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Bis[*o*-phenylenebis(dimethylarsine)]iron Complexes with NO, CO, CH_3CN, and Other Small Molecules

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The preparation and characterization of several new *o*-phenylenebis(dimethylarsine) (das) complexes of iron are reported including $[Fe(das)_2(NO)][ClO_4]$, $[Fe(das)_2(NO)Cl][ClO_4]_2$, $[Fe(das)_2(CO)Cl][B(C_6H_5)_4]$, $[Fe(das)_2(CH_3CN)Cl][B(C_6H_5)_4]$, $Fe(das)_2(N_3)_2$, $Fe(das)_2(NCO)_2$, $Fe(das)_2(NO_2)Cl$, and $[Fe(das)_2(NCS)_2]PF_6$. Pmr studies of the diamagnetic six-coordinate complexes show that they all have trans geometry. The pmr spectrum of $[Fe(das)_2(NO)]^+$ in DMSO-d_6, CD_3CN and C_6H_5CN indicates that it is fluxional and has trigonal-bipyramidal geometry. The geometries of the four different nitrosyl complexes *trans*-$[Fe(das)_2(NO)(NCS)]^{2+}$, *trans*-$[Fe(das)_2(NO)(NCS)]^+$, $[Fe(das)_2(NO)]^{2+}$, and $[Fe(das)_2(NO)]^+$ are accounted for by a molecular orbital scheme.

Introduction

Transition metals play a central role in mediating the reactions of many small molecules. Iron compounds are especially important, because they are involved in nitrogen reduction by nitrogenase and by Haber catalysts, in oxygen transport by hemoglobins and myoglobin, and in several important catalysts. However, there is only a limited understanding of the chemical transformations which small molecules undergo while they are attached to iron. The research described below was initiated to elucidate the chemistry of $\{FeXY\}^n$ complexes.[1]

The chemistry of *o*-phenylenebis(dimethylarsine) (das) complexes of iron was first studied by Nyholm,[2] who isolated and characterized $FeX_2(das)_2$ and $FeX_2(das)_2{}^+$. Subsequently, studies of their magnetic properties[3,4] as well as those of an iron(IV) complex showed that all are low spin. The ligand field spectra[5,6] and infrared spectra[7] of *trans*-$[FeX_2(das)_2]^{0,+}$ have also been thoroughly studied and many of their spectral bands assigned. In addition, several nitrosyl derivatives of the $Fe(das)_2$ fragment have been reported previously.[8-10] These prior studies indicated that a series of $Fe(NO)(das)_2$ complexes could be prepared in which the total number of electrons in the $\{FeNO\}^n$ group could easily be varied.

In spite of the large number of $Fe(das)_2$ complexes which have been reported, there has been little systematic investigation of the preparation and chemical reactivity of their complexes with small molecules such as NO, CO, N_2, or CH_3CN. Since das forms complexes with iron in several oxidation states (0, +1, +2, +3, and +4) the $Fe(das)_2$ complexes should be ideal for investigating the chemical and physical consequences of changing the number of electrons in an $\{FeXY\}^n$ group while keeping the other ligands the same. This paper describes the synthesis of a number of such das complexes and demonstrates that the chemical and physical properties of the $\{FeNO\}^n$ group (n = 6–8) do indeed differ dramatically. These $\{FeNO\}^n$ complexes and their properties may serve as a guide to understanding the chemistry of other $\{FeXY\}^n$ groups.

Experimental Section

Reagents and Characterization. The reactions and operations described below were carried out where necessary under oxygen-free nitrogen in Schlenkware[11] using standard inert-atmosphere techniques. All solvents were thoroughly degassed before use. Further purification of solvents and reagents was by standard methods. Nitric oxide was purified by passing it through molecular sieves (Linde 4A) at −78°. The ligand *o*-phenylenebis(dimethylarsine) was prepared according to literature methods.[12] The compounds were analyzed by Huffman Laboratories, Wheatridge, Colo., and Chemalytics, Inc., Tempe, Ariz., and the results are set out in Table I.

The infrared spectra were obtained as Nujol mulls between KBr plates or as KBr pellets using Perkin-Elmer Model 337 and Beckman Model IR-12 infrared spectrophotometers. The nmr spectra were obtained using the Varian Models T60 and HA100 spectrometers equipped with variable-temperature probes. TMS was used as an internal standard. Conductivity measurements were carried out by methods described elsewhere[13] using an International Instruments, Inc., Model RC-16B2 conductivity bridge and a Lab-Line Instruments, Inc., cell.

Preparation of Complexes. Dichlorobis[*o*-phenylenebis(dimethylarsine)]iron(II).[7] A solution of 2.70 g of $FeCl_3 \cdot 6H_2O$ in 100 ml of ethanol was stirred for 2 hr with 0.5 g of iron powder and 2 drops of perchloric acid. The colorless solution was filtered and 4.1 ml of das was added. The yellow slurry was warmed almost to boiling for 30 min and allowed to cool to room temperature. The yellow solid was collected on a frit washed with 50 ml of ethanol and dried *in vacuo*; yield 5.35 g 77%.

Diazidobis[*o*-phenylenebis(dimethylarsine)]iron(II). A solution of 0.50 g of $Fe(das)_2Cl_2$ in 90 ml of methanol was warmed with 0.5 g of sodium azide for 20 min. The green solid was collected and dried *in vacuo*; yield 0.23 g, 45%.

Diisothiocyanatobis[*o*-phenylenebis(dimethylarsine)]iron(II). A solution of 1.0 g of potassium thiocyanate in 20 ml of methanol was added to a warm solution of 0.35 g of $Fe(das)_2Cl_2$ in 40 ml of methanol. After 0.5 hr the solution was cooled, and the purple solid was collected and dried *in vacuo*. The product was recrystallized from chloroform–heptane; yield 0.30 g 81%.

Dicyanatobis[*o*-phenylenebis(dimethylarsine)]iron(II). Solutions of 0.35 g of $Fe(das)_2Cl_2$ in 50 ml of warm methanol and of 0.21 g of potassium cyanate in 40 ml of methanol were mixed and stirred for 1 hr. The green solid was collected by filtration, dried *in vacuo*, and recrystallized from chloroform–heptane; yield 0.15 g, 43%.

Chloronitrobis[*o*-phenylenebis(dimethylarsine)]iron(II). A solution of sodium nitrite (0.15 g) in methanol (10 ml) was added to a warm solution of $Fe(das)_2Cl_2$ (1.00 g) in methanol (50 ml). After stirring for 10 min the brown solid was collected, washed with 5 ml of cold methanol, and dried *in vacuo*; yield 0.82 g, 81%.

Chlorocarbonylbis[*o*-phenylenebis(dimethylarsine)]iron(II) Tetraphenylborate. A methanol solution (100 ml) of $Fe(das)_2Cl_2$ (0.70 g) and sodium tetraphenylborate (0.35 g) were stirred for 24 hr at *ca.* 50° under a carbon monoxide atmosphere. After cooling the solution to room temperature, the yellow crystals which formed were

Table I. Elemental Analysis

Complex	% C		% H		% halide		% N	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Fe(das)_2Cl_2$						10.60		
	34.35	34.48	4.62	4.42	10.15	10.42		
$Fe(das)_2(N_3)_2$	33.72	34.07	4.54	4.75		0.1 if any	11.80	11.18
$Fe(das)_2(NCS)_2$	35.51	35.60	4.34	4.24			3.76	3.47
$Fe(das)_2(NCO)_2$	37.12	36.55	4.53	4.35			3.94	3.71
$Fe(das)_2(NO_2)Cl$		33.82		4.10		5.55		1.52
	33.84	33.11	4.55	4.41	5.00	4.29	1.97	1.82
$[Fe(das)_2(CO)Cl]BPh_4$	53.46	53.25	5.19	5.28	3.51	3.72		
$[Fe(das)_2(CH_3CN)Cl]BPh_4 \cdot CH_3OH$	53.45	53.51	5.64	5.39	3.36	3.74	1.33	1.29
$[Fe(das)_2(CH_3CN)Cl]BPh_4 \cdot C_2H_5OH$	53.87	53.97	5.75	5.95	3.32	4.43	1.31	1.44
$[Fe(das)_2(NO)Cl]BPh_4$	52.17	51.42	5.18	5.26	3.50	4.12	1.38	1.42
$[Fe(das)_2(NO)Cl](ClO_4)_2$	26.90	26.51	3.62	3.41	11.93	12.43	1.57	1.18
$[Fe(das)_2NO][ClO_4]_2$	28.02	27.86	3.77	3.64			1.63	1.45
$[Fe(das)_2NO]ClO_4$	31.70	30.90	4.27	4.19			1.65	1.65
$[Fe(das)_2NO]BPh_4$	54.65	54.61	5.37	5.46			1.43	1.44
$[Fe(das)_2(NCS)_2]PF_6$	29.71	31.32	3.63	3.69			3.15	2.89
$[Fe(das)_2Cl_2]BF_4$	30.56	30.37	4.11	4.39	9.03	8.86		
$[Fe(das)_2Cl_2]PF_6$	28.45	29.01	3.83	4.01	8.40	8.23		

collected in a fritted funnel, washed with 5 ml of ethanol, and dried *in vacuo*. The sample was recrystallized from acetone–ethanol as deep yellow plates; yield 0.45 g, 44%.

Chloroacetonitrilebis[*o*-phenylenebis(dimethylarsine)]iron(II) Tetraphenylborate–Methanol. A solution of 0.70 g of $Fe(das)_2Cl_2$ in 50 ml of methanol was stirred for 30 min with 0.1 g of powdered zinc. The solution was filtered and 2 ml of acetonitrile was added. Upon addition of 0.35 g of sodium tetraphenylborate, pale purple crystals formed. After 10 min they were collected on a fritted funnel, washed with 5 ml of ethanol and dried *in vacuo*; yield 0.71 g, 67%.

The corresponding ethanol solvate, $[Fe(das)_2(CH_3CN)Cl]B(C_6H_5)_4 \cdot C_2H_5OH$, was prepared by dissolving 0.35 g of $Fe(das)_2Cl_2$ and 0.20 g of sodium tetraphenylborate in 10 ml of acetonitrile. The resultant solution was filtered and after the addition of 50 ml of ethanol, it was stored at −10° for 24 hr. The purple crystals which formed were collected, washed with 2 ml of ethanol, and dried *in vacuo*; yield 0.37 g, 69%.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]iron Tetraphenylborate. Nitric oxide was bubbled through a methanol solution (30 ml) of $Fe(das)_2Cl_2$ (0.36 g) for 15 min. Next, nitrogen was bubbled through the solution for 5 min to remove excess nitric oxide. The purple solution was then filtered and 0.20 g of sodium tetraphenylborate was added. The purple crystals which formed were collected, washed with 5 ml of methanol, and dried *in vacuo*; yield 0.46 g, 91%.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]iron Diperchlorate. Enough concentrated hydrochloric acid was added to just dissolve 0.44 g of $Fe(das)_2Cl(NO_2)$ in 10 ml of methanol. Orange crystals formed upon addition of 2 drops of 70% perchloric acid to the solution. The solution was cooled to 0° and the solid was removed by filtration, washed with 5 ml of methanol, and dried *in vacuo*; yield 0.53 g, 95%.

Nitrosylbis[*o*-phenylenebis(dimethylarsine)]iron Diperchlorate. The following synthesis of this complex is superior to that reported previously.[8] A solution of $Fe(H_2O)_6(ClO_4)_2$ (3.65 g or 10 mmol) in 175 ml of degassed ethanol was treated with 0.2 g of powdered zinc for 10 min until the solution was colorless. After filtration under N_2, 4.1 ml of das (20 mmol) was added to the solution, and NO was slowly bubbled through the solution for 15 min. During this time the initially colorless solution turned dark blue, and a blue solid began to form. After removal of the excess NO by purging with N_2, the solid was removed by filtration and washed with a 1:1 ether–ethanol mixture (10 ml) and dried under vacuum. The product is sufficiently pure for most purposes but can be recrystallized by Soxhlet extraction with acetone under N_2; yield 7.31 g or 85% based on das.

Nitrosylbis[*o*-phenylenebis(dimethylarsine)]iron Perchlorate. An acetone solution (50 ml) of $[Fe(das)_2NO](ClO_4)_2$ (0.86 g) was passed down a Jones reductor column[14] (1.5 × 20 cm) which had been previously rinsed with acetone. The solution which was purple initially was brown on emerging from the column. After adding 50 ml of ethanol, the volume of the solution was reduced to *ca.* 50 ml by vacuum distillation. The red-brown crystals which formed were removed by filtration and recrystallized from acetone–ethanol; yield 0.46 g, 61%.

Nitrosylbis[*o*-phenylenebis(dimethylarsine)]iron Tetraphenylborate. A solution of 0.70 g of $Fe(das)_2Cl_2$ in 100 ml of methanol was stirred under an atmosphere of nitric oxide for 30 min. Nitrogen was bubbled through the solution to remove excess nitric oxide and the solution was passed through a Jones reductor column. The yellow solution of $Fe(das)_2Cl_2$ turned purple on exposure to nitric oxide and brown upon reduction. Sodium tetraphenylborate (0.35 g) was added, and after several minutes light brown crystals began forming. The crystals were removed by filtration, washed with 2 ml each of ethanol and diethyl ether, and dried *in vacuo*; yield 0.67 g, 68%.

This complex was also prepared by passing a solution of 0.39 g of $[Fe(das)_2(NO)Cl]Cl_2$ in 50 ml of methanol down the Jones reductor column and adding 0.18 g of sodium tetraphenylborate; yield 0.38 g, 74%.

Diisothiocyanatobis[*o*-phenylenebis(dimethylarsine)]iron(III) Hexafluorophosphate. A slurry of 0.2 g of $Fe(das)_2(NCS)_2$ in 10 ml of methanol was treated with *ca.* 0.1 g of nitrosonium hexafluorophosphate. The solution was stirred for 1 hr and the solvent was decanted from the brown solid, washed with 3 ml each of methanol and ether, and dried *in vacuo*; yield 0.19 g, 79%.

Dichlorobis[*o*-phenylenebis(dimethylarsine)]iron(III) Tetrafluoroborate. A solution of 0.30 g of $Fe(das)_2Cl_2$ in 15 ml of 1:1 acetone–methanol was treated with 2 ml of 50% tetrafluoroboric acid. The red solution was filtered and nitrogen was bubbled through it until crystals had formed; yield 0.2 g, 62%.

Dichlorobis[*o*-phenylenebis(dimethylarsine)]iron(III) Hexafluorophosphate. Nitrosonium hexafluorophosphate (0.1 g) was added to 0.20 g of $Fe(das)_2Cl_2$ in 10 ml of acetonitrile. After 10 min of stirring, 30 ml of diethyl ether was added to cause crystallization. The red crystals were filtered, washed with 2 ml each of ethanol and diethyl ether, and dried *in vacuo*; yield 0.15 g, 62%.

Results

$Fe(das)_2X_2$ Complexes. The dichloro complex, $Fe(das)_2Cl_2$, appeared to us to be the best starting material for the synthesis of a series of bis[*o*-phenylenebis(dimethylarsine)] complexes of iron. Although the compound is relatively easily prepared, there is only brief reference to its synthesis.[7] $Fe(das)_2Cl_2$ was prepared from alcohol solutions in 75% yield provided an inert atmosphere was maintained to avoid oxidation to $[Fe(das)_2Cl_2]^+$. The presence of $[Fe(das)_2Cl_2]^+$ in solution is easily detected by its blood red color. Once formed, the dry solid, $Fe(das)_2Cl_2$, is stable under nitrogen or under vacuum. The odor of das is noticeable over samples of $Fe(das)_2Cl_2$ which have been exposed to air, but the extent of decomposition is minor.

The trans isomer of $Fe(das)_2Cl_2$ is the only one which was isolated from these reactions, while the cis isomer has not yet been prepared. The trans isomer is probably formed preferentially because of its insolubility. The cis and trans isomers of $Ru(das)_2Cl_2$ have both been reported;[15] and *cis*-$[Ru(das)_2Cl_2]$ is quite soluble in many organic solvents including

Table II. Nmr and Infrared Data

Compd	Solvent	$\delta(CH_3)$, ppm	ν,[a] cm^{-1}
$Fe(das)_2Cl_2$	CD_3OD	1.18	$\nu(Fe{-}Cl)$ 349[b]
	CD_3CN	1.20, 1.68, 1.75	
$Fe(das)_2(N_3)_2$			$\nu_{as}(N_3)$ 2130 vs
$Fe(das)_2(NCO)_2$	$CDCl_3$	1.60	$\nu(CN)$ 2225 vs
$Fe(das)_2(NCS)_2$	$CDCl_3$	1.65	$\nu(CN)$ 2085 vs
$Fe(das)_2Cl(NO_2)$	Insoluble		$\nu_{as}(NO_2)$ 1314, 1295; $\nu_s(NO_2)$ 1208; $\delta(ONO)$ 805; $\rho_\omega(NO_2)$ 605
$[Fe(das)_2(CH_3CN)Cl]BPh_4 \cdot CH_3OH$	CD_3CN	1.68, 1.77, 3.27[c]	$\nu(CN)$ 2240 w
	DMSO-d_6	1.02, 1.12, 1.92, 3.13[d]	
$[Fe(das)_2(CH_3CN)Cl]BPh_4 \cdot C_2H_5OH$	CD_3CN	1.12,[e] 1.67, 1.75, 3.50[e]	$\nu(CN)$ 2240 w
$[Fe(das)_2(CO)Cl]BPh_4$	Acetone-d_6	1.95, 2.00	$\nu(CO)$ 1930 vs
	DMSO-d_6	1.87, 1.90	
$[Fe(das)_2(NO)Cl]BPh_4$		Paramagnetic	$\nu(NO)$ 1620 vs
$[Fe(das)_2(NO)Cl](ClO_4)_2$	DMSO-d_6	2.20, 2.37	$\nu(NO)$ 1860 vs
$[Fe(das)_2NO]ClO_4$	CD_3CN	1.62, 1.77	$\nu(NO)$ 1690 vs
	Acetone-d_6	1.77, 1.87	
	DMSO-d_6	1.17, 1.60[f]	
$[Fe(das)_2NO]BPh_4$	CD_3CN	1.57, 1.73	$\nu(NO)$ 1710 vs
	DMSO-d_6	1.17, 1.60[f]	

[a] KBr pellet. Key: s, strong; v, very; w, weak; as, asymmetric. [b] Reference 7. [c] Methanol CH_3. [d] 1.02, 1.12, das CH_3; 1.92, CH_3CN; 3.13, CH_3OH. The resonances integrate 4:4:1:1. [e] 1.12, ethanol triplet; 3.50, ethanol quartet. [f] 1.17 resonance integrates 3 times as large as the 1.60 resonance.

methanol, but *trans*-[Ru(das)$_2$Cl$_2$] is very insoluble. The relative solubilities of *cis*- and *trans*-[FeCl$_2$(das)$_2$] should closely correspond to these ruthenium complexes. The crystal structures of Fe(das)$_2$Cl$_2$ have not been determined, but several different pieces of evidence allow the stereochemistry of these complexes to be confidently assigned. Infrared studies[7] of Fe(das)$_2$Cl$_2$ show that there is only a single iron–chlorine stretching frequency at 349 cm^{-1} which is strong evidence for trans geometry. The patterns of the methyl resonances in the pmr spectrum have been used to establish the structures of several cobalt(III)[16] and ruthenium(II)[17] complexes of das. For the cis isomers of M(das)$_2$X$_2$, four peaks are observed in the methyl region of the pmr spectrum, whereas only a single peak is observed for the trans isomers. The iron complexes Fe(das)$_2$X$_2$ all have single methyl resonances (Table II) and therefore must have trans configurations. Finally, the electronic spectra of Fe(das)$_2$X$_2$ were readily interpreted assuming tetragonal (trans) geometry.[5]

Studies of the properties of *trans*-[Fe(das)$_2$Cl$_2$] in solution show that the chlorides are quite labile. Its conductivity in methanol indicates that it is a 1:1 electrolyte even though only a single methyl resonance was observed in the pmr spectrum in this solvent. In acetonitrile conductance measurements indicate that one chloride is only partially dissociated. The observation of three peaks in the methyl region of the pmr spectrum in acetonitrile is consistent with these conductance studies. In CD$_3$CN, the single methyl resonance of *trans*-[Fe(das)$_2$Cl$_2$] is at 1.20 ppm, while *trans*-[Fe(das)$_2$(CD$_3$CN)Cl]$^+$ has two singlets of equal intensity at 1.68 and 1.75 ppm. Treatment of *trans*-[Fe(das)$_2$Cl$_2$] with Ag$^+$ in methanol yields [Ag(das)$_2$]$^+$. However, except for this one reaction with Ag$^+$, the loss of das is unimportant to the chemistry of Fe(das)$_2$Cl$_2$.

The solubility of *trans*-[Fe(das)$_2$Cl$_2$] in polar solvents such as alcohols is sufficient to carry out metathetical reactions. Both chlorides are readily displaced in these solvents by more polarizable anions. Reaction 1 occurs readily with azide, cyanate, and thiocyanate ions. The products obtained from these reactions are all diamagnetic. The single methyl resonance in the pmr spectra (Table II) as well as the single infrared bands at 2130, 2225, and 2085 cm^{-1} indicate that the *trans*-diacido geometry has been retained in the azide, cyanate, and thiocyanate derivatives, respectively. It has been concluded that the thiocyanate ligand is probably bound through nitrogen, because the low value (Table II) observed for ν_{CN} is that usually found for N-bonded thiocyanate.[18]

$$trans\text{-}[Fe(das)_2Cl_2] + 2X^- \rightarrow trans\text{-}[Fe(das)_2X_2] + 2Cl^- \quad (1)$$

Fe(das)$_2$XX′ Complexes. In only one case was a single chloride displaced from Fe(das)$_2$Cl$_2$ by another anion. The reaction between nitrite ion and *trans*-[Fe(das)$_2$Cl$_2$] in methanol yields primarily *trans*-[Fe(das)$_2$(NO$_2$)Cl]. Attempts to prepare Fe(das)$_2$(NO$_2$)$_2$ by further substitution with nitrite ion were unsuccessful, perhaps because of the very low solubility of *trans*-[Fe(das)$_2$(NO$_2$)Cl]. The monosubstituted complex was difficult to obtain in a pure form and was usually contaminated with *trans*-[Fe(das)$_2$Cl$_2$]. Because of its extreme insolubility in inert solvents, it could not be purified by recrystallization. The infrared spectrum of *trans*-[Fe(das)$_2$(NO$_2$)Cl] (Table II) indicates that the NO$_2^-$ ligand is coordinated through the nitrogen.[19] Treatment of this compound with acid leads to a trans-nitrosyl complex (*vide infra*), a reaction which has been observed for other nitro complexes.[20]

[Fe(das)$_2$X$_2$]$^+$ Complexes. The iron(II) complexes described above are generally sensitive to air oxidation or to oxidation by other good oxidants such as Cl$_2$, Br$_2$, NO$^+$, or even H$^+$.

$$trans\text{-}[Fe(das)_2X_2] + NO^+ \text{ or } H^+ \rightarrow trans\text{-}[Fe(das)_2X_2]^+ \quad (2)$$

The reactions between NO$^+$ or H$^+$ and *trans*-[Fe(das)$_2$X$_2$] were carried out in the absence of air, but the fate of the reduced NO$^+$ or H$^+$ species is not known. Since it is well-known that NO$^+$ can serve as a one-electron oxidant,[21] its reaction with *trans*-[Fe(das)$_2$Cl$_2$] is assumed to produce NO. Fractionation of the gaseous products from the reaction between H$^+$ and *trans*-[Fe(das)$_2$Cl$_2$] showed that H$_2$ was *not* a product of this reaction. Reaction 2 provides a route to *trans*-[Fe(das)$_2$(NCS)$_2$]$^+$ which could not be obtained from the reaction between *trans*-[Fe(das)$_2$Cl$_2$]$^+$ and NCS$^-$. Nyholm[2] found that the reaction between *trans*-[Fe(das)$_2$Cl$_2$]$^+$ and both NCS$^-$ and I$^-$ produced the iron(II) complexes, apparently *via* reduction of iron(III) by NCS$^-$ or I$^-$. Our attempts to prepare [Fe(das)$_2$I$_2$]$^+$ using reaction 2 were unsuccessful apparently because iodide was abstracted from the complex.

[Fe(das)$_2$(XY)X′]$^+$ Complexes. One chloride ion is also readily displaced from *trans*-[Fe(das)$_2$Cl$_2$] by neutral ligands, producing cationic complexes.

$$trans\text{-}[Fe(das)_2Cl_2] + XY \rightarrow trans\text{-}[Fe(das)_2(XY)Cl]^+ + Cl^- \quad (3)$$

The conductivity of *trans*-[Fe(das)$_2$Cl$_2$] in dilute solutions of acetonitrile ($\sim 10^{-3}$ *M*) corresponds to about 50% dissociation and suggested that an acetonitrile complex could be prepared. Addition of several per cent of acetonitrile and sodium tetraphenylborate to methanol solutions of *trans*-[Fe(das)$_2$Cl$_2$] rapidly produced crystals of *trans*-[Fe(das)$_2$(CH$_3$CN)Cl][BPh$_4$]. Although methanol solutions of *trans*-[Fe(das)$_2$Cl$_2$] indicate the dissociation of one chloride, addition of sodium tetraphenylborate to these solutions did *not* yield a methanol complex.

Carbon monoxide also displaces chloride from *trans*-[Fe(das)$_2$Cl$_2$] forming a chlorocarbonyl complex under rather mild conditions. Yellow crystals of *trans*-[Fe(das)$_2$(CO)Cl][BPh$_4$] were readily obtained from the reaction between a warm methanol solution of *trans*-[Fe(das)$_2$Cl$_2$] and sodium tetraphenylborate with carbon monoxide. Its carbonyl stretching frequency (1930 cm^{-1}) compares favorably with the analogous ruthenium complex,[22] *trans*-[Ru(das)$_2$(CO)Cl][BPh$_4$], (ν_{CO} 1950 cm^{-1}). Two singlets (intensity ratio 1:1) were observed[22] for *trans*-$[Ru(das)_2Cl(CO)]^+$ at 1.81 and 1.88 ppm in the methyl region of the pmr spectrum in DMSO-d_6, and the corresponding iron complex also has two singlets (intensity ratio 1:1) at 1.87 and 1.90 ppm. Cis complexes of $[Fe(das)_2(XY)Cl]^+$ would be expected to exhibit eight separate resonances in the methyl region of the pmr spectrum. Therefore, both the ruthenium and iron complexes have been assigned the trans configuration. The iron(0) complex $Fe(das)_2CO$ has been reported previously.[23] However, several attempts to prepare this Fe(0) complex by the reduction of *trans*-$[Fe(das)_2(CO)Cl]^+$ were unsuccessful.

We have shown above that under mild conditions one anion can easily be displaced from *trans*-$Fe(das)_2X_2$ by CO, CH_3CN, and CH_3OH. Consequently, numerous attempts were made to prepare *trans*-$[Fe(das)_2(N_2)X]^+$ by displacement of Cl^-, Br^-, CH_3CN, or CH_3COCH_3 from the corresponding iron(II) complexes. In one case, a band of medium intensity at 2040 cm^{-1} was observed in the ir spectrum, but an iron(II) complex of dinitrogen could not be isolated.

Iron Nitrosyl Complexes. Although these nitrosyl complexes were formed from many diverse reactions and have widely differing properties, the chemistry of all these nitrosyl complexes will be discussed in this section.

Methanol solutions of *trans*-$[Fe(das)_2Cl_2]$ rapidly react with nitric oxide producing das derivatives of the $\{FeNO\}^7$ group.

$$trans\text{-}[Fe(das)_2Cl_2] + NO \rightarrow trans\text{-}[Fe(das)_2(NO)Cl]^+ + Cl^- \qquad (4)$$

Reaction 4 is an example of chloride substitution and simultaneous oxidation of Fe(II) to Fe(III). The nitrosyl frequency (1620 cm^{-1}) of *trans*-$[Fe(das)_2(NO)Cl][BPh_4]$ is identical with that of *trans*-$[Fe(das)_2(NO)Cl][ClO_4]$ described previously.[8] Although the *trans*-$[Fe(das)_2(NO)Cl]^+$ complex is not new, the present method of synthesis is a considerable improvement over that previously reported. Further insight into this interesting nitrosylation reaction requires a detailed mechanistic study.

The very stable *trans*-$[Fe(das)_2(NO)Cl]^{2+}$ species is readily obtained by treatment of *trans*-$Fe(das)_2NO_2Cl$ with acid (*vide supra*). This nitrosyl complex was also expected to result from the direct reaction of NO with *trans*-$[Fe(das)_2Cl_2]^+$. Surprisingly, methanolic solutions of *trans*-$[Fe(das)_2Cl_2]^+$ do not react with NO, even though this Fe(III) complex is expected to be labile. It was also anticipated that *trans*-$[Fe(das)_2(NO)Cl]^{2+}$ could be obtained from the reaction between NO^+ and *trans*-$Fe(das)_2Cl_2$, but only *trans*-$[Fe(das)_2Cl_2]^+$ was isolated from this reaction.

The preparation of the five-coordinate derivative of the $\{FeNO\}^7$ group $[Fe(das)_2(NO)]^{2+}$ reportedly gave high yields of product (66%). However, our subsequent attempts to prepare this complex using the method previously described[8] failed completely. Consequently, an alternative preparative method for this complex was sought. Simple reversal of the order of addition of das and NO appears to have solved this synthetic difficulty. If 2 equiv of das/mol of iron are first added to a ethanolic solution of $Fe(H_2O)_6(ClO_4)_2$, then subsequent addition of NO to this solution produces $[Fe(das)_2(NO)][ClO_4]_2$ in reproducibly good yield.

The complex *trans*-$[Fe(das)_2(NO_2)Cl]$ proved to be a very useful starting material for the preparation of the das derivatives of the $\{FeNO\}^6$ group. This complex readily reacts with acid in acid–methanol mixtures forming $[Fe(das)_2(NO)Cl]^{2+}$.

$$trans\text{-}[Fe(das)_2(NO_2)Cl] + 2H^+ \rightarrow trans\text{-}[Fe(das)_2(NO)Cl]^{2+} + H_2O \qquad (5)$$

The $\{FeNO\}^6$ group in this diamagnetic complex is isoelectronic with that in $[FeNO(CN)_5]^{2-}$ and consequently has properties which are closely related to the pentacyano complex. The nitrosyl stretching frequency (1860 cm^{-1}) and high N(1s) binding energy (402.4 eV) of the das complex are consistent with the *formal* description of the complex as an NO^+ derivative of Fe(II), as is often given to $FeNO(CN)_5^{2-}$. The pmr spectrum of $[Fe(das)_2(NO)Cl]^{2+}$ in DMSO-d_6 consists of two singlets (intensity ratio 1:1) at 2.20 and 2.37 ppm. Consequently, $[Fe(das)_2(NO)Cl]^{2+}$ must have trans geometry. The relatively large separation between the two methyl resonances suggests that the NO group has a large deshielding effect on the adjacent methyl groups.

A fourth type of iron nitrosyl complex of das was prepared by the reduction of any of the other three Fe–das nitrosyls described above. Both the six-coordinate complexes and the five-coordinate complex are reduced by a Jones reductor forming $[Fe(das)_2(NO)]^+$ (eq 6). This new brown complex

$$[Fe(das)_2(NO)Cl]^{+\text{ or }2+} \xrightarrow{Zn\text{–}Hg} [Fe(das)_2(NO)]^+ \qquad (6)$$

is diamagnetic and can be isolated as either the perchlorate or tetraphenylborate salt. The solids are stable in air only for a few weeks. The infrared spectrum of $[Fe(das)_2(NO)]^+$ (ν_{NO} 1690 cm^{-1}) gives little insight into its geometry. However, there are several closely related complexes which are isoelectronic with this $\{FeNO\}^8$ complex of das. The cobalt complex, $[Co(das)_2(NO)]^{2+}$ is known to be trigonal bipyramidal with a linear Co–N–O group in the equatorial plane.[24] The diphos (diphos = 1,2-bis(diphenylphosphino)ethane) derivative of this $\{FeNO\}^8$ group has also been reported.[25] The diphos complex $[Fe(diphos)_2(NO)]^+$ has a slightly lower NO frequency (1681 cm^{-1}) and was originally suggested to have square-pyramidal geometry but was reassigned a trigonal-bipyramidal structure.[26] The analogous ruthenium complex $[Ru(diphos)_2(NO)]^+$ is known to be trigonal bipyramidal with a linear Ru–N–O group.[27] This information suggests that $[Fe(das)_2(NO)]^+$ is most likely trigonal bipyramidal and isostructural with $[Co(das)_2(NO)]^{2+}$.

Since pmr studies of $[Co(das)_2(NO)]^{2+}$ in CD_3CN and DMSO-d_6 have shown that it undergoes turnstile rotation and solvent exchange,[28] the temperature dependence of the pmr spectrum of $[Fe(das)_2(NO)]^+$ was investigated. Solutions of $[Fe(das)_2(NO)]^+$ in CD_3CN and in C_6H_5CN exhibit two singlets (intensity 1:1) in the methyl region of the pmr spectrum which are temperature dependent. In C_6H_5CN, the two peaks coalesce with increasing temperature, until a single broad peak is obtained at 75° (Figure 1). Increasing the temperature causes continued narrowing of this peak until the complex begins to decompose (~110°). For $[Fe(das)_2(NO)]^+$ however, in contrast with $[Co(das)_2(NO)]^{2+}$, only a small shift (2.9 Hz) of the coalesced single peak and of the average position of the two singlets was observed with temperature. Finally, the process which results in the coalescence of the two low-temperature peaks is relatively independent of solvent, since movement toward coalescence of these two peaks was observed over the same temperature range in DMSO-d_6, CD_3CN, and C_6H_5CN.

The chiral trigonal-bipyramidal complexes, $[Co(das)_2(NO)]^{2+}$ and $[Fe(das)_2(NO)]^+$, can have only C_2 symmetry and they would be expected to exhibit four peaks in the methyl region of the pmr spectrum (intensity ratio 1:1:1:1). The fact that only two methyl resonances are observed for each complex can be accounted for by a process which rapidly interconverts the "*d*" and "*l*" enantiomers of the TBP complexes *via* a complex with square-pyramidal geometry having an axial NO group. This square-pyramidal form can be either (1) a six-coordinate solvated intermediate, (2) a five-coordinate square-pyramidal intermediate, or (3) a square-pyramidal transition state. As we have already discussed, the square-pyramidal forms of these complexes should have two nonequivalent methyl groups (intensity ratio 1:1). Evidence was presented elsewhere[28] for the formation of a solvated

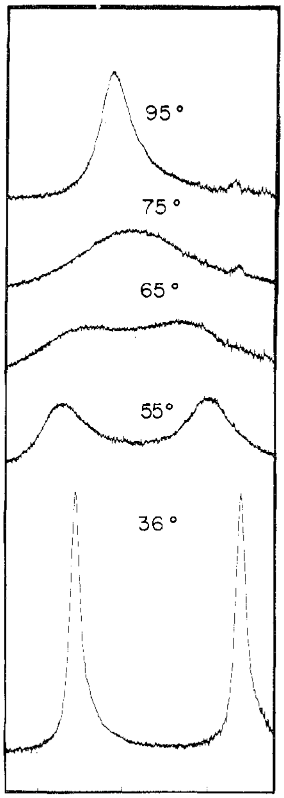
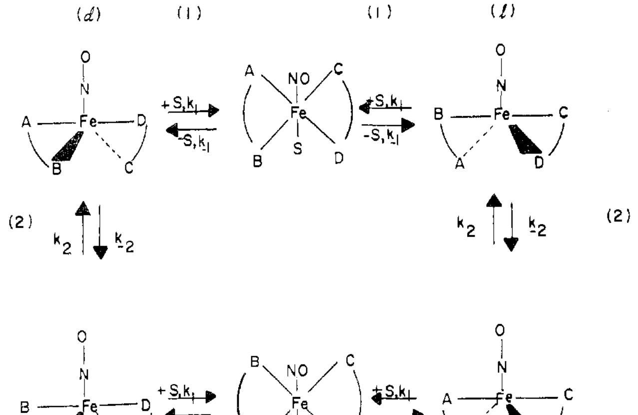


Figure 1. The temperature dependence of the pmr spectrum of $[Fe(NO)(das)_2][ClO_4]$ in C_6H_5CN. An activation energy of 12.6 kcal mol^{-1} was calculated for the process which equilibrates all of the methyl groups of $[Fe(NO)(das)_2][ClO_4]$ using the method outlined by H. S. Gutowski and C. H. Holm, *J. Chem. Phys.*, **25**, 1226 (1956).

Scheme I



species in the case of $[Co(das)_2(NO)]^{2+}$. The slight shifts of the average peak positions of the methyl resonances of $[Fe(das)_2(NO)]^+$ in C_6H_5CN suggest that some *trans*-$[Fe(das)_2(NO)(C_6H_5CN)]^+$, a six-coordinate solvated species, is in equilibrium with the pentacoordinate complex (process 1 of Scheme I) but to a lesser extent than the cobalt case.

The coalescence of the two peaks is indicative of a second dynamic process in solutions of $[Fe(das)_2(NO)]^+$. This process requires that all eight methyl groups of $[Fe(das)_2(NO)]^+$ become equivalent. The cobalt complex $[Co(das)_2(NO)]^{2+}$ behaved similarly. The two mechanisms which can account for the averaging of all eight of the methyl resonances of these complexes are turnstile rotation and Berry pseudorotation. For complexes of nonchelating ligands, Berry pseudorotation probably has a smaller activation energy.[29] However, in order to average all eight methyl groups of $[Fe(das)_2NO]^+$, a Berry pseudorotation process must pass through a trigonal-bipyramidal complex with NO axial and one das ligand diequatorial. Therefore, we prefer the turnstile rotation (process 2 of Scheme I) as the mechanism for averaging the methyl groups because two chelating ligands are attached to the metal. The insensitivity of the coalescence temperature of $[Fe(das)_2(NO)]^+$ to solvent (compared to $[Co(das)_2(NO)]^{2+}$) is also indicative of a lesser degree of solvation of the iron complex and is consistent with our failure thus far to isolate any six-coordinate complexes of the $[Fe(das)_2(NO)]^+$ group.

Table III

Complex	Electron confign	Stereo-chem-istry[a]	MNO angle, deg	ν_{NO}, cm^{-1}	Ref
$[Fe(NO)(das)_2(NCS)]^{2+}$	$\{FeNO\}^6$	Trans	180[b]	1885	*b*
$[Fe(NO)(das)_2(NCS)]^+$	$\{FeNO\}^7$	Trans	157[b]	1620	*c*
$[Fe(NO)(das)_2]^{2+}$	$\{FeNO\}^7$	TP	174[d]	1760	6
Fe(NO)(TPP)(NMeIm)	$\{FeNO\}^7$	Trans	142		32
Fe(NO)(TPP)	$\{FeNO\}^7$	TP	149	1700	30b, 31
$Fe(NO)[S_2CN(C_2H_5)]_2$	$\{FeNO\}^7$	TP	170	1673	*e*
$[Fe(NO)(das)_2]^+$	$\{FeNO\}^8$	(TBP)[f]	(180)[f]	1710	*c*
$[Co(NO)(das)_2]^{2+}$	$\{CoNO\}^8$	TBP	179	1852	24
$[Fe(NO)(diphos)_2]^+$	$\{FeNO\}^8$	(TBP)[f]	(180)[f]	1681	26
$[Ru(NO)(diphos)_2]^+$	$\{RuNO\}^8$	TBP	174	1673	27

[a] TP = tetragonal pyramid with axial NO; TBP = trigonal bipyramidal with equatorial NO. [b] K. F. Bizot, J. H. Enemark, and R. D. Feltham, unpublished results. [c] This work. [d] P. L. Johnson, J. H. Enemark, R. D. Feltham, and T. E. Nappier, unpublished results. [e] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958); M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967). [f] The structures of these complexes have not as yet been determined. Their stereochemistry and MNO bond angles have been assumed by comparison with the $\{CoNO\}^8$ and $\{RuNO\}^8$ complexes in this table.

Discussion

The synthesis of these four different types of iron–nitrosyl complexes provides an opportunity for a direct comparison of the structural, physical, and chemical properties of the $\{FeNO\}^n$ group. Because all of these complexes are low spin and have two das ligands and one nitrosyl ligand attached to the iron, any changes in the structure of the $\{FeNO\}^n$ group brought about by *changes* in intramolecular ligand–ligand repulsions should be negligible. Consequently, all of the observed changes in the $\{FeNO\}^n$ group are directly attributed to changes in the number of electrons, *n*. The structural effects of the number of electrons, *n*, in the $\{FeNO\}^n$ group are very evident from Table III. The bonding in complexes of the $\{FeNO\}^6$ and $\{FeNO\}^7$ groups has been discussed in detail elsewhere[30] but will be summarized here (Figure 2). Six-coordinate $\{FeNO\}^6$ complexes with approximately C_{4v} symmetry such as *trans*-$[Fe(das)_2(NO)Cl]^{2+}$ have the electron configuration $(2e)^4(1b_2)^2$. These molecular orbitals are mainly comprised of d_{xz}, d_{yz}, and d_{xy}, respectively, and are bonding or nonbonding. This electron configuration gives rise to a $^1A_1$ ground state, and consequently *trans*-$[Fe(das)_2(NO)Cl]^{2+}$ should be stable with a linear Fe–N–O group. However, a one-electron reduction to the $\{FeNO\}^7$ group will place one electron in an antibonding molecular orbital (either $3e(\pi^*\ NO)$ or $4a_1(d_{z^2})$, Figure 2). Population of the 3e orbital will cause bending of the Fe–N–O group, while population of $4a_1$ would cause the loss of one of the six ligands and distortion toward TBP geometry. Both five- and six-coordinate $\{FeNO\}^7$ complexes have been isolated. The five-coordinate $\{FeNO\}^7$ complex $[Fe(NO)(das)_2]^{2+}$ has TP geometry and an Fe–N–O angle of 174°. The Fe–N–O angle in the six-coordinate complex *trans*-$[Fe(NO)(NCS)(das)_2]^+$ is 157°. For another pair of $\{FeNO\}^7$ complexes, (nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenyl-

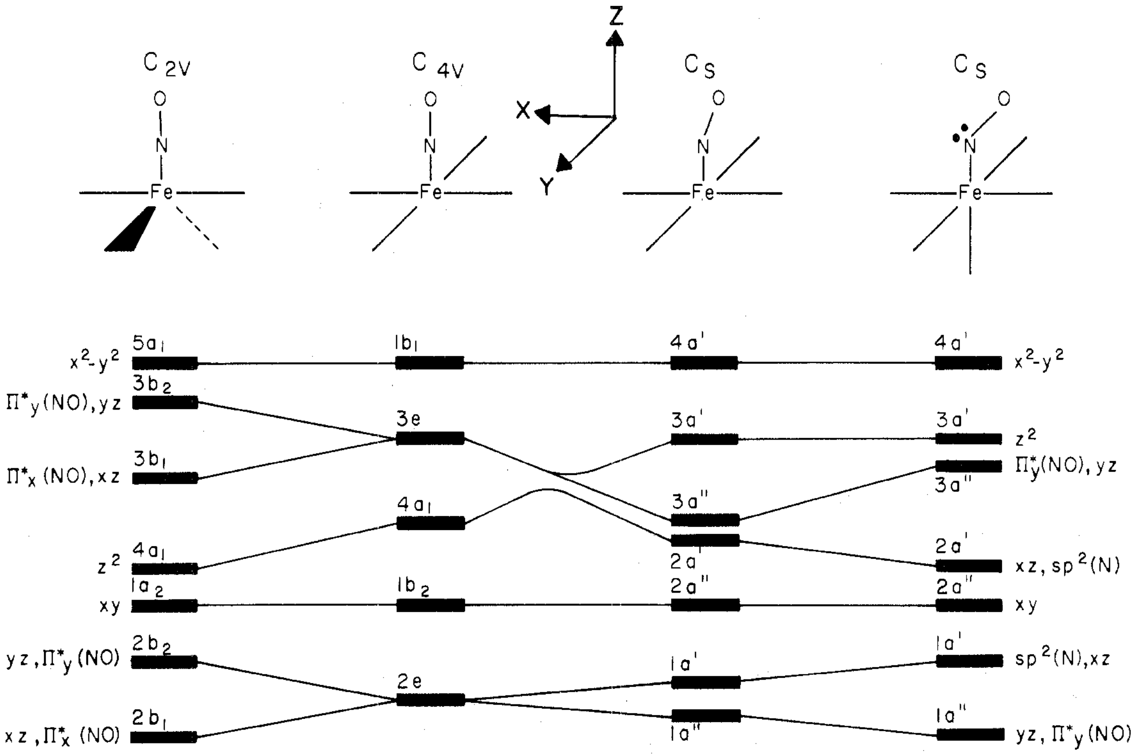


Figure 2. A molecular orbital diagram correlating the energy levels of the $\{FeNO\}^n$ group in ligand fields of various symmetries.

porphinatoiron, Fe(NO)(TPP),[31] and nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(1-methylimidazole)iron, Fe(NO)(TPP)-(NMeIm)[32]), the Fe–N–O angles are 149 and 142°, respectively. Consequently, the $4a_1$ and 3e orbitals must be close in energy, and their exact ordering will depend upon the strength of the ligand field established by the other ligands attached to the $\{FeNO\}^7$ group.

As has been pointed out elsewhere[30,32-35] bending of the $\{MNO\}^n$ group will allow orbitals which have π and σ symmetry to mix. In the present case, a component of the 3e orbital (π^* NO) may mix with $4a_1$. The degree of mixing will be dependent upon the relative energies of 3e and $4a_1$, which in turn will be strongly dependent upon the presence of a sixth ligand trans to the nitrosyl group.[30] With a sixth ligand in the trans-axial position, $4a_1(d_{z^2})$ should be higher in energy than 3e and a strongly bent FeNO group will result. However, removal of the trans-axial ligand will lower the energy of $4a_1$ relative to 3e with consequent increased mixing of $4a_1$ and 3e. Greater contribution of d_{z^2} to the highest occupied molecular orbital will result in increased bond angles of the FeNO group.

The reduction of any of the $\{FeNO\}^6$ or $\{FeNO\}^7$ complexes by Zn–Hg leads to the five-coordinate derivative of the $\{FeNO\}^8$ group, $[Fe(das)_2(NO)]^+$. Other five-coordinate complexes of $\{MNO\}^8$ groups have TBP geometry with linear MNO groups if $4a_1$ is lower than 3e, TP geometry with strongly bent MNO groups if 3e is lower than $4a_1$ (Figure 2), and geometry distorted between TBP and TP with intermediate bond MNO angles if 3e and $4a_1$ are degenerate. The evidence presented above favors assigning TBP geometry with a linear Fe–N–O group to $[Fe(das)_2(NO)]^+$ although the data are insufficient to draw final conclusions regarding its structure. Complete X-ray structure determinations of these complexes are in progress and will be the subjects of future reports.

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Registry No. $Fe(das)_2Cl_2$, 14127-26-5; $Fe(das)_2(N_3)_2$, 53966-27-1; $Fe(das)_2(NCS)_2$, 53966-28-2; $Fe(das)_2(NCO)_2$, 53966-29-3; $Fe(das)_2(NO_2)Cl$, 53966-30-6; $[Fe(das)_2(CO)Cl]BPh_4$, 53966-32-8; $[Fe(das)_2(CH_3CN)Cl]BPh_4 \cdot CH_3OH$, 53966-15-7; $[Fe(das)_2(CH_3CN)Cl]BPh_4 \cdot C_2H_5OH$, 53966-16-8; $[Fe(das)_2(NO)Cl]BPh_4$, 53966-12-4; $[Fe(das)_2(NO)Cl](ClO_4)_2$, 36236-95-0; $[Fe(das)_2NO](ClO_4)_2$, 54002-69-6; $[Fe(das)_2NO]ClO_4$, 54002-72-1; $[Fe(das)_2NO]BPh_4$, 54002-71-0; $[Fe(das)_2(NCS)_2]PF_6$, 53966-25-9; $[Fe(das)_2Cl_2]BF_4$, 37817-55-3; $[Fe(das)_2Cl_2]PF_6$, 53966-26-0.

References and Notes

(1) *n* is the number of d electrons when the XY ligand is *formally* considered to be coordinated as :X≡Y:. Thus, $\{FeNO\}^6$ represents the $N{\equiv}O^+$ derivative of Fe(II), $[FeNO]^{3+}$, while $\{FeNCCH_3\}^6$ represents the acetonitrile derivative of Fe(II), $[FeN{\equiv}CCH_3]^{2+}$.
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Ligand Field Interpretation of High-Spin Trigonal-Bipyramidal Cobalt(II) Complexes

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Single-crystal polarized spectra have been recorded for a high-spin trigonal-bipyramidal CoNS$_3$Br chromophore. These spectra as well as those of the chromophores CoNP$_3$Br and CoNN$_3$Br have been interpreted on the basis of ligand field and angular overlap parameters. These parameters, which have been estimated either from metal–ligand orbital overlaps or from the experimental transitions, are quite meaningful for the interpretation of the coordination bond. In particular, it appears that the metal to ligand π bonding is significant for both sulfur and phosphorus donor atoms. A comparison between the point charge model where the radial integral ratio I_2/I_4 is held constant within a given chromophore and the angular overlap model is presented.

Introduction

High-spin trigonal-bipyramidal cobalt(II) complexes are particularly well suited for testing theoretical models, in that their electronic spectra show at least four well-separated absorption bands in the region 5–25 K.[1-5] Detailed assignments of these spectra can be obtained from single-crystal studies with polarized light when the crystal structure is known. Until now, single-crystal electronic spectra have been recorded for the [Co(NCS)Me$_6$tren]SCN·H$_2$O[2] (Me$_6$tren = tris(2-dimethylaminoethyl)amine, chromophore CoN$_5$) and [CoBr(NP$_3$)]PF$_6$[3] (NP$_3$ = tris(2-diphenylphosphinoethyl)amine, chromophore CoNP$_3$Br) complexes. We report here single-crystal spectra of the [CoBr(NS$_3$)]PF$_6$ (NS$_3$ = tris(2-*tert*-butylthioethyl)amine, chromophore CoNS$_3$Br) complex.[6]

The X-ray structure is known also for the trigonal-bipyramidal [CoBr(Me$_6$tren)]Br complex[7] (chromophore CoNN$_3$Br) which crystallizes in the cubic system and therefore cannot be investigated by means of single-crystal spectroscopy. However, the spectral assignment of this complex is supported by the assignment of the spectra of the thiocyanate analog. Therefore there are three chromophores, CoNN$_3$Br, CoNS$_3$Br and CoNP$_3$Br, which have been shown to be similar in geometry,[6-8] to have the same axial donor atoms (N and Br), and to have spectral assignments supported by single-crystal studies. A comparison of the electronic transitions of these three complexes is quite instructive as well as the interpretation of the transition energies in terms of angular overlap parameters,[9-11] which can give significant information on the coordination bond.[12]

Experimental Section

Single crystals of [CoBr(NS$_3$)]PF$_6$ were grown by slow evaporation of acetone–ethanol solutions. Thin plates were obtained which crystallize[6] in the space group $P2_1/n$; $a = 27.420$ Å, $b = 11.923$ Å, $c = 17.082$ Å, $\beta = 102.4°$, and $Z = 8$. In the unit cell there are two asymmetric units CoBr(NS$_3$) which are slightly misaligned. The two Co–Br axes, assumed as z axes for the molecular coordinate systems, form an angle of 12°. The squares of the projections of the z axes along the crystal axes are reported in Table I.

Table I. Squares of the Projections of the Co–Br Axes along the Crystal Axes

	a	b	c^*
Co$_1$–Br$_1$	0.43	0.00	0.57
Co$_2$–Br$_2$	0.48	0.02	0.49

The polarized electronic spectra were recorded with the apparatus previously described[3] along the a and b crystal axes.

Results and Discussion

Electronic Spectra. Figure 1 reports the electronic spectra of the CoNS$_3$Br chromophore recorded with the light polarized parallel to a and b crystal axes.

According to the figures of Table I the spectrum recorded with the electric vector of polarized light parallel to b has to be $\perp$ polarized, while the spectrum parallel to a has to be almost equally $\parallel$ and $\perp$ polarized. Since the ground level of a Co(II) complex in C_{3v} symmetry is expected to be $^4A_2$, the bands at 5.2, 11.8, and 18.8 kK can be assigned to the $^4A_2 \rightarrow {}^4E$ transitions. The lack of neat polarization properties for the $^4A_2 \rightarrow {}^4E$ transitions is not uncommon, as transitions to degenerate levels are very sensitive to low-symmetry components.[2,3,13,14] The main difference in the spectrum recorded parallel to a, as compared to that parallel to b, is the appearance of the 13.8-kK band. With the figures of Table I in mind this is reasonably assigned to a polarized $^4A_2 \rightarrow {}^4A_2$ transition.

The present assignment corresponds quite closely to those previously proposed for the analogous CoNN$_3$Br and CoNP$_3$Br chromophores,[2,3] as shown in Figure 2 and Table II. Although these three chromophores can be described as trigonal bipyramidal, they show significant departures from D_{3h} symmetry. In fact the N$_{ax}$–Co–L$_{eq}$ angle (α) is in every case less than 90°. The most highly distorted in this sense is the CoNP$_3$Br chromophore, where the angle α is 74° and the Co–N distance is so large (Table III) that the chromophore