molybdenum tetrachloride"–arsine oxide reaction and (2) attempting the preparation of I by more reliable methods.

Results and Discussion

The Reaction Products of "Molybdenum Tetrachloride" and Triphenylarsine Oxide.—We have carried out the above reaction in the manner described by HT *11* times using several different samples of "tetrachloride." A variety of products were obtained, a few of which do resemble the materials reported by HT. The experimental results are summarized in Table I along with the *published* results of HT for comparison. We find that even discounting the colored or initially oily products, the solute materials from reactions 8–11 (Table I) do not have a reproducible analysis. Furthermore reaction 1 provides evidence that $(C_6H_5)_3As(OH)Cl$ may be a prominent constituent of all of these products. Fraction a had a very similar melting point and infrared absorption spectrum to an authentic sample of $(C_6H_5)_3As(OH)Cl$ prepared from the arsine oxide with hydrogen chloride.

We cannot state exactly what the precipitated products are other than suggest they are probably mixtures of $MoO_2Cl_2[(C_6H_5)_3AsO]_2$ and/or $MoOCl_4\cdot(C_6H_5)_3AsO$ with $(C_6H_5)_3As(OH)Cl$. Nevertheless we can state that *our results are similar to those of HT in all important particulars.* They inform[3] us that they attempted the reaction 19 times and succeeded in getting a white solid only 4 times. Green oils were obtained on the other occasions and they attribute these failures to the impurity of the "tetrachloride." As will be seen below, the important conclusion at this stage is that the molybdenum halide we used in our work is the same as the "molybdenum tetrachloride" used by HT, since our results are *sufficiently* similar to theirs.

The Nature of "Molybdenum Tetrachloride."—We were unable to determine the oxidation state of molybdenum in the products owing to interference by the

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[1] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 947 (1962).
[2] S. M. Horner and S. Y. Tyree, *ibid.*, **1**, 122 (1962).
[3] S. Y. Tyree, private communication, 1966.

TABLE I

REACTION PRODUCTS OF "MOLYBDENUM TETRACHLORIDE" AND EXCESS TRIPHENYLARSINE OXIDE

Reaction	Nature of initial products	Treatment before analysis	Mp, °C	Infrared absorption bands, 800–900 cm^{-1}			Analyses, %				
							C	H	As	Cl	Mo
1	(a) White finely divided ppt, plus colorless crystals on standing	. . .	171	823	858	898	58.9	4.5	20.4	9.7	0.3
	(b) Green oil	Re-pptd from acetone with ether	171				. . .	. . .	. . .	. . .	. . .
2	Pale green oil	Vacuum drying	150	. . .	. . .	. . .	47.4	3.4	14.2	19.4	6.0
3	Pale green oil	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
4	Red-brown oil	Vacuum drying	. . .	848	873	. . .	54.3	4.3	18.8	6.1	6.8
5	Red-brown oil	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
6	Very pale green solid	None	148	828	845	898	54.5	4.1	17.7	8.2	2.7
7	Very pale green solid	None	. . .	843	868	894	52.2	4.1	17.7	7.9	4.3
8	Gray-white solid	None	158	845	865	891	55.5	4.2	19.2	9.45	5.4
9	Gray-white solid	None	150	844	867	893	49.7	3.9	16.0	15.0	7.4
10	White solid	None	. . .	849	876	. . .	52.5	4.2	18.3	9.9	7.2
11	White solid	None	120–150	. . .	. . .	. . .	. . .	. . .	. . .	8.0	. . .
HT	White solid	None	161–163	848	878	900	53.5	3.81	. . .	9.42	6.24
HT										9.93	6.81
HT										9.45	6.88
HT										9.18	
Calculated for $(C_6H_5)_3As(OH)Cl$			171 (lit.)	823	858		60.3	4.5	21.0	9.8	0.0
Calculated for $MoCl_4 \cdot [(C_6H_5)_3AsO]_4$							56.7	4.0	19.7	9.3	6.3

arsine oxide, and we subsequently attempted to demonstrate the oxidation of the "tetrachloride" by arsine oxide. During this work we found: (a) the "tetrachloride" contains molybdenum with an apparent oxidation state of +5.5, despite a resemblance to $MoCl_4$ in composition; (b) carbon tetrachloride solutions of the "tetrachloride" displayed infrared absorption bands at 909, 961, 988, and 1008 cm^{-1} characteristic of Mo–O groups; (c) authentic molybdenum(IV) chloride is completely insoluble in carbon tetrachloride.[4] This was confirmed by repeating the preparation of Larson and Moore, although our product obviously contained some of the carbonaceous impurity referred to by these workers.

It is worth noting that $MoCl_5$, $MoOCl_4$, and MoO_2Cl_2 are all soluble in carbon tetrachloride, the first two giving reddish solutions, and that it is unlikely that a tetrachloride of a lower transition metal would be soluble in nonpolar solvents.

Tyree and his associates have reported two original methods for the preparation of molybdenum(IV) chloride[5,6] and used both sources for the "tetrachloride" in the synthesis of I. They are (1) the chlorination of molybdenum(IV) oxide in refluxing hexachlorobutadiene and (2) the action of carbon tetrachloride on molybdenum(IV) oxide in sealed ampoules at 250–300°. It is remarkable that these methods could give *pure* molybdenum(IV) chloride, *free* from pentachlorides and oxychlorides; *e.g.*, the enthalpies of formation of $MoOCl_4$ (154), MoO_2Cl_2 (173), and $MoCl_5$ (126) are all greater than that of $MoCl_4$ (114 kcal $mole^{-1}$).[7] Method 1 is not now considered reliable[1] as it appears to give a mixture of "tetrachloride" and pentachloride. The product from method 2 contains unchanged molybdenum(IV) oxide,[1,7] so that a variation of the method passing carbon tetrachloride at 300° over molybdenum(IV) oxide has been recommended.[7] The product then is *a mixture of chlorides and oxychlorides,* although sublimation leaves a residue of pure molybdenum(IV) chloride.[7]

Tyree and his associates report *no molybdenum oxidation numbers* for chlorides prepared by methods 1 or 2. For selected samples, *i.e.* "for a good preparation,"[2] the total molybdenum plus chloride content is *always a few per cent less than that required for molybdenum(IV) chloride; viz.,* see Table II. We suggest that the "tetrachloride" prepared by HT and ourselves by method 2 is largely a mixture of $MoCl_5$ and MoO_2Cl_2 (or $MoOCl_4$); *e.g.*, a 70–30% mixture of the first two chlorides would have an apparent composition of $MoCl_{4.1}O_{0.6}$, giving an apparently satisfactory Cl/Mo ratio for molybdenum(IV) chloride, but being about 4% deficient in molybdenum and chlorine and having a molybdenum oxidation number of +5.3.

TABLE II

ANALYTICAL DATA FOR "MOLYBDENUM TETRACHLORIDE"

Prepn method	% Cl	% Mo	Deficiency from 100%	Ref
MoO_2–Cl_2–C_4Cl_6 (1)	59.78	39.24	0.98	2
MoO_2–CCl_4 (2)	58.31, 58.73	39.67, 40.17	1.56	2
MoO_2–CCl_4 (2)	57.6	39.0	3.4	7

It is possible there is some molybdenum(IV) chloride present in preparations by method 2, but it is likely to be insoluble in carbon tetrachloride.[5] The

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[4] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **3**, 285 (1964).

[5] T. E. Austin and S. Y. Tyree, *J. Inorg. Nucl. Chem.*, **14**, 141 (1960).

[6] E. R. Epperson and H. Frye, *Inorg. Nucl. Chem. Letters*, **2**, 223 (1966).

[7] S. A. Shchukarev, *et al.*, *Russ. J. Inorg. Chem.*, **5**, 802 (1960).

TABLE III

REACTION PRODUCTS OF MOLYBDENUM(V) CHLORIDE AND EXCESS TRIPHENYLARSINE OXIDE

Reaction no.	Nature of product	Mp, °C	Infrared absorption bands, cm^{-1}			Analyses, %				
						C	H	As	Cl	Mo
1	White solid	120	...	...	...				8.8	
2	White solid	120	840	870	897	54.2	4.6	17.3	7.8	6.55
3	White solid	162	848	866	893	54.40	3.96	21.5	9.1	8.45

carbon tetrachloride extracts of such preparations, used by HT to synthesize I, probably contained only molybdenum pentachloride and oxychlorides. We assume that the distinctive red color of such a solution was principally due to molybdenum(V) chloride.

The Reaction of Molybdenum(V) Chloride with Excess Triphenylarsine Oxide.—The reaction was carried out in the same manner as the HT synthesis of I, save for the replacement of the "tetrachloride" by molybdenum(V) chloride. The red carbon tetrachloride solution was decolorized and a pure white, flocculent precipitate was immediately formed. The appearance of the reaction differs in no way from that reported by HT, or from our reactions 10 and 11 (Table I), except that the precipitate had a much cleaner appearance. These observations lead us to reject the explanation given by HT[1,3] for the numerous failures of their synthesis of I to give pure white solids. They suggest that the purity of the tetrachloride is critical and that the yield of a pure white precipitate with the arsine oxide is indicative that the requisitely pure tetrachloride is being used.

The reaction products from molybdenum(V) chloride are given in Table III, and it will be seen that these differ very little from the materials reported by HT (*viz.*, see Table I). Furthermore a similar reaction using excess triphenylphosphine oxide proceeds with slow decolorization and the eventual formation of a yellow precipitate of $MoO_2Cl_2[(C_6H_5)_3PO]_2$. *Anal.* Calcd for $MoO_2Cl_2[(C_6H_5)_3PO]_2$: C, 57.2; H, 4.2; Cl, 9.4; P, 8.2. Found: C, 57.2; H, 4.2; Cl, 10.0;[7] P, 9.3. These results are identical with those of HT with "tetrachloride" and excess phosphine oxide.[1]

The Reaction of Authentic Molybdenum(IV) Chloride with Triphenylarsine Oxide.—Fowles, *et al.*, have reported[8] a number of authentic molybdenum(IV) chloride adducts, with appropriate oxidation numbers and magnetic moments, of the form $MoCl_4L_2$ prepared by a replacement reaction in chloroform solution: $MoCl_4L'_2 + 2L \rightarrow MoCl_4L_2 + 2L'$ (L' is *n*-propylcyanide). The method overcomes the insolubility of molybdenum(IV) chloride in nonpolar solvents. We have attempted to prepare I by Fowles' method in order to confirm our prediction that I does not exist. We recognize that merely unsuccessful efforts to precipitate I from solution are not sufficient evidence as to its nonexistence—it must be shown that I cannot appear from such solutions.

We have been unable to get a molybdenum(IV)–arsine oxide adduct by the Fowles method. Dilute solutions give no precipitate and concentrated ones turn green giving green precipitates containing molybdenum(V) (visible spectroscopy). Triphenylphosphine oxide, on the other hand, produces no significant oxidation of molybdenum(IV) and gives a very small yield of yellow precipitate—too small for proper identification—but presumably it is $MoCl_4[(C_6H_5)PO]_2$. We consider it significant that although 2:1 adducts of molybdenum(IV) with triphenylphosphine, triphenylarsine, and phosphine oxide have been reported, there is no mention[8] of a triphenylarsine oxide adduct.

We have examined dilute $MoCl_4(n\text{-}C_3H_7CN)_2$–$(C_6H_5)_3AsO$ chloroform solutions over a range of arsine oxide/molybdenum ratios (R) by quantitative infrared spectroscopy. Triphenylarsine oxide displays a doublet band (*viz.*, see Figure 1) at 876 and 888 cm^{-1} which obeys Beer's law, E_M (888 cm^{-1}) = 300. Mixtures of low R display a broad band, 860-cm^{-1}, maximum, which we assign to the arsine oxide coordinated to molybdenum. In general, the doublet and broad bands appear together with relative intensities dependent on R (Figure 1). It is possible to estimate the molarities of free and combined arsine oxide from such spectra if some judgment is exercised in resolving the two overlapping bands. However, we find that the final conclusions are not affected by different resolutions, and the results remain at all times approximate since slow oxidation of molybdenum(IV) and consumption of arsine oxide occur even in dilute solution.

Our results are given in Table IV. The ratio of *combined* arsine oxide to molybdenum (B/A) never exceeds 2.0 by a significant amount even in large excesses of arsine oxide. The results are evidence for the adduct $MoCl_4 \cdot [(C_6H_5)_3AsO]_2$ which is itself entirely plausible in view of similar $MoCl_4L_2$ complexes previously reported.[8] If a tetrakis(arsine oxide) adduct were present in these chloroform solutions, it must now be supposed to be in small concentration and in equilibrium with the observed bis(arsine oxide) adduct. This is equivalent to saying that the tetrakis adduct is dissociated by chloroform, a nonligand, and therefore the tetrakis adduct is quite unstable. The possibility of a *stable* tetrakis adduct at high concentrations of arsine oxide is also ruled out by the rapid oxidation occurring which could, just conceivably, result from a species of high coordination number. We conclude that a stable tetrakis(arsine oxide) adduct of molybdenum(IV) does not exist.

Theory

The nonexistence of I is not an important fact in itself but amply demonstrates the impotence of conventional valence theories to detect curious, and

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[8] E. A. Allen, K. Feenan, and G. W. A. Fowles, *J. Chem. Soc.*, 1636 (1965).

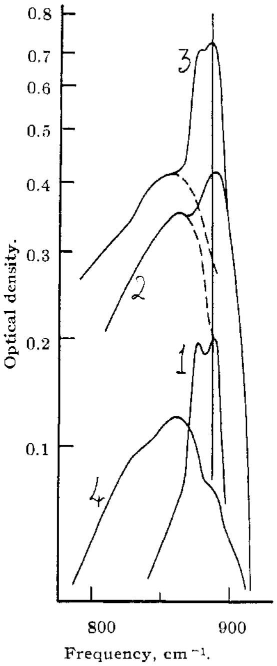

Figure 1.—Infrared absorption spectra of triphenylarsine oxide and mixtures with bis(propyl cyanide)molybdenum(IV) chloride: 1, triphenylarsine oxide; 2, molybdenum(IV)–arsine oxide mixture, 0.0075 *M*–0.0068 *M;* 3, molybdenum(IV)–arsine oxide mixture, 0.0068 *M*–0.0130 *M;* 4, molybdenum(IV)–arsine oxide mixture, 0.0054 *M*–0.023 *M*.

Table IV

Quantitative Infrared Spectroscopy of Molybdenum(IV)–Arsine Oxide Solutions in Chloroform

Molar ratio (*R*)	Concn, $M \times 10^3$ Mo(IV) [A]	Arsine oxide	Optical density (888 cm⁻¹) Obsd	Correction[a]	Concn of arsine oxide, *M* Free	Combined [B]	B/A
0.91	7.5	6.85	0.07	−0.05	0.4	6.4	0.85
1.9	6.75	13.0	0.42	−0.22	4.0	9.0	1.3
3.0	6.1	18.5	0.57	−0.25	6.6	11.9	1.95
4.3	5.5	23.5	0.74	−0.28	9.7	13.8	2.5
5.2	2.75	14.2	0.41	0[b]	8.6	5.6	2.0
8.2	2.5	20.2	0.65	0[b]	14.7	5.5	2.2
10.6	1.8	18.5	0.67	0[b]	15.3	3.2	1.8

[a] Contribution from adduct to be deducted. [b] Small and difficult to estimate.

hence possibly mistaken, structures in transition element chemistry and so prompts confirmatory experiments. We believe the situation results from a disregard of fundamental factors that determine molecular geometry.

Although it has been pointed out a number of times that there is no recognizable difference between ionic and covalent bonding (if polarity is not confused with ionicity) and that it is difficult to attach any meaning to "percentage ionic character," it is scarcely appreciated that as a consequence Pauling electronegativity,[9] χ, cannot have the interpretation given it by conventional theory, *i.e.*, a measure of *electroaffinity*.

We view χ as a measure of "nucleopositivity"—*the ability of atomic cores to repel neighboring cores.* We discover that this interpretation has already been proposed by Cottrell and Sutton.[10] The internuclear repulsive energy between the atomic cores of A and B can be shown to be $2\chi_A\chi_B$ and the origin of the Pauling equation, $D_{AB} - {}^1/_2(D_{AA} + D_{BB}) = (\chi_A - \chi_B)^2$, becomes obvious. The way is then clear to recognizing a number of important correlations between CN and χ, which have enabled one of us to formulate a simple model for CN valid over a wide area of chemistry. *A major factor determining CN is the magnitude of the internuclear energy.* It is postulated that the total internuclear energy of atom A (N_A) surrounded by *m* atoms of type A, *n* of type B, etc., can be expressed

$$2m\chi_A^2 + 2n\chi_A\chi_B + 2p\chi_A\chi_C + \ldots = N_A$$

N_A is a characteristic constant for a particular class of elements coordinated by particular kinds of atoms, *e.g.*, transition elements coordinated by second-period nonmetals. It is not appropriate to discuss the theory in detail here, but its results for molybdenum chlorides may be of interest as a typical but specific illustration. Adopting the appropriate valence-state χ_{Mo} value, the equation $2m\chi_{Mo}^2 + 2n\chi_{Mo}\chi_{Cl} = 55$ may be solved if one of the CN (*m*, the Mo:Mo CN, or *n*, the Cl:Mo CN) is specified. The results are given in Table V.

Table V

CN in Molybdenum Chlorides Predicted by Theory

Chloride	Mo valence state	χ_{Mo}	Mo:Mo CN (*m*)	Cl:Mo CN (*n*)
$MoCl_6$	6	1.58	*0*[b]	5.7
$MoCl_5$	5	1.52	*0*	5.9
$MoCl_4$	6[a]	1.58	0	*6*[b]
$MoCl_4$			1.3	*5*
$MoCl_3$	6[a]	1.47	0.2	*6*
$MoCl_3$			2.2	*5*
$MoCl_2$	6[a]	1.37	1.2	*6*
$MoCl_2$			3.4	*5*

[a] Mo–Mo bonding assumed to take place. [b] The values in *italics* are the assumed CN.

The model accounts for a number of facts in a most original way: (1) there is no stable $MoCl_6$ since $n \ngtr 5.7$ even if $m = 0$; (2) $MoCl_5$ contains no Mo–Mo bond (*i.e.*, $d_{MoMo} > 2.7$ A) since $m = 0$ if $n = 6.0$; (3) $(MoCl_2)_x$ must display Mo–Mo bonds (*i.e.*, $d_{MoMo} \sim 2.7$ A) since *m* is significantly large for $n = 6, 5$, etc. The structure of molybdenum(II) chloride has not been determined directly, but by analogy with its derivatives likely to be of the form $[(Mo_6Cl_8)Cl_4]_x$ where $n = 5$ and $m = 4$. This is consistent with one prediction of the theory, $n = 5.0$ and $m = 3.4$. Molybdenum(III) chloride has a layer structure with $n = 6$ and $m = 1$ ($d_{MoMo} = 2.76$ A). The theory is unsatisfactory here since for $n = 6$ it predicts a very long Mo–Mo distance, say about 3.0 A, with $m < 1$. Molybdenum(IV) chloride is of unknown structure, but on general grounds it is likely to be chains or layers of $MoCl_6$ octahedra with $d_{MoMo} > 2.7$ A. This is consistent with one possibility of the theory. It has been suggested[11] that $MoCl_4$ may be formulated as Mo_3Cl_{12}

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(9) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

(10) T. L. Cottrell and L. E. Sutton, *Proc. Roy. Soc.* (London), **A207**, 49 (1951).

(11) R. Cotton and R. L. Martin, *Nature*, **207**, 141 (1965).

with a similar structure to the $Re_3Cl_{12}^{3-}$ group, *i.e.*, $n = 5$ and $m = 2$. Our theory suggests that this is unlikely, and the proper elucidation of the structure will provide a useful test of this theory.

Consider now an adduct of $MoCl_4$ with oxygen donor atoms. The relevant N_{Mo} for such a coordination sphere cannot be specified *a priori* but is probably in the region 55–62 ev which is appropriate for most metal chlorides and oxides. It is then impossible for molybdenum(IV) to be surrounded by eight chlorine or oxygen atoms, unless some Mo–Cl or Mo–O bonds are unusually long. However, it is doubtful whether the term "eight-coordinate molybdenum(IV)" would have much significance in the latter case. The molybdenum(IV) tetrachloride–oxygen donor adducts so far reported appear to be six-coordinate. The occurrence of eight-coordinate fluoro- and cyanatomolybdates is no less than the proverbial exception to prove the rule. These molybdates usually contain an alkali element which is assigned a very low χ. The low internuclear repulsion exerted by the alkali offsets and allows higher repulsion by molybdenum with a high CN. Unusually high CN can be thus estimated in the simpler ternary halides.

Experimental Section

The preparation, purification, analysis, and handling of the materials followed conventional methods or those described in the text. Where appropriate, moisture and air were rigorously excluded. The product of molybdenum(IV) oxide and carbon tetrachloride at 250–300° ("molybdenum tetrachloride") was red-black needles soluble in carbon tetrachloride. The following percentages and oxidation numbers were found for four samples: (1) Cl, 62%; Mo, 38.9%; (2) Cl, 56.5%; Mo oxidation no., 5.6 (assuming 39% Mo); (3) oxidation no., 5.4; (4) oxidation no., 5.6. (The last two results are from assays on carbon tetrachloride solutions of the product.)

Molybdenum(IV) chloride was prepared by the reduction of molybdenum(V) chloride by refluxing benzene.[4] There is a tendency to produce carbonaceous by-products, and consequently this material was not obtained in a pure form. The product was a black powder completely insoluble in carbon tetrachloride. *Anal.* Calcd for Cl_4Mo: Cl, 59.6; Mo, 40.3. Found: Cl, 54.4; Mo, 37.4; Cl/Mo = 4.0; Mo oxidation no., 4.1.

Bis(*n*-propyl cyanide)molybdenum(IV) chloride appeared as red-brown needles from a mixture of molybdenum(V) chloride and *n*-propyl cyanide after 24 hr at room temperature. *Anal.* Calcd for $C_8H_{14}Cl_4N_2Mo$: Cl, 37.8; Mo, 25.5; Mo oxidation no., 4.0. Found: Cl, 37.3; Mo, 24.6; Mo oxidation no., 3.9.

Molybdenum(V) chloride was Molybdenum Climax material, resublimed.

Infrared spectroscopy was conducted in a Perkin-Elmer Model 21 double-beam spectrophotometer, with matched NaCl window cells of 0.15-cm path length.

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The Reaction of $K_3W_2Cl_9$ with Pyridine and Its Homologs

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The reaction of $K_3W_2Cl_9$ (obtained from an improved synthesis) with pyridine has been investigated. The only isolable product was the diamagnetic $W_2Cl_6(py)_4$. Similar products were obtained from reactions with 4-picoline and 4-isopropylpyridine. The structures are presumed to consist of two octahedra sharing a common edge, and result from the breaking of one bridge bond in the $W_2Cl_9^{3-}$ ion. In the reaction with 4-isopropylpyridine, two isomeric compounds have been isolated. The similarity of the electronic spectra of one of these with that of $W_2Cl_6(py)_4$ suggests that these have an identical skeletal arrangement. Similarly the spectrum of the other isomer compares favorably to the product obtained from the reaction of $K_3W_2Cl_9$ with 4-picoline. The electronic spectrum of the $W_2Cl_9^{3-}$ ion is briefly discussed.

Introduction

The $W_2Cl_9^{3-}$ ion, one of the simplest examples of a metal cluster, is known[1] to consist of two octahedra sharing a common trigonal face. This structure suggests that there may be reactions in which the peripheral halogen atoms are preferentially removed with respect to the bridging atoms. Indeed, Jonassen, Cantor, and Tarsey[2] reported the isolation of diamagnetic $W_2Cl_6(py)_3$ by the reaction of pyridine with the potassium salt of the binuclear ion. It was postulated that the bridging arrangement in this compound was identical with that within the $W_2Cl_9^{3-}$ ion.

This reaction would appear to belong to an important general class of reactions which can occur with metal cluster compounds, namely those which leave the bridging arrangement completely intact. A recent example of this type is the reaction of phenyldiethylphosphine with the trigonal cluster, Re_3Cl_9, to form Re_3Cl_6(phenyldiethylphosphine)$_3$. X-Ray analysis[3] confirmed the preservation of the Re_3Cl_9 ring system. Another general class of reactions would include those which proceed with partial destruction of the bridging arrangement. While polymeric metal halides are not metal clusters, some of their reactions fall within this category. For example $CrCl_3$, a substance consisting of infinite chains of octahedra sharing common trigonal faces, is reported[4] to react with alkylphosphines

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[1] W. H. Watson, Jr., and J. Waser, *Acta Cryst.*, **11**, 689 (1958).

[2] H. B. Jonassen, S. Cantor, and A. R. Tarsey, *J. Am. Chem. Soc.*, **78**, 271 (1956).

[3] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

[4] K. Issleib and H. O. Fröhlich, *Z. Anorg. Allgem. Chem.*, **298**, 84 (1959).