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## Chelates of $\beta$ -Diketones. VI. Synthesis and Characterization of Dimeric Dialkoxo-Bridged Iron(III) Complexes with Acetylacetonone and 2,2,6,6-Tetramethylheptane-3,5-dione (HDPM)

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Received October 18, 1971

A series of compounds assigned the structure  $[L_2FeOR]_2$  where L is the enolate of acetylacetonone or dipivaloylmethane (HDPM) and R is  $CH_3$ ,  $C_2H_5$ , and  $i-C_3H_7$  has been prepared and characterized. They are obtained by the oxidation of ferrous compounds in alcoholic solutions containing free ligand and bases or directly from ferric compounds. These dimers are weakly antiferromagnetic ( $-J \cong 10 \text{ cm}^{-1}$ ). Their infrared and optical spectroscopic properties are reported.

### Introduction

In the course of a study of the mechanism of oxidation of iron(II) chloride in nonaqueous solvents,<sup>3,4</sup> we observed large enhancement in the rates of oxygen consumption upon addition of  $\beta$ -diketones, such as HDPM (2,2,6,6-tetramethylheptane-3,5-dione) and amines. In a typical experiment the rate of oxidation of a 0.1 M solution of iron(II) chloride in methanol at 30° was increased at least 300-fold by addition of 0.3 mol each of HDPM and piperidine. Furthermore, a golden yellow product precipitated from the solution almost immediately. Initially, we suspected that the material might be an intermediate in the oxidation process, for example  $(DPM)_2FeOFe(DPM)_2$ . However, an exhaustive search for evidence for a peroxide structure, or unusual oxidizing properties, proved to be negative. We then found that the same material could be formed from iron(III) chloride, HDPM, and piperidine in methanol solution. The alternative method of preparation, in conjunction with properties reported in this paper, led to assignment of the structure as  $[(DPM)_2FeOCH_3]_2$ . The analogous dimer containing ethoxy groups is produced if the reactions are carried out in ethyl alcohol.

Similar materials resulting from the oxygenation of other ferrous chelates have been reported by other workers. Emmert and coworkers<sup>5</sup> have produced a variety of alkoxo-bridged ferric  $\beta$ -diketones by a similar procedure. For example, the oxygenation of  $(acac)_2Fe(py)_2$  in various alcohols yielded crystalline materials of composition  $(acac)_2FeOR$ . These products were characterized only by melting point and elemental analysis, although we presume that the structures are analogous to those that we have studied. More recently, Lever, Lewis, and Nyholm have reported that the oxygenation of  $(N-picO)_2Fe(H_2O)_2$  in  $CH_3OH$  yields a crystalline product of composition  $(N-picO)_2FeOCH_3$ .<sup>6</sup> They proposed a polymeric structure to account

for its reduced effective moment of 5.09 BM (spin-only  $\mu_{\text{eff}} = 5.92 \text{ BM}$  for  $S = 5/2$ ).

We report here the synthesis and spectroscopic and magnetic characterization of dimeric dialkoxo-bridged iron(III) chelates with DPM or acac as the nonbridging ligand.

### Experimental Section

**Preparation of Compounds.**  $[(acac)_2Fe(OC_2H_5)]_2$ .—This compound was prepared by the procedure of Emmert, *et al.*<sup>5</sup> Orange crystals were obtained and recrystallized from anhydrous ethanol (mp 158°, lit. mp 159°).

A simpler preparation results from the reaction of sodium ethoxide with an equimolar amount of the readily available  $Fe(acac)_3$ . An instantaneous reaction occurs with either concentrated ethanolic solutions or slurries of  $Fe(acac)_3$ . The dimeric product is less soluble than its precursor and approximately 75% yields of the crude material are obtainable by filtration of the cooled ( $\sim 0^\circ$ ) reaction mixtures. The product is dried under vacuum at room temperature or in a stream of dry  $N_2$ . The crude product was purified as above and is identical with the material obtained by Emmert's method.

This procedure appears to be general for the production of related dimers from the appropriate tris  $\beta$ -diketonate and alkoxide salt.<sup>7</sup>

$[(acac)_2Al(OC_2H_5)]_2$ .—This compound was prepared from  $Al(acac)_3$  and sodium ethoxide following the procedure used for  $[(acac)_2Fe(OC_2H_5)]_2$ ; mp 154°C. An alternative preparation involving the reaction of  $Al(OC_2H_5)_3$  with two moles of ligand has been described by Mehrotra and Mehrotra.<sup>8</sup> This material has been reported to be dimeric in boiling benzene.<sup>9</sup> Both preparations give material having identical melting points and infrared spectra.

$[(acac)Fe(OCH_3)]_2$ .—Following the procedure of Emmert and coworkers,<sup>5</sup> the oxygenation of a methanolic solution of  $(acac)_2Fe(py)_2$  results in a bright yellow product. The material is presumably polymeric since it is essentially insoluble in boiling polar organic solvents such as  $CH_3OH$ ,  $CHCl_3$ , and acetone and chars without melting. A similar yellow powder can be formed from the reaction of a methanolic solution of  $Fe(acac)_3$  with 2 equiv of methoxide ion.

$Fe(DPM)_3$  and  $[(N-picO)_2Fe(OCH_3)]_2$ .—These compounds were prepared according to literature methods.<sup>3,6</sup>

$[(DPM)_2Fe(OR)]_2$  (R =  $CH_3$ ,  $C_2H_5$ , and  $i-C_3H_7$ ). (1) **By the Oxidation of Ferrous Chloride in an Alcohol in the Presence of DPM.**—Fifteen milliliters of the appropriate dry alcohol 0.3 M in both HDPM and piperidine was saturated at 1 atm and 30° with oxygen. To this solution solid  $FeCl_2 \cdot 2H_2O$  ( $1.75 \times 10^{-3}$  mol,  $\sim 0.12 \text{ M}$ ) was added with stirring. Immediate  $O_2$  consumption and product precipitation occurred. After 30 min the reaction was nearly complete with 20 ml ( $0.8 \times 10^{-3}$  mol) of  $O_2$  absorbed. When the solution was stirred another 30 min, less than 1 additional ml of  $O_2$  was absorbed. The suspended orange

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 (4) G. S. Hammond and C.-H. S. Wu, *Advan. Chem. Ser.*, **No. 77**, 186 (1968).  
 (5) B. Emmert and W. Seebode, *Ber.*, **71**, 242 (1938), and references therein.  
 (6) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 5262 (1962).

(7) L. Leichter and H. J. Schugar, unpublished results.  
 (8) R. K. Mehrotra and R. C. Mehrotra, *Can. J. Chem.*, **39**, 795 (1961).  
 (9) R. C. Mehrotra, *Inorg. Chim. Acta Rev.*, **1**, 99 (1967).

TABLE I  
 PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound	Mp, °C	Mol wt at 37°		Calcd			Found			$\mu_{2980}^{\text{DPT}}$ BM
		Calcd	Found	C	H	Fe	C	H	Fe	
$[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$	208–213 <sup>a</sup>	906.8	911	60.92	9.11	12.31	61.01	9.02	12.13	5.09
$[(\text{DPM})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$	226–230 <sup>a</sup>	934.9	872	61.66	9.29	11.95	61.47	8.90	12.39	5.02
$[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]_2$	216–220 <sup>a</sup>	962.9	921	62.36	9.42	11.60	62.15	9.46	11.86	5.09
$\text{Fe}(\text{DPM})_3$	163	605.6	605	65.44	9.48	9.22	65.10	9.25	9.31	5.90
$[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$	158 <sup>a</sup>	598.2	479	...	...	...	...	...	...	4.94
$[(\text{acac})_2\text{Al}(\text{OC}_2\text{H}_5)_2]_2$	154	540	<i>b</i>	...	...	...	...	...	...	Diagram
$[(N\text{-picO})_2\text{Fe}(\text{OCH}_3)_2]_2$	...	726.2	Insol	...	...	...	...	...	...	5.14

<sup>a</sup> Melts with decomposition. <sup>b</sup> Dimeric.<sup>9</sup>

precipitate was collected, thoroughly washed with alcohol in small portions, and dried at room temperature under vacuum over  $\text{P}_2\text{O}_5$  (yield 75%). If water is added to the red filtrate,  $\text{Fe}(\text{DPM})_3$  forms. The same product is formed when the ratio of  $\text{FeCl}_2$  to DPM is varied between 1:2 and 1:3.

(2) From Iron(III) Chloride, HDPM, Piperidine, and ROH.—To a filtered dry solution of ferric chloride in the appropriate alcohol (*e.g.*,  $1.6 \times 10^{-3}$  mol in 20 ml of alcohol) was added a solution of  $3.2 \times 10^{-3}$  mol of freshly distilled HDPM and  $6 \times 10^{-3}$  mol of purified piperidine in 5–10 ml of the same alcohol. The solution was stirred at room temperature. The product precipitated immediately and was collected by filtration, thoroughly washed with numerous portions of the alcohol, and dried over  $\text{P}_2\text{O}_5$  under vacuum at room temperature. Yields were 90, 70, and 12% from methanol, ethanol, and 2-propanol, respectively.

The dimeric iron(III) alkoxide complexes are stable in the absence of moisture. The moisture sensitivity of the solids is such that inert-atmospheric techniques are not required in low-humidity environments. However, solutions of these dimers are readily decomposed by moisture to yield the tris  $\beta$ -diketonates as a major product along with insoluble residues. In addition, heating of the apparently anhydrous solutions often results in disproportionation to the tris chelates and unidentified materials.

**Physical Measurements.**—Molecular weights were determined in  $\text{CHCl}_3$  by vapor-phase osmometry (Hewlett-Packard 301 A). Infrared spectra were obtained on a Model 225 Perkin-Elmer spectrophotometer using KBr pellets, mineral oil mulls on CsI plates, and freshly prepared  $\text{CHCl}_3$  solutions. Optical spectra were measured on a Cary 14 RI spectrophotometer in  $\text{CHCl}_3$  and cyclohexane solutions and in KBr pellets. Variable-temperature magnetic susceptibility data were obtained on a PAR FM-1 vibrating-sample magnetometer. Melting points were measured with a Du Pont 900 dta apparatus and in melting point capillary tubes with conventional techniques. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories. Selected physical constants and analytical data are summarized in Table I.

## Results and Discussion

**Structural Formulation and Infrared Spectra.**—The molecular weight data given in Table I establish the dimeric nature of the  $(\beta\text{-dik})_2\text{Fe}(\text{OR})$  complexes. The infrared spectra of representative dimers are shown in Figure 1. For purposes of comparison, the spectrum of  $\text{Fe}(\text{DPM})_3$  is included. As all significant spectral features of the tris monomeric chelates are present in the spectra of the corresponding dimeric materials, we have chosen to summarize the data by listing only the new absorption bands of the dimeric chelates (Table II).

The first point to note is that the absorption peaks associated with the ligated acac and DPM are essentially identical in both the monomeric and corresponding dimeric materials. Thus the structures of the dimeric complexes are probably as shown in Figure 2, in which the  $\beta$ -diketonates are nonbridging ligands. As discussed below, the magnetic measurements are also in accord with the suggested structure.

The dominant feature among the new infrared absorptions (Table II) is the appearance of one or more

 TABLE II  
 INFRARED SPECTRA<sup>a</sup>

$[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$	235, 371, 486 s, 580, 1048 s, 1434
$[(N\text{-picO})_2\text{Fe}(\text{OCH}_3)_2]_2$	312, 392 s, 501 s, 1031 s
$[(\text{acac})_2\text{Fe}(\text{OCH}_3)_2]_2$	332 s, 1050 s, 1450
$[(\text{DPM})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$	220, 265 s, 332, 495, 583, 586, 889 s, 1047 s, 1096 s, 1160, 1460
$[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$	245, 265, 330, 472 s, 502 s, 885, 1048 s, 1091 s, 1160, 1460, 1471
$[(\text{acac})_2\text{Al}(\text{OC}_2\text{H}_5)_2]_2$	346, 428, 458, 538 s, 600 s, 751, 898, 1059 s, 1106, 1170, 1489
$[(\text{acac})_2\text{Al}(\text{OC}_2\text{H}_5)_2]_2^b$	150 s, 338, 345, 374, 438, 608, 992 s, 1078, 1177
$[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]_2$	225, 245, 295, 352, 582 s, 825, 945 s, 1120 s, 1462

<sup>a</sup> The only peaks reported are those not found in corresponding monomers; positions in  $\text{cm}^{-1}$ ; s = strong band. <sup>b</sup> Raman spectral data.

strong bands in the region  $800\text{--}1200\text{ cm}^{-1}$  whose positions depend upon the particular alkoxo group but are relatively independent of the nature of both the non-bridging ligands and the central metal ion. In the methoxo-bridged materials, a single band appears at  $1030\text{--}1050\text{ cm}^{-1}$ . For the ethoxides, three bands located near 890, 1050, and  $1100\text{ cm}^{-1}$  are prominent spectral features. A fourth band of lower intensity located at about  $330\text{ cm}^{-1}$  is also displayed by all the alkoxides. Both of the isopropoxides studied have significant new bands near 800 and  $930\text{ cm}^{-1}$ .

For the simplest case of the methoxo dimers, the band at  $\sim 1030\text{--}1050\text{ cm}^{-1}$  corresponds to the C–O stretch typically found near  $1050\text{ cm}^{-1}$  in alcohols.<sup>10</sup> For the ethoxo-bridged dimers, the strong absorption at  $\sim 1050\text{ cm}^{-1}$  is also assigned to a C–O stretch. The neighboring band at about  $1100\text{ cm}^{-1}$  and an additional band at  $\sim 890\text{ cm}^{-1}$  are characteristic of the ethoxo group. For instance, ethanol has strong absorptions at 1081, 1050, and  $876\text{ cm}^{-1}$  and  $\text{Si}(\text{OC}_2\text{H}_5)_4$  has strong absorptions at 1105 and  $1082\text{ cm}^{-1}$  along with a weak band at  $880\text{ cm}^{-1}$ . For the cases of the polynuclear compounds  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ta}(\text{OC}_2\text{H}_5)_5$ , and  $\text{Nb}(\text{OC}_2\text{H}_5)_5$ , Barraclough, *et al.*,<sup>11</sup> assigned two C–O modes at  $\sim 1030$  and  $1070\text{ cm}^{-1}$ . As partial hydrolysis of these materials resulted only in the disappearance of the band at  $1030\text{ cm}^{-1}$ , the two bands were suggested to originate from the bridging and terminal ethoxide groups, respectively.

A variety of isopropoxides display strong absorption at  $\sim 1000\text{ cm}^{-1}$  that is presumably due to the C–O

(10) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 31.

(11) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

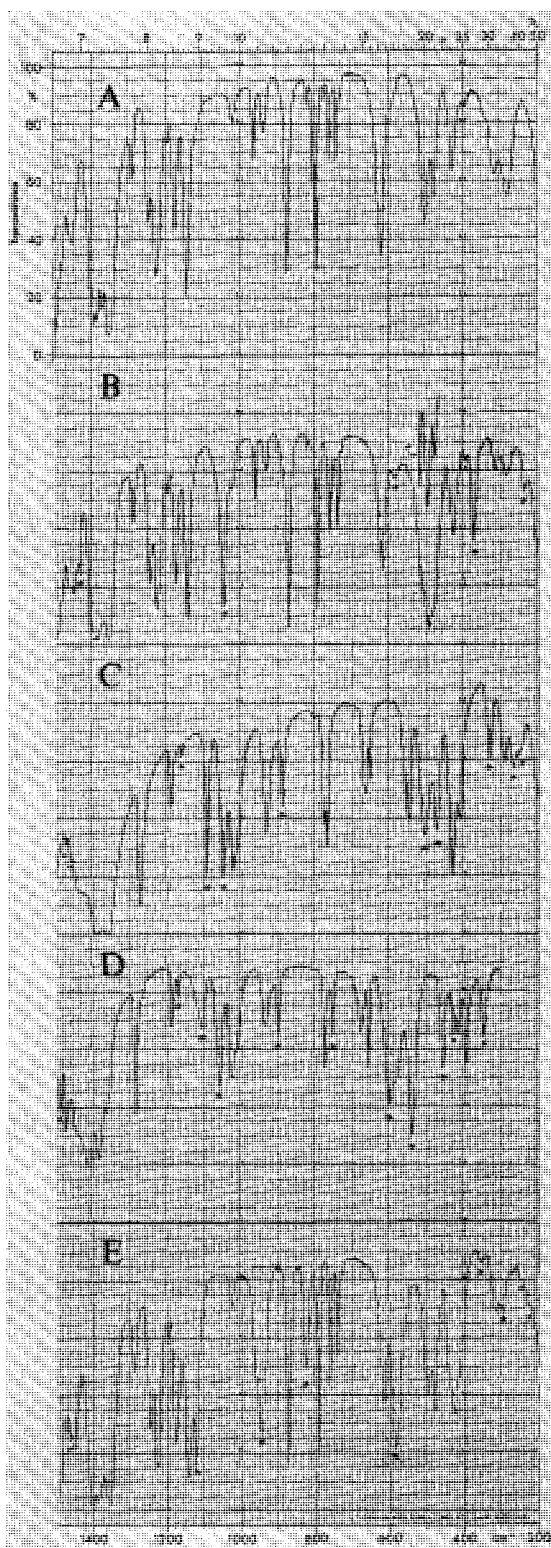


Figure 1.—Infrared spectra: (A)  $\text{Fe}(\text{DPM})_3$ ; (B)  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]$  (insert near  $500\text{ cm}^{-1}$  shows the improvement in resolution at  $\sim 78^\circ\text{K}$ ); (C)  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]$ ; (D)  $[(\text{acac})_2\text{Al}(\text{OC}_2\text{H}_5)_2]$ ; (E)  $[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]$ .

stretch found at  $1070\text{ cm}^{-1}$  in 2-propanol. Barraclough, *et al.*,<sup>11</sup> have located a band at  $1001\text{--}1036\text{ cm}^{-1}$  assigned to the C–O frequency for the isopropoxides of Ti(IV), Al(III), Zr(IV), and Ta(V). Similar results for the first two materials have been obtained by Bell, *et al.*<sup>12</sup> The latter workers also have located an anal-

(12) J. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *Anal. Chem.*, **25**, 1720 (1953).

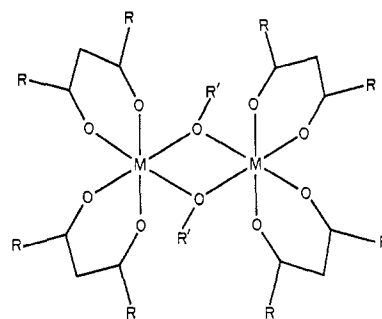


Figure 2.—Proposed structure of  $[(\beta\text{-dik})_2\text{MOR}]_2$ .

ogous band at  $\sim 1000\text{ cm}^{-1}$  in  $\text{P}[\text{OCH}(\text{CH}_3)_2]_3$ . (Interestingly, no such absorption was found for the analogous borate.) All the various isopropoxides (and 2-propanol itself) show additional absorption features at  $\sim 950$  and  $\sim 840\text{ cm}^{-1}$ . On this basis we assign the strong band at  $1012\text{ cm}^{-1}$  to a  $(\text{CH}_3)\text{CH}-\text{O}$  stretch for  $[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]$ . Apparently, additional absorptions at  $\sim 950$  and  $\sim 840\text{ cm}^{-1}$  are also characteristic of the isopropyl group. The bands at  $945$  and  $825\text{ cm}^{-1}$  exhibited by  $[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]$  are therefore also assigned to the alkoxide groups.

Nakamoto and coworkers<sup>13</sup> have recently identified the Fe–O absorption frequencies in  $\text{Fe}(\text{acac})_3$  through isotopic substitution. A band at  $300.5\text{ cm}^{-1}$  displayed the maximum shift upon isotopic substitution and was accordingly assigned as the Fe–O stretch. Smaller shifts were observed for the bands appearing at  $436$ ,  $551$ ,  $562$ , and  $655\text{ cm}^{-1}$ .

The dialkoxo-bridged ferric dimers display two or more bands in the low-energy region which have appropriate energies for Fe–O stretching modes. However, several ligand modes also are found in this spectral area. Thus a reliable band assignment scheme for the low-energy region must await appropriate isotopic substitution data. Also presented without commentary are the Raman bands displayed by  $[(\text{acac})_2\text{Al}(\text{OC}_2\text{H}_5)_2]$  which are not found for  $\text{Al}(\text{acac})_3$ .

The infrared spectrum of  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]$  was also examined at  $\sim 80^\circ\text{K}$ . With the exception of improved band resolution, the most striking spectral feature at  $80^\circ\text{K}$  is the  $12\text{-cm}^{-1}$  shift to higher energy of the  $502\text{-cm}^{-1}$  band. Greater than average shifts were also observed for the  $1090\text{-}$  and  $1048\text{-cm}^{-1}$  bands ( $5\text{--}6\text{ cm}^{-1}$ ). Other spectral bands displayed shifts of  $-2$  to  $+3\text{ cm}^{-1}$ . Therefore the largest shifts in the dimer spectrum all involve bands which are not present in  $\text{Fe}(\text{acac})_3$ . Regarding other ferric dimers, large low-temperature shifts have been observed<sup>14</sup> for the Fe–O–Fe stretch at  $858\text{ cm}^{-1}$  in  $\text{enH}_2[(\text{HEDTAFe})_2\text{O}] \cdot 6\text{H}_2\text{O}$  (where  $\text{enH}_2^{2+}$  is ethylenediammonium and HEDTA is *N*-hydroxyethylethylenediaminetriacetate)<sup>15</sup> and the bridging O–H frequency at  $947\text{ cm}^{-1}$  in  $[(\text{pic})_2\text{Fe}(\text{OH})_2]$ .<sup>16</sup>

**Magnetic Susceptibility.**—A feature common to all the dialkoxo-bridged iron(III) dimers is a room-temperature magnetic moment in the range  $4.9\text{--}5.2\text{ BM}$

(13) K. Nakamoto, C. Udovich, and J. Takemoto, *J. Amer. Chem. Soc.*, **92**, 3973 (1970).

(14) H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *ibid.*, in press.

(15) H. J. Schugar, C. Walling, R. Jones, and H. B. Gray, *ibid.*, **89**, 3712 (1967).

(16) H. J. Schugar, G. R. Rossman, and H. B. Gray, *ibid.*, **91**, 4564 (1969).

per iron, a value somewhat lower than the 5.9 BM observed for the corresponding tris monomers and other monomeric, octahedral high-spin Fe(III) complexes (see Table I). Furthermore, Figure 3 shows that all of

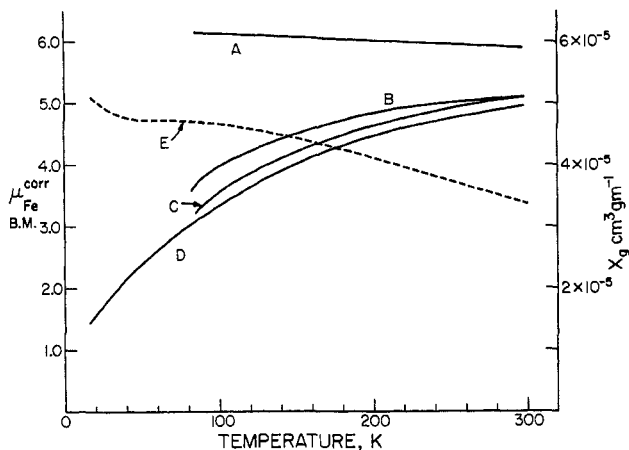
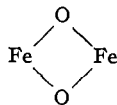


Figure 3.—Temperature dependence of the magnetic moments: (A)  $\text{Fe}(\text{DPM})_3$ ,  $\mu$  vs.  $T$ ; (B)  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$ ,  $\mu$  vs.  $T$ ; (C)  $[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]_2$ ,  $\mu$  vs.  $T$ ; (D)  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ ,  $\mu$  vs.  $T$ ; (E)  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ ,  $\chi_g$  vs.  $T$ .

these dimers display a magnetic moment which decreases with temperature. Such behavior is characteristic of an antiferromagnetically coupled system. The magnetic moment per iron vs. temperature curves for  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$  and  $[(N\text{-picO})_2\text{Fe}(\text{OCH}_3)_2]_2^{17}$  are nearly identical as are the curves for  $[(\text{DPM})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ ,  $[(\text{DPM})_2\text{Fe}(\text{O}-n\text{-C}_3\text{H}_7)_2]_2^{18}$  and  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ . A representative  $\chi_g$  vs.  $T$  curve (for  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ ) is also included in Figure 3. See Table III for additional magnetic susceptibility data.

Adopting the standard spin-spin coupling model with a perturbing Hamiltonian  $-2JS_1 \cdot S_2$  and  $S_1 = S_2 = 5/2$ , the experimental data for  $[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ ,  $[(\text{DPM})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ , and  $[(\text{DPM})_2\text{Fe}(\text{O}-n\text{-C}_3\text{H}_7)_2]_2$  are adequately fit by  $g = 2.0$ ,  $\text{TIP} = 0$ , and  $J = -11 \text{ cm}^{-1}$ . Similarly  $J \approx -8.5 \text{ cm}^{-1}$  for  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$  and  $[(N\text{-picO})_2\text{Fe}(\text{OCH}_3)_2]_2$  and for  $[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]_2$   $J \approx -10 \text{ cm}^{-1}$ . The extent of antiferromagnetic interaction in the dialkoxo dimers is considerably smaller than for oxo-bridged Fe(III) systems but is comparable to that found in dihydroxo-bridged Fe(III) dimers ( $J \approx -8 \text{ cm}^{-1}$ ).<sup>14-16</sup> Apparently the antiferromagnetic interaction in systems of the type shown in Figure 2 is primarily characteristic of the



structural unit and relatively insensitive to the nature of  $R'$  and the nonbridging ligands. Insensitivity to the nature of the nonbridging ligands has also been observed for a series of dimers containing the approximately linear Fe-O-Fe structural unit.<sup>14</sup>

(17)  $[(N\text{-picO})_2\text{Fe}(\text{OCH}_3)_2]_2$  has not been fully characterized. The magnetic susceptibility data lend support to the tentative dimeric formulation.

(18)  $[(\text{DPM})_2\text{Fe}(\text{O}-n\text{-C}_3\text{H}_7)_2]_2$ , although not fully characterized, has been prepared using the techniques reported here. The reddish orange solid melts with decomposition at 180–200°. On the basis of the magnetic susceptibility data it is presumed to be a dialkoxo-bridged dimer.

TABLE III  
MAGNETIC SUSCEPTIBILITY DATA

	Temp, °K	$10^5 \chi_g$ , $\text{cm}^3 \text{g}^{-1}$	$\mu^{\text{cor}}$ , BM
$[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$	298	33.8	4.95
	252	37.1	4.76
	199	41.2	4.45
	149	44.2	3.99
	101	46.4	3.36
$[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$	50.5	47.4	2.41
	298	23.4	5.09
	246	27.4	5.00
	198	31.9	4.84
	149	36.5	4.47
$[(\text{DPM})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$	101	42.5	3.97
	298	22.0	5.02
	246	24.7	4.83
	199	26.9	4.52
	149	29.1	4.06
$[(\text{DPM})_2\text{Fe}(\text{O}-n\text{-C}_3\text{H}_7)_2]_2$	101	29.9	3.40
	298	20.1	4.88
	246	22.6	4.69
	199	25.1	4.44
	149	27.4	4.01
$\text{Fe}(\text{DPM})_3$	101	28.4	3.36
	298	23.4	5.89
	246	29.6	6.00
	199	37.1	6.03
	149	50.7	6.08
$[(N\text{-picO})_2\text{Fe}(\text{OCH}_3)_2]_2$	91	86.2	6.17
	298	29.9	5.11
	246	35.1	5.03
	199	40.1	4.83
	149	46.7	4.50
$[(\text{DPM})_2\text{Fe}(\text{O}-i\text{-C}_3\text{H}_7)_2]_2$	101	53.5	3.97
	298	21.9	5.09
	246	24.6	4.89
	199	27.2	4.62
	149	30.0	4.19
	101	31.5	3.54

TABLE IV  
ELECTRONIC SPECTRAL DATA

Complex and conditions	$\lambda_{\text{max}}$ , nm	$10^{-3}\epsilon$ , $\text{cm}^{-1}$	$\epsilon$	Assignment, ${}^6A_1 \rightarrow$
$\text{Fe}(\text{DPM})_3$ Cyclohexane soln, room temp	$\sim 1010$	9.90	0.5	${}^4T_1$
	$\sim 755$	13.2	1.2	${}^4T_2$
	425	23.5	3,910	$a$
	357	28.0	4,120	$a$
	275	36.4	30,600	$a$
$[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$ Cyclohexane soln, room temp	$\sim 935$	10.7	1.0	${}^4T_1$
	$\sim 710$	14.1	2.0	${}^4T_2$
	418	23.9	2,350	$a$
	353	28.3	3,150	$a$
	272	36.8	20,000	$a$
$\text{Fe}(\text{acac})_3$ Acetone soln, room temp <sup>b</sup>	1025	9.760	0.45	${}^4T_1$
	760	13.160	0.70	${}^4T_2$
	433	23.12	3,400	$a$
	352	28.41	3,250	$a$
	$[(\text{acac})_2\text{Fe}(\text{OC}_2\text{H}_5)_2]_2$ CHCl <sub>3</sub> soln, room temp	$\sim 990$	10.1	0.7
$\sim 725$		13.8	0.7	${}^4T_2$
428		23.4	...	$a$
352		28.4	...	$a$
KBr pellet, 78°K		$\sim 950$	10.5	...
	$\sim 735$	13.6	...	${}^4T_2$
	436	22.0	...	$a$
	355	28.2	...	$a$

<sup>a</sup> Intraligand or charge-transfer band. <sup>b</sup> From ref 19.

**Electronic Spectra.**—The electronic spectral data are summarized in Table IV and a representative monomer-dimer comparison is shown in Figures 4 and 5 for  $\text{Fe}(\text{DPM})_3$  and  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]_2$ . The intraligand and charge-transfer bands in the two visible and ultraviolet spectra (Figure 4) are very similar, as would be expected for the structure shown in Figure 2. Two low-energy bands (near-ir) in each complex are of low intensity and most probably are due to spin-forbidden

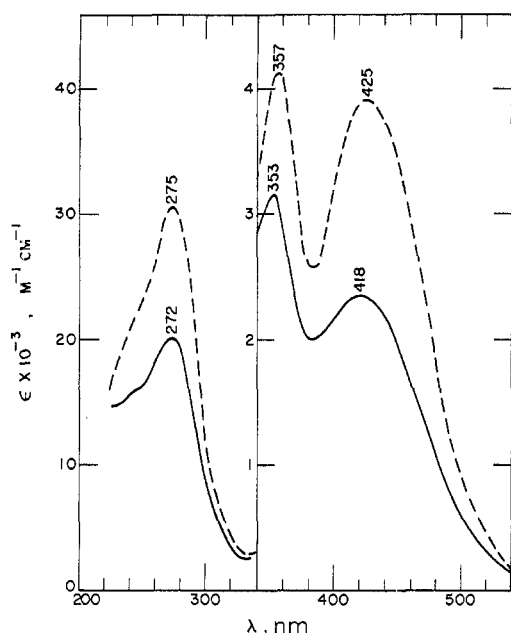


Figure 4.—Ultraviolet and visible spectra of  $\text{Fe}(\text{DPM})_3$  (broken line) and  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)]_2$  in cyclohexane solution.  $\epsilon$  is based on formula weight per iron(III).

d-d transitions (Figure 5). Following Piper and Carlin,<sup>19</sup> these bands are assigned to the d-d transitions  ${}^6A_1 \rightarrow {}^4T_1$  and  ${}^6A_1 \rightarrow {}^4T_2$ , respectively. The somewhat higher energies of the dimer d-d bands as compared to the corresponding monomer could be due to a smaller ligand field strength for bridging alkoxide than for  $\beta$ -diketonate. This conclusion is not firm, however, because small differences in interelectronic repulsions in the two cases could also lead to shifts of the magnitude observed.

It is important to note that there is no evidence in the electronic spectra of the dialkoxo-bridged dimers for

(19) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

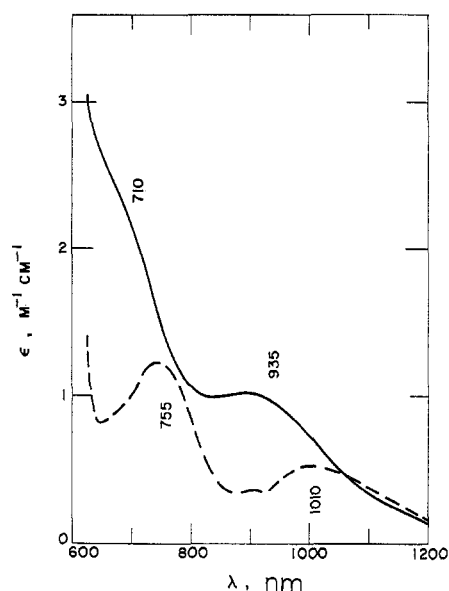


Figure 5.—Near-infrared (ligand field) spectra of  $\text{Fe}(\text{DPM})_3$  (broken line) and  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)]_2$  in cyclohexane solution.  $\epsilon$  is based on formula weight per iron(III).

either substantial intensity enhancements of the spin-forbidden d-d bands or simultaneous pair excitations such as found in certain oxo-bridged Fe(III) dimers.<sup>14,20</sup> Such special spectral features are apparently properties of antiferromagnetically coupled systems with  $-J$  values considerably in excess of  $10 \text{ cm}^{-1}$ .

**Acknowledgments.**—Research at the California Institute of Technology was supported by grants from the National Institutes of Health and the National Science Foundation. Research at Rutgers University was supported by the Rutgers Research Council and a Petroleum Research Fund starter grant.

(20) H. J. Schugar, G. R. Rossman, J. Thibeault, and H. B. Gray, *Chem. Phys. Lett.*, **6**, 26 (1970).

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## Synthetic Aspects of the Reaction between Azide Ion and $\text{Ru}(\text{bipy})_2(\text{NO})\text{X}^{2+}$ ( $\text{X} = \text{Cl}, \text{NO}_2$ ). Substitution-Induced Nitro-Nitrito Isomerism

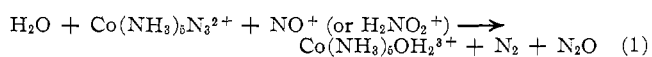
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Received August 30, 1971

The reaction  $\text{Ru}(\text{bipy})_2(\text{NO})\text{X}^{2+} + \text{N}_3^- + \text{S} \rightarrow \text{Ru}(\text{bipy})_2\text{SX}^+ + \text{N}_2 + \text{N}_2\text{O}$  ( $\text{S} = \text{solvent}$ ;  $\text{X} = \text{Cl}, \text{NO}_2$ ) has been used to prepare a series of solvent complexes. For  $\text{X} = \text{NO}_2$ , mixtures of nitro and nitrito isomers are obtained as products. Displacement of coordinated acetone in  $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{X}^+$  has provided a general route to the cis complexes  $\text{Ru}(\text{bipy})_2\text{YX}^{+6}$  ( $\text{Y} = \text{neutral or anionic ligand}$ ). During the substitution reactions of  $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{NO}_2^+$ , nitrito-nitro interconversion also occurs.

### Introduction

Haim and Taube<sup>2</sup> have shown that coordinated azide can be nitrosated



(1) National Science Foundation undergraduate research participant, summer 1970.

(2) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

In nonaqueous solvents using  $\text{NO}^+\text{ClO}_4^-$  as the nitrosating agent, labile solvent complexes are obtained,  $\text{Co}(\text{NH}_3)_6\text{S}^{3+}$  ( $\text{S} = \text{triethyl phosphate, sulfolane, etc.}$ ),<sup>3,4</sup> which are useful synthetic intermediates.<sup>3-5</sup> The intermediates allow synthetic control because un-

(3) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, **5**, 1091 (1966).

(4) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1174 (1968).

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