

0.63 mdyn/Å for the Rh-Fe bond force constant, if one ignores the presence of all other atoms. On the other hand, the force constant will have a value of 1.3 mdyn/Å if one considers it as a diatomic molecule with two atoms of atomic weights equal to those of the Rh(CO)₂ and Fe(CO)₃ moieties but ignores the effect of C₇H₇ ligand. The first value of the force constant so obtained is close to that reported for the Mn-Mn bond while the second value is closer to that reported for the Fe-Fe bond in similar compounds.⁴ The intensity of the Raman band increases upon moving into the regions of higher absorption (Figure 1). The band observed with the 4579-Å line is 7 times stronger than that observed with the 5145-Å line. This is in agreement with the current literature on resonance Raman spectra.⁷

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Registry No. (CO)₂Rh·C₇H₇·Fe(CO)₃, 51608-48-1.

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The Binuclear Molybdenum(III)-Aquo Ion

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Reduction of acid solutions of molybdenum(VI) by a cadmium reductor or a Jones reductor produces green solutions of molybdenum(III).¹ Similar green solutions are produced by electrolytic reduction of Mo(VI) in HCl (2–4 M).² Forster and Fricke³ attributed the green color to a hexa-aquomolybdenum(III) ion. Wardlaw and coworkers⁴ believed that the main species in these solutions were MoO(H₂O)₅⁺ and MoO(H₂O)₄Cl. Hartmann and Schmidt² measured the absorption spectra of the green solutions of molybdenum(III) in HCl, HBr, and H₂SO₄ and reported similar spectra for these three acids. The authors concluded from this similarity that the three solvents contained one and the same species, namely, a green hexa-aquo ion Mo(H₂O)₆³⁺. Bowen and Taube⁵ investigated the products of the aquation of the hexachloromolybdenum(III) ion in the noncomplexing acid solutions of *p*-toluenesulfonic acid (HPTS) and trifluoromethylsulfonic acid. They separated the aquation products by ion-exchange chromatography and identified a pale yellow tripositive ion as Mo(H₂O)₆³⁺. These results were confirmed by other investigators^{6–8} and could not be reconciled with Hartmann's assignment of a hexa-aquo structure to the green Mo(III) species, since existence of two isomeric hexa-

aquomolybdenum(III) ions was ruled out. It was also pointed out⁵ that the strong absorption of the green species at 600 nm was incompatible with a Mo(H₂O)₆³⁺ structure in view of the position of Mo in the second row of the transition elements. Bowen and Taube⁵ concluded that the green species was a condensation product of Mo(III). A di- μ -oxo structure was recently proposed⁹ for the green Mo^{III}-EDTA complex [Mo₂O₂EDTA(H₂O)₄]¹²⁻. Haight and Boston¹⁰ suggested that the related structure Mo₂O₂²⁺ could be attributed to Hartmann's green species. The present investigation was undertaken in order to identify this green molybdenum(III) species.

Experimental Section

Materials. "Baker Analyzed" Na₂MoO₄ and Fluka HPTS were used. BioRad Dowex 50-X2 cation-exchange resin was used both for ion-exchange columns and for batch equilibration experiments. All ion-exchange separations and batch experiments were conducted under nitrogen at ~2°. All Mo(III) solutions prepared by reduction of Mo(VI) in HPTS were 0.01 M in Mo and 1 M in acid. Mo(III) preparations in other acids were 0.01 M in Mo and in acid concentrations as specified.

Analytical Work. The oxidation number of the blue-green ion was determined as follows. Aliquots of the green species eluted from the ion-exchange column were discharged into excess Fe(III) before and after reduction with a Jones reductor (to Mo(III)) and the Fe(II) resulting from oxidation of Mo to Mo(VI) was titrated with KMnO₄. Analyses of samples that were rereduced gave identical titer with those of the original green solution, thus confirming the oxidation state of +3 for this ion. The oxidation state did not change in solutions kept for 1 week under nitrogen. KMnO₄ titrations of solutions containing HPTS were conducted at 0°. Under these conditions, no oxidation of HPTS occurred. In the ion-exchange batch experiments, Mo(III) was analyzed spectrophotometrically at 624 nm or 360 nm. A Cary 14 spectrophotometer was used for all spectral measurements. An Alpha Scientific magnetic susceptibility instrument with a Model 6000 electromagnet was used for the magnetic measurements.

Results and Discussion

Preliminary experiments indicated that the green Mo(III) solutions in hydrochloric and sulfuric acids contained a mixture of molybdenum(III) species, whereas the solution obtained by reduction of Mo(VI) in HPTS contained a single Mo(III) species. A solution of 0.01 M Mo(III) in 1 M HPTS, prepared by a Jones reductor, was diluted with water and absorbed on a cooled Dowex 50-X2 cation-exchange column. All operations following the reduction were carried out under nitrogen. A sharp blue-green band was absorbed on the column and could not be eluted with 2 M HPTS but could be slowly eluted with 3 M HPTS, indicating an ionic charge of 4+. The absorption spectrum (Figure 1) had three maxima at 360 nm (ϵ 306), at 572 nm (ϵ 39), and at 624 nm (ϵ 43). Identical results were obtained when a cadmium reductor was used instead of the Jones reductor.

Charge Per Molybdenum Atom. A solution of 0.01 M Mo(III) in 1 M HPTS was diluted with water and absorbed on the cation-exchange column. Elution with 1 M HPTS removed the Zn²⁺ ion (introduced by the Jones reductor), and the blue-green band was eluted with 3 M HPTS. This fraction was diluted with water and reabsorbed on a small cation-exchange column until all the H⁺ ions were replaced by molybdenum ions. The absorbed molybdenum was eluted with acid and the number of millimoles of molybdenum in the eluent was determined. The capacity of the column was determined by elution of the acid form with

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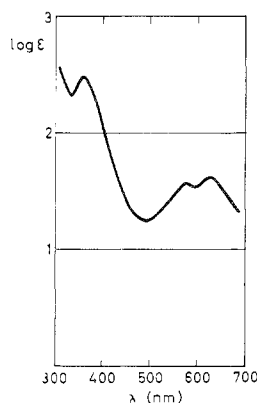


Figure 1. Spectrum of binuclear Mo(III) in 1 M HPTS.

NaCl and titration of the acid. The charge per Mo atom was determined by dividing the capacity of the resin by the number of moles of Mo atoms eluted from it. A charge of $(2.07 \pm 0.16)+$ was obtained from five experiments.

Ionic Charge of the Blue-Green Ion. The ionic charge was determined by the method of Cady and Connick.¹¹ Solutions of freshly eluted Mo(III) in known concentrations of HPTS were equilibrated with given weights of air-dried resin of known capacity for 20 min and then analyzed. The solutions were diluted and again equilibrated and analyzed. Concentrations were chosen to minimize the changes in activity coefficients of Mo(III) and H^+ in the resin phase by keeping the mole fractions of Mo(III) and H^+ nearly constant. Activity coefficients for the species in solution can be assumed to be almost constant within the concentration range used.¹¹

The charge per molybdenum ion $b+$ was derived from the expression

$$\frac{[Mo^{b+}]_{resin} [H^+]^b}{[Mo^{b+}] [H^+]^b_{resin}} = K$$

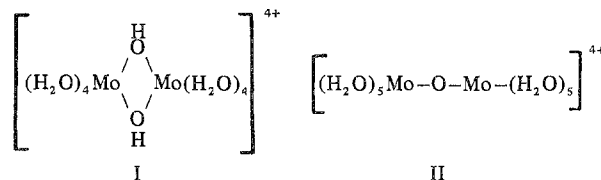
by using pairs of batch experiments at two different hydrogen ion concentrations (before and after dilution). A charge of $(3.7 \pm 1.0)+$ was obtained from four pairs of batch experiments.

Magnetic Susceptibility Measurements. The Gouy method was used with 0.1 M $NiCl_2$ as the calibrant. At a field strength of 5900 G, the increase in weight of the 0.1 M $NiCl_2$ solution was 6.9 ± 0.1 mg (compared to a water reference), and the decrease in weight of a solution containing 0.025 M Mo(III) in 3 M HPTS was 12.2 ± 0.1 mg. The decrease in weight of a blank solution of 3 M HPTS was also 12.2 ± 0.1 mg. These results indicate that the blue-green molybdenum(III) ion is diamagnetic.

The charge of $(2.07 \pm 0.16)+$ per molybdenum atom and the total ionic charge of $(3.7 \pm 1.0)+$ prove that this species is a binuclear tetrapositive ion. This ionic charge is consistent with the ion's elution behavior with 3 M acid. Although the total ionic charge cannot be determined with high precision by the method of Cady and Connick (especially in the case of highly charged ions) because of the unknown variation of the activity coefficients in the resin phase, it can be used with confidence for deciding between the ionic charges of 2+, 4+, or 6+, as only multiples of 2+

are allowed by the charge of 2+ per molybdenum atom.

Two structures should be considered (I and II). We favor



structure I, the analog of the chromium(III) dimer,¹²⁻¹⁴ but the present data including the diamagnetism of the ion do not rule out structure II.

Green Molybdenum(III) Species in HCl and H_2SO_4 . Mo(VI) (0.01 M) in 4 M HCl was reduced by a cadmium reductor in order to obtain a solution identical with Hartmann's green solution (see ref 2, Figure 7). After dilution with water and absorption on a cation-exchange column, two distinct bands were observed—an upper blue-green band and a lower bright green band. The column was rinsed with water until free of Cl^- ions. The lower band was eluted with 2 M HPTS while the upper band remained on the column. The blue-green band was then eluted with 3 M HPTS. Its absorption spectrum was identical with that of the blue-green ion separated from the Mo(III) solution in HPTS (Figure 1). The absorption spectrum of the bright green ion eluted with 2 M acid had maxima at 362, 589, and 631 nm. It was determined that this ion was a chloro complex; Cl^- was precipitated with a silver nitrate reagent after the Mo(III) was oxidized to Mo(VI) by hydrogen peroxide. The elution behavior indicated a charge of 3+ for the lower band. The 3+ chloro ion is probably a monosubstituted di- μ -ol-aquo ion in which one H_2O group in structure I is replaced by a Cl^- ligand.

Mo(III) (0.01 M) in 2 M HCl was reduced, absorbed, and separated as above. The same fractions were obtained as in the 4 M HCl solution, but the percentage of the chloro complex was lower and that of the blue-green ion higher than in the 4 M solution.

Mo(VI) (0.01 M) in 2 M H_2SO_4 was reduced by a cadmium reductor to obtain the solution investigated by Hartmann (see ref 2, Figure 9). The diluted solution was passed through a cation exchanger without being absorbed by it, indicating a zero-charged or negatively charged species. The absorption spectrum had maxima at 356 and 651 nm in good agreement with Hartmann's results. When 0.01 M Mo(III) in 0.5 M H_2SO_4 was reduced and absorbed on a cation-exchange column, only a part of it passed through the column and two distinct bands were observed—a broad bright green band and a narrow sharp blue-green band above it. The column was rinsed with water until no free sulfate could be detected. The lower band was easily eluted with 1 M HPTS, indicating a charge of 2+. The spectrum had maxima at 356 and 641 nm and a weak shoulder at 595 nm. After oxidation with H_2O_2 , it gave a positive sulfate test with $BaCl_2$ indicating that this species was a sulfato complex. The sharp blue-green band was eluted with 3 M HPTS and its spectrum was identical with that of Mo(III) in HPTS (Figure 1). The 2+ sulfato cation is probably a monosulfato substitution product of structure I, and the neutral or nega-

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tive species could be a di- or trisulfato substitution product.

All the green species have the same high absorption band at around 360 nm (which is not found in hexa-aquomolybdenum(III)⁵⁻⁸). This band is probably characteristic of the di- μ -ol-molybdenum(III) structure. The two peaks of the aquo ion at 571 and 624 nm are shifted toward the red in the chloro and sulfato species in agreement with the position of these ligands in the spectrochemical series.

The similarities of the spectra in H₂SO₄ and HCl misled Hartmann and Schmidt to interpret them as belonging to the same species (see ref 2, Figures 7 and 9). One can observe several differences between these spectra, some of which were noted by the authors themselves, such as the disappearance of the peak at 580 nm in 2 M HCl. These and other spectral differences can be understood by considering the change in the relative concentrations of the different species which compose these solutions.

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New Route to Thiocarbonyl Complexes of Iridium(III) and Rhodium(III)

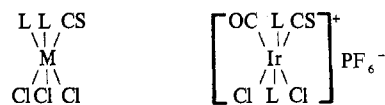
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The recent report¹ of the syntheses of thiocarbonyl complexes of chromium, molybdenum, and tungsten utilizing thiophosgene (CSCl₂) as thiocarbonylating agent prompts us to report our studies of reactions of thiophosgene with some complexes of group VIII metals. Ethyl (or methyl) thiocloroformate has been used to synthesize the thiocarbonyl cation C₅H₅Fe(CO)₂CS⁺.² Reactions of metal complexes with carbon disulfide and triphenylphosphine have been previously employed to synthesize thiocarbonyl complexes of rhodium, ruthenium, and iridium.³⁻⁵

We now report the facile and relatively high yield syntheses of thiocarbonyl complexes of iridium(III) and rhodium(III) by the three-fragment oxidative addition of thiophosgene to Ir(PPh₃)₂(N₂)Cl, [Ir(PPh₃)₂(CO)(CH₃CN)]PF₆, and Rh(PPh₃)₃Cl. The addition of the three fragments of thiophosgene and the loss of the labile ligands dinitrogen, acetonitrile, and triphenylphosphine lead to the formation of the six-coordinated products **1A**, **2**, and **1B**. The proposed structures for the thiocarbonyl complexes are depicted.



1A, M = Ir; L = PPh₃
1B, M = Rh; L = PPh₃

2, L = PPh₃

The CS stretching frequencies in the mull spectra of the iridium(III) complexes (at 1368 cm⁻¹ for **1A** and at 1409 cm⁻¹ for **2**) are increased from 1332 cm⁻¹ for Ir(PPh₃)₂(CS)Cl due to decreased back-donation from the Ir(III) as compared to Ir(I). The ν (CS) at 1409 cm⁻¹ for **2** is at a higher frequency than the ν (CS) observed in the 1263–1381-cm⁻¹ region for cationic five-coordinated iridium(I) thiocarbonyl complexes [Ir(CO)₂(CS)(PR₃)₂]⁺ where R = phenyl or cyclohexyl.⁶ The ν (CS) at 1409 cm⁻¹ for [Ir(PPh₃)₂(CO)(CS)Cl₂]⁺ is the highest frequency yet reported for metal-thiocarbonyl complexes. This high frequency reflects the small amount of back-donation from Ir(III) to CS in the cationic complex. The ν (CO) at 2127 cm⁻¹ for **2** is also much higher than the ν (CO) in the 2036- to 2066-cm⁻¹ region observed for cationic iridium(I) complexes [Ir(CO)₂(CS)(PR₃)₂]⁺.⁶ The significantly higher frequency for the ν (CO) band at 2127 cm⁻¹ in [Ir(PPh₃)₂(CO)(CS)Cl₂]⁺ than in [Ir(PPh₃)₂(CO)₂Cl₂]⁺⁷ (at 2050 and 2007 cm⁻¹) is also indicative of the greater effectiveness of the thiocarbonyl group compared to the carbonyl group in removing electron density from the central metal. The rhodium(III) compound **1B** similarly has ν (CS) at 1364 cm⁻¹ increased from 1299 cm⁻¹ for Rh(PPh₃)₂(CS)Cl. Compound **1B** can be prepared by the oxidative addition reaction of chlorine and Rh(PPh₃)₂(CS)Cl.⁸ The proposed structures for **1A**, **1B**, and **2** are suggested from the dependence of the metal-chlorine stretching frequencies on ligands trans to the chlorine ligand.⁹ The Cl ligand trans to CO or CS gives rise to ν (Ir-Cl) in the 290–310-cm⁻¹ region, whereas Cl trans to PPh₃ gives ν (Ir-Cl) in the 270–280-cm⁻¹ region.

The reactions of thiophosgene with other group VIII metal complexes were explored briefly. Reactions of CS-Cl₂ with [Rh(CO)₂Cl]₂ and with [Rh(CO)₂(PPh₃)₂Cl]₂ in benzene gave immediately dark-brown solids which had ν (CO) in the 2090–2100-cm⁻¹ region but no strong absorption in the 1000–1420-cm⁻¹ region other than bands due to triphenylphosphine. The reaction of CS-Cl₂ with Ir(CO)(PPh₃)₂Cl in benzene gave a red-brown Ir(III) complex with ir frequencies at 1358 (vs), 2014 (s), and 2065 (c) cm⁻¹. Similarly, the reaction of CSCl₂ with Rh(CO)(PPh₃)₂Cl in benzene or dichloromethane gave red-brown solids with ir frequencies at 1364 and 2085 cm⁻¹ expected for a Rh(III) complex with CO and CS ligands. The rhodium(III) complex additionally had bands at 1102 (m) and 1112 (sh) cm⁻¹ which may be ascribed to π -CS₂ coordination. Attempts to recrystallize these products from various solvents gave solids which had the ν (CS) band at 1358 and 1364 cm⁻¹ diminished in intensity, and further characterization of these compounds was not pursued.

The reaction of CSCl₂ and Pt(PPh₃)₃ in benzene gave two isolable products: one which was brown and had ir bands characteristic of the PPh₃ ligand and a second lighter brown solid which in addition to PPh₃ bands had a ν (CS) band at

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