**Table II.** Magnetic Susceptibility Data for the Complexes

| Complex | Temp, °K | $10^6 \times \chi_M^{corr}$, cgsu | $\mu_e$, BM |
|---|---|---|---|
| $Cu^{II}$(pyrr–propanolamine) | 294 | 78 | 0.44 |
| | 265 | 44 | 0.34 |
| | 228 | 23 | 0.24 |
| | 189 | 16 | 0.20 |
| | 120 | 4 | 0.11 |
| $Cu^{II}$(pyrr–ethanolamine) | 293 | 1521 | 1.89 |
| | 265 | 1731 | 1.92 |
| | 228 | 2090 | 1.96 |
| | 189 | 2645 | 2.00 |
| | 152 | 3396 | 2.03 |
| | 120 | 4348 | 2.05 |
| | 78 | 6958 | 2.08 |
| $Cu^{II}$(pyrr–isopropanolamine) | 296 | 1370 | 1.80 |
| | 261 | 1628 | 1.84 |
| | 223 | 1856 | 1.82 |
| | 184 | 2408 | 1.88 |
| | 148 | 3056 | 1.90 |
| | 117 | 3915 | 1.91 |
| | 78 | 6163 | 1.96 |

angle to ferromagnetic coupling as represented in the work of Hatfield, *et al.*[5] The possibility exist that all four copper(II) ions could be ferromagnetically coupled in our complexes. The interpretation of tetramers is not without controversy even when the structure is known.[10,11] The use of the Bleaney and Bowers equation to approximate the true situation is fairly successful in the case of the weakly tetrameric acetylacetonemono(*o*-hydroxyanil)copper(II) complex. In this case this leads to $J$ values of +22 and +124 $cm^{-1}$ for Cu(pyrr–ethanolamine) and Cu(pyrr–isopropanolamine), respectively. The esr spectra of the tetramers are similar to the spectrum of dimeric Cu(pyrr–propanolamine). Cu(pyrr–isopropanolamine) has bands at 750, 1680, 3300, 5000, and 6560 G. Resolution is not as good in the case of Cu(pyrr–ethanolamine) but the spectrum is similar. There has been little work with the spin quintet; however a recent report is available.[12] The transitions observed in these spectra could be associated with the $M_s = 0$ and $\pm 1$ part of the spin quintet. The transitions associated with $M_s = \pm 2$ of the spin quintet, when seen, are usually at higher fields than employed with this spectrometer. The transition at 1680 G is assigned to $\Delta M_s = 2$.

In conclusion the important difference brought about by changes in the aminoalkoxide chain on the properties of Cu(acac–alcoholamine) complexes is retained in the Cu(pyrr–alcoholamine) complexes. The change to a five-member ring has affected these properties only in changes of bond angles. The effect of the bond angles on the magnitude of the interaction is consistent with the correlation recently refined by Hatfield, *et al.*,[5] in that the magnitude of $J$ increases as the bond angle decreases. The spectral changes are consistent with going from a square-planar to a distorted trigonal-bipyramidal arrangement of atoms around copper.

**Acknowledgments.** This research was supported by the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund. The authors wish to acknowledge preliminary discussions with Professor J. A. Bertrand at the start of this work.

**Registry No.** Cu(pyrr–propanolamine), 37820-94-3; Cu(pyrr–ethanolamine), 51380-64-4; Cu(pyrr–isopropanolamine), 51380-65-5.

---

(10) E. Sinn, *Inorg. Chem.*, 9, 2376 (1970).

(11) W. E. Hatfield and G. W. Inman, *Inorg. Chem.*, 9, 2379 (1970).

(12) M. Y. Okamura and B. M. Hoffman, *J. Chem. Phys.*, 51, 3128 (1969).

---

Contribution from the Department of Chemistry,
San Diego State University, San Diego, California 92115

# Kinetics of the Reduction of Hexaammineruthenium(III) Ion by Vanadous Ion

Charles A. Jacks and Larry E. Bennett*

*Received January 7, 1974* AIC40004R

The relative Marcus theory[1] has proven remarkably successful in rationalizing the rates of a substantial number of outer-sphere redox reactions between transition metal complexes.[2,3] For reactions satisfying the Marcus relationship, the rate ratio for the reactions of two reductants with a common oxidant should depend only on the self-exchange rates and the difference in reduction potentials for the reductant couples (if small $f$ terms are neglected).[2,4] Thus, reduction by $V(H_2O)_6{}^{2+}$ has been found to be 10–60 times faster than by $Cr(H_2O)_6{}^{2+}$ with a number of oxidants.[4] Heretofore, a notable exception appeared to be $Ru(NH_3)_6{}^{3+}$, with a reported rate of reaction with $V(H_2O)_6{}^{2+}$ ($80\ M^{-1}\ sec^{-1}$, $I = 0.176$ ($ClO_4^-$))[5] being slightly lower than with $Cr(H_2O)_6{}^{2+}$ ($99\ M^{-1}\ sec^{-1}$, $I = 0.079$ ($ClO_4^-$)).[6] In connection with other studies we have investigated the vanadium reaction and measured a rate constant which yields a ratio to the chromous reaction of 13, *i.e.*, within the range observed with other oxidants.

## Experimental Section

**Materials.** Solutions of vanadyl perchlorate were obtained by the reduction of reagent grade vanadium pentoxide at a platinum electrode in excess perchloric acid or from R. G. Linck, who prepared it by ion exchange from vanadyl sulfate (negative barium sulfate test). Reduction to $V(H_2O)_6{}^{2+}$ using either solution, under nitrogen or argon and either by electrolysis at a mercury cathode or with amalgamated zinc, gave indistinguishable kinetic results.

Initial concentrations of $V(H_2O)_6{}^{2+}$ were determined by spectrophotometry after reaction with excess $Co(NH_3)_5Cl^{2+}$ in perchloric acid or by assaying the remaining $CrO_4{}^{2-}$ in alkaline solution ($\epsilon_{372}$ 4815[7]) after oxidation to $VO_2{}^+$ with excess $HCrO_4{}^-$ in perchloric acid, with good agreement between the methods.

The $Ru(NH_3)_6Cl_3$ salt was obtained from Matthey Bishop, recrystallized by the Armor procedure,[8] and tested spectrophotometrically for purity.

**Kinetic Measurements.** The desired ionic strength was obtained by addition of standardized perchloric acid and dilution with doubly distilled water, making allowance for the production of $Zn^{2+}$ and the consumption of acid during reduction to $V(H_2O)_6{}^{2+}$. The initial acidities of $V(H_2O)_6{}^{2+}$ solutions ranged from 0.040 to 0.099 $M$ while those of $Ru(NH_3)_6{}^{3+}$ solutions ranged from 0.094 to 0.100 $M$. For runs at pH 3, $VO^{2+}$ was reduced to $V(H_2O)_6{}^{2+}$ in acidic solutions followed by adjustment with concentrated sodium hydroxide. The $Ru(NH_3)_6{}^{3+}$ solutions were made up initially at pH 3 using sodium perchlorate and perchloric acid. In all cases, chloride was present only from the ruthenium salt. Vanadium(II) solutions were used within 2 hr to minimize oxidation by perchlorate ion; results with the older solutions were identical with those obtained 15 min after complete reduction.

Syringe techniques were used to transfer deoxygenated (with chromous-washed nitrogen or argon) solutions to a Durrum-Gibson

---

(1) (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964), and references therein; (b) N. Sutin, *Annu. Rev. Nucl. Sci.*, 12, 285 (1962); (c) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966.

(2) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 303 (1972).

(3) L. E. Bennett, *Progr. Inorg. Chem.*, 18, 1 (1973).

(4) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 10, 2635 (1971).

(5) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, 86, 1686 (1964).

(6) J. F. Endicott and H. Taube, *Inorg. Chem.*, 4, 437 (1965).

(7) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 48, 414 (1952).

(8) J. N. Armor, Ph.D. Thesis, Stanford University, 1970; described by J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, 12, 639 (1973).

stopped-flow spectrophotometer equilibrated within 0.1° of the desired temperature. The increase in absorbance at 275 nm, a peak for both $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_6{}^{3+}$, was routinely monitored with indistinguishable results from that observed in one run at 395 nm, a shoulder for $Ru(NH_3)_6{}^{2+}$. Data were either recorded photographically from a storage oscilloscope or collected and analyzed using an interfaced Varian 620/i computer.

Small absorbance changes and decreased signal to noise ratios accompanied experiments at low ruthenium concentrations. In instances where scope and computer analyses gave differing results, acceptance was based on reproducibility among replicate runs and minimal deviations from linearity in the kinetic plots.

Several experiments with low concentrations (1-5 $\mu M$) of copper(II) perchlorate added to the $Ru(NH_3)_6{}^{3+}$ solutions resulted in no detectable differences in the observed rates. The use of platinum rather than stainless steel syringe needles similarly had no observable effect on measured rate constants.

## Results

Plots of ln $(A_t - A_\infty)$ *vs.* time were linear through at least 90% of reaction with $[V(H_2O)_6{}^{2+}]$ in tenfold or greater excess, yielding the pseudo-first-order constants which are plotted *vs.* $[V(H_2O)_6{}^{2+}]$ in Figure 1. Since second-order rate constants were independent of acidity over the range $1 < \mathrm{pH} < 3$, the slope of this plot corresponds to a rate coefficient, $k = (1.26 \pm 0.02) \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$, in the rate law

$$d[Ru(NH_3)_6{}^{2+}]/dt = k[Ru(NH_3)_6{}^{3+}][V(H_2O)_6{}^{2+}]$$

over this acidity range at $I = 0.10$ and 25°. Preliminary kinetic studies duplicating conditions previously reported ($[H^+] = 2 \times 10^{-3}\ M, I = 0.176$, perchlorate[5]) yielded rate constants of about $1.5 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$. Our rate constant increased somewhat with chloride concentration but a systematic study of such anion effects was not pursued.

Experiments over a range of temperatures from 12.6 to 44.6° yielded the data in Table I. A least-squares analysis of the corresponding linear Eyring plot yielded $\Delta H^\ddagger = 0.6 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -42 \pm 2$ eu.

## Discussion

Several factors operate in concert to exclude the possibility of ligand bridging in this reaction: (a) the rate of ligand exchange on either complex is substantially slower than the redox rate; (b) the ruthenium complex presents no binding site; (c) the water ligands on vanadium are expected to be very inefficient bridging ligands;[4] and (d) the activation parameters are not typical of those characteristic of inner-sphere reactions of $V(H_2O)_6{}^{2+}$.[2,3,9-12] We conclude that the reaction proceeds unambiguously by an outer-sphere mechanism.

In an attempt to evaluate the activation parameters we have derived the following relationships from the relative Marcus theory[1]

$$\Delta S^\ddagger{}_{\mathrm{VRu}} = f(\Delta S^\circ{}_{\mathrm{VRu}} + \Delta S^\ddagger{}_{\mathrm{VV}} + \Delta S^\ddagger{}_{\mathrm{RuRu}})$$

$$\Delta H^\ddagger{}_{\mathrm{VRu}} = f(\Delta H^\circ{}_{\mathrm{VRu}} + \Delta H^\ddagger{}_{\mathrm{VV}} + \Delta H^\ddagger{}_{\mathrm{RuRu}})$$

where $f$ is nominally ~0.5. While these relationships have not yet been subjected to extensive experimental tests, the apparent applicability of the corresponding free energy relationship[1-3] suggests their provisional consideration.

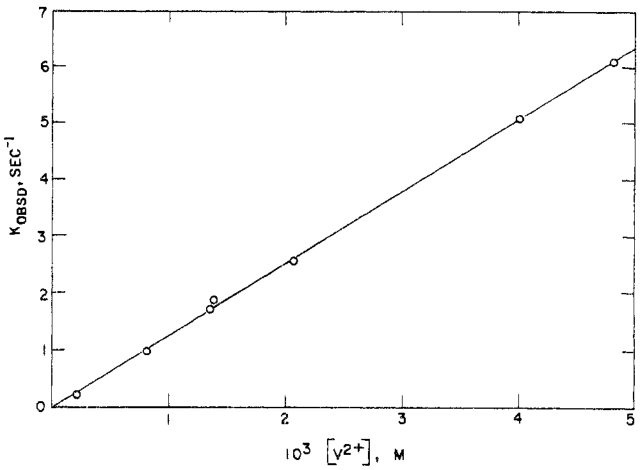

**Figure 1.** Plot of $k_{\mathrm{obsd}}$ *vs.* vanadous ion concentration at 25.0°, $I$ = 0.10. Least-squares line represents the equation $k_{\mathrm{obsd}} = 1.26 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}\ [V^{2+}]$.

**Table I.** Temperature Dependence of the $V(H_2O)_6{}^{2+}$-$Ru(NH_3)_6{}^{3+}$ Reaction[a]

| Temp, °C | $10^{-3}k$, $M^{-1}$ sec$^{-1}$ | Temp, °C | $10^{-3}k$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| 12.6 | 1.16 | 35.3 | 1.34 |
| 25.0 | 1.26 | 40.0 | 1.41 |
| 31.8 | 1.31 | 44.6 | 1.46 |

[a] $\Delta H^\ddagger = 0.6 \pm 0.1$ kcal/mol. $\Delta S^\ddagger = -42 \pm 2$ eu.

Absolute entropy changes of −47.5 eu for conversion of $V(H_2O)_6{}^{2+}$ to $V(H_2O)_6{}^{3+}$ and 4.1 ± 1.9 eu for conversion of $Ru(NH_3)_6{}^{3+}$ to $Ru(NH_3)_6{}^{2+}$ (each on a scale where $S^\circ{}_{H^+}$ = 5.5 eu and $S^\circ{}_{H_2}$ = 31.2 eu) have been recorded.[13-15] To the extent that these values are approximately applicable under our conditions, a contribution of $f\Delta S^\circ{}_{\mathrm{VRu}} \approx -43.4/2$ to $\Delta S^\ddagger{}_{\mathrm{VRu}}$ can be estimated. This contribution arises from an adjustment of the nuclear coordinates of the surrounding media, as well as the first coordination sphere, to an electronic distribution in the reacting species such that the charges on the $ML_6$ species are intermediate between 2+ and 3+.[1a] The entropy differences suggest that the increased vibration-orientation polarization of the medium around vanadium in the activated complex is not compensated for by the smaller decrease in polarization around ruthenium.

The use of $\Delta S^\ddagger{}_{\mathrm{RuRu}} = -11$ eu[16] and $\Delta S^\ddagger{}_{\mathrm{VV}} = -24.9$ eu[17] in the above equations would include ~13 units of rotational and translational entropy loss which must necessarily accompany formation of the $V(H_2O)_6{}^{2+}$-$Ru(NH_3)_6{}^{3+}$ collision complex.[1,3] However, while the ruthenium value applies to an outer-sphere reaction and comparable media, an inner-sphere mechanism has not been excluded for the vanadium self-exchange which was studied at $I = 2.0\ M$. Thus, on the order of −10 eu in $\Delta S^\ddagger{}_{\mathrm{VRu}}$ might remain unaccounted for in terms of molecular events which could be related to an empirically uniform[18,19] but poorly understood decrease in partial

---

(9) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968).

(10) N. Sutin, *Accounts Chem. Res.*, 1, 225 (1968).

(11) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, 51, 289 (1969).

(12) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, 7, 250, 2678 (1968).

(13) (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 68, 228 (1964); (b) T. W. Newton and S. W. Rabideau, *ibid.*, 63, 365 (1959).

(14) D. K. Lavallee, C. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 12, 570 (1973). The partial entropy change observed here for the ruthenium couple is surprisingly less negative than that recorded for the analogous cobalt couple,[15a] perhaps in part because of anomalies with ruthenium, or of media differences, as is also the case with our reaction, from the standard entropy changes normally recorded for $I = 0$.[15b]

(15) (a) P. A. Rock, *Inorg. Chem.*, 7, 837 (1968); (b) J. J. Kim and P. A. Rock, *ibid.*, 8, 563 (1969).

(16) T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

(17) K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 80, 5921 (1958).

(18) T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, No. 71, 268 (1967).

(19) R. G. Linck in "Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971.

molar entropy on forming highly charged activated complexes.

Values for $\Delta H^{\ddagger}_{\mathrm{RuRu}} = 10.3$ kcal/mol and $\Delta H^{\ddagger}_{\mathrm{VV}} = E_a - RT = 12.6$ kcal/mol have been reported.[16,17] (While previous reservations regarding the vanadium value remain in effect, the outer-sphere $\Delta H^{\ddagger}_{\mathrm{VV}}$ at $I = 0.10$ is not likely to be greatly different.) A $\Delta H^{\circ}_{\mathrm{VRu}}$ of $-20.6$ kcal/mol can be estimated from reduction potentials given below and $\Delta S^{\circ}_{\mathrm{VRu}}$, again assuming applicability to our conditions. The low $\Delta H^{\ddagger}_{\mathrm{VRu}}$ appears understandable then in terms of a ~10-kcal combined self-exchange contribution which is compensated by an almost equal counter contribution from $\Delta H^{\circ}_{\mathrm{VRu}}$. In terms of the absolute Marcus theory[1-3] the molecular source would appear to reside primarily in a first-coordination-sphere (or outer-sphere) rearrangement barrier which has been diminished relative to the self-exchange reactions, as a result of the ground-state difference in redox orbital energies which is also reflected in the favorable net potential. (This represents an extension of previous analyses.)[20,21]

Finally, we have calculated an unambiguously outer-sphere, *apparent* self-exchange rate for the vanadium couple under our conditions ($I = 0.10$) from[1,3]

$$\log k_{\mathrm{VV}} = 2 \log k_{\mathrm{VRu}} - \log k_{\mathrm{RuRu}} - \frac{\Delta E^{\circ}}{0.059} - \log f$$

where $\log k_{\mathrm{RuRu}}$ and $E^{\circ}_{1/2}(\mathrm{Ru})$ are estimated at $I = 0.10$ as 3.5 and 0.078 V, respectively, from data at other ionic strengths;[19] $E^{\circ}_{1/2} = -0.255$ V for the vanadium couple;[22] and $\log f = -0.4$. The resulting value for $k_{\mathrm{VV}}$ of $3 \times 10^{-3}$ $M^{-1}$ sec$^{-1}$ ($1.1 \times 10^{-3}$ if the $\log f$ term is ignored) seems more appropriate for use in the Marcus theory context at $I = 0.10$ than the value of $1 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$ obtained at $I = 2.0$.[19]

**Acknowledgments.** Support for this research from the National Science Foundation (Grant GP-12223) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with appreciation.

**Registry No.** $V(H_2O)_6^{2+}$, 15696-18-1; $Ru(NH_3)_6^{3+}$, 18943-33-4.

---

(20) (a) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970; (b) *Pure Appl. Chem.*, 24, 289 (1970).

(21) A. Anderson and N. A. Bonner, *J. Amer. Chem. Soc.*, 76, 3826 (1954).

(22) G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta*, 36, 1089 (1953).

---

Contribution No. 2374 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

## Alternate Routes to the $Mo_2Cl_9^{3-}$ and $Mo_2Br_9^{3-}$ Anions

W. H. Delphin and R. A. D. Wentworth*

*Received January 11, 1974* AIC40021G

The preparation of the anion $Mo_2X_9^{3-}$ (X = Cl or Br) has been achieved by several different routes: (1) the reaction of $MoX_3$ and CsX in a sealed tube at about 800°;[1] (2) the electrolytic oxidation of $Mo_2Cl_8^{3-}$ in aqueous HCl solutions;[2] (3) the addition of alkylammonium or alkali metal halides to aqueous HX solutions of Mo(III);[3] and (4) the oxidative displacement of CO from $Mo(CO)_4Cl_3^-$ by $MoCl_6^{2-}$ in $CH_2Cl_2$ solutions.[4] The last reaction, which was designed specifically to achieve the desired synthesis, is typified by a change in the oxidation state of each reacting metal atom such that the oxidation states of the metal atoms in the product are identical, *i.e.*, +3. Other examples of this kind of reaction are the preparations of $WCl_4$ and $WCl_5$ by the reaction of stoichiometric proportions of $WCl_6$ and $W(CO)_6$ and $MoCl_4$ from $MoCl_5$ and $Mo(CO)_6$.[5] We have continued to investigate reactions such as these in order to determine their utility in the preparation of polynuclear halomolybdates. We report in this paper the following successful reactions conducted in $CH_2Cl_2$ solutions.

$$6MoCl_5 + 4Mo(CO)_5Cl^- + 11Cl^- \rightarrow 5Mo_2Cl_9^{3-} + 20CO \qquad (1)$$

$$3MoBr_4 + Mo(CO)_5Br^- + 5Br^- \rightarrow 2Mo_2Br_9^{3-} + 5CO \qquad (2)$$

Reaction 1 gave $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ in high yield (83%), but difficulties encountered in working up an alkylammonium salt of $Mo_2Br_9^{3-}$ probably account, at least in part, for the lower yield (54%) obtained from reaction 2.

These reactions demonstrate the scope and utility of the method since the expected products could be obtained starting with either Mo(IV) or Mo(V) halides and suitable adjustment of the stoichiometry of the reactants. These oxidation-reduction reactions are undoubtedly driven by the release of CO. However, each probably proceeds through a complex series of intermediates and no mechanistic interpretation will be attempted. It is noteworthy that attempts to produce $MoCl_6^{3-}$ by increasing the proportion of $Cl^-$ in reaction 1 failed since the product was again $Mo_2Cl_9^{3-}$.

### Experimental Section

**Reagents and Procedures.** Samples of $MoCl_5$ were prepared *by halogenation of the metal.*[6] *The preparation of* $MoBr_4$ *was* accomplished by exhaustive bromination (2 hr at room temperature) of $Mo(CO)_6$ in the absence of a solvent.[7] Alkylammonium salts of $Mo(CO)_5X^-$ (X = Cl or Br) were prepared by the reaction of the halide with $Mo(CO)_6$.[8] 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.** $\mathbf{[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9}$. A solution of $[(n\text{-}C_4H_9)_4N]Mo(CO)_5Cl$ (1.67 mmol) and $[(n\text{-}C_4H_9)_4N]Cl$ (4.76 mmol) was prepared in $CH_2Cl_2$ (~40 ml). Solid $MoCl_5$ (2.51 mmol) was then added to this solution. After 38 hr evolution of CO had ceased with a total of 6.00 mmol (72%) measured. The solution was filtered yielding $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ (0.68 mmol). *Anal.* Calcd for $C_{48}H_{108}N_3Mo_2Cl_9$: Mo, 15.5; Cl, 25.8. Found: Mo, 15.8; Cl, 25.6. The filtrate was diluted to 50.0 ml and aliquots of this solution were used for quantitative spectroscopic analyses. An infrared spectrum indicated that the only CO-containing species was $Mo(CO)_6$ (0.28 mmol). The only chromophoric species evident in the visible spectrum was $Mo_2Cl_9^{3-}$ (1.06 mmol). The total yield of $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ was 83% (1.74 mmol).

$\mathbf{[(n\text{-}C_4H_9)_4N]_3Mo_2Br_9}$. A freshly prepared sample of $MoBr_4$

---

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

(2) M. J. Bennet, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, 8, 1060 (1969).

(3) (a) P. W. Smith, Ph.D. Thesis, University College, London, 1962; (b) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc. A*, 57 (1969).

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

(5) R. E. McCarley, private communication.

(6) R. Colton and I. B. Tomkins, *Aust. J. Chem.*, 19, 1143 (1966).

(7) W. Hieber and E. Romberg, *Z. Anorg. Allg. Chem.*, 221, 321 (1935).

(8) E. W. Abel, I. S. Butler, and J. E. Reid, *J. Chem. Soc.*, 2068 (1963).

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