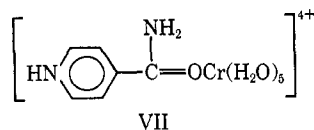As already noted, the rate of aquation of the isoamide 5+ species is similar to that observed for

VII

For the latter complex at 1 M H$^+$ the dominant path appears to be independent of (H$^+$), and the specific rate by this path[1] at 25° is 6.5×10^{-5} sec^{-1}, compared to 1.02×10^{-5} sec^{-1} for the isoamide 5+ species under the same conditions. The values of $\Delta H^{\ddagger}$ do, however, differ significantly; they are 21.9 ± 0.5 kcal/mol for the former complex and 27 ± 2 kcal/mol for the latter, and some influence on the rate of aquation of the group on the pyridine nitrogen has to be admitted.[28] This is borne out by the present studies on the rate of aquation of the isoamide 6+ species. Again at 1 M H$^+$, but at 24° rather than 25°, the specific rate is 2.8×10^{-5} sec^{-1}. The effects are in the direction of the expected diminishing inductive effects for H$^+$, Ru(III), and Ru(II) but, in view of the differences in $\Delta H^{\ddagger}$ registered, are not entirely to be disposed of quite this simply.

(28) The ionic strengths do differ in the studies done on VII, and those described in this paper. They are 1.00 and 0.100, respectively, but since the activated complexes have the same charges as do the reactants, it is unlikely that the differences can be ascribed to ionic medium effects.

A Nuclear Magnetic Resonance Line-Broadening Study of the Azidopentaaquochromium(III) Ion in Aqueous Perchloric Acid

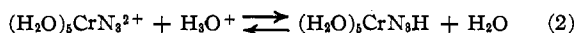BY R. J. BALAHURA AND R. B. JORDAN*

The solvent proton nmr line broadening caused by (H$_2$O)$_5$CrN$_3$$^{2+}$ has been studied in aqueous perchloric acid at 3.0 m ionic strength. Studies were carried out at 0, 20, and 36° with varying HClO$_4$ concentrations and between 0 and 70° at 0.082 m HClO$_4$. No evidence was found for proton exchange from coordinated N$_3$H. The exchange of coordinated water protons by acid-catalyzed and uncatalyzed paths has been observed. The general behavior is thus similar to that observed previously for Cr(OH$_2$)$_6$$^{3+}$. However the (H$_2$O)$_5CrN_3$$^{2+}$ ion has a short electron spin relaxation time. As a result, when chemical exchange is fast, the line broadening is controlled by the inner-sphere relaxation time.

The rate laws for hydrolysis of azide complexes of chromium(III),[1] cobalt(III),[2] and iron(III)[3] have been found to contain a term first order in hydrogen ion. This term has been associated with the reaction

$$MN_3H + H_2O \longrightarrow MOH_2 + HN_3 \qquad (1)$$

The original intention of this work was to measure the rate and possibly the equilibrium constant for the reaction

$$(H_2O)_5CrN_3{}^{2+} + H_3O^+ \rightleftharpoons (H_2O)_5CrN_3H + H_2O \qquad (2)$$

In principle the results could be used to assess the basicity of the coordinated azide ion and to obtain a specific rate constant for reaction 1.

Consideration of the previous work of Swift, *et al.*,[4,5] on Cr(OH$_2$)$_6$$^{3+}$ indicated that proton exchange from the more basic azide ligand might be measurable. Initial results were qualitatively consistent with proton exchange by reaction 2 with partial saturation of the equilibrium in 3 M HClO$_4$. However more detailed analysis and temperature studies have shown that only coordinated water proton exchange causes the observed nmr line broadening. The kinetic parameters for water proton exchange have been determined and are compared to similar results for other hydrated metal ions.

A rather unexpected feature of the (H$_2$O)$_5$CrN$_3$$^{2+}$ system is that the electron spin relaxation time is too short to permit observation of an epr signal for the complex ion in solution. As a consequence the transverse relaxation time of the coordinated water protons is unexpectedly long and inner-sphere relaxation becomes a controlling factor for the observed line broadening under certain conditions.

Experimental Section

Solutions of azidopentaaquochromium(III) perchlorate were prepared by the reaction of chromium(III) perchlorate and sodium azide in aqueous solution. Solutions of ((H$_2$O)$_5$CrN$_3$)(ClO$_4$)$_2$ were obtained by ion-exchange separation of the reaction mixture as described by Swaddle and King.[1] The product was identified by comparison of the visible spectrum to that

* To whom correspondence should be addressed.
(1) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).
(2) G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963).
(3) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).
(4) T. J. Swift and T. A. Stephenson, *ibid.*, **5**, 1100 (1966).
(5) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Amer. Chem. Soc.*, **89**, 1611 (1967).

reported by Swaddle and King.[1] The perchloric acid concentration in the solutions of $((H_2O)_5CrN_3)(ClO_4)_2$ was determined by potentiometric titration with sodium hydroxide.

The nmr samples were prepared by adding perchloric acid, water, and chromium complex solution to the appropriate amount of LiClO₄ to give a final ionic strength of 3.0 m. The final solution was weighed in order to determine the molality of the species. In a few samples with $[H^+] > 3\ m$ the ionic strength is given by the HClO₄ concentration.

In the concentration study samples were prepared and stored at 0° for not more than 1 hr before running the nmr spectra. The spectra of any one sample were run at 0, 20, and 36° in turn. In order to check the method and minimize hydrolysis effects at high acid concentrations fresh samples were prepared and run immediately at 20° and also at 36°. Results indicated that hydrolysis was not a problem.

The samples for the temperature study were prepared and pre-equilibrated in a water bath at the required temperature before running the spectrum. The nmr spectrometer probe was also at the required temperature. A second spectrum recorded about 20 min after the first showed no significant change for temperatures up to 50°. At 60° the second spectrum had a 5% (3 Hz) greater full width at half-height. At 70° several spectra were recorded and the value of $\Delta\nu_{obsd}$ was determined by extrapolation to zero time.

All nmr spectra were recorded on a Varian A 56/60 spectrometer equipped with the standard nitrogen gas temperature control system.

Results

The nmr line broadening is related to the solvent proton transverse relaxation time (T_{2p}) by

$$(T_{2p})^{-1} = \pi(\Delta\nu_{obsd} - \Delta\nu_{sol}) \qquad (3)$$

where $\Delta\nu_{obsd}$ is the full width at half-height of the solvent resonance in the presence of the paramagnetic ion and $\Delta\nu_{sol}$ is the line width in the solvent without the paramagnetic ion.

The variation of the concentration-normalized $(T_{2p})^{-1}$ with hydrogen ion molality at 0 and 36° is shown in Figure 1. Similar results have been obtained at 20°.
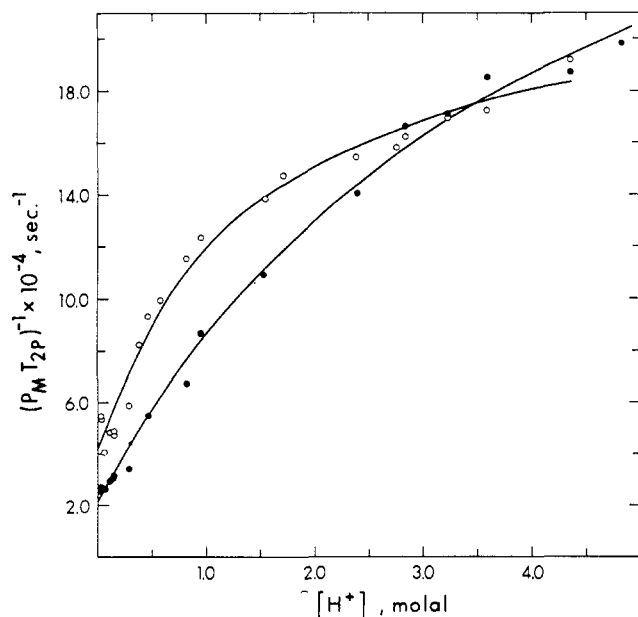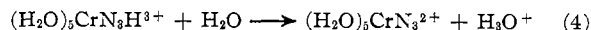

Figure 1.—Variation of $(P_M T_{2p})^{-1}$ with hydrogen ion molality at 36° (O) and 0° (●). Lines are final best fit curves as described in text.

Qualitatively the leveling off of the line broadening at high acid concentrations could be attributed to saturation of the equilibrium represented by eq 2. Then the chromium species is largely in the form of $(H_2O)_5Cr$-N_3H^{3+} and the limiting broadening at high acid would give the rate constant for the reaction

$$(H_2O)_5CrN_3H^{3+} + H_2O \longrightarrow (H_2O)_5CrN_3^{2+} + H_3O^+ \qquad (4)$$
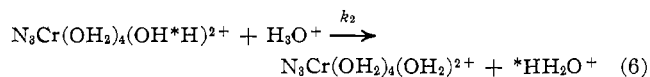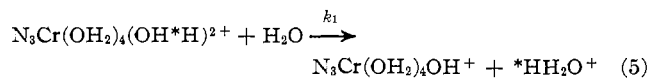
However it is obvious from Figure 1 that this limiting rate must be larger at 0° than at 36° to explain the data. Thus the rate constant would appear to have a negative activation enthalpy of about -4 kcal mol⁻¹.

It was also found that the line-broadening variation with hydrogen ion concentration gave an acid dissociation constant, for $(H_2O)_5CrN_3H^{3+}$, of 1.99 m at 36°. The value increases to 4.35 m at 20°. These results would require that nonlinearity should have been observed in the dependence of the hydrolysis rate constant on $[H^+]$ at acid concentrations of ~0.5 M at 30°. The effect should be apparent at even lower acidity at 50 and 70°. In fact no such nonlinearity appears in the data of Swaddle and King.[1]

It was concluded from the preceding arguments that proton exchange from coordinated hydrazoic acid does not explain the observed line broadening.

A consistent and reasonable interpretation of the results is possible in terms of proton exchange from coordinated water molecules. The following exchange reactions have been considered

$$N_3Cr(OH_2)_4(OH^*H)^{2+} + H_2O \xrightarrow{k_1}$$
$$N_3Cr(OH_2)_4OH^+ + {}^*HH_2O^+ \qquad (5)$$

$$N_3Cr(OH_2)_4(OH^*H)^{2+} + H_3O^+ \xrightarrow{k_2}$$
$$N_3Cr(OH_2)_4(OH_2)^{2+} + {}^*HH_2O^+ \qquad (6)$$

Then

$$(\tau_M)^{-1} = k_1 + k_2[H_3O^+] \qquad (7)$$

Then the exchange lifetime of a proton in the coordination sphere of the paramagnetic ion is given by

$$(\tau_M)^{-1} = k_1 + k_2[H^+] \qquad (8)$$

The nmr line broadening may be described by[6]

$$(P_M T_{2p})^{-1} = (T_{20})^{-1} + (\tau_M + T_{2M})^{-1} \qquad (9)$$

where T_{2M} is the transverse relaxation time of the protons in the coordination sphere of the metal ion, T_{20} is the outer-sphere contribution to the observed line broadening, and P_M is the ratio of the concentration of exchanging protons on the metal ion to the concentration of protons in the free solvent. It has been assumed that all 10 coordinated water protons are exchanging, so that $P_M = 10[Cr(III)][2[H_2O] + H^+]^{-1}$; however, if only trans or only cis water protons are exchanging,[7] the factor of 10 would be replaced by 2 or 8, respectively.

(6) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 185.

The temperature dependence of the parameters in eq 8 and 9 have been assumed to have the form

$$k_1 = C_1 T \exp(-\Delta H_1^*/RT)$$

$$k_2 = C_2 T \exp(-\Delta H_2^*/RT) \quad (10)$$

$$(T_{20})^{-1} = C_0 \exp(E_0/RT)$$

$$(T_{2M})^{-1} = C_M \exp(E_M/RT)$$

The $(T_{20})^{-1}$ term has been determined from a series of trial least-squares fits of the temperature study results (Figure 2). It was assumed that the k_2 contribu-
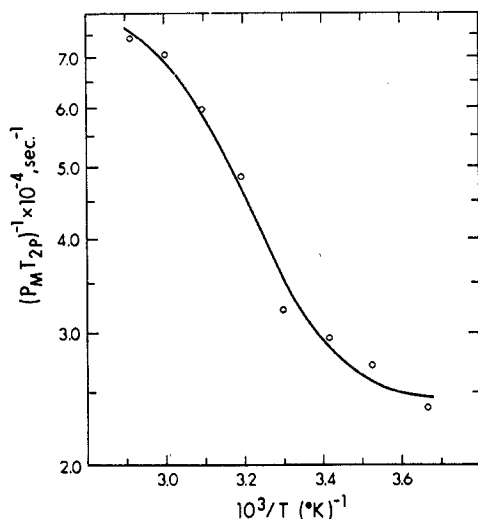

Figure 2.—Variation of $(P_M T_{2p})^{-1}$ with temperature; $[H^+]$ = 0.082 m. Smooth line is the final best fit curve to the data.

tion was negligible since the study was at low acid[8] (0.082 m) and that $E_0 = E_M = 2.20$ kcal mol^{-1}. Then various fixed values of C_M were chosen to observe their effect on the fit and the value of C_0. A generally reasonable fit was obtained with $C_M = 5 \times 10^3$ sec^{-1} which gave $C_0 = 3.35 \times 10^2$ sec^{-1}. Then at 0, 26, and 36°, $(T_{20})^{-1}$ is 1.85×10^3, 1.40×10^3, and 1.15×10^3, respectively.

The concentration study data were treated by subtracting the appropriate value of $(T_{20})^{-1}$ from the observed $(T_{2p}P_M)^{-1}$ and fitting the resultant value by a least-squares method to the extreme right-hand term in eq 9 to obtain T_{2M}, k_1, and k_2 at 0, 20, and 36°. The results are shown in Table I along with the appropriate temperature parameters as determined from the plots shown in Figure 3. The good linearity of the plots in Figure 3 is partly fortuitous but it is gratifying that no abnormalities appear.

In order to determine if the concentration and temperature studies are consistent, the latter results were refitted using the values in Table I for k_1 and k_2 and allowing C_0, C_M, and $E_0 = E_M$ to vary. The best fit parameters are $C_0 = 7.86$ (6.65–9.07) $\times$ 10^2 sec^{-1}, $C_M = 5.99$ (5.86–7.86) $\times$ 10^3 sec^{-1}, and $E_0 = E_M$, 1.82 (1.67–1.88) kcal mol^{-1}.

(8) This assumption is not completely justified but has little effect on the analysis because $(\tau_M)^{-1}$ is smaller than $(T_{20})^{-1}$ at low temperature in any case.

TABLE I
PARAMETERS FROM LEAST-SQUARES FITTING OF THE CONCENTRATION STUDY[a,b]

Temp, °C	k_1, sec^{-1}	k_2, m^{-1} sec^{-1}	$(T_{2M})^{-1}$, sec^{-1}
0	2.66 × 10^3	7.96 × 10^4	3.52 × 10^5
20	1.20 × 10^4	1.24 × 10^5	2.72 × 10^5
36	3.35 × 10^4	1.77 × 10^5	2.18 × 10^5
ΔH^*, kcal mol^{-1}	11.7	3.2	
ΔS^*, eu	3	−24	
E_M, kcal mol^{-1}			2.3
C_M, sec^{-1}			5.46 × 10^3

[a] The temperature dependences of k_1, k_2, and $(T_{2M})^{-1}$ are plotted in Figure 3. [b] Values are calculated assuming all 10 coordinated water protons are exchanging.
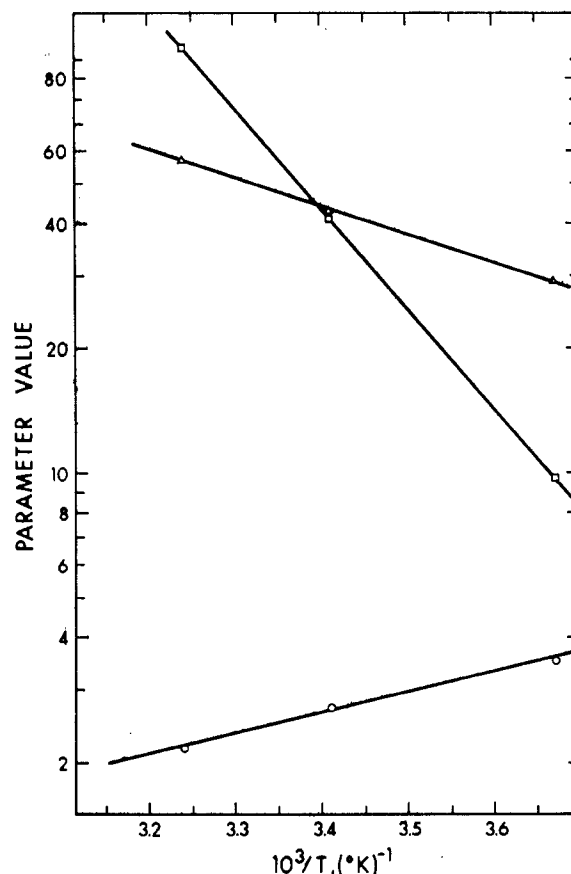

Figure 3.—Temperature dependence of the parameters from the concentration study: □, k_1/T, sec^{-1} deg^{-1}; △, $10^{-1} \times k_2/T$, m^{-1} sec^{-1} deg^{-1}; O, $10^{-5} \times (T_{2M})^{-1}$, sec^{-1}. Values obtained by fitting data at 0, 20, and 36° as described in text.

The values of $(T_{2M})^{-1}$ at 0, 20, and 36° calculated from this best fit are about a factor of 2 smaller than those from the concentration study but the errors are large and the 95% confidence limits almost overlap. This disagreement is probably not significant however since the $(T_{2M})^{-1}$ parameters from the temperature study depend on the bending at high temperature in Figure 2 and a rather long extrapolation to 36° is required.

The $(T_{20})^{-1}$ values used originally are about 20% lower than those calculated at 0, 20, and 36° from the refitted temperature data. However the original values

are well within 95% confidence limits of the new values. If a significant disagreement had been observed at this point, the whole procedure could be repeated to give self-consistency.

Conclusions

The results of this study indicate that the nmr line broadening caused by the $(H_2O)_5CrN_3^{2+}$ ion is largely associated with water proton exchange. The failure to detect exchange from coordinated N_3H may be due to the high acidity of the coordinated acid or to a long relaxation time for the proton of coordinated N_3H. Therefore it is not possible to establish even any limits for the acidity of coordinated hydrazoic acid.

The rate constants and ΔH^* values in Table I show the expected variation, if only charge effects are considered, when compared to rates for $Cr(OH_2)_6^{3+}$ obtained by Swift, *et al.*,[4,5] and in these laboratories[9] using nmr line broadening, and by Rich, Cole, and Eyring[10] using the dissociation field relaxation method. It should be noted that a recent T_1 nmr study of Melton and Pollak[11] has yielded quite different exchange rate parameters.

(9) R. J. Balahura, unpublished results, indicated that $k_1 = 1.32 \times 10^5$ sec^{-1} at 33°, for $Cr(OH_2)_6^{3+}$ in perchloric acid, in good agreement with results from ref 5.

(10) L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, **73**, 713 (1969).

(11) B. F. Melton and V. L. Pollak, *ibid.*, **73**, 3669 (1969).

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Molybdenum(II)–Isocyanide Complexes

BY FLAVIO BONATI* AND GIOVANNI MINGHETTI

MoL_5X_2 (L = isocyanide, X = Cl, Br) are prepared from $Mo(CO)_4X_2$ and the ligand. They are characterized through infrared and nuclear magnetic resonance spectra and conductance data. The presence of a possible seven-coordinate molybdenum(II) is suggested.

While zerovalent molybdenum–isocyanide complexes, *e.g.*, $Mo(CO)_{6-n}L_n$ ($n = 1, 2, 3, 6$)[1–5] and $Mo(NO)_2L_2$-Cl_2[6] (L = isocyanide), are well known, molybdenum(IV) compounds are dubious, and only three complexes are known[7] where molybdenum has the formal oxidation state +2: these complexes contain a π-C_5H_5 ring. The recent preparation of $Mo(CO)_4X_2$ compounds[8] prompted us to try their reaction with isocyanide and a novel type of molybdenum(II) compounds, MoL_5X_2, is reported here.

Experimental Section

Isocyanides were prepared according to Ugi.[9] Molybdenum tetracarbonyl halides were prepared according to Colton[8] and used immediately.

Molybdenum analysis[10] was carried out gravimetrically as $MoO_2(oxinate)_2$, after destroying the sample with H_2SO_4–KNO_3; halogen analysis, as silver halide, after decomposing the sample in a melt of KNO_3–Na_2CO_3.

* To whom correspondence should be addressed.

(1) L. Malatesta, A. Sacco, and M. Gabaglio, *Gazz. Chim. Ital.*, **82**, 548 (1952).

(2) W. Hieber and D. von Pigenot, *Chem. Ber.*, **89**, 616 (1956).

(3) G. Cetini, O. Gambino, and M. Castiglioni, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Natur.*, **97**, 1131 (1963).

(4) F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961); F. Bonati and G. Minghetti, *J. Organometal. Chem.*, **22**, 195 (1970).

(5) H. D. Murdoch and R. Henzi, *ibid.*, **5**, 166 (1966).

(6) F. Canziani, U. Sartorelli, and F. Cariati, *Ann. Chim. (Rome)*, **54**, 1354 (1964).

(7) C. E. Coffey, *J. Inorg. Nucl. Chem.*, **25**, 179 (1963); K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organometal. Chem.*, **1**, 51 (1963).

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

(9) I. Ugi and R. Meyer, *Org. Syn.*, **41**, 101 (1964).

(10) R. G. W. Hollingshead, "Oxine and Its Derivatives," Butterworths, London, 1954.

Diamagnetism in the solid state was checked with a Gouy balance. The ¹H nmr spectra were recorded by Dr. G. Bonora on a Perkin-Elmer R-10 instrument at 60.0 Mc; the solvent was always $CDCl_3$, with tetramethylsilane as internal standard. Molecular weight determinations were carried out on a Mechrolab osmometer in chloroform solution at 37°.

The compounds are stable in the solid state but not in solution as evidenced, *inter alia*, by the change of molar conductance with time.

Pentakis(cyclohexyl isocyanide)dibromomolybdenum(II).—Cyclohexyl isocyanide (2.5 ml) was dissolved in acetone (3 ml); the solution was added to a solution of tetracarbonyldibromomolybdenum(II), prepared[8] from hexacarbonylmolybdenum(0) (1.0 g), in acetone (*ca.* 100 ml). After 10 min the solution was concentrated under reduced pressure; the scarce precipitate which formed was filtered and identified as $Mo(CO)_6$ by the infrared spectrum. The filtered solution was evaporated to dryness under vacuum; the residual thick oil was dissolved in ethanol and treated with ether, under scratching. A yellow powder was obtained, filtered (0.79 g), and crystallized from ethanol–diethyl ether to yield the pure yellow compound. *Anal.* Calcd for $C_{30}H_{55}Br_2MoN_5$: C, 52.45; H, 6.9; N, 8.7. Found: C, 52.63; H, 7.51; N, 8.55. ν_{max} 2136 cm^{-1}, very broad and unresolved ($CHCl_3$). A freshly prepared 6.54×10^{-4} *M* nitrobenzene solution gave a conductance value of 33 ohm^{-1} cm^2 mol^{-1}, which dropped to 16.1 after 18 hr.

Pentakis(*p*-tolyl isocyanide)dibromomolybdenum(II).—An acetone (40 ml) solution of tetracarbonyldibromomolybdenum(II), prepared[8] from hexacarbonylmolybdenum(0) (1.0 g), was added to an acetone (3 ml) solution of *p*-tolyl isocyanide (2.5 ml).

The yellow precipitate was then filtered and crystallized from dry chloroform–petroleum ether (bp 40–70°) to yield a yellow compound (0.37 g), mp 157°. *Anal.* Calcd for $C_{40}H_{35}Br_2MoN_5$: C, 57.0; H, 4.15; N, 8.32; Br, 19.0. Found: C, 56.21; H,