present, completing a distorted octahedron about Na(5).

Sodium–water distances in other compounds are comparable and vary widely, such that a standard sodium–water distance is difficult to ascertain. Sodium–water distances in some other highly hydrated sodium salts are 2.41–2.49 Å in $Na_2S \cdot 9H_2O$ and $Na_2Se \cdot 9H_2O$,[28] 2.41–2.50 Å in $Na_2SiO_3 \cdot 9H_2O$,[27] 2.36–2.82 Å in $Na_2SiO_3 \cdot 6H_2O$ and $Na_2GeO_3 \cdot 6H_2O$,[18] and 2.39–2.46 Å in $Na_2B_4O_7 \cdot 10H_2O$.[30] In the compound $2Co(en)_3Cl_3 \cdot NaCl \cdot 6H_2O$, isolated sodium–water octahedra are present; the sodium–oxygen distances are all equivalent, being 2.62 Å.[31]

The results of chemical analyses[10] require that six sodium ions exist in the asymmetric unit of the structure. That only five were found is attributed to disorder. In fact, difference maps show marked elongation of the Na(4) peak, and the Na(5) peak height is even lower than most oxygen peaks. The high calculated temperature factors of these two atoms are consistent with partial site occupation, since no allowance was made for the latter in the calculations. To satisfy stoichiometry and electrical neutrality, additional sodium ions would have to be disordered among interstices between water molecules or between anion oxygen atoms and water molecules. The contacts between anion atoms and water molecules, given in Table VII, and between water molecules, given in Table VIII, are long enough to permit interstitial sodium ions. If such a site were occupied with 20% probability, the electron density therein would be comparable to that of a lithium ion and thus would not be detectable with certainty in the presence of so many heavy atoms.

The high temperature factors of some of the water molecules are attributed to partial site occupation, consistent with the efflorescence of the compound. Allowing for a sixth water molecule coordinated to Na(5), there are 25 water molecules in the asymmetric unit, in agreement with the stoichiometry.

The success of the structure determination supports the correlation of structure and properties used in the solution of the structure. The octahedral coordination of manganese(IV) is to be expected on the basis of its d^3 electron configuration, because of its high crystal field stabilization energy with respect to other geometries. It would be interesting to carry out a complete structure determination of the 9-molybdomanganate(IV) anion, $MnMo_9O_{32}{}^{6-}$, and then compare the geometries of the manganese(IV) in the niobate and molydate and correlate them with spectroscopic and magnetic data. (Only a two-dimensional heavy-atom determination of the $MnMo_9O_{32}{}^{6-}$ structure was carried out by Waugh, *et al.*[32]).

Acknowledgment.—This research was supported in part by the Advanced Research Projects Agency under Grant SD-131.

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[32] J. L. T. Waugh, D. P. Shoemaker, and L. Pauling, *Acta Cryst.*, **7**, 438 (1954).

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Transition Metal Nitrosyls. VIII. Complexes of Chromium and Molybdenum

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Several new nitrosyl complexes of chromium and molybdenum have been synthesized including *trans*-$[CrClNO(das)_2]ClO_4$, *cis,cis*-$MoCl_2(NO)_2(das)$, and *cis,cis*-$MoCl_2(NO)_2(en)$. The chromium complex *trans*-$CrClNO(das)_2{}^+$ has a doublet ground state and the esr spectrum shows hyperfine splitting due to both the nitrogen and arsenic nuclei. The measured values of the isotropic hyperfine parameters are $A_{As} = 35$ G and $A_N = 5$ G. The molybdenum compounds are diamagnetic and slowly isomerize to the mononitrosyl hyponitrito complexes $\{[MoClNO(das)]_2N_2O_2\}Cl_2$ and $\{[MoClNO(en)]_2N_2O_2\}Cl_2$. The first-order rate constants for these isomerization reactions at 25° are 1.10×10^{-4} and 1.13×10^{-5} sec^{-1}, respectively.

Introduction

The past several papers in this series have described the preparation and characterization of mononitrosyl derivatives of iron and cobalt.[2,3] These iron and cobalt nitrosyl complexes, stabilized with *o*-phenylenebis(dimethylarsine) (das) and ethylenediamine (en), have structures in which the metal, nitrogen, and oxygen atoms are not collinear.[4] The best *formalism* for discussing these compounds is the valence bond structure in which an $N{=}O^-$ group is bound to the metal *via* the nitrogen atom. This description is explicit in demand-

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[1] (a) Taken in part from the Ph.D. Thesis of W. S., University of Arizona, 1967; Shell Fellow, 1966–1967; (b) NSF Undergraduate Research Participant, 1965.

[2] W. Silverthorn and R. D. Feltham, *Inorg. Chem.*, **6**, 1662 (1967).

[3] R. D. Feltham and R. S. Nyholm, *ibid.*, **4**, 1334 (1965).

[4] L. Dahl, private communication.

ing that there be a double bond between the nitrogen and the oxygen and, moreover, that the nitrogen must utilize sp^2-hybrid orbitals to accommodate the two electron pairs which are not involved in the bonding between the nitrogen and the oxygen, $>N{=}O$. Clearly this is a rather crude description, but it has the advantage of explaining many of the physical and chemical properties of transition metal nitrosyls with NO stretching frequencies near 1600 cm^{-1}. The nitrosyl group is covalently bound to the metal, and as much σ bonding as is necessary can be accommodated by this particular valence bond description. However, the π bonding must be minimal for this valence bond description to be useful.

The iron and cobalt complexes with the composition $MNOX(das)_2^+$ have been shown to have a structure in which the halogen, X^-, is *trans* to the nitrosyl group, while the M–N–O angle is approximately 150°.[4] This structure is in complete accord with the description outlined above, leading to an assignment of III for the oxidation numbers of the metals in $MNOX(das)_2^+$. Therefore, the iron(III) and cobalt(III) have the electron configurations t_{2g}^5 and t_{2g}^6, respectively. Consequently, these metals will be unable to form π bonds with the filled π orbitals on the $N{=}O^-$, since the t_{2g} levels are essentially filled and the π orbitals on the $N{=}O^-$ are also filled. Accordingly, these investigations have been extended to chromium, molybdenum, and tungsten which may have fewer electrons in the t_{2g} orbitals and might therefore be capable of forming π bonds with $N{=}O^-$. The results of these investigations are described below.

Experimental Section

Materials and Analyses.—The nitric oxide from Matheson was purified by passing it through a CO_2–acetone trap. The solvents were freed of water by drying over molecular sieves. The chromium, molybdenum, and tungsten carbonyls were obtained from Alfa Inorganics, while the nitrosyl chloride was obtained from Matheson. The compounds were analyzed by Huffman Laboratories, Wheatridge, Colo.

Preparation of Compounds.—As in the previous papers, all of the reactions were carried out under nitrogen which was carefully freed of oxygen. While most of these compounds are stable as dry solids, in solution they are rather oxygen sensitive, so that special glassware must be utilized for all of the operations with these compounds.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]chromium Perchlorate.—Approximately 3 g of anhydrous chromous chloride was slurried in 300 ml of oxygen-free AR acetone and the solution was heated to boiling in a large Schlenk tube.[5] The slurry was then cooled to room temperature, and NO was passed into the system. When equilibrium between the solution and NO was reached, 2 ml of *o*-phenylenebis(dimethylarsine) dissolved in 20 ml of acetone was added in 5-ml portions. After each addition, the solution was reequilibrated with NO. On completion of the addition of *o*-phenylenebis(dimethylarsine), the solution was filtered under nitrogen in order to remove any undissolved chromium salts. The filtrate was then evaporated to half its original volume under vacuum and allowed to stand overnight before being filtered again. The resulting filtrate was then stripped to approximately 15 ml and allowed to stand for 2 hr. The solution was then filtered and 1.6 g of a light green solid was collected and dried at 60° under vacuum. To the final 15 ml of filtrate was added 200 ml of diethyl ether which resulted in another 0.9 g of solid. These last two fractions were then dissolved in 30 ml of methanol, and $NaClO_4$ was added. Upon cooling, a yellow crystalline solid formed, while a second crop of crystals was obtained by evaporating the filtrate to half its original volume. After recrystallization from dichloromethane–hexane, 0.5 g of complex was obtained.

Anal. Calcd for $\{CrClNO[C_6H_4(As(CH_3)_2)_2]_2\}ClO_4$: C, 30.4; H, 4.1; Cl, 9.0; N, 1.8. Found: C, 30.9; H, 4.5; Cl, 9.4; N, 1.9. $\chi_g = 0.95 \times 10^{-6}$ cgsu; $\mu = 1.70$ BM.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]chromium.—A solution containing 0.2 g of $[CrClNO(das)_2]ClO_4$ in 10 ml of methanol was treated with small portions of finely ground sodium dithionite. The solid sodium dithionite slowly turned yellow and then bright orange as the solution was stirred and heated for 0.5 hr. The orange solid was filtered and dried at 60° under vacuum. The compound was recrystallized from dichloromethane giving 60 mg of bright orange complex.

Anal. Calcd for $CrClNO[C_6H_4[As(CH_3)_2]_2]_2$: C, 34.8; H, 4 7; Cl, 5.1; N, 2.0. Found: C, 34.1; H, 4.8; Cl, 5.3; N, 2.2. The compound is diamagnetic.

***cis*-Dichlorodinitrosyl[*o*-phenylenebis(dimethylarsine)]molybdenum. Method 1.**—$Mo(NO)_2Cl_2$ was prepared as described by Cotton and Johnson[6] by the reaction of NOCl with molybdenum hexacarbonyl. *o*-Phenylenebis(dimethylarsine) (2.1 g) was slowly added to 20 ml of a methanol solution containing 0.8 g of $Mo(NO)_2Cl_2$. After stirring for a few minutes, a light green crystalline solid separated and was removed by filtration. The complex was recrystallized from methanol, then filtered and washed with ether, and dried under vacuum at 100°.

Method 2.—This same compound can be prepared by treating NOCl with $Mo(CO)_2(das)_2$. NOCl was slowly passed into a solution of 0.68 g of $Mo(CO)_2(das)_2$ dissolved in dichloromethane. An immediate reaction occurred with the evolution of gas and a color change from yellow to green. On standing, a green solid precipitated. After removal of the solvent under vacuum, the complex was recrystallized from ethanol.

Anal. Calcd for $MoCl_2(NO)_2[C_6H_4(As(CH_3)_2)_2]$: C, 23.4; H, 3.1; Cl, 13.8; N, 5.5; O, 6.2. Found: C, 23.4; H, 3.6; Cl, 13.7; N, 5.5; O, 6.4. The compound is diamagnetic.

***cis*-Dichlorodinitrosylethylenediaminemolybdenum.**—Ethylenediamine (0.17 g) was added to 10 ml of a solution containing 0.65 g of $Mo(NO)_2Cl_2$. After stirring for several minutes, a green precipitate formed and was removed by filtration. On standing, another crop of well-formed green needles was obtained from the filtrate. These materials were combined and recrystallized from methanol. The infrared spectrum indicated that methanol was present in the solid complex.

Anal. Calcd for $MoCl_2(NO)_2(C_2H_4N_2H_4)\cdot 0.5CH_3OH$: C, 9.9; H, 3.3; Cl, 23.4; N, 18.5. Found: C, 10.1; H, 3.3; Cl, 24.8; N, 18.8. The compound is diamagnetic.

Dichlorohyponitritonitrosyl[*o*-phenylenebis(dimethylarsine)]-molybdenum.—During the preparation of $Mo(NO)_2Cl_2$, it was noted that the filtrates turned yellow on standing in the absence of air. Accordingly, the filtrates from several preparations were combined and evaporated to dryness. The yellow material thus obtained was recrystallized from methanol. The concentration dependence of the conductance in methanol is consistent with a 2:1 electrolyte.[7]

Anal. Calcd for $\{MoCl_2NO[C_6H_4(As(CH_3)_2)_2]\}_2[N_2O_2]$: C, 23.4; H, 3.1; Cl, 13.8; N, 5.5; O, 6.2. Found: C, 23.4; H, 3.6; Cl, 13.4; N, 4.8; O, 7.0. The compound is diamagnetic.

Attempted Preparation of Tungsten Complexes.—The reaction between NOCl and $W(CO)_6$ has been described previously by Cotton and Johnson.[6] The green complex formed from this reaction was reported by these authors as $W(NO)_2Cl_2$. In all of the reactions between $W(CO)_6$ and NOCl, a green material was obtained, but it had properties which differed markedly from those

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[5] R. B. King, "Organometallic Synthesis," Vol. 1, Academic Press, New York, N. Y., 1965.

[6] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

[7] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

reported in ref 6. This green material readily lost NOCl under vacuum and was thereby converted into a brown material which had the infrared spectrum reported previously for $W(NO)_2Cl_2$. Although completely satisfactory analyses were never obtained due to the instability of these materials, the initial green complex had the approximate composition $W(NO)_3Cl_3$ while the brown material gave elemental analyses corresponding to $W(NO)_2Cl_2$. Several reactions of both the green and the brown materials were attempted, but the brown material was too insoluble to react, while the green material lost NOCl and oxidized all of the ligands which were added.

Physical Measurements.—The infrared spectra were measured using a Perkin-Elmer Model 337 spectrophotometer. The X-ray photographs were obtained using a Phillips powder camera 11.48 cm in diameter. The magnetic balance consisted of a Varian 4-in. magnet equipped with constant $H(dH/dx)$ pole pieces and a Cahn microbalance. The esr measurements were carried out on solutions of these compounds using a Varian E3 spectrometer equipped with a Fieldial regulator.

Results and Discussion

Chromium Complexes.—Nitric oxide reacts smoothly with chromous salts in aqueous solution to form the $CrNO^{2+}$ species along with a variety of other materials. When the reaction between NO and $CrCl_2$ was carried out in acetone, there was much less difficulty in isolating the nitrosyl complexes from these solutions. The chloride, $CrCl_2NO(das)_2$, could be isolated from these solutions but proved difficult to purify. However, the addition of sodium perchlorate to the solutions obtained from the addition of *o*-phenylenebis(dimethylarsine) to $CrCl_2NO$ in acetone gave immediate precipitation of the perchlorate salt. As first obtained, this compound is green owing to contamination with an intensely colored blue material. Recrystallization or successive recrystallizations from dichloromethane led to the complete removal of this blue material and gave light yellow crystals of $[CrClNO(das)_2]ClO_4$. There was not enough of the dark blue contaminant for analysis, but an infrared spectrum of this blue material showed that it contained a coordinated nitrite group and very little *o*-phenylenebis(dimethylarsine).

The X-ray powder pattern of $[CrClNO(das)_2]ClO_4$ obtained from this reaction was compared with those of the preceding members of this series of nitrosyl complexes *trans*-$[FeClNO(das)_2]ClO_4$ and *trans*$[CoClNO(das)_2]ClO_4$. All three compounds have the same powder patterns and therefore must be isomorphous. The structure of the iron compound *trans*-$[FeBrNO(das)_2]ClO_4$ has been determined by X-ray diffraction techniques.[4] The essential structural features of the iron complex show it to be six-coordinate, with the halogen *trans* to the nitrosyl group. The single crystals used for this X-ray study were disordered, so that the bond distances and bond angles for the Fe–N–O atoms could not be precisely determined. However, the three atoms are not collinear and the angle formed by these three atoms is near 150°. Since there is a disorder problem in all of the complexes, the similarity of the powder patterns can be interpreted in the following way. The chromium complex must have the chloride *trans* to the nitrosyl group and is six-coordinate. However, the Cr–N–O angle could be 180° or less than 180° since it is the nitrosyl group that is disordered. Similar disordering has been found in several nitrosyl complexes with bent M–NO groups.[8,9]

Magnetically, the $CrNO^{2+}$ complex is quite interesting. The compounds containing this complex ion which have thus far been prepared are all paramagnetic, with one unpaired electron per chromium. The static magnetic susceptibility of the *o*-phenylenebis(dimethylarsine) complex was measured at room temperature and found to be 1.70 BM. This value is very near the value of 1.73 BM which is expected for one unpaired spin with no orbital contribution to the susceptibility. The esr spectrum of this complex has also been measured in solution in dichloromethane (Figure 1). The spectrum consists of thirteen equally spaced lines of unequal intensity. The figure shows all thirteen, even with the low intensity of the two end lines. Each of these thirteen lines is also split into three equally spaced lines of equal intensity. Besides these lines, there are also some relatively weak satellites with similar patterns which can also be observed on the exterior of the intense central lines. Unfortunately, these lines are complicated by the presence of the weak lines of the main group, and their positions could therefore not be measured accurately. The thirteen hyperfine lines clearly arise from the interaction of the unpaired electron with the arsenic nuclei. Elemental arsenic consists exclusively of ^{75}As which has a nuclear spin of $^3/_2$, so that the total spin of the four coordinated arsenic atoms is $I = 6$. Thus, one expects $2I + 1$ or thirteen lines of unequal intensity as is observed. The splitting of each of these thirteen lines into a triplet is caused by interaction with the nitrogen nucleus ($I = 1$). The esr data for this compound are reported in Table I.

TABLE I

ELECTRON SPIN RESONANCE PARAMETERS FOR $CrNO^{2+}$ COMPLEXES

Species	g(av)	A_n, G	A_{other}, G	Ref
trans-$[CrClNO(das)_2][ClO_4]$	2.00	5	37.5 (^{75}As)	*a*
$Cr(CN)_5NO^{3-}$	1.99	5.3	11 (^{13}C)	*b*
$Cr(NO)(NH_3)_5^{2+}$	1.98	...	...	*c*
$Cr(NO)(H_2O)_5^{2+}$	1.97	6.4	...	*c*

[a] This work. [b] P. T. Monoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966). [c] L. S. Meriwether, S. D. Robinson, and G. Wilkinson, *J. Chem. Soc.*, 1488 (1966).

Arsenic hyperfine splitting[10] of 9582 Mc sec^{-1} has been observed in pyramidal AsO_3^{2-} and $NiCl_2(das)_2^+$. The large hyperfine coupling between the unpaired electron and the arsenic nucleus which was observed in AsO_3^{2-} can be taken as a measure of the coupling between the arsenic nucleus in a tetrahedral environment and the electron when the spin density at the arsenic is approximately 1. A crude measure of the spin density on the arsenic in $CrClNO(das)_2^+$ can be

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(8) P. R. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(9) G. R. Davies, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 81 (1968).

(10) (a) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964); (b) P. Kreisman, R. Marsh, J. Preer, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 1067 (1968).

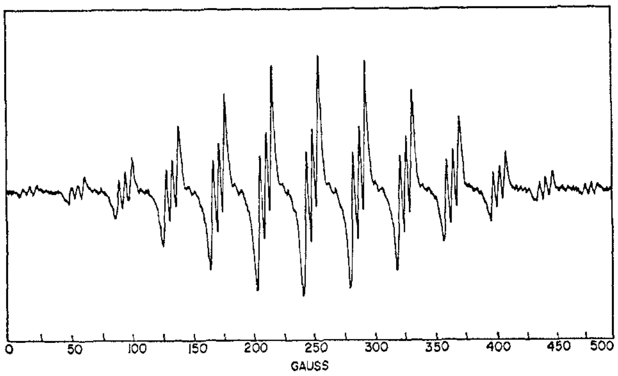

Figure 1.—The esr spectrum of *trans*-[CrClNO(das)$_2$]ClO$_4$ in CH$_2$Cl$_2$.

obtained from A_{As} by comparison with that observed for AsO$_3^{2-}$. The ratio $A_{\mathrm{complex}}/A_{\mathrm{AsO_3^{2-}}}$ indicates a spin density on each arsenic in the complex of less than 2%. Although this estimate should not be taken literally, it certainly indicates only a small amount of delocalization of the unpaired spin onto the *o*-phenylenebis(dimethylarsine) ligand. This small arsenic hyperfine coupling constant is consistent with the failure to observe any proton hyperfine interaction with the unpaired spin in this chromium complex.

The visible spectrum of [CrClNO(das)$_2$]ClO$_4$ was obtained both in solution and from the reflectance of the pure solid. The spectral data are compared with those for Cr(CN)$_5$NO^{3-} in Table II. There are some similarities between the spectra of these two chromium nitrosyls which should be noted. Both complexes have a rather weak absorption band in the region between 10 and 13 kK. There are two additional transitions in the two complexes which occur near the same energies (22 and 26 kK) but have distinctly disparate extinction coefficients. Manoharan and Gray have assigned the spectrum of Cr(CN)$_5$NO^{3-} to the excited states of Cr(I). While the spectrum of the complex CrCl(NO)(das)$_2^+$ has some similarities with that of Cr(CN)$_5$NO^{3-}, there are also significant differences between the spectra of these two nitrosyl complexes.

TABLE II

ELECTRONIC SPECTRA OF CrNO^{2+} SPECIES

Compd	NO (cm^{-1})	Absorption max, kK (ϵ)[a]	Ref
[CrClNO(das)$_2$)]ClO$_4$	1690	10.5 (40), 17.6,[b] 21.7 (1200), 25.6 (1800), 30.3 (1600), 37.7 (30,000)	*c*
Na$_3$[Cr(CN)$_5$NO]	1645	13.7 (8), 22.2 (72), 27.32 (59), 37.3 (1100), 43.98 (3600)	*d*

[a] The units are l. mol^{-1} cm^{-1}. [b] Observed in reflectance only. [c] This work. [d] See footnote *b* of Table I.

The electronic ground state of Cr(CN)$_5$NO^{3-} has been assigned as $^2B_2$ (d_{xz}^2, d_{yz}^2, d_{xy}) on the basis of its esr spectrum,[11-13] visible spectrum, and SCCC–MO calculations. On this basis, the unpaired electron resides in the d_{xy} orbital in the electronic ground state. While it would be tempting to regard Cr(CN)$_5$NO^{3-} and CrCl(NO)(das)$_2^+$ as isoelectronic, the subtle differences between these complexes may be significant. Consider the possibility in which Cr(III) is coordinated to N═O$^-$. In D$_{4h}$ symmetry, if the tetragonal field (covalent bonding) is large enough to cause spin pairing (*ca.* 13 kK in the *o*-phenylenebis(dimethylarsine) complexes), then the electron configuration of the highest filled orbitals would be either $(d_{xz}, d_{yz})^3$ or d_{xz}^2, $(d_{xz}, d_{yz})^1$, with the unpaired electron residing in the d_{xz}, d_{yz} orbitals. The first spin-allowed transition for such a Cr(III) complex would be $(d_{xz}, d_{yz})^3$ (^2E) → $(d_{xz}, d_{yz}, d_{xy})^3$ ($^2A_2$, 2^2B_1, or $^2B_2$) or would be d_{xy}^2, $(s_{xz}, d_{yz})^1$ (^2E) → $(d_{xz}, d_{yz}, d_{xy})^3$ ($^2A_2$, 2^2B_1, or $^2B_2$). The lowest electronic transition of Cr(CN)$_5$NO^{3-} has been assigned by Gray to $^2B_2 \rightarrow {}^2E$ on the basis of polarization studies. Thus these electron configurations cannot be distinguished *experimentally* by the present spectral data. However, the two possible ground states $^2B_2$ [d_{xz}^2, d_{yz}^2, d_{xy}] and ^2E [$(d_{xz}, d_{yz})^3$ or d_{xy}^2, $(d_{xz}, d_{yz})^1$] should have different *g* tensors. Single crystals of this complex diluted in a diamagnetic host lattice are now being grown to investigate the magnetic anisotropy of this complex.

The infrared spectrum of CrClNO(das)$_2^+$ has a single NO stretching frequency at 1690 cm^{-1} which is characteristic for the *o*-phenylenebis(dimethylarsine)nitrosyl complexes, MXNO(das)$_2^+$. This low frequency, along with the structural similarities between the iron, cobalt, and chromium compounds, is strongly suggestive that the Cr–N–O angle is less than 180°. Evidence has been presented[14-16] both for and against the linearity of the Cr–N–O bond in Cr(CN)$_5$NO^{3-}. This question remains unresolved.

The complex CrClNO(das)$_2^+$ is readily reduced to the neutral compound by dithionite ion and other reducing agents. The orange compound thus obtained, CrClNO(das)$_2$, was found to be diamagnetic and to have an NO stretching frequency 100 cm^{-1} lower than the cationic species. Since relatively small amounts of this compound were available, it has not been further characterized.

Molybdenum Complexes.—Various attempts have been made to prepare the molybdenum and tungsten complexes analogous to the chromium compounds discussed above. The compound Mo(NO)$_2$Cl$_2$ was found to react readily with *o*-phenylenebis(dimethylarsine) and ethylenediamine forming the emerald green compounds MoCl$_2$(NO)$_2$(das) and MoCl$_2$(NO)$_2$(en), respectively. The infrared spectra of both of these complexes consist of two strong bands near 1700 cm^{-1} in addition to the spectral characteristics of the other ligands. The presence of these two well-separated bands indicates that the two nitrosyl groups are *cis* to one another. Recrystallization from various solvents

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(11) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).
(12) J. J. Fortman and R. G. Hayes, *J. Chem. Phys.*, **43**, 15 (1965).
(13) J. A. Kuska and M. T. Rogers, *ibid.*, **42**, 3034 (1965).
(14) D. A. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc.*, 364 (1964).
(15) B. A. Goodman, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.*, 994 (1966).
(16) B. R. McGarvey, private communication.

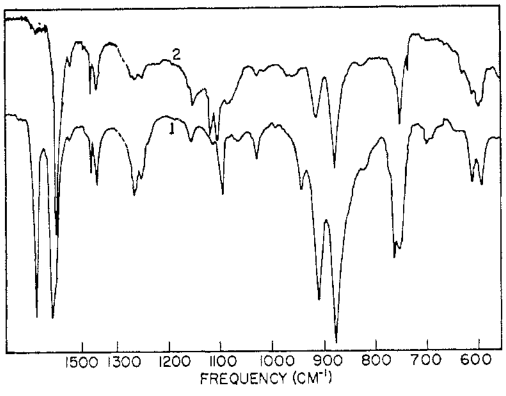


Figure 2.—The infrared spectra of (1) $MoCl_2(NO)_2$(das) and (2) $\{[MoCl_2(NO)(das)]_2N_2O_2\}Cl_2$ in KBr pellets.

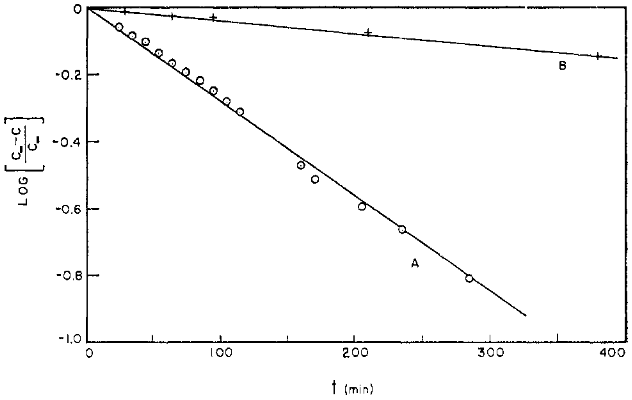
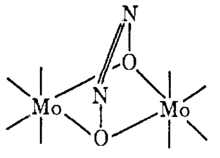


Figure 3.—The isomerization of 4.96×10^{-5} *M* $MoCl_2(NO)_2$(das) (A) and 3.44×10^{-5} *M* $MoCl_2(NO)_2$(en) (B) in methanol at 25°.

failed to change the infrared or visible spectrum of either of these complexes, which makes it unlikely that more than one isomer is present. However, the steric arrangement of these nitrosyl groups must be considered uncertain. These compounds are rather stable toward oxidation, even in solution as is the chromium compound discussed above. However, solutions of these compounds do undergo a rather slow but dramatic color change in solution, even when oxygen is rigorously excluded. After standing for several days, solutions of the green complexes $MoCl_2(NO)_2$(das) and $MoCl_2(NO)_2$(en) in methanol became yellow. The yellow compound which was obtained from the methanol solution of $MoCl_2(NO)_2$(das) was purified by recrystallization from methanol. The elemental analyses of this yellow complex indicated that it has the same composition as the green complex. The infrared spectrum of the yellow isomer has a single NO stretching frequency at 1650 cm^{-1} (Figure 2). A closely related mononitrosylmolybdenum complex has recently been reported by Johnson.[17] In addition, there are three absorption bands at 1160, 1030, and 970 cm^{-1} which are not present in the green isomer and are typical of the hyponitrite ion.[18] These facts are consistent with a structure in which both oxygens of the hyponitrite ion form bridges between the two molybdenum atoms



The conductance of both the yellow and green isomers was measured. Both of the green isomers are nonelectrolytes in methanol while the yellow isomer of $MoCl_2(NO)_2$(en) has $\Lambda_e = 133$ cm² mho equiv^{-1} in methanol and $MoCl_2(NO)_2$(das) has $\Lambda_e = 147$ cm² mho equiv^{-1} in methanol. Thus, the conductance of these compounds could be utilized to investigate the isomerism from the green to the yellow forms. The green dinitrosyl complexes were dissolved in methanol, and the conductance was measured as a function of time (Figure 3). A good first-order plot of the conductance data was obtained over more than 3 half-lives for both $MoCl_2(NO)_2$(das) and $MoCl_2(NO)_2$(en). The first-order rate constants at 25° were found to be 1.10×10^{-4} sec^{-1} for $MoCl_2(NO)_2$(das) and 1.13×10^{-5} sec^{-1} for $MoCl_2(NO)_2$(en). The fact that these rates are strongly dependent upon the amine and arsine ligands suggests that, of the two possible *cis* isomers, these compounds consist of the isomer in which a chloride is *trans* to the amine or arsine ligand and consequently *cis* to the other chloride. Moreover, the relative rates of the reactions are similar to those usually found for compounds containing arsenic or nitrogen *trans* to the leaving group.[19] This reaction can be visualized as taking place in two steps. In the first step, the chloride *trans* to ethylenediamine or *o*-phenylenebis(dimethylarsine) dissociates giving a pentacoordinate or weakly solvated species which then rapidly reacts with a second molecule of the complex giving a dimer with a chloride bridge. This chloride-bridged dimer then rearranges expelling another chloride ion and leaving a hyponitrite-bridged dimer in which two coordination positions of each molybdenum are occupied by the hyponitrite bridge. The exact structure of the hyponitrite-bridged dimer cannot be determined on the basis of the above evidence, but the proposed structure is consistent with the information available and with the known chemistry of metal nitrosyls.

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