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Stereospecific Formation of Face-Shared Bioctahedra and Trioctahedra by Oxidative Displacement of CO from the $Mo(CO)_4Cl_3^-$ Anion

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The reaction of $MoCl_6^{2-}$ or $MoCl_6^-$ with $Mo(CO)_4Cl_3^-$ in CH_2Cl_2 results in the formation of $Mo_2Cl_9^{3-}$ and $MoCl_9^{2-}$, respectively. The temperature dependence of the magnetic moment of the latter is shown to be in accord with the thermal equilibrium $S = {}^1/_2 \rightleftarrows S = {}^3/_2$, while its infrared spectrum can be readily assigned assuming a bioctahedral, D_{3h} structure. It is easily reduced to $Mo_2Cl_9^{3-}$. The reaction of $Mo_2Cl_9^{2-}$ with $Mo(CO)_4Cl_3^-$ leads to $Mo_3Cl_{12}^{3-}$ whose trinuclear structure was verified from conductivity measurements. Both the electronic and the infrared spectra are in accord with a linear, trioctahedral, face-shared structure (unlike $Re_3Cl_{12}^{3-}$). Magnetic moments in solution are in qualitative agreement with the thermal equilibrium $S = {}^1/_2 \rightleftarrows S = {}^3/_2$.

Introduction

There is increasing evidence that certain oxidation–reduction reactions involve dinuclear-bridged intermediates. Commonly, these intermediates have a single bridge but two and three bridges have been proposed in certain cases.[1] If one of the metal atoms in the bridged intermediate has a formal oxidation state after electron transfer which results in lability, then a relatively short lifetime can be expected for the intermediate. If, however, both metal atoms are found in inert oxidation states after electron transfer, then the intermediate can become a stable product, as is the case with $(NC)_5Fe\text{-}CN\text{-}Co(CN)_5^{6-}$.[2]

The utility of these principles should extend beyond the mechanistic sense to the rational syntheses of bridged compounds. Indeed, the preparations of $Mo_2Cl_9^{n-}$ ($n = 2$ or 3), previously described in a brief communication,[3] were readily achieved by the oxidative displacement of CO from $Mo(CO)_4Cl_3^-$ by $MoCl_6^{(n-1)-}$ in CH_2Cl_2 according to

$$MoCl_6^{2-} + Mo(CO)_4Cl_3^- \rightarrow Mo_2Cl_9^{3-} + 4CO \qquad (1)$$

$$MoCl_6^- + Mo(CO)_4Cl_3^- \rightarrow Mo_2Cl_9^{2-} + 4CO \qquad (2)$$

The general mechanism for this reaction is based on the presumption that $MoCl_6^{(n-1)-}$ can displace CO in a stepwise fashion from a trigonal face on the exterior of $Mo(CO)_4Cl_3^-$.[4] Since electron transfer should accompany bridge formation, the additional CO ligand which remains after bridge formation should be readily lost because of the rather high formal oxidation state of the metal atom to which it is attached. The proposed mechanism is then

$$MoCl_6^{(n-1)-} + Mo(CO)_4Cl_3^- \xrightarrow{-3CO} Cl_3MoCl_3Mo(CO)Cl_3^{n-} \xrightarrow{-CO} Cl_3MoCl_3MoCl_3^{n-} \qquad (3)$$

The stability of $Mo_2Cl_9^{3-}$ toward bridge rupture under the conditions of the reaction is derived not only from the inert d^3 configurations which both metal atoms possess but also from the ligand-deficient system in which the reaction was conducted. The latter probably becomes increasingly important in accounting for the stability of $Mo_2Cl_9^{2-}$ which should be somewhat more labile since the metal atoms formally have both d^3 and d^2 configurations.

A logical extension of this mechanism involves the oxidative displacement of CO from $Mo(CO)_4Cl_3^-$ by $Mo_2Cl_9^{2-}$. Since the latter should possess two trigonal faces (assuming a confacial bioctahedral structure) and is easily reduced, the reaction was expected to proceed according to

$$Mo_2Cl_9^{2-} + Mo(CO)_4Cl_3^- \rightarrow Mo_3Cl_{12}^{3-} + 4CO \qquad (4)$$

where the product should have a linear trioctahedral structure containing two shared faces rather than a triangular one as is the case with $Re_3Cl_{12}^{3-}$.[5]

These reactions and the characterization of their products are now described in detail.

Experimental Section

Reagents and Procedures. Samples of $MoCl_5$ were prepared by halogenation of the metal.[6] Samples of $[(n\text{-}C_3H_7)_4N]_2MoCl_6$ were isolated from CH_2Cl_2 solutions containing stoichiometric quantities of $[(n\text{-}C_3H_7)_4N]Cl$ and $MoCl_4(CH_3CN)_2$. The latter was obtained from the reaction of $MoCl_5$ with acetonitrile.[7] Solutions of $Mo(CO)_4Cl_3^-$ were prepared by the reaction of $Mo(CO)_6$ with Cl_2 followed by the addition of a stoichiometric quantity of an appropriate alkylammonium halide.[8] The reagent grade acetonitrile used in the conductivity studies was dried over P_2O_5 and fractionally distilled.

The reactions which follow were conducted under conditions previously described.[9] The compounds which were isolated from these reactions were always washed with the cold distillate from the mother liquor and dried under vacuum.

Preparation of Compounds. $Mo_2Cl_9^{3-}$. A solution of $[(n\text{-}C_3H_7)_4N]Mo(CO)_4Cl_3$ (1.76 mmol) in CH_2Cl_2 (~25 ml) was prepared. To this solution was added solid $[(n\text{-}C_3H_7)_4N]_2MoCl_6$ (1.76 mmol). Evolution of CO ceased after 30 hr with 6.12 mmol gas measured (87%). The solution was filtered yielding $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$ (0.83 mmol) as an orange solid. *Anal.* Calcd for $C_{36}H_{84}N_3Mo_2Cl_9$: Mo, 18.1; Cl, 30.2. Found: Mo, 18.3; Cl, 29.6. The infrared spectrum of the filtrate revealed $Mo(CO)_6$ (0.14 mmol) while an unknown chromophore was found in the visible spectrum.

$Mo_2Cl_9^{2-}$. To a solution of $[(n\text{-}C_4H_9)_4N]Mo(CO)_4Cl_3$ (3.63 mmol) and $[(n\text{-}C_4H_9)_4N]Cl$ (4.03 mmol) in CH_2Cl_2 was added $MoCl_5$ (3.62 mmol). The evolution of CO was vigorous and complete within 24 hr. The compound was obtained in quantitative yield as green crystals upon addition of ether. *Anal.* Calcd for $C_{32}H_{72}N_2Mo_2Cl_9$:

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[1] For example, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley-Interscience, New York, N. Y., 1967, p 479.

[2] A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

[3] W. H. Delphin and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, **95**, 7920 (1973).

[4] This statement assumes the availability of a trigonal face containing only three CO ligands. The structure of $W(CO)_4Br_3^-$ has been shown to be a capped octahedron with four CO ligands occupying a trigonal face: M. G. B. Drew and A. P. Wolters, *J. Chem. Soc., Chem. Commun.*, 457 (1972). However, stereochemical nonrigidity is not precluded and is in fact common to many seven-coordinate systems.

[5] (a) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc., London*, 116 (1963); (b) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Amer. Chem. Soc.*, 85, 1349 (1963); *Inorg. Chem.*, 2, 1166 (1963).

[6] R. Colton and I. B. Tomkins, *Aust. J. Chem.*, 18, 447 (1965).

[7] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 4531 (1964).

[8] J. A. Bowden and R. Colton, *Aust. J. Chem.*, 21, 2657 (1968).

[9] W. H. Delphin and R. A. D. Wentworth, *Inorg. Chem.*, 12, 1914 (1973).

C, 38.59; H, 7.24; N, 2.81; Cl, 32.06; Mo, 19.3. Found: C, 38.40; H, 7.49; N, 2.81; Cl, 32.10; Mo, 19.3.

$Mo_3Cl_{12}^{3-}$. (a) A fresh solution of $[(n\text{-}C_4H_9)_4N]Mo(CO)_4Cl_3$ (5.50 mmol) and $[(n\text{-}C_4H_9)_4N]Cl$ (2.76 mmol) was prepared. After addition of a 2.73-mmol sample of $MoCl_5$, vigorous evolution of CO commenced. The solution was initially dull green, but after about 10 min it became red and remained that color throughout the remainder of the reaction. The solution was evaporated to about half the original volume; then ether (~10 ml) was added to produce an oil. The mother liquor was decanted and the oil was caused to solidify by addition of another 10-ml portion of ether. *Anal.* Calcd for $C_{48}H_{108}N_3Mo_3Cl_{12}$: C, 40.0; H, 7.50; N, 2.92; Mo, 20.0; Cl, 29.6. Found: C, 40.3; H, 7.95; N, 2.68; Mo, 19.5; Cl, 28.9.

(b) To a solution of 0.718 mmol of $[(n\text{-}C_4H_9)_4N]Mo(CO)_4Cl_3$ was added 0.706 mmol of $[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$. This solution was stirred for 16 hr at the end of which 2.64 mmol of CO was measured (92%). The solution was filtered yielding a very small amount of solid. Dilution of the filtrate to 25.0 ml and subsequent inspection of the infrared and visible spectra revealed $Mo(CO)_6$ (0.041 mmol) and $[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$ (0.662 mmol), respectively, as the only species.

Reaction of $Mo_2Cl_9^{2-}$ with Sn. A solution of $[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$ (5.80×10^{-2} mmol) in 20.0 ml of CH_2Cl_2 was treated with an excess of Sn powder and a 1-ml CH_2Cl_2 solution containing excess $[(n\text{-}C_4H_9)_4N]Cl$. On mixing, the solution changed from yellow-green to red. The solution was filtered and diluted to 25.0 ml. The visible spectrum indicated only $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ (5.71×10^{-2} mmol).

Physical Measurements. Magnetic susceptibilities were measured with the Faraday balance previously described.[10] Infrared spectra were obtained in Nujol mulls between polyethylene plates using a Perkin-Elmer Model 621 spectrophotometer. The electronic spectra were recorded using a Cary Model 14 spectrophotometer.

Conductance measurements were obtained with a General Radio Co. impedance bridge (Type 1608-A) which provided compensation for the capacitance effects within the system. The conductance cell was of the type which has been previously described[11] but a tube (2 cm in diameter and 5 cm in length) topped with a 50-ml bulb replaced the flask in the earlier designs. The bulb was added after it was found that the conductance of a solution with a constant concentration of electrolyte decreased asymptotically to a constant value as the volume was increased. Thereafter, all conductance measurements were obtained from solutions whose volumes were greater than that which was described above. In each experiment, a known quantity of the sample was placed in the cell which was immersed in an oil bath at 25.00 ± 0.05°. After the cell was connected to a buret filled with CH_3CN, the entire system was maintained under nitrogen which was saturated with CH_3CN. Appropriate quantities of the solvent were added to the cell from the buret and the conductance was measured after temperature equilibration. The approximate concentration range which was available under these conditions was from 1.0×10^{-3} to 4×10^{-4} equiv $l.^{-1}$. The procedure was checked by measuring the conductances of CH_3CN solutions of $[(n\text{-}C_4H_9)_4N]ClO_4$ for which excellent values of the equivalent conductivities are available.[12] A plot of $c\Lambda/1000$ against L, where c is the equivalent concentration, Λ is the literature value of the equivalent conductivity, and L is the experimentally determined conductance, was strictly linear. This experiment also afforded the cell constant (0.6577) from the reciprocal of the slope. It should be noted that the values of Λ were obtained by a least-squares fit of the literature data using the Onsager equation $\Lambda - \Lambda_0 = Bc^{1/2}$, where Λ_0 is the limiting conductivity at infinite dilution.

The theoretical slope of the Onsager equation was calculated[13] from the dielectric constant and viscosity of the solvent, the temperature, the observed value of Λ_0, the charges on the ions, and the single-ion conductivities. Since the single-ion conductivity of $(n\text{-}C_4H_9)_4N^+$ has been previously determined,[12] the value for each anion was obtained from $\lambda_-^0 = \Lambda_0 - \lambda_+^0$.

Results and Discussion

The Reactions. Reaction 1 at ambient conditions gives the desired orange $Mo_2Cl_9^{3-}$ ion as a salt of an alkylammonium cation in 47% yield. Initial experiments indicated that reaction 2, again at ambient conditions, gave green $Mo_2Cl_9^{2-}$ in high yield. Subsequent experiments, including the one described above, were based on *in situ* generation of $MoCl_6^-$ from equivalent quantities of $MoCl_5$ and Cl^-. Yields in excess of 98% were found. Since the products from reactions 1 and 2 are those which were expected, there is strong probability that the mechanisms of their formation are closely similar to if not identical with the proposed mechanism shown in reaction. The lower yield of $Mo_2Cl_9^{3-}$ compared to that of $Mo_2Cl_9^{2-}$ may reflect the increased electrostatic repulsion experienced by $Mo(CO)_4Cl_3^-$ in reacting with $MoCl_6^{2-}$ compared with $MoCl_6^-$.

Since it was found that $Mo_2Cl_9^{2-}$ is easily reduced to $Mo_2Cl_9^{3-}$ by Sn in CH_2Cl_2 or even by acetonitrile, reaction 4 was regarded with optimism. When $MoCl_6^{2-}$ and $Mo(CO)_4Cl_3^-$ were allowed to react in a 1:2 ratio, red $Mo_3Cl_{12}^{3-}$ was obtained. Since the reaction solution passed from its initial color through green, the color of $Mo_2Cl_9^{2-}$, and finally to red, reaction 3 was presumed to occur initially, followed by reaction 4. Complete support for this conjecture was obtained by allowing $Mo_2Cl_9^{2-}$ and $Mo(CO)_4Cl_3^-$ to react with the stoichiometry of reaction 4, whereupon $Mo_3Cl_{12}^{3-}$ was again obtained (93% yield). The proposed mechanism of the reaction suggests that $Mo_3Cl_{12}^{3-}$ should possess a linear trioctahedral structure.

Table I. Electronic Spectra

Compd	Absorptions,[a] $cm^{-1} \times 10^3$
$[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$	23.30 (573), 18.95 (638), 15.4 (33), 13.5 (25), 13.2 (23), ~12.8 (16)
$[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$	15.28 (265), 12.80 (171), 10.25 (163)
$[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$	23.80 (1292), 18.90 (810), 14.6 (50), 13.4 (52), 12.8 (85)

[a] Extinction coefficients are given in parentheses. All spectra were obtained in CH_2Cl_2 solutions.

The Products. $Mo_2Cl_9^{3-}$ and $Mo_2Cl_9^{2-}$. The crystal structure of $Cs_3Mo_2Cl_9$ has been reported previously.[14] The accessible portion of the electronic spectrum of that compound[15] compares favorably with that of $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$, which is given in Table I. The spectrum of the latter is also compared in Figure 1 to that of $MoCl_6^{3-}$, which has two bands corresponding to spin-allowed ligand field transitions between 18,000 and 24,000 cm^{-1} and two bands resulting from spin-forbidden transitions below 15,000 cm^{-1}. Since a remarkable correlation in band positions occurs between 18,000 and 24,000 cm^{-1}, it is clear that no marked sensitivity to symmetry differences or magnetic exchange occurs for these transitions. It would appear then that this band system is diagnostic of $Mo^{III}Cl_6$ units whether in mononuclear or polynuclear anions and it should be a useful tool for deductions of structure. Further support for this contention is provided by compounds of other metal atoms. A comparison of the spectra of $TiCl_6^{3-}$ and $Ti_2Cl_9^{3-}$, VCl_6 and $V_2Cl_9^{3-}$, or $CrCl_6^{3-}$ and $Cr_2Cl_9^{3-}$ has indicated that a similar relationship exists for all observed ligand transitions in which no spin change occurs.[16] Returning to the band systems which exist below 15,000 cm^{-1} for the Mo anions, no correlation in either band position or intensity occurs.

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(11) H. M. Daggett, E. J. Bair, and C. A. Kraus, *J. Amer. Chem. Soc.*, 73, 799 (1951).

(12) J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, 87, 2529 (1965).

(13) The method of calculation is given by S. Glasstone, "Introduction to Electrochemistry," Van Nostrand, New York, N. Y., 1949, p 90.

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(15) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, 8, 1226 (1969).

(16) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, 7, 1606 (1968).

Table II. Magnetic Moments at Various Temperatures

$[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$[a]	T, °K	302	230	204	154	86			
	μ(obsd), BM	1.29	1.10	0.84	0.43	0			
$[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$[a]	T, °K	300	271	236	188	159	140	119	95
	μ(obsd), BM	2.06	1.94	1.87	1.78	1.71	1.65	1.63	1.61
	μ(calcd), BM	2.06	1.98	1.88	1.76	1.71	1.65	1.63	1.61
$[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$[b]	T, °K	302	261	231	197	178	148	135	103
	μ(obsd), BM	2.02	1.81	1.69	1.57	1.52	1.45	1.42	1.34

[a] Magnetic moments were computed for the dinuclear unit. [b] Magnetic moments were computed for the trinuclear unit.

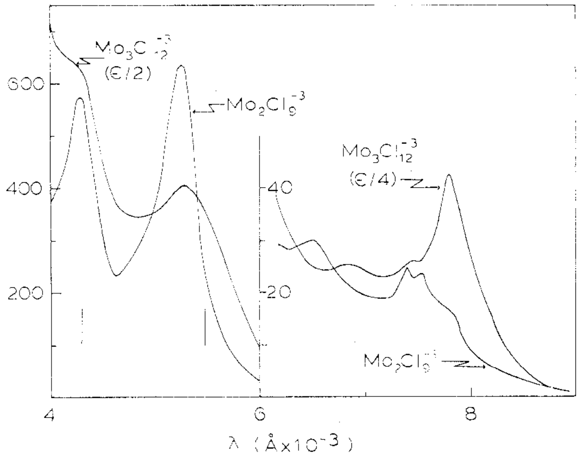

Figure 1. A comparison of the electronic spectra of $Mo_2Cl_9{}^{3-}$ and $Mo_3Cl_{12}{}^{3-}$ in CH_2Cl_2 solutions with that of $MoCl_6{}^{3-}$ (indicated by vertical lines) in aqueous solution. The latter, which also has a weak band at 9500 cm^{-1}, is taken from C. Furlani and O. Piovesano, *Mol. Phys.*, 9, 341 (1965).

Table III. Infrared Spectra

Compd	Absorption max (cm^{-1}) and assignment			
	ν(A_2'')	ν(E')	ν(A_2'')	ν(E')
$[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$	318 s	290 s	245 m	220 w
$[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$	345 s	305 s	250 m	225 w
	ν(A_{2u})	ν(E_u)	ν(A_{2u})	ν(E_u)
$[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$	335 s	295 s	244 s	227 s

While of interest in understanding the spectra of systems coupled by magnetic exchange, they can serve no useful purpose until a complete theoretical interpretation has been advanced.[17]

The paramagnetism found at room temperature for $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$ disappears completely at 86°K (Table II) which is consistent with the expected antiferromagnetic behavior.[15,18] A comparison of the limited data in Table II with the extensive data[18] for several salts of $Mo_2Cl_9{}^{3-}$ indicates that the paramagnetism of $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$ is very similar to that of the $[(C_2H_5)_4N]^+$ salt. Consequently, it is estimated that the total width of the manifold of spin states resulting from magnetic exchange is approximately 3000 cm^{-1}. This estimate is rendered doubly crude because it does not account for possible coupling throughout the crystalline lattice, a situation which must prevail with diamagnetic $Cs_3Mo_2Cl_9$[15] unless marked structural changes in the anion accompany substitution of one cation for another.

The infrared spectrum of $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$, listed in Table III, contains two principal bands at 318 and 290 cm^{-1} and weaker bands at 245 and 220 cm^{-1}. Similar bands, although shifted, also appear in the spectra of alkylammonium salts of $Cr_2Cl_9{}^{3-}$ and $W_2Cl_9{}^{3-}$. Using the results of a normal-coordinate analysis for each of these anions,[19] the strong absorptions in the spectrum of $Mo_2Cl_9{}^{3-}$ are assigned readily to modes of A_2'' and E' symmetries, respectively. Terminal Cl–Mo stretching motions are involved primarily in these modes. Similarly the absorptions at 245 and 220 cm^{-1} are assigned to A_2'' and E' modes arising principally from bridging Cl–Mo stretching motions. The infrared spectrum of $[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$ compares favorably to that of $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$ which suggests similar structures and which permits similar assignments (Table III). The general shift to higher wave number which is found in the spectrum of the oxidized anions is compatible with an increase in the average oxidation state of the metal atoms.

The electronic spectrum of $Mo_2Cl_9{}^{2-}$ (Table I) is not similar to that of $W_2Cl_9{}^{2-}$, which has bands (and extinction coefficients) at 13,530 (1040) and 17,200 (1700) cm^{-1} with a shoulder at about 25,600 cm^{-1}.[20] However, the spectra of $Mo_2Cl_9{}^{3-}$ and $W_2Cl_9{}^{3-}$ are also widely disparate.[10,15]

The temperature dependence of the magnetic moment of $[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$ is given in Table II. The overall variation clearly reflects a thermal equilibrium between at least two paramagnetic states with the ground state having a magnetic moment of about 1.6 BM. This value would be characteristic of a state with $S = {}^1/_2$ and $g < 2$. Analysis of the magnetic data was accomplished using the equation

$$\mu_{\text{obsd}} = [(\mu_0{}^2 + 2\mu_1{}^2e^{-x})/(1 + 2e^{-x})]^{1/2}$$

where x is $\Delta E/kT$; ΔE is the energy difference between the triplet and singlet states, while μ_1 and μ_0 are their respective magnetic moments. The calculated results given in Table II were obtained from $\mu_0 = 1.61$ BM, $\mu_1 = 3.60$ BM, and $\Delta E = 490$ cm^{-1}. Thus, the results are in full accord with the thermal equilibrium $S = {}^1/_2 \rightleftarrows S = {}^3/_2$. The simplest model for antiferromagnetic exchange within this system would predict a manifold of spin states with $S = {}^1/_2, {}^3/_2$, and ${}^5/_2$. The experimental results agree with this model providing only the $S = {}^1/_2$ and $S = {}^3/_2$ states, whose separation is $-2J$ (or ΔE as above), are appreciably populated throughout the temperature range which was examined. Since the separation of the $S = {}^3/_2$ and $S = {}^5/_2$ states would be $-4J$ or 980 cm^{-1}, population of the $S = {}^5/_2$ state would be negligible.

$Mo_3Cl_{12}{}^{3-}$. Conductivity measurements of $[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$ over a range of concentrations in CH_3CN have established that this salt is a 3:1 electrolyte. The value of the slope, B, obtained from the Onsager equation compares[21] very favorably to that obtained for $[(n\text{-}C_4H_9)]_3Mo_2Cl_9$ (Table IV). The observed values of the slopes obtained for both of these salts also compare fairly well with the calculated values (*cf.* Experimental Section) for a 3:1 electrolyte. The deviations between the observed and calculated values

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(17) Magnetic exchange between nearest neighbors can cause both enhancement of intensity and band shifts in transitions which are nominally forbidden by the spin selection rules for a single atom. This subject is reviewed by L. L. Lohr, *Coord. Chem. Rev.*, 8, 241 (1972).

(18) I. E. Grey and P. W. Smith, *Aust. J. Chem.*, 22, 121 (1969).

(19) R. J. Zeigler and W. M. Risen, *Inorg. Chem.*, 11, 2796 (1972).

(20) R. Saillant and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, 91, 2174 (1969).

(21) For a general discussion of the method see R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Table IV. Comparison of Conductivity Data

Compd	Λ_0, cm^2 ohm^{-1} equiv^{-1}	Slope, *B*	
		Obsd	Calcd
$[(n\text{-}C_4H_9)_4N]ClO_4$[a]	164	327	373
$[(n\text{-}C_4H_9)_4N]_2NiS_4C_4(CN)_4$[b]	190	790	770
$[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$	172	952	1110
$[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$	152	900	1020

[a] The limiting equivalent conductance, Λ_0, and the slope were obtained from the simple Onsager equation using the data in ref 12. [b] A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

probably should be ascribed to small amounts of ion pairing or unknown deficiencies in the theory. No detectable dissociation of the anions occurs since the electronic spectra of both salts in CH_3CN agree within experimental error with those obtained in CH_2Cl_2. Furthermore, the addition of excess $[(n\text{-}C_4H_9)_4N]Cl$ to the CH_3CN solutions did not produce shifts in the band positions.

The general mechanism proposed for reaction 4 suggests that $Mo_3Cl_{12}^{3-}$ should have a linear, trioctahedral structure containing two shared faces. Although $Mo_3Cl_{12}^{3-}$ and triangular $Re_3Cl_{12}^{3-}$ are both trinuclear anions of the same stoichiometry and charge, there is no reason that they should be isostructural since their d-orbital occupancies are unequal. Since $Re_3Cl_{12}^{3-}$ is believed to owe its stability to completely filled bonding orbitals and completely empty antibonding orbitals,[22] it follows that $Mo_3Cl_{12}^{3-}$ with three less electrons would suffer a considerable loss in stability if the triangular structure were adopted. Attempts to reduce $Mo_3Cl_{12}^{3-}$ with Sn metal in CH_2Cl_2 solutions containing $[(n\text{-}C_4H_9)_4N]Cl$ have been unsuccessful.

The infrared spectrum of $[(n\text{-}C_4H_9)_4N]_3Mo_3Cl_{12}$ is given in Table III. While differences do exist, certain similarities between spectra of $Mo_2Cl_9^{3-}$ and $Mo_3Cl_{12}^{3-}$ are apparent. In each case two strong bands are observed between 280 and 350 cm^{-1}, the region of the spectrum assigned to terminal Cl–Mo stretching frequencies. The spectrum of triangular $Re_3Cl_{12}^{3-}$ has two strong bands and two of medium intensity in the same region.[23] Assuming a linear, trioctahedral structure for $Mo_3Cl_{12}^{3-}$ (D_{3d}) stretching motions of the terminal Cl–Mo bonds would lead to two infrared-active modes of A_{2u} and E_u symmetries. Furthermore, these modes would be expected to occur at frequencies which more or less match those of the corresponding A_2'' and E' modes found for $Mo_2Cl_9^{3-}$. As shown in Table III, this is the case. Additional correlation also occurs at 244 and 227 cm^{-1}, but these bands are somewhat more difficult to assign since four infrared-active modes ($2\ A_{2u} + 2\ E_u$) are to be expected for stretching of the bridging Cl–Mo bonds. The assignments in Table III are based on the assumption of accidental degeneracy of the A_{2u} modes at 244 cm^{-1} and the E_u modes at 227 cm^{-1}. The high intensity of these absorptions is compatible with this assumption. Alternatively, however, it is completely possible that the two additional bands occur at lower wave numbers and were not observed. The limit of these measurements was about 200 cm^{-1}. Nevertheless, since the spectrum is totally dissimilar to triangular $Re_3Cl_{12}^{3-}$ and since it can be assigned adequately to a D_{3d} structure, it is assumed that $Mo_3Cl_{12}^{3-}$ has a linear, trioctahedral structure.

Further support for this conclusion rests on a comparison of the electronic spectra of $Mo_3Cl_{12}^{3-}$ between 18,000 and 24,000 cm^{-1} with those of $MoCl_6^{3-}$ and $Mo_2Cl_9^{3-}$ (Table I and Figure 1). Since band positions again remain remarkably invariant, it is clear that $Mo_3Cl_{12}^{3-}$ probably contains $Mo^{III}Cl_6$ units. This probable criterion is met with a linear, trioctahedral structure but would not be the case with a triangular structure.

Measurements of the magnetic moment from 100 to 300°K (Table II) indicated a definite temperature dependence, with the extrapolated value at 0° being approximately 1.1-1.2 BM. Since $Mo_3Cl_{12}^{3-}$ has an odd number of electrons, the low-temperature limit of the magnetic moment should correspond to a value which is appropriate for a state with $S = {}^1/_2$, assuming antiferromagnetic coupling within the trinuclear anion and no antiferromagnetic coupling throughout the crystalline lattice. The latter will cause a further reduction in the observed magnetic moment. This situation must prevail with this salt of $Mo_3Cl_{12}^{3-}$. No attempt to sort out the two types of coupling has been made. However, the magnetic moment of this compound in CH_2Cl_2 has been measured very recently by the nmr method[24] at 100 MHz. The magnetic moment varies from 2.5 BM at 291°K to 2.1 BM at 189°K which is the lowest temperature accesible with this solvent. These values, which are in considerable excess of those obtained with the solid compound within the same temperature range,[25] are in full accord with the thermal equilibrium $S = {}^1/_2 \rightleftarrows S = {}^3/_2$.

Conclusions

The general mechanism proposed in reaction 3 adequately accounts for the syntheses of the confacial, bioctahedral anions $Mo_2Cl_9^{3-}$ and $Mo_2Cl_9^{2-}$ by reactions 1 and 2. The extension of that mechanism has led to the synthesis of $Mo_3Cl_{12}^{3-}$ by reaction 4. All experimental data are in accord with a linear, trioctahedral structure for that anion. It remains to be seen whether larger polynuclear anions, such as $Mo_4Cl_{15}^{3-}$, can be obtained by these methods.

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Registry No. $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$, 52523-48-5; $[(n\text{-}Bu_4H_9)_4N]_2Mo_2Cl_9$, 52523-49-6; $[(n\text{-}B_4H_9)_4N]_3Mo_3Cl_{12}$, 52523-50-9; $[(n\text{-}C_3H_7)_4N]Mo(CO)_4Cl_3$, 52392-78-6; $[(n\text{-}C_3H_7)_4N]_2MoCl_6$, 52392-79-7; $MoCl_5$, 10241-05-1.

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(25) It has become increasingly clear that magnetic moments which have been obtained from solid salts of $M_2Cl_9^{3-}$ (M = Cr, Mo, and perhaps W) reflect varying and virtually unknown degrees of coupling throughout the lattice. To circumvent this difficulty, solution studies of these compounds are now in progress.