Mononuclear and Oxide-Bridged Binuclear Iron(III) Complexes Containing the Cyclic Tetradentate Schiff Base Derived from o-Aminobenzaldehyde

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Iron(III) complexes of the tetradentate macrocyclic ligand tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine (TAAB), have been prepared by the template reaction of o-aminobenzaldehyde with an iron salt. Two types of compounds were isolated and characterized: dimeric $Fe_2(TAAB)_2OX_4 \cdot 4H_2O$, $X^- = NO_3^-$ and ClO_4^-, which contain the Fe–O–Fe bridging group, and mononuclear compounds $Fe(TAAB)FX_2 \cdot 2H_2O$, $X^- = NO_3^-$ and ClO_4^-. $Fe_2(TAAB)_2O(NO_3)_4 \cdot 4H_2O$ reacts with methoxide ions giving the neutral compound $[Fe(TAAB)(OCH_3)_2]_2O$ where two methoxide ions are added to the macrocycle, forming α-amino ether linkages. The Fe–O–Fe linkage in these binuclear compounds is unusually difficult to cleave; only acidic fluoride media appear to cause cleavage. The compounds were characterized by elemental analysis, IR spectra, mass spectra, conductivity studies, molecular weight determination, and magnetic susceptibility measurements over the temperature range from 80 to 300 K.

Introduction

The self-condensation reaction of o-aminobenzaldehyde in the presence of metal ions provides one of the best examples of metal ion template reactions.[2-6] In the absence of metal ions, o-aminobenzaldehyde condenses with itself and forms a variety of polycyclic structures including a polycyclic trimer (I) which contains no C=N groups.[7] Condensation in the

I
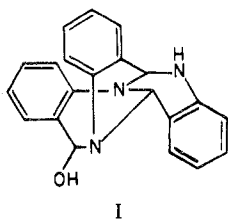
presence of some metal ions leads to the formation of complexes with the closed tetradentate Schiff base macrocyclic ligands tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine (TAAB) (II)[2,6] and/or the corresponding tridentate macro-
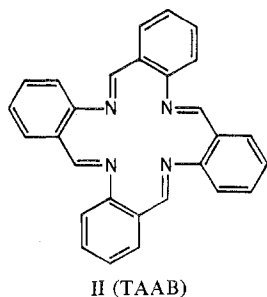

II (TAAB)

cyclic ligand[3-5] tribenzo[b,f,j][1,5,9]triazacycloduodecine (TRI) (III). TAAB complexes have been characterized with

III (TRI)
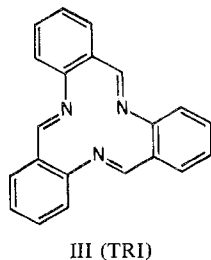
the metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pd^{2+}, and Co^{3+}. The species $Ni(TRI)^{2+}$,[2,3] $Ni(TRI)_2^{2+}$,[4] and $Co(TRI)_2^{3+}$[5] have been prepared and characterized. X-ray crystal structure determinations on $Ni(TAAB)(BF_4)_2$,[8] $Ni(TAAB)I_2 \cdot H_2O$,[8] $Ni(TRI)(NO_3)_2 \cdot 3H_2O$,[9] and $Co(TRI)_2(ClO_4)_3 \cdot 3H_2O$[10] have confirmed the structures of the TAAB and TRI ligands.

TAAB contains a 16-membered ring which is the same as the theoretical tetraaza[16]annulene (IV). In its complexes

IV   V
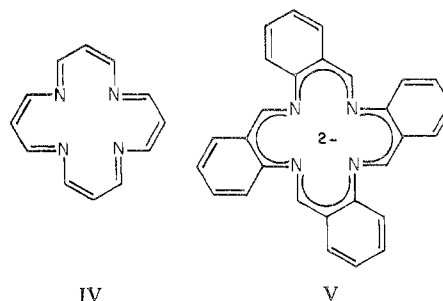
TAAB is subject to two-electron reductions[11] producing the dianion (V), which is a structural analogue of the porphine ligand of heme proteins. For this reason, the iron complexes of TAAB are of special interest. However, synthetic difficulties have prevented synthesis of Fe–TAAB complexes prior to this report. Here we describe the preparation, characterization, and chemical properties of two types of Fe(III)–TAAB complexes: binuclear, $Fe_2(TAAB)_2OX_4 \cdot 4H_2O$ and [Fe-$(TAAB)(OCH_3)_2]_2O$, and mononuclear, $Fe(TAAB)FX_2 \cdot 2H_2O$, $X^- = NO_3^-$ and ClO_4^-.

Results and Discussion

Initial Condensation Product. o-Aminobenzaldehyde and several iron(II) and iron(III) salts were permitted to react under a variety of conditions. Reaction with anhydrous iron(II) chloride in ethanol under a protective nitrogen atmosphere results in the formation of a black-green crystalline condensation product. Infrared spectra, analytical data, and chemical evidence show that this product contains the closed tetradentate macrocycle TAAB and that it may be formulated as $Fe(TAAB)FeCl_4$. The same material was obtained from the reaction of iron(II) chloride with $Zn(TAAB)ZnCl_4$ or trisanhydro trimer (structure I) in ethanol under similar conditions. Infrared data are in accord with this formulation. The absence of bands that could be attributed to the stretching and deformation frequencies of the $-NH_2$ group or the stretching frequency of the C=O group and the presence of a strong absorption at 1563 cm^{-1}, assigned as a coordinated, conjugated C=N stretching mode, strongly indicate the formation of a cyclic product containing Schiff base linkages. However, as has previously been shown in the case of the Co^{3+} derivatives it is not possible to distinguish between TAAB and TRI on the basis of IR evidence alone.[5]

The initial condensation product, $Fe(TAAB)FeCl_4$, was used as a starting material for the preparation of other iron derivatives of TAAB. Under anhydrous conditions and a protective nitrogen atmosphere, metathesis with NCS^- from

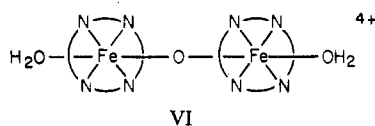**Table I.** Magnetic Data^a for the Dimeric Iron(III) Complexes

Compd	Temp, K	$10^6 \chi_M'$, cgsu	μ_{eff}, μ_B
Fe$_2$(TAAB)$_2$O(NO$_3$)$_4$·4H$_2$O	304.7	1284	1.77
($J = -110.9$ cm^{-1})	296.8	1283	1.75
	262.4	1249	1.61
	248.2	1223	1.56
	241.1	1205	1.53
	228.3	1196	1.48
	201.9	1126	1.35
	164.8	977.9	1.14
	147.0	855.6	1.00
	125.7	768.2	0.88
	119.7	689.6	0.81
	90.5	488.5	0.60
	83.5	418.8	0.53
Fe$_2$(TAAB)$_2$O(ClO$_4$)$_4$·4H$_2$O	297.2	2286	2.33
($J = -64.8$ cm^{-1})	241.1	2261	2.09
	192.3	2195	1.84
	170.2	2173	1.72
	141.7	2054	1.53
	119.6	1937	1.36
	83.2	1717	1.07
[Fe(TAAB)(OCH$_3$)$_2$]$_2$O	292.3	1168	1.65
($J = -117.6$ cm^{-1})	250.1	1079	1.47
	219.0	1034	1.35
	200.0	966.0	1.24
	173.2	914.1	1.13
	142.8	802	0.96
	123.8	698.0	0.83
	85.1	489.5	0.51
Fe(TAAB)F(NO$_3$)$_2$·2H$_2$O	297.5	3542	2.90
	229.0	3752	2.62
	192.5	3863	2.44
	151.2	4047	2.21
	128.4	4147	2.07
	115.9	4277	1.99
	105.7	4387	1.93
	89.3	4717	1.83
Fe(TAAB)F(ClO$_4$)$_2$·2H$_2$O	298.3	2694	2.54
	225.1	2920	2.29
	177.8	3147	2.12
	156.9	3254	2.02
	135.4	3481	1.94
	120.4	3589	1.86
	90.4	4030	1.71

^{a} All data are calculated per iron atom.

Figure 1. Temperature dependence of the magnetic susceptibility of Fe$_2$(TAAB)$_2$O(NO$_3$)$_4$·4H$_2$O ($J = -110.9$ cm^{-1}).

acetonitrile yields Fe(TAAB)(NCS)$_2$ containing Fe(II).[12] Exposure of methanol solutions of Fe(TAAB)FeCl$_4$ to the air produces oxo-bridged iron(III) compounds.

The Dimeric Cations Fe$_2$(TAAB)$_2$O^{4+}. The metathetical reaction of Fe(TAAB)FeCl$_4$ with AgNO$_3$ in acidic methanol in the presence of air leads to oxidation of Fe(II) to Fe(III) and gives an oxo-bridged dimeric cation Fe$_2$(TAAB)$_2$O^{4+}. The nitrate salt Fe$_2$(TAAB)$_2$O(NO$_3$)$_4$·4H$_2$O was isolated as deep red crystals. The analogous perchlorate salt was prepared from nitrate by metathesis from water or methanol after addition of a small amount of HClO$_4$.

These species can be formulated as dimers Fe$_2$-(TAAB)$_2$OX$_4$·4H$_2$O, X = NO$_3$ and ClO$_4$ (VI), on the basis

H$_2$O—[Fe]—O—[Fe]—OH$_2$ 4+

VI

of elemental analysis, conductivity studies, infrared spectra, mass spectra, and cryomagnetic measurements. The infrared spectra of these dimeric compounds are similar to those of Fe(TAAB)FeCl$_4$ and other known M(TAAB)$^{2+}$, M = Ni, Cu, Co, Zn, complexes for they contain the characteristic ligand bands (due to TAAB). These include absorptions at ~1613
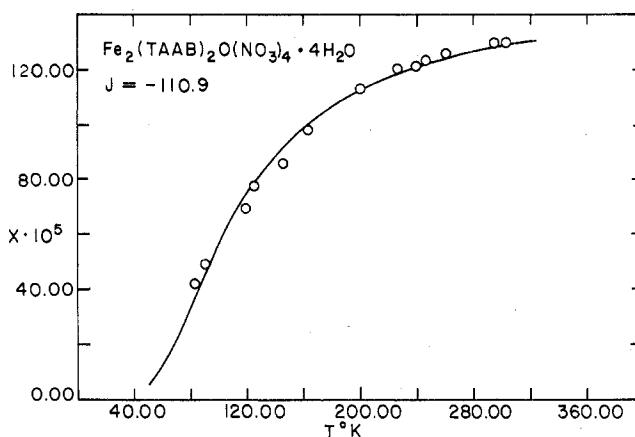
and 1590 cm^{-1} which represent the vibrational modes of ortho-disubstituted benzene, a band at ~1568 cm^{-1} assigned to the -C=N- stretching vibrational mode and a band at ~780 cm^{-1} assigned as a C-H out-of-plane deformation mode of benzene rings. In addition to these bands, the infrared spectrum of Fe$_2$(TAAB)$_2$OX$_4$·H$_2$O displays other characteristic absorptions which provide further evidence for the bridged structure of these compounds. A broad band in the region 3500–3200 cm^{-1} is assigned to the H$_2$O stretching vibrational modes. The absorption pattern of the IR spectrum near 1100 and 1400 cm^{-1} indicates that ClO$_4^-$ and NO$_3^-$ are not coordinated.[13,14] In addition, the spectra of both the nitrate and the perchlorate salts display a strong band at 810 cm^{-1} which is attributed to the asymmetric Fe–O–Fe stretching mode. Significantly, this band is not present in the spectra of Fe(TAAB)FeCl$_4$ and Fe(TAAB)FX$_2$H$_2$O. The presence of a strong band in the region 780–850 cm^{-1} is reported to be characteristic of the presence of the Fe–O–Fe moiety[13-19] and ^{18}O isotopic exchange experiments have confirmed this assignment.[20] The molar conductance of Fe$_2$(TAAB)$_2$O-(NO$_3$)$_4$·4H$_2$O in water is in the range expected for 4:1 electrolytes. The equation which relates the equivalent conductance (Λ_e) of a solution of an electrolyte to its equivalent concentration (C_{eq}) is
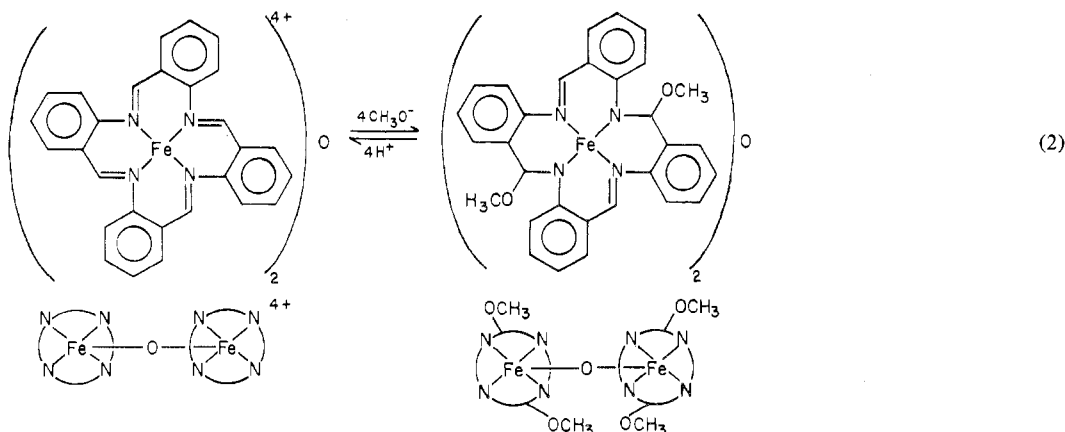
$$\Lambda_0 - \Lambda_e = BC_{eq}^{1/2}$$

where Λ_0 is equivalent conductance at infinite dilution.[21]

Conductance studies on Fe$_2$(TAAB)$_2$O(NO$_3$)$_4$·4H$_2$O over the concentration range 0.4×10^{-3}–1.2×10^{-3} M gave data showing a linear graph of ($\Lambda_0 - \Lambda_{eq}$) vs. $C_{eq}^{1/2}$. The slope of the line (B) was found to be 540 which is in the range expected for 4:1 electrolytes.[21]

The Neutral Dimer [Fe(TAAB)(OMe)$_2$]$_2$O. Previous reports have shown that M(TAAB)X$_2$ (M = Ni or Cu) reacts with nucleophiles, such as methoxide ion, forming neutral species where two such nucleophiles have added, one to each of two azomethine linkages of the macrocycle[22,23] as shown in eq 1.·

(1)
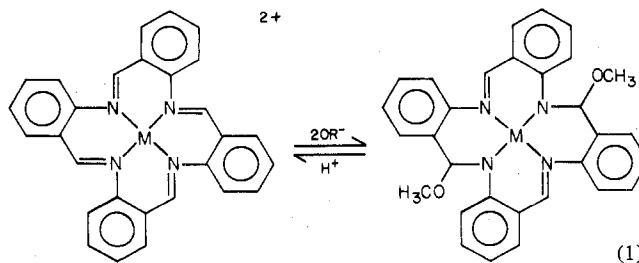
The resulting macrocycle, TAAB(OCH$_3$)$_2$, may be viewed as containing two azomethine donors and two anionic, depro-

tonated α-amino ether donors. This kind of nucleophilic addition reaction has been observed for the dimeric compound $Fe_2(TAAB)_2O(NO_3)_4 \cdot 4H_2O$. This substance reacts with methoxide ions giving the neutral dimeric species [Fe-(TAAB)(OCH_3)_2]_2O where methoxides are incorporated in two of the azomethine linkages of each TAAB macrocycle (eq 2). Although stereoisomerism is theoretically possible for this structure,[22] no indication of the phenomenon was found.

[Fe(TAAB)(OCH_3)_2]_2O is obtained from the reaction of $Fe_2(TAAB)_2O(NO_3)_4$ with NaOCH_3 in methanol as a dark brown crystalline solid that is soluble in chloroform and acetone, slightly soluble in methanol, and insoluble in water. Chemical analysis, including oxygen and methoxy determinations, is in good agreement with this formulation. Molecular weight determination in chloroform confirms the dimeric structure of the compound: calcd for [Fe(TAAB)(OCH_3)_2]O, 1077; found, 1038, 1080. The compound is unstable in acidic media where it rapidly eliminates methanol and reverts to the parent dimeric cation $Fe_2(TAAB)_2O^{4+}$.

The IR spectrum of [Fe(TAAB)(OMe)_2]_2O is similar to those of the Cu and Ni compounds with the same kind of ligand, M(TAAB)(OCH_3)_2,[23] confirming that methoxide ions are incorporated in two of the azomethine linkages of each TAAB macrocycle. A band at 1568 cm^{-1} originally present in $Fe_2(TAAB_3)_2O^{4+}$ and assigned to the C=N vibrational mode is shifted toward lower energy (1523 cm^{-1}) and is assigned as a stretching vibration of the two remaining azomethine linkages. The presence of methoxy groups is indicated by the appearance of new bands at 1050, 1386, 1358, and 1470 cm^{-1} and in the region 2850–3000 cm^{-1}. The spectrum also shows the absence of bands due to NO_3$^-$ and water. A characteristic band arising from antisymmetric vibration of the Fe–O–Fe moiety in [Fe(TAAB)(OCH_3)_2]_2O is found at 840 cm^{-1}. Mass spectral measurements on [Fe(TAAB)-(OCH_3)_2]_2O confirm the presence of the TAAB macrocycle in this compound. Relatively intense m/e peaks were found at 412 and 467; these correspond to TAAB$^+$ and Fe(TAAB)$^+$, respectively. No m/e peaks (309 or 364) corresponding to TRI$^+$ and Fe(TRI)$^+$ were observed. The most intense mass peak does not correspond to the intact dimer but rather to an ion of the formulation Fe(TAAB)$^+$.

Magnetic Properties of the Dimers. Two types of oxygen-bridged dimeric iron(II) compounds are well-known. The most common involve linear Fe–O–Fe bridges.[15,16,19,24] The dimeric Fe(III) compound [Fe(pic)_2OH]_2 is illustrative of species containing dihydroxo bridges[24]
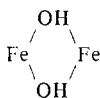
The magnetic behavior of this compound is considerably

different from those of systems containing linear Fe–O–Fe bridges. The value of the magnetic moment varies from ∼5 μ_B at room temperature to ∼1 μ_B at 20 K. The coupling constant J is reported to have a value of –8 cm^{-1}. It was calculated from cryomagnetic data, assuming a spin–spin coupled ($^5/_2$, $^5/_2$) system. The magnetic behaviors of dimeric Fe(III) compounds containing the linear Fe–O–Fe bridge are distinctive and useful in characterizing similar systems. All such compounds have room-temperature magnetic moments which are considerably lower than the spin-only value of 5.9 μ_B for high-spin Fe(III) ($S = ^5/_2$). They usually fall in the range around 2.0 μ_B. These magnetic moments are strongly temperature dependent and their values decrease to ∼0.6 μ_B at 80 K. These cryomagnetic properties are best interpreted assuming a binuclear spin-free model[15]

$$\chi_M = \left(\frac{g^2 N\beta^2}{3kT}\right)\frac{55 + 30\exp(10X) + 14\exp(18X) + 5\exp(24X) + \exp(28)X}{11 + 9\exp(10X) + 7\exp(18X) + 5\exp(24X) + 3\exp(28X) + \exp(30X)} + N(\alpha) \qquad (3)$$

$X = -J/kT$, and g is the spectroscopic splitting factor, β is the Bohr magneton, k is the Boltzmann constant, T is temperature, and $N(\alpha)$ is the temperature-independent paramagnetic term. The values of J calculated from eq 1 are usually in the range from 85 to 120 cm^{-1}.

The cryomagnetic properties of the dimeric compounds $Fe_2(TAAB)_2OX_4 \cdot 4H_2O$, X = NO_3$^-$ and ClO_4$^-$, and [Fe-(TAAB)(OCH_3)_2]_2O have been investigated over the temperature range ∼80–300 K and the results are presented in Table I. The three compounds exhibit the general behavior expected for linear oxide-bridged structures. The magnetic susceptibility data have been fitted to the simple binuclear model involving exchange between two Fe(III) ions having $S = ^5/_2$. The values of J calculated using eq 3 are given in Table I and are in the range typical of systems containing the Fe–O–Fe linkage. A plot of χ_M' vs. T for $Fe_2(TAAB)_2O$-$(NO_3)_4 \cdot 4H_2O$ together with the theoretical curve (assuming $J = -110.9$ cm^{-1}) appears in Figure 1.

Cleavage of the Fe–O–Fe Bridge. We have found that the Fe–O–Fe linkage in the binuclear complexes Fe_2-$(TAAB)_2OX_4 \cdot 4H_2O$ and [Fe(TAAB)(OCH_3)_2]_2O is unusually difficult to cleave. Several attempts were made to break this bond without success. For example, a boiling water solution of $Fe_2(TAAB)_2O(NO_3)_4 \cdot 4H_2O$, after the addition of concentrated HClO_4, HCl, or HBr, yields the corresponding dimeric salts Fe(TAAB)_2OX_4 \cdot 4H_2O, X = ClO_4, Cl, and Br. Vigorous treatments such as dissolving $Fe_2(TAAB)_2O$-$(NO_3)_4 \cdot 4H_2O$ in 47% HBr or bubbling gaseous HCl through

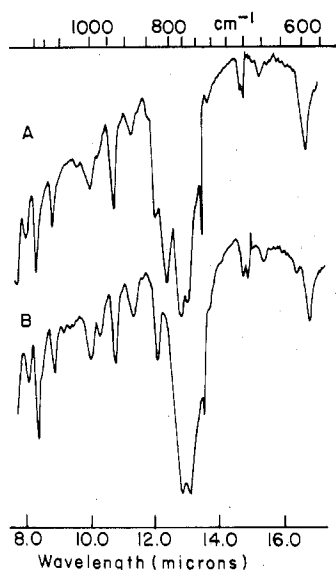**Figure 2.** Infrared spectra of the oxo-bridged and mononuclear complexes in the range 600–1100 cm^{-1}: A, $Fe_2(TAAB)_2O$-$(NO_3)_4 \cdot 4H_2O$; B, $Fe(TAAB)F(NO_3)_2 \cdot 2H_2O$.

water solutions of the dimer compound also gave the corresponding dimeric salts. The neutral dimeric compound $[Fe(TAAB)(OCH_3)_2]_2O$ has shown the same stability for the Fe–O–Fe moiety. An acetone solution of $[Fe(TAAB)-(OCH_3)_2]_2O$ gave dimeric $Fe_2(TAAB)_2O(ClO_4)_4$ after addition of $HClO_4$.

The cleavage of the Fe–O–Fe bond was achieved only in acidic fluoride media. On reaction of a water solution of $Fe_2(TAAB)_2O(X)_4 \cdot 4H_2O$, X = NO_3^- and ClO_4^-, with HF at room temperature for 6 h the cleavage of Fe–O–Fe bond was achieved and the compounds $Fe(TAAB)FX_2 \cdot 2H_2O$, X = NO_3^- and ClO_4^-, were isolated as crystalline materials. The compounds are slightly soluble in water and methanol but hydrolysis occurs after a short time with regeneration of oxygen-bridged dimeric compounds (eq 4). The absence of

$$2Fe(TAAB)FX_2 \cdot 2H_2O + 3H_2O \rightarrow Fe_2(TAAB)_2OX_4 \cdot 4H_2O$$
$$+ 2HF \qquad (4)$$
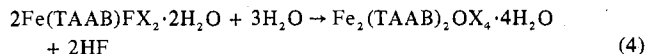
Fe–O–Fe moieties in these mononuclear compounds was confirmed on the basis of analytical data, infrared spectra, and magnetic susceptibility measurements. Chemical analysis shows that anion:iron ratio is 3:1. The infrared spectra of the fluoride derivatives are very similar to those of the binuclear compounds. They contain all of the bands that are characteristic of the macrocycle and the corresponding anions. They also show that neither NO_3^- nor ClO_4^- is coordinated. The most characteristic feature of these spectra is an absorption pattern around 800 cm^{-1}. A band at 810 cm^{-1}, originally present in the spectra of binuclear compounds and assigned as the Fe–O–Fe vibrational mode, was not found in the spectra of the mononuclear compounds. Figure 2 shows the IR spectra of $Fe_2(TAAB)_2O(NO_3)_4 \cdot 4H_2O$ and $Fe(TAAB)F(NO_3)_2 \cdot 2H_2O$ over the range 600–1200 cm^{-1}. A strong band at 780 cm^{-1} present in the spectra of both compounds is assigned to the out-of-plane C–H deformation of the benzene ring.

There are two spin multiplets which are possible for the ground state of iron(III) in octahedral symmetry: doublet, $S = {}^1/_2$, or sextet, $S = {}^5/_2$.[25,26] However, complexes in fields of lower symmetry may also exhibit a quartet ground term with $S = {}^3/_2$.[26] Room-temperature magnetic moment determinations (Table I) indicate that mononuclear compounds $Fe(TAAB)FX_2 \cdot 2H_2O$, X = NO_3^- and ClO_4^-, contain low-spin iron(III) with a doublet ground state, $S = {}^1/_2$. In this case μ_{eff} should be temperature dependent and follow approximately a Kotani-type curve,[27] e.g., should be in the range 1.73–2.55
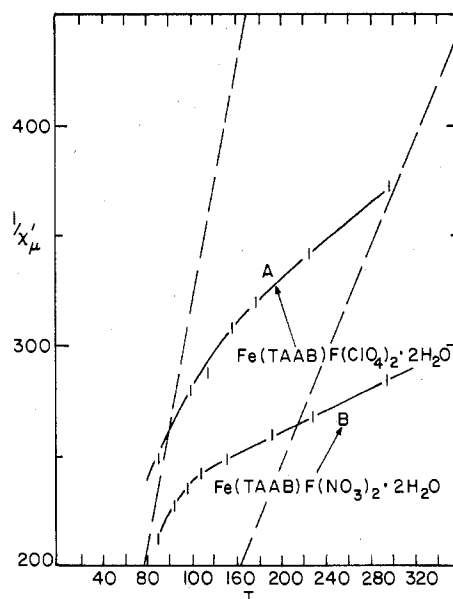

Figure 3. Temperature dependence of the magnetic susceptibility of the mononuclear complexes: A, $Fe(TAAB)F(ClO_4)_2 \cdot 2H_2O$; B, $Fe(TAAB)F(NO_3)_2 \cdot 2H_2O$.

μ_B. The magnetic properties of $Fe(TAAB)FX_2 \cdot 2H_2O$ have been investigated from 90 to 300 K and the data are reported in Table I. Their magnetic moments are temperature dependent and increase with temperature from 1.71 (90.4 K) and 1.83 (89.3 K) to 2.54 (298.3 K) and 2.90 μ_B (297.5 K) for the ClO_4^- and NO_3^-, respectively. Graphs of $1/\chi_M$ vs. temperature are given in Figure 3. The broken lines represent the theoretical values of $1/\chi_M$ for moments of 1.73 and 2.55 μ_B, the range which is expected for a doublet ground state of Fe(III). The slopes of the experimental curves indicate that the values of magnetic moments do not fall below the spin-only value for one unpaired electron within the temperature range from 90 to 120 K. At higher temperatures, the slopes change and the magnetic moments increase, finally reaching a value of 2.90 μ_B for the NO_3^- salt, which is higher than the expected range of values for low-spin Fe(III) at that temperature. This excessive value for the magnetic moments may indicate the occurrence of an equilibrium between low- and high-spin forms. The cryomagnetic properties of mononuclear compounds $Fe(TAAB)FX_2 \cdot 2H_2O$, X = NO_3^- and ClO_4^-, differ sharply from those of the binuclear compounds Fe_2-$(TAAB)_2OX_4 \cdot 4H_2O$, X = NO_3^- and ClO_4^-, and [Fe-$(TAAB)(OCH_3)_2]_2O$. This combined with the infrared data mentioned earlier proves that the Fe–O–Fe linkage has been eliminated in forming the mononuclear fluoride derivatives.

Experimental Section

Materials. o-Aminobenzaldehyde was prepared by the method of Smith and Opie.[28] $Zn(TAAB)ZnCl_4$ was prepared by reaction of anhydrous $ZnCl_2$ with o-aminobenzaldehyde in ether.[29] All other chemicals were of reagent grade. Elemental analyses were determined by Bernhard Microanalytical Laboratory, Müllheim, West Germany; Galbraith Laboratories, Inc., Knoxville, Tenn.; and Chemalytics Laboratory, Tucson, Ariz.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer. Nujol and hexachlorobutadiene mulls and potassium bromide pellet techniques were employed. The electronic spectra were recorded on a Cary Model 14R spectrometer. Molecular weights were determined in chloroform solution with a Mechrolab Model 301A vapor pressure osmometer. The instrument was calibrated with solutions of benzil of known concentrations. Conductivity measurements were made on water solutions in a standard 15-mL cell with an Industrial Instruments conductivity bridge. The mass spectra were obtained using an AEI MS9 mass spectrometer. Magnetic measurements, as a function of

temperature between 80 and 300 K, were made using the Faraday method.[30] Forces exerted on the samples were measured with a Cahn RH automatic electrobalance. Temperatures were measured using a copper–constantan thermocouple previously calibrated with a platinum resistance thermometer. The equipment was calibrated with $HgCo(NCS)_4$ and $Ni(en)_3S_2O_3$ in the range 80–300 K at a number of field strengths. The molar diamagnetic corrections for ligands were calculated from Pascal's constants.[31]

Reaction of *o*-Aminobenzaldehyde with Anhydrous Iron(II) Chloride. *o*-Aminobenzaldehyde (16.0 g, 0.14 mol) was dissolved in 40 mL of absolute ethanol in a 500-mL, two-necked, round-bottomed flask. The flask was fitted with a condenser and a bubbler with ground-glass joints. Nitrogen was bubbled through the solution and the mixture was heated to reflux while it was stirred. In a glove box, anhydrous iron(II) chloride (8.9 g, 0.07 mol) was dissolved in 300 mL of ethanol which had been deaerated previously with nitrogen and which contained 0.3 mL of concentrated HCl. This solution was added to the stirred, refluxing *o*-aminobenzaldehyde solution under nitrogen protection. Special precaution was taken to avoid exposure of the solutions to the air. A few minutes after addition of the iron(II) chloride, the reaction solution changed from red, to brown, and then to a final dark green color. A black-green precipitate appeared after 10 min. The reaction mixture was refluxed and stirred under the continuous nitrogen stream for 6 h. After being chilled, the solution was filtered in a glovebox, washed with ethanol, and dried in vacuo at room temperature. A black-green powder (3.7 g) was isolated. Anal. Calcd for $Fe_2C_{28}H_{20}N_4Cl_4$: C, 51.26; H, 3.0; N, 8.54; Cl, 21.62; Fe, 15.50. Found: C, 49.31; H, 3.17; N, 8.71; Cl, 19.89; Fe, 14.98.

Reaction of Zn(TAAB)ZnCl₄ with Anhydrous Iron(II) Chloride. This preparation is similar to that above, except that $Zn(TAAB)ZnCl_4$ was used instead of *o*-aminobenzaldehyde. $Zn(TAAB)ZnCl_4$ (1.0 g, 0.0015 mol) was suspended in 50 mL of absolute ethanol, which was acidified with a few drops of concentrated hydrochloric acid. The suspension was deaerated by bubbling with nitrogen and brought to reflux. Iron(II) chloride (1.0 g, 0.0078 mol) was added and the reaction was held at reflux under nitrogen for 6 h. After a few minutes, the color of the solution changed from yellow to deep brown. Within 30 min, all of the $Zn(TAAB)ZnCl_4$ was dissolved and a black precipitate had appeared. The black-green precipitate was filtered under nitrogen and dried in vacuo over P_4O_{10} at room temperature; yield ~90% based on $Zn(TAAB)ZnCl_4$.

Fe₂(TAAB)₂O(NO₃)₄·4H₂O. The black-green material (3.0 g) from above, which was assumed to be $Fe(TAAB)FeCl_4$, was partially dissolved in 950 mL of absolute methanol to which 1 mL of concentrated nitric acid had been added. Silver nitrate (3.5 g), partially dissolved in 40 mL of methanol, was added and the reaction mixture was stirred for 1 h. The precipitated silver chloride was removed by filtration, and the deep red solution was concentrated to three-fourths of its original volume and chilled overnight. Red crystals were isolated by suction filtration. These were washed with anhydrous methanol; yield 0.6 g. Addition of ether to the filtrate yielded another crop of the red product (0.6 g). The product was recrystallized three times from methanol which was acidified with nitric acid. The pure red crystals were dried at room temperature in vacuo over P_4O_{10}. Anal. Calcd for $Fe_2(C_{28}H_{20}N_4)O(NO_3)_4\cdot4H_2O$: C, 52.84; H, 3.81; N, 13.21; Fe, 8.78. Found: C, 52.87; H, 3.73; N, 13.10; Fe, 8.22.

Fe₂(TAAB)₂O(ClO₄)₄·4H₂O. A 0.25-g sample of Fe_2-$(TAAB)_2O(NO_3)_4\cdot4H_2O$ was dissolved in 120 mL of water. The clear solution was boiled for 5 min and 60% $HClO_4$ (0.5 mL) was added dropwise. Stirring was continued for a few minutes and, after cooling of the mixture, red crystals appeared. They were recrystallized from methanol by the addition of 2–3 drops of 60% $HClO_4$. These red crystals were filtered, washed with methanol, and dried in vacuo over P_4O_{10} at room temperature. Anal. Calcd for $Fe_2(C_{28}H_{20}N_4)_2O$-$(ClO_4)_4\cdot4H_2O$: C, 47.31; H, 3.40; N, 7.88; Cl, 9.98; Fe, 7.86. Found: C, 47.24; H, 3.28; N, 8.10; Cl, 9.78; Fe, 7.73.

[Fe{TAAB(OCH₃)₂}]₂O. A solution of $Fe_2(TAAB)_2O(NO_3)_4\cdot4H_2O$ (0.5 g, 0.000 39 mol) in methanol was added to a solution prepared

by dissolving 150 mg of sodium metal in 50 mL of absolute methanol. The color of the solution changed from deep red to olive green. After 2 h of stirring black crystals appeared. They were filtered, washed with methanol, and dried in vacuo over P_4O_{10} at room temperature. Anal. Calcd for $Fe_2(C_{30}H_{26}N_4O_2)_2O$: C, 66.91; H, 4.88; N, 10.41; O, 7.43; Fe, 10.37; OCH_3, 11.51; mol wt 1077. Found: C, 67.05; H, 4.96; N, 10.21; O, 7.30; Fe, 10.28; OCH_3, 10.78; mol wt 1080.

Fe(TAAB)F(NO₃)₂·2H₂O. To a solution prepared by dissolving $Fe_2(TAAB)_2O(NO_3)_4\cdot4H_2O$ (0.4 g) in 200 mL of water, 48% HF (3 mL) was added. After 30 min of stirring, a pale brown precipitate appeared. The stirring was continued for an additional 6 h. The brown precipitate was filtered, washed with a small amount of water, and vacuum-dried over P_4O_{10} at room temperature. Anal. Calcd for $C_{28}H_{24}N_6O_8FFe$: C, 51.95; H, 3.74; N, 12.98; F, 2.93; Fe, 8.62. Found: C, 52.10; H, 3.84; N, 12.81; F, 2.80; Fe, 8.48.

Fe(TAAB)F(ClO₄)₂·2H₂O. This compound was prepared in the same manner as the preceding substance except that Fe_2-$(TAAB)_2O(ClO_4)_4\cdot4H_2O$ was used. Anal. Calcd for $C_{28}H_{24}N_4O_{10}FCl_2Fe$: C, 46.56; H, 3.35; N, 7.76; F, 2.63; Cl, 9.82; Fe, 7.73. Found: C, 46.65; H, 3.24; N, 7.66; F, 2.46; Cl, 9.63; Fe, 7.54.

Registry No. $Fe_2(TAAB)_2O(NO_3)_4$, 62601-31-4; Fe_2-$(TAAB)_2O(ClO_4)_4$, 62601-30-3; [Fe(TAAB)(OCH₃)₂]₂O, 50431-07-7; Fe(TAAB)F(NO₃)₂, 62571-29-3; Fe(TAAB)F(ClO₄)₂, 62571-28-2; Fe(TAAB)FeCl₄, 62571-26-0; Zn(TAAB)ZnCl₄, 62571-24-8; *o*-aminobenzaldehyde, 529-23-7.

References and Notes

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