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Metal Nitrosyls. VII. Stabilization of Mononitrosyl Complexes of Iron[1a]

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A new series of iron nitrosyl compounds has been prepared using *o*-phenylenebis(dimethylarsine) as the stabilizing ligand (L). These nitrosyl complexes have the general formula $[FeXNOL_2]^+$ in which X is a halide. One pentacoordinate complex, $[FeNOL_2]^{2+}$, and one complex anion, $[FeX_2(NO)_2]^-$, have also been isolated and characterized. Measurements of the infrared spectra, conductances in solution, magnetic susceptibilities, and X-ray powder patterns have established that these cations are monomeric with the coordinated nitrosyl group *trans* to the halide. These properties are conveniently interpreted in terms of a complex in which Fe(III) is bonded to $(N{=}O)^-$.

Introduction

There is both chemical and physical evidence that the bonding between the metal and the NO group is strongly influenced by the coordination number of the metal, the steric arrangement of the other ligands attached to the metal, the charge on the complex, and the number of d electrons present on the metal. The cobalt nitrosyl complexes[1] with ethylenediamine and *o*-phenylenebis(dimethylarsine) (das) such as $[CoBrNO(das)_2]^+$ were shown to have Co(III) coordinated to $(N{=}O)^-$. To investigate the effects which charge and number of d electrons have on the bonding between the metal and the nitrosyl group, the iron nitrosyl complexes with *o*-phenylenebis(dimethylarsine) have been prepared. These compounds and their properties are reported below.

Experimental Section

Materials and Analyses.—The reactions and operations described below were carried out using nitrogen freed from oxygen by passing it over a bed of "BTS" catalyst obtained from Badische-Anilin and Soda Fabric, New York, N. Y. The anhydrous iron halides were obtained from Alfa Inorganics, Inc., while ferrous perchlorate hexahydrate was obtained from G. Frederick Smith Chemical Co. The nitric oxide obtained from Matheson was purified by passing it through a Dry Ice trap. The compounds were analyzed for C, H, N, O, and halogen by Huffman Laboratories, Wheatridge, Colo. The oxygen content of several of these compounds has also been independently determined by neutron activation.

Preparation of Compounds.—All manipulations of these materials were carried out under nitrogen in specially designed glassware. The general procedure for preparing the complexes consisted of dissolving the anhydrous iron halide or the hydrated perchlorate in oxygen-free methanol, passing NO through the solution until no further absorption of NO was noted, and then slowly adding a solution of *o*-phenylenebis(dimethylarsine) in methanol dropwise. It is important to have a continuous flow of NO into the reaction vessel during the addition of *o*-phenylenebis(dimethylarsine) because of the slow equilibration of the iron nitrosyl species in solution.

When isolated from methanol, all of the Fe(III) species contain residual methanol which cannot be removed by drying under vacuum at 60°. The methanol can only be removed by recrystallization. The procedure for recrystallization of all of these compounds consists of dissolving about 1 g of the complex in 50 ml of oxygen-free dichloromethane, filtering, and cooling the filtrate to −76°. Hexane is then slowly added (20–50 ml), while the solution is allowed to warm to room temperature. The resultant crystalline solid is then removed by filtration, washed with 50% dichloromethane–hexane, and dried at 60° under vacuum. $[FeBr_2(das)_2][FeBr_4]$ and $[CoBr_2(das)_2]Br$ were prepared using the methods of Nyholm.[2,3]

Nitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Diperchlorate.—$Fe(ClO_4)_2 \cdot 6H_2O$ (2.5 g) was dissolved in 90 ml of methanol and equilibrated with NO. A total of 2.0 g of *o*-phenylenebis(dimethylarsine) dissolved in 20 ml of oxygen-free methanol was added dropwise. The complex precipitates as a dark blue crystalline compound. The complex was filtered under nitrogen, washed with several small portions of oxygen-free methanol, and dried under vacuum at 60° overnight (yield 2.0 g; 66% based on das). The dry solid is quite air stable, but solutions are readily oxidized by air. The compound was recrystallized from dichloromethane–hexane. These perchlorates were not found to be explosive under ordinary conditions but were handled only in small quantities.

Anal. Calcd for $[FeNO(C_6H_4[As(CH_3)_2]_2)_2][ClO_4]_2$: C, 28.0; H, 3.8; Cl, 8.2; N, 1.6; O, 16.8. Found: C, 28.1; H, 4.0; Cl, 8.4; N, 1.4; O, 15.7.[4] $\chi_g = 2.05 \times 10^{-6}$ cgs unit; $\mu = 2.32$ BM; $\Lambda_0 = 172$ cm² mhos equiv⁻¹ in methanol.

Bromonitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Perchlorate.—To a slurry of 1.0 g of $[FeNO(das)_2][ClO_4]_2$ in 50 ml of methanol was added 0.012 g of LiBr. The mixture was heated to boiling and then cooled to 0°. After cooling, the dark green crystalline solid was removed by filtration, washed with a little methanol, and dried under vacuum (0.9 g, 90% based on $[FeNO(das)_2][ClO_4]_2$). The complex was recrystallized from dichloromethane–hexane.

Anal. Calcd for $[FeBrNO(C_6H_4[As(CH_3)_2]_2)_2]ClO_4$: C, 28.7; H, 3.9; Br, 9.5; Cl, 4.2; N, 1.7; O, 9.8. Found: C, 28.8; H, 4.1; Br, 9.5; Cl, 4.4; N, 1.6; O, 10.0. $\chi_g = 1.10 \times 10^{-6}$ cgs unit; $\mu = 1.80$ BM; $\Lambda_0 = 105.2$ cm² mhos equiv⁻¹ in methanol.

Chloronitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Perchlorate.—The procedure used for preparing the bromide was followed.

Anal. Calcd for $[FeClNO(C_6H_4[As(CH_3)_2]_2)_2ClO_4$: C, 30.3; H, 4.1; Cl, 8.9; N, 1.8; O, 10.3. Found: C, 30.5; H, 4.3; Cl, 9.2; N, 1.7; O, 10.1.

Cyanonitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Perchlorate.—The procedure used for preparing the bromide was followed, except the solution was evaporated under vacuum to 10 ml and the yellow solid removed by filtration. This complex was then recrystallized from dichloromethane–hexane.

Anal. Calcd for $[Fe(CN)(NO)C_6H_4[As(CH_3)_2]_2)_2]ClO_4$: C,

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(1) (a) Presented in part before the division of Inorganic Chemistry, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. Previous paper: R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4**, 1334 (1965). (b) Shell Research Fellow, 1966–1967.

(2) R. S. Nyholm, *J. Chem. Soc.*, 851 (1950).

(3) R. S. Nyholm, *ibid.*, 2070 (1950).

(4) The sample exploded during pyrolysis so that some error in the oxygen analysis is expected.

32.2; H, 4.1; Cl, 4.5; N, 3.6. Found: C, 32.3; H, 4.3; Cl, 6.3;[5] N, 3.6.

Bromonitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Bromide.—Anhydrous ferrous bromide (1.5 g) was dissolved in 75 ml of methanol, and NO_2-free NO was passed into the solution until the solution would no longer absorb NO. A solution of 4.0 g of *o*-phenylenebis(dimethylarsine) was then added *dropwise* with prior equilibration of the solution with NO after each addition. After about half of the *o*-phenylenebis(dimethylarsine) solution was added, a wine-colored solid had formed and no further absorption of NO was noted. The rest of the *o*-phenylenebis(dimethylarsine) was then added rapidly, the solution was stirred for 5 min, and 75–100 ml of diethyl ether was added with stirring to the green solution. The resulting solid was removed by filtration and dried at 60° under vacuum. This complex was then recrystallized from dichloromethane–hexane (yield 50% based on *o*-phenylenebis(dimethylarsine)).

Anal. Calcd for $[FeBrNO(C_6H_4[As(CH_3)_2]_2)_2]Br$: C, 29.4; H, 3.9; Br, 19.5; N, 1.7; O, 2.0. Found: C, 29.5; H, 3.9; Br, 19.1; N, 1.5; O, 1.9.

Iodonitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Iodide.—The procedure used to prepare $[FeBrNO(das)_2]Br$ was also used to prepare this green complex (yield 50% based on *o*-phenylenebis(dimethylarsine)). Both the elemental analysis and the infrared spectrum show the presence of methanol in the complex.

Anal. Calcd for $[FeINO(C_6H_4[As(CH_3)_2]_2)_2]I \cdot CH_3OH$: C, 26.7; H, 3.9; N, 1.5; O, 3.4. Found: C, 26.6; H, 3.7; N, 1.2; O, 3.5.

Bromonitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Dibromodinitrosyliron(III).—It was noted in the preparation of $[FeXNO(das)_2]X$ that halfway through the addition of *o*-phenylenebis(dimethylarsine), a dark wine-colored solid always appeared, and that no further NO absorption could be observed. This wine-colored solid prepared in either methanol or tetrahydrofuran was removed by filtration and recrystallized from dichloromethane–hexane. The compound is fairly stable as a crystalline solid, but must be stored under nitrogen and is stable in solution only in absence of air.

Anal. Calcd for $[FeBrNO(C_6H_4[As(CH_3)_2]_2)_2][FeBr_2(NO)_2]$: C, 23.7; H, 3.2; Br, 23.7; N, 4.2; O, 4.7. Found: C, 24.5; H, 3.6; Br, 23.0; N, 3.8; O, 5.0. $\chi_g = 2.34 \times 10^{-6}$ cgs unit; μ $([FeBr_2(NO)_2]^-) = 1.83$ BM.

Iodonitrosyldi[*o*-phenylenebis(dimethylarsine)]iron(III) Diiododinitrosyliron(III).—Method 1. This compound was prepared exactly as was the bromide, by passing NO into solutions of ferrous iodide in methanol and adding *o*-phenylenebis(dimethylarsine) slowly.

Method 2. The compound is also readily prepared by allowing $[Fe(NO)_2I]_2$ to react with *o*-phenylenebis(dimethylarsine) in hexane. Excess *o*-phenylenebis(dimethylarsine) was added dropwise to a solution of 0.1 g of $[Fe(NO_2)I]_2$ in 20 ml of hexane. The purple-colored precipitate was removed by filtration and recrystallized from dichloromethane–hexane.

Anal. Calcd for $[FeINO(C_6H_4[As(CH_3)_2]_2)_2][FeI_2(NO)_2]$: C, 20.9; H, 2.8; N, 3.6; O, 4.2. Found: C, 21.2; H, 3.2; N, 3.2; O, 4.8. $\chi_g = 1.83 \times 10^{-6}$ cgs unit.

Physical Measurements.—The infrared spectra were obtained using a Perkin-Elmer Model 337 infrared spectrophotometer. The reflectance spectra were measured on a Zeiss PMQ-II equipped with a standard reflectance attachment and a specially fabricated PbS detector for measurements from 4 to 15 kK. The solution spectra and transmission spectra of solids were recorded using a Cary Model 14 spectrophotometer. The samples of the solid compounds were prepared by mixing the powdered sample with fluorocarbon grease and sandwiching them between two transparent quartz disks 2 mm thick. The reference was prepared by mulling lithium fluoride with the fluorocarbon grease and sandwiching this mull between two 2-mm thick quartz disks. The conductivity measurements were carried out using the methods previously described.[6] The magnetic susceptibilities were obtained at room temperature using the Gouy method. The X-ray photographs were obtained using a Phillips powder camera 11.48 cm in diameter.

Results

The elemental analyses establish unequivocally that the reaction between nitric oxide and ferrous salts in the presence of *o*-phenylenebis(dimethylarsine) results in compounds with the composition $FeX_2NO(das)_2$. It is well known[7] that reactions of nitric oxide can also lead to hyponitrites which are isomeric with the nitrosyl group. In order to distinguish between a coordinated nitrosyl group and a hyponitrite dimer containing two iron atoms, the conductivity in solution and X-ray powder patterns of the crystalline solids were obtained. In methanol $[FeNO(das)_2][ClO_4]_2$ is a 2:1 electrolyte and $[FeBrNO(das)_2]Br$ is a 1:1 electrolyte, thus proving that these compounds exist as monomers in solution.

The monomeric composition and *trans* stereochemistry of the crystalline solids have been established by a comparison of the X-ray powder patterns of these nitrosyls with $[FeX_2(das)_2]X$ and with $[CoX_2(das)_2]X$. With the exception of $[FeClNO(das)_2]ClO_4$ and $[FeINO(das)_2]I$, all of these iron nitrosyls have powder patterns which are almost identical with those of the halide complexes of iron and cobalt mentioned above. Moreover, single crystals of *trans*-$[CoBr_2(das)_2Br]$ have been grown which contain 1–5% of $[FeBrNO(das)]_2Br$. These single crystals are currently being investigated by epr, but the preliminary results show that the iron nitrosyl complex has substituted directly in the lattice for the cobalt host. Thus all of the nitrosyl compounds mentioned above contain the six-coordinate monomeric cation, $[FeXNO(das)_2]^+$, in which the halide is *trans* to the nitrosyl group.

The composition of the first compounds formed, $Fe_2X_3(NO)_3(das)_2$, from the reaction between *o*-phenylenebis(dimethylarsine), NO, and ferrous salts required that they be further investigated. When $Fe_2X_3(NO)_3(das)_2$ is dissolved in methanol at room temperature, and lithium perchlorate is added,, the perchlorate salt of *trans*-$[FeXNO(das)_2]^+$ is immediately precipitated from solution in essentially quantitative yield (based on the above formulation). Numerous attempts were made to isolate the anion from these solutions by using large cations such as $(CH_3)_4N^+$, K^+ and Ba^{2+}, but all these attempts have thus far failed.

Nyholm[2] has isolated an iron compound, $[FeBr_2(das)_2][FeBr_4]$, of similar composition from the reaction between $FeBr_3$ and *o*-phenylenebis(dimethylarsine). This compound has been shown by Nyholm to contain the $[FeBr_4]^-$ ion. This compound was prepared again, and its X-ray powder pattern compared with that of $Fe_2X_3(NO)_3(das)_2$. The powder patterns are almost identical, and the compounds have essentially the same structure. If this conclusion is correct, in addition to the NO frequency of $[FeBrNO(das)_2]^+$

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(5) Pyrolysis and examination of the resultant gases indicates the presence of dichloromethane.

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

(7) R. D. Feltham, *Inorg. Chem.*, **3**, 1038 (1964).

at 1625 cm^{-1}, there should be two additional bands in the infrared spectrum of this compound due to the anion $[FeBr_2(NO)_2]^-$. Two strong bands are found in the infrared spectra of both $[FeBrNO(das)_2][FeBr_2(NO)_2]$ and $[FeINO(das)_2][FeI_2(NO)_2]$ in addition to the absorption band due to the cation (Figure 1). Although this evidence is somewhat indirect, these compounds almost certainly contain the $[FeX_2(NO)_2]^-$ ion.

The isolation of intermediates with the composition $[FeXNO(das)_2][FeX_2(NO)_2]$ was quite unexpected in view of the earlier report[8] that solutions of ferrous salts react with nitric oxide to give complexes with the composition FeX_2NO. Since only solids of indefinite composition had been isolated by Griffith, solutions containing ferrous salts and nitric oxide were investigated by examining their infrared spectra. These complex anions are obtained from either methanol or tetrahydrofuran, but the latter solvent was chosen for experimental convenience. Ferrous bromide in tetrahydrofuran was equilibrated with NO and the infrared spectrum of this solution was obtained (Figure 2). Clearly, there is one predominant nitrosyl species present in this solution. Since the single NO frequency corresponds well to those reported[8] for other mononitrosyls of the type $[Fe(NO)(solvent)_5]^{2+}$, this absorption band was ascribed to $FeBr_2NO(THF)_x$. Addition of 1 equiv of *o*-phenylenebis(dimethylarsine) to this solution results in the formation of $[FeBrNO(das)_2][FeBr_2(NO)_2]$ (Figure 2), which is readily identified by its three nitrosyl bands.

One explanation of these results is that the *o*-phenylenebis(dimethylarsine) reduces $FeBr_2NO$ to FeBrNO followed by the oxidation of FeBrNO with more NO to give $FeBr(NO)_2$, which then reacts with o-phenylenebis(dimethylarsine) to give $[FeBrNO(das)_2][FeBr_2(NO)_2]$. To test this hypothesis, $[FeI(NO)_2]_2$ was prepared,[9] dissolved in hexane, and allowed to react with *o*-phenylenebis(dimethylarsine). This reaction gave $[FeINO(das)_2][FeI_2(NO)_2]$ in good yield.

Since it is believed[10] that nitrosyl groups can be protonated in solution, the magnetic susceptibility of these compounds was determined. The compounds $[FeXNO(das)_2]X$ and $[FeNO(das)_2][ClO_4]_2$ have magnetic moments near 2.0 BM corresponding to a doublet ground state. The dinitrosyl anions $[FeX_2(NO)_2]^-$ should have one unpaired electron per iron as well. The magnetic susceptibility of $[FeBrNO(das)_2][FeBr_2(NO)_2]$ was determined, and after correcting for the contribution of the cation to the total susceptibility, the magnetic moment of $[FeBr_2(NO)_2]^-$ was found to be 1.8 BM. Again, the susceptibility is in agreement with that expected for one unpaired electron and further verifies the composition of the anionic species present in these complexes.

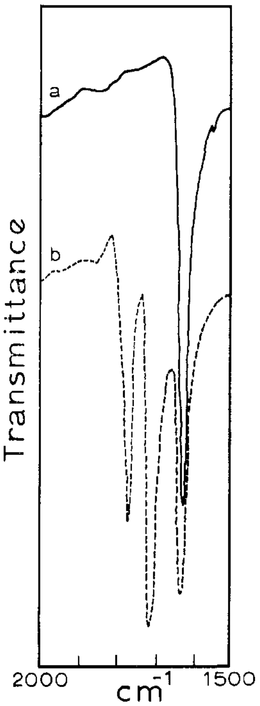

Figure 1.—The NO stretching region (a) of $[FeBrNO(das)_2][ClO_4]$; (b) of $[FeBrNO(das)_2][FeBr_2(NO)_2]$.

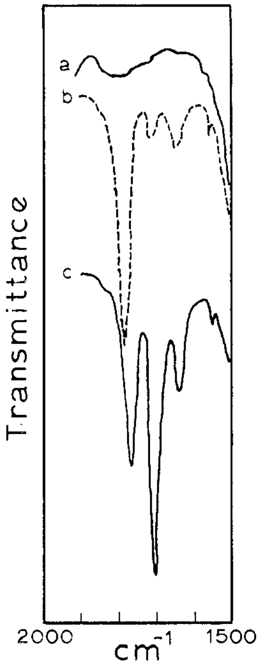

Figure 2.—The NO stretching region of tetrahydrofuran solutions (a) saturated with NO, (b) containing 0.01 *M* $FeBr_2$ saturated with NO, and (c) containing 0.01 *M* $FeBr_2$ saturated with NO to which *o*-phenylenebis(dimethylarsine) has been added.

When ferrous perchlorate is treated with NO and *o*-phenylenebis(dimethylarsine), a compound with the composition $[FeNO(das)_2][ClO_4]_2$ is formed. The compound must be recrystallized from dichloromethane–hexane to remove the last traces of methanol and can then be obtained analytically pure. With this composition, the diperchlorate could be either five-coordinate, six-coordinate with a perchlorate occupying the sixth coordination position, or six-coordinate polymers with the nitrosyl serving as the bridging group. In solution, the diperchlorate is a 2:1 electrolyte and reacts immediately in the cold with halide ions to form $[FeXNO(das)_2]^+$. If the perchlorate ion were coordinated to the metal, the symmetry of the perchlorate ion should deviate strongly from T_d. It has been shown[11] that this deviation from tetrahedral symmetry leads to additional absorption bands in the infrared spectra of complexes in which the perchlorate ion is coordinated to the metal. A comparison of the infrared spectrum of $[FeNO(das)_2][ClO_4]_2$ with that of $[FeXNO(das)_2][ClO_4]$ gave no evidence for any additional absorption bands (Figure 3). This evidence is completely consistent with the properties expected for a pentacoordinate complex. Some of the important properties of these compounds are summarized in Table I.

Discussion

Transition metal nitrosyls are normally classified on the basis of their NO stretching frequencies as co-

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(8) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 3993 (1958).

(9) W. Hieber and J. S. Anderson, *Z. Anorg. Allgem. Chem.*, **211**, 132 (1933).

(10) P. Hammerich, D. V. DerBartanian, C. Veeger, and J. D. W. van Voorst, *Biochim. Biophys. Acta*, **77**, 564 (1963).

(11) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

TABLE I

THE NO FREQUENCIES AND ELECTRONIC ABSORPTION SPECTRA OF THE IRON NITROSYL COMPLEXES

Compound	ν_{NO}, cm^{-1}	Absorption maxima, kK (ϵ)[b]			
trans-[FeClNO(das)$_2$]ClO$_4$[a]	1620	10.6(...)	13.7(...)	17.5(...)	24.5(...)
trans-[FeBrNO(das)$_2$]Br	1625	10.6(170)	13.5(sh)	17.3(190)	24.0(sh)
trans-[FeINO(das)$_2$]I	1640	10.5(350)	13.0(sh)	16.8(380)	Unobsd
[FeNO(das)$_2$][ClO$_4$]$_2$	1760	6.05(...)	16.7(...)	17.9(...)	

[a] Observed as reflectance spectra only. [b] The units are l. mole^{-1} cm^{-1}.

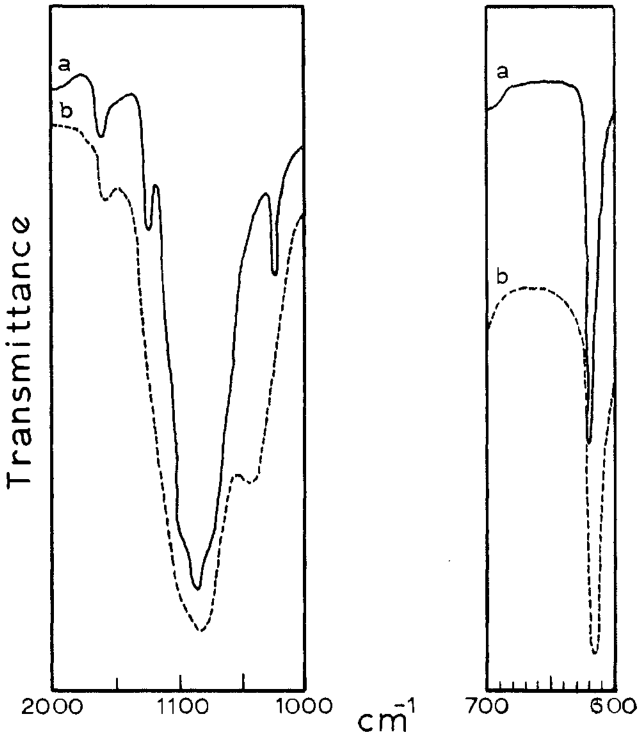

Figure 3.—The ClO$_4^-$ infrared absorption bands of (a) [FeBrNO(das)$_2$][ClO$_4$]; (b) [FeNO(das)$_2$][ClO$_4$]$_2$.

ordination compounds containing either the (NO)$^+$ group (ν_{NO} from 1500 to 2000 cm^{-1}) or the (NO)$^-$ group (ν_{NO} from 1080 to 1500 cm^{-1}).[12] This classification has been criticized on several grounds.[1,13,14] The most important of these criticisms is that compounds with NO frequencies between 1080 and 1500 cm^{-1} have been shown not to contain the NO group, but rather to be either hyponitrites, nitrito, or nitro compounds. Clearly, the use of the infrared stretching frequency as the sole criterion for determining the oxidation number of the nitrosyl group in these complexes is undesirable.

Manoharan and Gray[15] have shown that an LCAO–MO description of [Fe(CN)$_5$NO]$^{2-}$ successfully accounts for the limited observations of the spectral properties of this ion. It is readily apparent from the general properties of complexes containing NO that the nitrosyl group is covalently bound to the metal. However, the spectral properties of this series of *o*-phenylenebis(dimethylarsine)–nitrosyl complexes with *low NO frequencies* (ν_{NO} 1500–1600 cm^{-1}) can be described using a much less ambitious model.[1,16] It is initially assumed that the gross position of the NO stretching frequency in the infrared spectrum has a qualitative relationship to the NO bond multiplicity. In the case of the iron complexes [FeXNO(das)$_2$]$^+$ the NO stretching frequencies range from 1600 cm^{-1} in the cyanide to 1640 cm^{-1} in the iodide. This is the region of the infrared spectrum normally associated with double bonds.[17] If this assumption is correct, then the complex can be considered to contain an (N=O)$^-$ bonded to Fe(III), and it should be possible to interpret the electronic spectra of these iron complexes on this basis. The spectra of the closely related cobalt compounds[1] [CoXNO(das)$_2$]$^+$ and [CoXNO(en)$_2$]$^+$ were readily classified as electronic transitions of Co(III) d^6.

The reflectance spectrum of [FeClNO(das)$_2$]ClO$_4$ is shown in Figure 4. There are several qualitative features of importance which should be noted. The sharp transitions in the region between 4 and 6 kK have been identified as overtone or combination bands of *o*-phenylenebis(dimethylarsine). The spectrum of a pure sample of *o*-phenylenebis(dimethylarsine) shows very sharp absorptions in this region at 4.06, 4.15, 4.22, 4.30, 4.40, 4.50, 4.61, 5.75, and 5.97 kK. These *o*-phenylenebis(dimethylarsine) absorptions are very sharp and of relatively low intensity, and their positions are relatively insensitive to the chemical environment of *o*-phenylenebis(dimethylarsine). Thus, these vibrational absorptions are easily distinguished from electronic transitions (especially spin-forbidden transitions) which also occur in this region of the spectrum

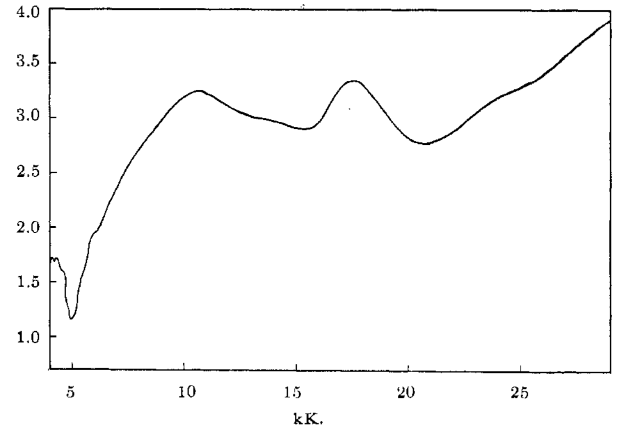

Figure 4.—The reflectance spectrum of [FeClNO(das)$_2$][ClO$_4$].

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[12] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

[13] R. D. Feltham, *Inorg. Chem.*, **3**, 1038 (1964).

[14] P. Gans, *Chem. Commun.*, 144 (1965).

[15] P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965).

[16] R. D. Feltham and W. Silverthorn, Proceedings of the Ninth International Conference on Coordination Chemistry, Helvitica Chimica Acta, Basle, 1966.

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

in the *o*-phenylenebis(dimethylarsine) complexes. The four broad absorption bands between 6 and 30 kK are electronic transitions of the complex. A detailed examination of the electronic spectra of these iron nitrosyl complexes will be presented in a subsequent paper.

Acknowledgments.—The authors are indebted to Professor M. Wacks for the analysis of oxygen in these complexes by neutron activation. The authors gratefully acknowledge the National Science Foundation (Grant GP-5752) for support of this work.

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The Electronic Absorption Spectrum and Bonding in the $Cu_2Cl_6^{2-}$ Dimer

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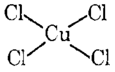
The electronic absorption spectra of several red copper(II) chloride compounds containing planar $Cu_2Cl_6^{2-}$ dimers have been measured. In addition to the normal charge-transfer and d–d transitions typical of square-planar $CuCl_4^{2-}$ ions, a new band, characteristic of the dimeric species, is present at 19,000 cm^{-1}. This band is polarized parallel to the Cu–Cu direction of the dimer. A molecular orbital description of the bonding in the dimer is presented and the origin of the anomalous 19,000-cm^{-1} band is explained.

Introduction

Recent investigations into the structural and spectral properties of copper(II) chloride complexes have revealed several heretofore unknown geometrical configurations.[1-9] Among those of particular interest have been the square-planar $CuCl_4^{2-}$ ion[4-6,8] (I) and the planar $Cu_2Cl_6^{2-}$ dimer[1-3] (II) The first of these has provided the opportunity to study in detail the properties of a simple square-planar species and contrast them with the properties of the more thoroughly studied distorted tetrahedral $CuCl_4^{2-}$ ion.[10-16] The second species is of interest because of the unusual optical[2,3] and magnetic properties[2,17-19] involved in the dimeric nature of the complexes. Since the $Cu_2Cl_6^{2-}$ dimer can be simply visualized as being formed by the union of two $CuCl_4^{2-}$ ions by the sharing of a pair of bridging chlorines, it makes it possible to correlate the properties of the dimer with the simpler monomer and sort out the features which are uniquely characteristic of the dimer. This article will report on an investigation of the electronic absorption spectrum of the $Cu_2Cl_6^{2-}$ dimer and an interpretation of its properties in terms of a simple molecular orbital correlation diagram.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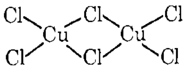
II

The compounds studied included $LiCuCl_3 \cdot 2H_2O$,[1] $KCuCl_3$,[2] $(CH_3)_2NH_2CuCl_3$,[3,20] and $(CH_3)_2CHNH_3CuCl_3$.[20] All four compounds are a deep garnet red and, when examined with polarized light, show strong yellow-red or green-red pleochroism.[3] For the case of the first three compounds, where the structure is known, it has been shown that compounds appear red when the electric vector of the polarized light is nearly parallel to the Cu–Cu direction.

Experimental Section

All compounds were prepared as described in previous work.[1-3,20] For each compound, except $KCuCl_3$, it was possible to obtain quite large crystals by slow evaporation of water or ethanol (or mixtures of the two) solutions in a desiccator with the use of a suitable desiccant. Thin single crystals for spectra work were ground or etched with an appropriate solvent. It was not always possible to obtain crystals thin enough for investigation of the visible and ultraviolet regions owing to the larger extinction coefficients for bands in this area. For these compounds, the spectra were obtained by the use of mineral oil and/or hexachlorobutadiene mulls. Since no isomorphous compounds exist, it was not possible to use a diluent technique. All spectra were recorded using a Cary Model 14 spectrophotometer. The results are summarized in Table I. For comparison purposes, the bands present in a typical square-planar complex, $(C_2H_5NH_3)_2CuCl_4$, are also given.

The polarization properties of the 19,000-cm^{-1} band were investigated using a polarizing microscope. The necessary

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