C. The equation for the square of the magnetic moment of a tetrahedral A_4 array (with $S = {}^3/_2$), if $x = J/kT$, can be written

$$\mu_{\text{eff}}^2 = g^2\left\{\begin{array}{l}\dfrac{546\exp(42x) + 990\exp(30x) + 1080\exp(20x) + 840\exp(12x)}{13\exp(42x) + 33\exp(30x) + 54\exp(20x) + 70\exp(12x)} \\[2ex] \dfrac{+330\exp(6x) + 54\exp(2x)}{+55\exp(6x) + 27\exp(2x) + 4}\end{array}\right.$$

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Seven-Coordination in Some Mononuclear and Binuclear Iron(III) Complexes Containing a Pentadentate Macrocyclic Ring

BY S. MARTIN NELSON AND DARYLE H. BUSCH

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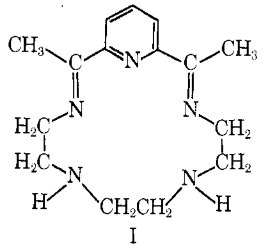
The preparations and properties of two novel series of seven-coordinate iron(III) complexes are reported. In both series, the stereochemistry involves pentagonal-bipyramidal coordination about the iron atom with the five donor atoms of a pentadentate macrocycle occupying a single plane and monodentate groups above and below that plane. The macrocycle is 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (ligand B). Monomeric $FeBX_2Y$ compounds are formed for X = Cl, Br, I, or NCS and Y = ClO_4, BF_4, or NCS. The species are high spin and act as uni-univalent electrolytes in nitromethane. Dimeric $[XBFe\text{–}O\text{–}FeBX]Y_2$ (X = ClO_4 or NCS; Y = ClO_4) involves spin–spin coupling across the Fe–O–Fe linkage.

Introduction

Considerable interest attaches to the synthesis of transition metal compounds in which the metal atom exhibits high coordination numbers, *i.e.*, greater than 6.[1] Until recently, known examples of seven-coordination were limited mostly to elements of the second and third transition series and to elements of the lanthanides and actinides, in combination with fluorine or oxygen. In such compounds, the metal–ligand bond is relatively polar and the cation:anion size ratio is generally large; high coordination numbers are therefore to be expected.

The past few years have seen the synthesis of a number of seven-coordinate transition metal complexes containing ligands which favor the formation of covalent bonds. Typical ligands in compounds of this class are carbon monoxide, cyanide, and chelating tertiary arsines. For the first transition metal series seven-coordination is now known for titanium[2] (in $TiCl_4(TAS)$), vanadium[2,3] (in $VCl_4(TAS)$ and $(C_6H_5)_3PAuV(CO)_6$), and chromium[4] (in $[Cr(DAS)_2(CO)_2I]I$). (DAS and TAS are bidentate and tridentate tertiary arsines.) It seems probable that in this class of compound the coordination number of 7 is related to the availability of at least three d orbitals for d^3sp^3 hybridization and also to the π-acceptor capacity of some of the ligands, which permits the withdrawal of excess charge away from the metal.

The manganese(II) and iron(III) complexes with ethylenediaminetetraacetic acid and *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid, studied by Hoard and coworkers,[5] are conveniently considered as constituting a third class of seven-coordinate compounds. With these metal ions the hexadentate ligands are not well suited to coordinate in an octahedral fashion. The distortion the ligands impose is such that an extra coordination site is made available for a molecule of water. In these cases seven-coordination is a consequence of ligand geometry and metal ion size. The compounds to be described in this paper also fall in this class.[6] Here, a pentadentate macrocycle, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (ligand B, structure I),



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[1] E. Muetterties, *Quart. Rev.* (London), **21**, 109 (1967).

[2] R. J. H. Clark, M. L. Greenfield, and R. S. Nyholm, *J. Chem. Soc.*, *A*, 1254 (1966).

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[4] J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 3009 (1964).

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[6] A preliminary account has appeared: S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.*, 641 (1966).

holds the five-coordinating nitrogen atoms in an essentially planar arrangement thereby allowing the close approach of two coordinating anions to the metal ion, above and below the plane of the ring. Structure determinations on two of the compounds have been reported.[7]

Results and Discussion

Two types of complexes have been prepared and investigated. These include mononuclear and binuclear substances. In most cases, the mononuclear complexes, of stoichiometry $FeBX_2Y$ (X = Cl, Br, I, or NCS; Y = ClO_4, BF_4, or NCS), were prepared from the previously reported[8] complex $Fe_2B_2O(ClO_4)_4 \cdot H_2O$. Treatment of acidified solutions of the latter with NaX yields stable, colored, crystalline compounds of the formula $FeBX_2Y$ (See Table I). Analytical data and preparative details are given in the Experimental Section.

Infrared spectral analysis confirms that the macrocyclic ligand B remains intact on formation of the $FeBX_2Y$ derivatives from the parent complex $FeB(OH)(ClO_4)_2$. A strong absorption attributable to the >C=N group occurs at 1655 cm^{-1}. The single sharp peak at 3270 cm^{-1} suggests the presence of secondary but not primary amine groups. All of the vibrations expected for the substituted pyridine were observed. The regularity of the infrared spectra shows that all of the compounds are of related structures.

TABLE I

PROPERTIES OF THE MONONUCLEAR COMPLEXES $[FeBX_2]Y$

	Color	μ_{eff},[a] BM	Λ_M,[b] ohm^{-1}
$[FeBCl_2]ClO_4$	Yellow	5.73	86
$[FeBCl_2]BF_4$	Yellow	...	91
$[FeBBr_2]ClO_4$	Orange	5.65	89
$[FeBI_2]ClO_4$	Dark green	5.78	87
$[FeB(NCS)_2]ClO_4$	Deep red[c]	5.82	89
$[FeB(NCS)_2]NCS$	Deep red[c]	...	85

[a] Corrected for diamagnetism of ligands, at 23–29°. [b] Measured at 10^{-3} *M* in nitromethane, at 25°. [c] Large crystals appear green.

All the $FeBX_2Y$ compounds have room-temperature magnetic moments (Table I) fairly close to the value of 5.92 BM predicted for high-spin iron(III). This is in contrast to the room-temperature moment of 1.86 BM previously found for the compound of empirical formula $FeB(OH)(ClO_4)_2$.

The observation that the $FeBX_2Y$ complexes are most easily isolated as monoperchlorates and that their colors are dependent on the nature of X first suggested that the complexes contain the seven-coordinate $FeBX_2^+$ cation.[6] The persistence of the seven-coordinate structure in solution has been confirmed by electrical conductance measurements in nitromethane which show that all of the complexes behave as uni-univalent electrolytes (see Table I). The molar conductances in nitromethane show little dependence on concentration (one example is illustrated in Figure 1) indicating negligible dissociation of the complex cation in this solvent. In water, on the other hand, the observed molar conductances increase rapidly with decreasing concentration. For $[FeBCl_2]ClO_4$, for example, Λ_M increases from 362 ohm^{-1} at 5 × 10^{-3} *M* to 572 ohm^{-1} at 4.7 × 10^{-5} *M*, indicating extensive dissociation of coordinated halide in dilute solution.

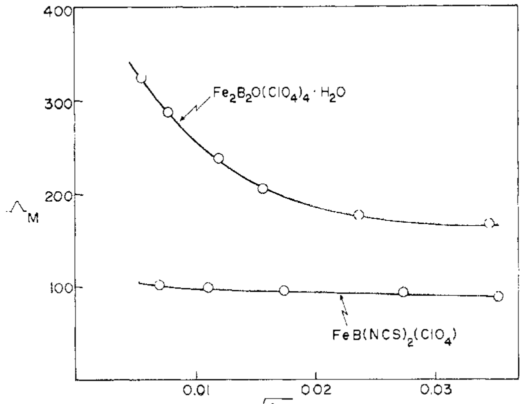

Figure 1.—Variation of Λ_M with concentration for $[FeB(NCS)_2]ClO_4$ (lower curve) and $Fe_2B_2O(ClO_4)_4 \cdot H_2O$ (upper curve) in nitromethane.

The complexes are soluble in polar organic solvents, as well as in water, and electronic spectral studies indicate that no significant decomposition or dissociation of the complex ion occurs in nitromethane or in acetone. All of the complexes exhibit strong absorption in the visible and near-ultraviolet regions. Spectral data are summarized in Table II. The high extinction coefficients and the movement of the band to lower energies with an increase in the reducing power of the coordinated anion suggest that the bands are charge transfer in origin. Indeed, the iodo complex shows spectral changes with time that are consistent with the occurrence of an oxidation–reduction reaction, involving electron transfer from iodide to metal, and the accompanying formation of iodine. In water, the extensive dissociation that occurs is accompanied by a decrease in the intensity of the charge-transfer bands and their complete disappearance in dilute solution. Such dilute solutions show absorption bands only at 273 and 217 mμ, these features being common to all of the complexes and arising presumably from the hydrated cation $FeB(H_2O)_2^{3+}$. Addition of excess NaX partially restores the charge-transfer bands. The equilibrium

$$2H_2O + FeBX_2^+ \rightleftharpoons FeB(H_2O)_2^{3+} + 2X^-$$

is thus indicated. Qualitative estimates of the degree of dissociation of the different complexes in aqueous solution indicate that the formation constants decrease in the sequence NCS > Cl > Br > I. The electrical conductance data for aqueous solutions noted above are entirely consistent with the occurrence of this equilibrium in aqueous solution. On the foregoing evidence it is concluded that the metal atom is seven-coordinate in these complexes both in solution and in the solid state.

Infrared spectra are also consistent with the general

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[7] E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, **89**, 720 (1967).

[8] J. D. Curry and D. H. Busch, *ibid.*, **86**, 592 (1964).

TABLE II

ELECTRONIC SPECTRA OF THE COMPLEXES

Complex	Solvent	λ_{max}, mμ (ϵ_M)
$[FeBCl_2]ClO_4$	Acetone	362 (6000)
$[FeBBr_2]ClO_4$	CH_3NO_2	442 (15,000)
$[FeBI_2]ClO_4$	CH_3NO_2	630 (5600), 565 sh
$[FeB(NCS)_2]ClO_4$	CH_3NO_2	489 (15, 000)
$[FeBCl_2]ClO_4$	H_2O	273 (9700), 216 (28,000)
$[FeBBr_2]ClO_4$	H_2O	273 (9600), 217 (26,000)
$[FeBI_2]ClO_4$	H_2O	275 (9500), 218 (30,000)
$[FeB(NCS)_2]ClO_4$	H_2O	273 (9500), 217 (30,000)
$Fe_2OB_2(ClO_4)_4 \cdot H_2O$	Acetone	480 sh, 367 (4500)
$Fe_2OB_2(ClO_4)_4 \cdot H_2O$	Water	480 sh, 365 (~4200), 275 (9000)

occurrence of the $FeBX_2^+$ cation in these complexes. The perchlorates show strong absorption at 1100 and 620 cm^{-1} (see Figure 2) which may be attributed to the ν_3 and ν_4 fundamental modes of ionic perchlorate.[9] The infrared spectrum of $[FeBCl_2]BF_4$, having strong absorption at 1020–1120 cm^{-1} (ν_3) and weaker absorptions at 522 cm^{-1} (ν_4, ^{11}B) and 533 cm^{-1} (ν_4, ^{10}B), similarly indicates ionic BF_4.[10] More significantly, the spectrum of $[FeB(NCS)_2]ClO_4$ shows a single NCS antisymmetric stretching vibration at 2037 cm^{-1}, whereas in $[FeB(NCS)_2]NCS$, a second weaker band occurs at 2055 cm^{-1}. These two bands can be assigned to nitrogen-coordinated NCS and to ionic NCS, respectively (KNCS, in KBr, absorbs at 2053 cm^{-1}).[11]

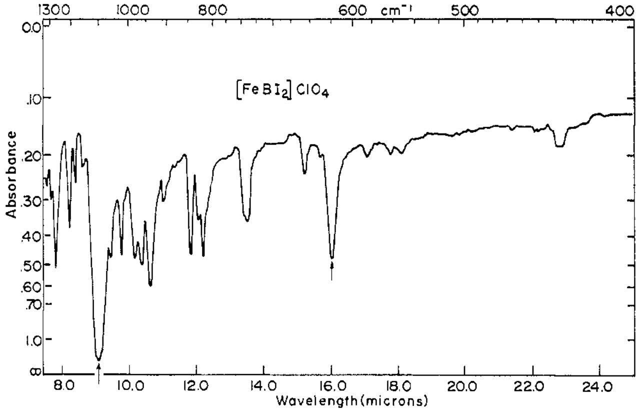

Figure 2.—Infrared spectrum of a Nujol mull of $[FeBI_2]ClO_4$.

Recognition that the $[FeBX_2]Y$ complexes are seven-coordinate (prior to the X-ray work[7]) prompted a reexamination of the parent complex which had been formulated as $FeB(OH)(ClO_4)_2$.[6,12] On the basis of the room-temperature magnetic moment (1.86 BM) and electrical conductance in water (λ_M = 220 ohm^{-1} at 31° for a 10^{-3} *M* solution, calculated as a monomer) this compound was first thought to contain six-coordinate iron(III) in a doublet ground state.[8] In the light of the foregoing results for the mononuclear complexes it seemed that an alternative dimeric structure, involving antiferromagnetic exchange interaction between hydroxo- or oxo-bridged iron atoms, might account better for the observed moment at room temperature and at the same time preserve the sevenfold coordination recognized to exist in $FeBX_2^+$. Measurement of the temperature dependence of the magnetic susceptibility over the range from 106 to 316°K confirmed the occurrence of predicted exchange interaction.[8,13] The magnetic results combined with the structural work of Fleischer and Hawkinson[7] show that spin–spin exchange involves coupling across a linear oxygen bridge.

Analytical and infrared data revealed that the binuclear complex may be isolated in one of several forms, $Fe_2OB_2(ClO_4)_4 \cdot xH_2O$, which differ in the number of water molecules associated with them. Thus, a band of variable intensity occurred at 3430 cm^{-1} in the infrared spectra of crystals which were air dried or stored over phosphoric oxide for short periods. In oven-dried material (110° for 12 hr or more), however, this band was almost completely absent and oxygen analysis also indicated the absence of water. The infrared spectrum in the 1200–900-cm^{-1} region also varied with the method of drying. Figure 3 is an infrared spectrum of a Nujol mull of a sample which had been stored over phosphoric oxide for 12 hr and which showed a band of moderate intensity at 3430 cm^{-1}. It can be seen that the strong perchlorate absorption (1200–900 cm^{-1}) is

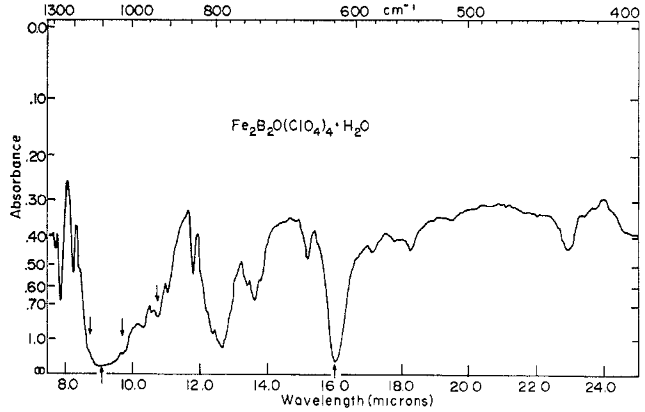

Figure 3.—Infrared spectrum of a Nujol mull of $Fe_2B_2O(ClO_4)_4 \cdot H_2O$.

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[9] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); A. F. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

[10] N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

[11] P. O. Kinell and B. Strandberg, *Acta Chem. Scand.*, **13**, 1607 (1959).

[12] *Caution!* $FeB(OH)(ClO_4)_2$ has been found to detonate violently when touched by a metal spatula, presumably because of electrical discharge. Like many perchlorate salts, these substances should be regarded as treacherous explosives.

[13] These studies have been supplanted by the more extensive work of Reiff, *et al.*, who have measured the susceptibility over the temperature range from 20 to 289°K: *cf.* W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **90**, 6347 (1968).

much broader and more complicated than in the spectrum of the mononuclear complex, $[FeBI_2]ClO_4$ (Figure 2), which contains only ionic perchlorate. In Figures 2 and 3 the upward pointing arrows indicate the positions where ionic perchlorate (in $[FeBI_2](ClO_4)$ absorbs; the downward pointing arrows indicate the positions where monodentate perchlorate C_{3v} symmetry) is reported[9] to absorb strongly. The spectrum of Figure 3 is thus best interpreted in terms of overlapping modes due to both coordinated and ionic perchlorates. This form of the complex, with which most of the work described in this paper was carried out, is believed to be the monohydrate, $[FeB(ClO_4)\text{–}O\text{–}FeB(ClO_4)](ClO_4)_2 \cdot H_2O$. Spectra of the same sample taken in potassium bromide disks exhibited a profile, in the 1200–900-cm^{-1} region, intermediate between those shown in Figures 2 and 3, and it may be that in this medium coordinated perchlorate is partially replaced by bromide ion. Nujol mulls of anhydrous specimens dried at 110° also indicated coordinated perchlorate. On the other hand, crystals which were air dried showed stronger absorption at 3430 cm^{-1} and a profile in the 1200–900-cm^{-1} region similar to that of Figure 2, indicating the presence of ionic perchlorate as well as a higher water content. The specimen examined by Fleischer and Hawkinson contained coordinated water, not perchlorate ion, and must therefore have been of this form, though the infrared spectrum of this same specimen is not available. It appears, therefore, that the bridged dimer first separates from aqueous solution as $[FeB(H_2O)\text{–}O\text{–}FeB(H_2O)](ClO_4)_4$ but that on heating or storage over desiccant the coordinated water becomes wholly or partially replaced by perchlorate ion.

Figure 3 shows an intense broad absorption centered at 792 cm^{-1} which is absent from the spectra of the mononuclear complexes. Absorption in this region has been attributed to metal–oxygen–metal antisymmetric stretching modes in systems where there is some metal–oxygen double bonding.[14] On the other hand, systems containing the bent M–(OH)–M grouping are reported to absorb at substantially lower frequencies (about 540–580 cm^{-1}). Thus, the present example confirms the assignment of the M–O–M absorption.

It has already been noted that the molar conductance of the binuclear complex in water was previously reported to be 440 ohm^{-1} (calculated on a binuclear formula). This value is greatly in excess of that to be expected for the uni-bivalent electrolyte structure having coordinated anions. However, measurements over a range of concentrations established a marked concentration dependence. For example, λ_M equals 359 ohm^{-1} in 2×10^{-3} *M* solution and 503 ohm^{-1} in 1.6×10^{-4} *M* solution. This suggests *either* ion-pair association *or* an equilibrium involving coordination of the anion. The conductance data indicate little association of any kind in dilute aqueous solution. In nitromethane, on the other hand, the equilibrium produces almost complete association at concentrations greater than about 10^{-3} *M*. Figure 1 shows that at these concentrations λ_M has effectively leveled out at 165 ohm^{-1}, a value in accord with the structure $[(ClO_4)BFe\text{–}O\text{–}FeB(ClO_4)]^{2+}$ but not the structure $[(\text{solvent})BFe\text{–}O\text{–}FeB(\text{solvent})]^{4+}$.

A second bridged complex $[(NCS)BFe\text{–}O\text{–}FeB(NCS)](ClO_4)_2$ has been isolated. This compound exhibits infrared absorption characteristic of ionic perchlorate only. The intense broad band assigned to the Fe–O–Fe antisymmetric stretch is retained, though shifted to 788 cm^{-1}. A single intense band at 2040 cm^{-1} supports the assignment of coordinated thiocyanate. The molar conductance is 170 ohm^{-1} in 10^{-3} *M* nitromethane solution as expected for a uni-bivalent electrolyte.

Electronic spectral data for the dimeric perchlorate in acetone and in water are given in Table II. Unlike the mononuclear complexes the same spectrum is obtained initially in water as in polar organic solvents. However, the spectrum of a water solution changes with time. Thus, the apparent molar extinction coefficient of the 365-mμ band fell from about 4200 after 15 min to about 100 after 16 hr. The absorption in the 300–500-mμ region is clearly a property of the Fe–O–Fe linkage since it does not occur in the aqueous spectra of the mononuclear complexes and as demonstrated by the observation that the magnetic moment in water at 20° increases with time from 3.6 BM at a time of 3 hr after preparation of the solution to a final value of 5.7 BM after 22 hr. This confirms the existence of a monomer–dimer equilibrium.

From the single-crystal X-ray study of $[FeB(NCS)_2]ClO_4$ all five nitrogen atoms of the macrocyclic ligand B define a single plane and the two thiocyanate groups are nitrogen coordinated in *trans* positions normal to the plane.[7] The stereochemistry is therefore pentagonal bipyramidal. It is clear that the occurrence of seven-coordination is a consequence of the conformation of the macrocyclic ligand. This being so, it is to be expected that seven-coordination will be found in complexes of this ligand with other metal ions since the stereochemical preference of the ligand will often predominate over that of the metal atom. There are, however, two important requirements for the metal ion. It must be of a suitable size and it must be capable of acting as a template for the condensation of the diketone with the polyamine.

Experimental Section

Materials.—2,6-Diacetylpyridine and triethylenetetramine were obtained from the Aldrich Chemical Co. and were used as received. Elemental analyses were carried out by Galbraith Laboratories Inc. and by the Bernhardt Microanalytical Laboratory.

Preparation of Complexes.—$[Fe_2B_2(ClO_4)_2O](ClO_4)_2 \cdot H_2O$ was prepared as described previously.[8] The crude brown product was recrystallized from a water–methanol mixture. The anhydrous complex was obtained by heating the monohydrate at 110° for 12 hr. *Anal.* Calcd for $Fe_2B_2O(ClO_4)_4$: C, 33.61; H, 4.33; N, 13.06; Cl, 13.23; O, 25.37. Found: C, 33.45; H, 4.89; N, 12.55; Cl, 13.38; O, 25.91.

$[FeB(NCS)_2]NCS$.—This compound was prepared by the same procedures as $Fe_2B_2O(ClO_4)_4 \cdot H_2O$ except that NaNCS was used in place of $NaClO_4$. After air oxidation a small amount of in-

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[14] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.*, 472 (1966).

soluble brown material, probably iron(III) oxide, was removed and the filtrate was acidified with a few drops of concentrated HCl. The solution immediately turned dark red and on standing and cooling it deposited dark green needles. These were washed with water and dried over phosphoric oxide. *Anal.* Calcd for $[FeB(NCS)_2]NCS$: C, 42.94; H, 4.60; N, 22.25; S, 19.11; Fe, 11.09. Found: C, 41.95; H, 4.51; N, 21.50; S, 18.47; Fe, 11.02.

$[FeBX_2]ClO_4$ (X = Cl, Br, I, or NCS).—The same general method of preparation was employed for all four complexes. A 2.18-g amount of $Fe_2B_2O(ClO_4)_4 \cdot H_2O$ was dissolved in water with warming. The hot solution was acidified with 3–4 drops of 60% $HClO_4$ and filtered into a warm, aqueous solution of NaX (~0.01 mol). The bromide separated immediately; the other complexes separated on standing and cooling. They were recrystallized from hot water containing 1 drop of 60% $HClO_4$. *Anal.* Calcd for $[FeBCl_2]ClO_4$: C, 35.87; H, 4.48; N, 13.84; Cl, 20.99. Found: C, 36.07; H, 4.64; N, 14.02; Cl, 21.30. Calcd for $[FeBBr_2]ClO_4$: C, 30.48; H, 3.79; N, 11.71; Cl, 5.86; Br, 27.06. Found: C, 30.62; H, 3.94; N, 11.90; Cl, 6.02; Br, 27.16. Calcd for $[FeBI_2]ClO_4$: C, 26.40; H, 3.40; N, 10.29; I, 37.20. Found: C, 26.33; H, 3.43; N, 9.81; I, 38.20. Calcd for $[FeB(NCS)_2]ClO_4$: C, 37.50; H, 4.23; N, 18.0; S, 11.8; Cl, 6.51; Fe, 10.20. Found: C, 38.76; H, 4.38; N, 18.59; S, 12.10; Cl, 6.41; Fe, 10.54.

$[FeBCl_2]BF_4$.—The method of preparation was the same as that for $[FeB(NCS)_2]NCS$ except that $NaBF_4$ was used instead of NaNCS. Some insoluble material remaining after air oxidation was removed and the filtrate was acidified with a few drops of concentrated HCl. On standing, yellow crystals separated. They were recrystallized from hot water containing 1 drop of concentrated HCl. *Anal.* Calcd for $[FeBCl_2]BF_4$: C, 37.00; H, 4.76; N, 14.39; F, 15.61. Found: C, 35.83; H, 4.46; N, 14.00; F, 15.84

$[Fe_2B_2(NCS)_2O](ClO_4)_2$.—A 0.5-g amount of $[FeB(NCS)_2]ClO_4$ was dissolved in 50 ml of methanol and a 20% ethylenediamine solution was added dropwise until the red color disappeared, then 5 drops more were added. The filtered solution was set aside, and when the volume had fallen to about 10 ml, the brown crystals were isolated by filtering and washed with water, ethanol, and ether. *Anal.* Calcd for $[Fe_2B_2(NCS)_2O](ClO_4)_2$: C, 38.86; H, 4.69; N, 16.99; S, 6.48; Cl, 7.17; O, 14.55. Found: C, 38.44; H, 5.10; N, 16.36; S, 6.03; Cl, 7.10; O, 14.54.

Magnetic Measurements.—For the mononuclear complexes magnetic susceptibility measurements were made at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. Measurements of the variation of the magnetic susceptibility of $Fe_2B_2O(ClO_4)_4 \cdot H_2O$ as a function of temperature between 106 and 316°K were made using a modification[15] of the apparatus described by Figgis and Nyholm.[16] Diamagnetic corrections for ligand and anions were calculated from Pascal's constants. The value of the molar susceptibility derived for ligand B is -161.3×10^{-6} cgsu.

Conductance Measurements.—Molar conductances were measured at 1000 cps and 25° using an Industrial Instruments Inc. Model RC-16B conductivity bridge and a cell having a constant of 1.469. Deionized water was used for preparing aqueous solutions, and nitromethane was dried over molecular sieves for at least 48 hr before use.

Electronic Spectra.—A Cary Model 14 recording spectrophotometer with 1-cm matched silica cells was used for all electronic spectral determinations.

Infrared Spectra.—These were measured over the range 4000–400 cm^{-1} using a Perkin-Elmer Model 337 grating spectrophotometer. Samples were prepared both in potassium bromide pellets and in Nujol mulls.

Acknowledgment.—The support of the National Science Foundation is gratefully acknowledged. The assistance of Mr. Philip Bryan during the early stages of this investigation is deeply appreciated.

[15] J. A. Burke, Jr., Ph.D. Thesis, The Ohio State University, 1963.

[16] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Photochemical Reactions of Cobalt(III) β-Ketoenolates in Organic Solvents[1]

BY NICOLAE FILIPESCU[2] AND HLA WAY

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Tris(acetylacetonato)cobalt(III), tris(benzoylacetonato)cobalt(III), and tris(dibenzoylmethanato)cobalt(III) have been photolyzed in different organic solvents. The complexed Co(III) ion is reduced photochemically to Co(II) with simultaneous oxidative fragmentation of one β-ketoenolate group. The reaction was partly reversible in the presence of oxygen. The quantum yields were found to be wavelength dependent and ranged from around 10^{-3} for excitation in the first d–d band to 0.6 in the ultraviolet region. A reaction mechanism consistent with the identified photoproducts is proposed.

An increasing number of papers have been published during the past 10 years on the photolysis of transition metal complexes in aqueous solutions.[3–5] However, very little is known about the photochemistry of transition metal chelates in nonpolar or less polar organic solvents. Presently we wish to report on the photochemical behavior of three cobalt(III) β-ketoenolates on exposure to near-ultraviolet irradiation in various organic solvents. A number of secondary reactions such as thermal and photoaquation or hydrolysis may be absent in nonpolar solvents, the role of which was expected to be less significant to the photochemical process than that of water.

The tris chelates of cobalt(III) with acetylacetone, $Co(acac)_3$, benzoylacetone, $Co(bzac)_3$, and dibenzoyl-

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[1] Taken in part from the dissertation submitted by H. W. to the Graduate School of The George Washington University in partial fulfillment for the degree of Doctor of Philosophy.

[2] Author to whom correspondence should be directed.

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