ring can be significantly increased by substitution of a strongly electron-donating group *para* to the nitroso moiety. However, even with this enhancement, the complexes formed are of low coordination number with respect to the ligand. It appears that even weakly coordinating anions such as nitrate and chloride can compete favorably with NODMA for coordination sites. It is interesting to compare this type of ligand with the pyridine N-oxides which have received much interest. The same resonance forms are available to nitrosobenzene as to pyridine N-oxide and coordination is through the N–O group. However, the infrared stretching frequencies indicate considerably more double-bond character in the nitroso compound. The N–O stretching frequency appears at around 1250 cm^{-1} in pyridine N-oxide[28] and at about 1500 cm^{-1} in nitrosobenzene.[13] The phenyl group seems to act as more of an electron sink to the nitroso compound whose dipole moment of 3.14 D[15] is less than that of pyridine N-oxide in which the value is 4.24 D.[29] Apparently this stabilization of the double-bonded N–O group decreases the basicity of the nitroso group toward metal ions relative to pyridine N-oxide. This decrease in basicity does not seem to be a steric problem since the N–O group is well removed from the benzene ring. Complexes with pyridine N-oxide easily exhibit coordination numbers of 6 with metal ions except when a strongly electron-withdrawing group such as nitro is substituted in the *para* position in pyridine N-oxide. Substitution of the dimethylamino group in the *para* position in nitrosobenzene greatly increases the dipole moment and seems to enhance the relative basicity of the nitroso group. This increased basicity is reflected in the fact that we were unable to obtain complexes using similar experimental techniques with nitrosobenzene.

Acknowledgment.—The authors are grateful for the support of this work by NIH Grant No. 1805 FRO-7092.

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A Novel Series of Six-Coordinated Iron(II) Diimine Complexes with Half-Quenched Spin

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Received March 15, 1968

The magnetic behavior of seven new six-coordinated iron(II) complexes having the general formula $Fe^{II}(diimine)_2X_2$, where X_2 stands for bidentate oxalate^{2-} and malonate^{2-} or two F^- ligands, has been studied. Between 77 and 300°K, the susceptibilities follow the Curie–Weiss law, $\chi_m = C_m/(T - \Theta)$, with Θ between -9 and $-51°$. The magnetic moments at 293°K are ~3.90 BM, corresponding to two unpaired electrons with a contribution of ~1.0 BM from second-order Zeeman effect. The agreement between corresponding moment values of the solid and in solution excludes the possibility that the rare $S = 1$ condition of iron(II) arises from intermolecular exchange interactions. Mössbauer effect studies result in isomer shifts $\delta = 0.33 \pm 0.04$ mm/sec, consistent with $S = 1$, and ΔE_Q between 0.18 and 0.31 mm/sec giving evidence for a very small electric field gradient. The electronic and epr spectra are briefly reported. The two Fe–O and the Fe–F stretching modes located in the infrared spectrum at 522, 340, and *ca.* 495 cm^{-1}, respectively, indicate that the compounds are *cis* monomeric. The unit cell of $[Fe(phen)_2ox] \cdot 5H_2O$ is extended along the *b* axis; the crystals are triclinic, with space group $P\bar{1}$ or P1 and $Z = 16$.

Introduction

Most simple mononuclear iron(II) complexes may be divided into two classes on the basis of their magnetic behavior: (i) high-spin compounds with four unpaired electrons exhibiting a quintet ground state ($S = 2$), *e.g.*, $Fe(H_2O)_6^{2+}$ and $FeCl_4^{2-}$, in which case the magnetic moment is 4.9–5.5 BM at room temperature and temperature dependent, following a curve as described previously;[3] (ii) low-spin compounds with all electrons paired and thus with a singlet ground state ($S = 0$) as in $Fe(CN)_6^{4-}$, compounds of this type showing a contribution from second-order Zeeman effect resulting in μ_{eff} values of up to 1.0 BM. Deviations from the normal high-spin and low-spin patterns may be encountered in six-coordinated iron(II) if the ligand field strength Δ approaches the mean spin-pairing energy π for the d^6 configuration, where $\pi = (5/2)B + 4C$, B and C being the Racah parameters. Thus the unusual μ_{eff} *vs.* T curves of certain diisothiocyanato- and diisoselenocyanatobis(diimine) complexes of iron(II), which were recently studied by the present authors,[4-6] are caused by transitions between the ground states $^5T_2$ and $^1A_1$.[7]

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[7] Within the approximation of O_h symmetry.

Although, besides the ^5D ground state, excited states of multiplicities 3 and 1 exist in the free iron(II) ion, it has been shown[8] that a state with two unpaired electrons ($S = 1$) cannot become the ground state in ligand fields of *strict octahedral* symmetry. However, inspection of the Tanabe–Sugano diagrams for the d^6 configuration[9] shows that, at the crossover point of $^5T_2$ and $^1A_1$, the lowest triplet state ($^3T_1$) is not far above the ground state. A lowering of symmetry will cause the $^3T_1$ to split, and, thus, close to $\Delta = \pi$, the stabilization of a triplet ground state might result.

In the course of our studies on $^5T_2$–$^1A_1$ transitions, we have prepared a novel series of iron(II) compounds in which a state of half-quenched spin, very likely a low-symmetry component of $^3T_1$, forms the electronic state of lowest energy. These new compounds are the oxalato- and malonatobis(diimine) complexes of iron(II), the diimines used being 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dmph), and 2,2′-dipyridyl (dipy). The complexes have been characterized chemically and their electronic ground states established by magnetic susceptibility and ^{57}Fe Mössbauer effect studies. In addition, electronic, vibrational infrared, and paramagnetic resonance absorption spectra have been used to obtain additional information on stereochemistry and bonding.

Experimental Section

(a) **Preparations.**—The bis(diimine) complexes $Fe^{II}(diimine)_2X_2$ (X = 0.5 oxalate, 0.5 malonate, and F) were prepared from iron(II) oxalate, $FeC_2O_4 \cdot 2H_2O$, the pyridine adduct of iron(II) malonate, $FeCH_2C_2O_4 \cdot py \cdot H_2O$, and anhydrous iron(II) fluoride, FeF_2, respectively, by the following method.[10,11] The initial iron(II) salt and a little more than a threefold molar quantity of the diimine were dissolved in a few milliliters of water, heated on a steam bath for several hours, and filtered, thereby forming a concentrated solution of the tris complex $[Fe^{II}(diimine)_3]X_2$. From this solution, dropwise addition of acetone precipitated the corresponding bis(diimine) complex $[Fe^{II}(diimine)_2X_2] \cdot nH_2O$. The crystals were collected, recrystallized from water, and reprecipitated from a water–acetone mixture with acetone or from a methanolic solution with ethanol. A detailed description of the preparative procedure for these compounds will be reported elsewhere.

To avoid any possible oxidation, the compounds were stored under prepurified dry nitrogen. However, no detectable decomposition was observed on samples exposed for a prolonged period to dry air. The compounds are generally soluble to some extent in water and alcohols and particularly well soluble in methanol, subsequently being affected by solvolysis.

The following representative compounds have been prepared and studied in some detail. Microanalyses were carried out both at the Institute of Inorganic Chemistry, University of Greifswald, and by Dr. F. Pascher, Microanalytical Laboratory, Bonn, Germany.

(1) **Oxalatobis(1,10-phenanthroline)iron(II) Pentahydrate.**—*Anal.* Calcd for $FeC_{26}H_{16}N_4O_4 \cdot 5H_2O$: C, 52.55; H, 4.42; N, 9.43; Fe, 9.40; H_2O, 15.13. Found: C, 52.68; H, 4.28; N, 9.42; Fe, 9.55; H_2O, 15.29.

(2) **Malonatobis(1,10-phenanthroline)iron(II) Heptahydrate.**—*Anal.* Calcd for $FeC_{27}H_{18}N_4O_4 \cdot 7H_2O$: C, 50.32; H, 5.01; N, 8.70; Fe, 8.66; H_2O, 19.57. Found: C, 50.66; H, 4.97; N, 8.58; Fe, 8.76; H_2O, 19.33.

(3) **Oxalatobis(4,7-dimethyl-1,10-phenanthroline)iron(II) Tetrahydrate.**—*Anal.* Calcd for $FeC_{30}H_{24}N_4O_4 \cdot 4H_2O$: C, 56.96; H, 5.10; N, 8.86; O, 20.22; Fe, 8.83; H_2O, 11.38. Found: C, 55.25; H, 4.96; N, 8.96; O, 20.15; Fe, 8.94; H_2O, 11.50.

(4) **Malonatobis(4,7-dimethyl-1,10-phenanthroline)iron(II) Heptahydrate.**—*Anal.* Calcd for $FeC_{31}H_{26}N_4O_4 \cdot 7H_2O$: C, 53.15; H, 5.76; N, 8.00; O, 25.10; Fe, 7.97; H_2O, 18.00. Found: C, 52.76; H, 5.16; N, 8.17; O, 24.74; Fe, 7.77; H_2O, 17.67.

(5) **Oxalatobis(2,2′-dipyridyl)iron(II) Trihydrate.**—*Anal.* Calcd for $FeC_{22}H_{16}N_4O_4 \cdot 3H_2O$: C, 51.78; H, 4.35; N, 10.98; Fe, 10.94; H_2O, 10.56. Found: C, 51.82; H, 4.38; N, 10.82; Fe, 11.12; H_2O, 10.31.

(6) **Malonatobis(2,2′-dipyridyl)iron(II) Trihydrate.**—*Anal.* Calcd for $FeC_{23}H_{18}N_4O_4 \cdot 3H_2O$: C, 52.69; H, 4.61; N, 10.69; Fe, 10.65; H_2O, 10.31. Found: C, 52.65; H, 4.49; N, 10.54; Fe, 10.60; H_2O, 10.20.

(7) **Difluorobis(1,10-phenanthroline)iron(II) Tetrahydrate.**—*Anal.* Calcd for $FeC_{24}H_{16}N_4F_2 \cdot 4H_2O$: C, 54.72; H, 4.59; N, 10.63; Fe, 10.59; F, 7.21; H_2O, 13.69. Found: C, 53.96; H, 4.62; N, 10.08; Fe, 10.27; F, 7.09; H_2O, 13.67.

(b) **Instrumentation.**—Magnetic susceptibilities between 77 and ~400°K were measured on polycrystalline samples, as described previously,[3,4] by the Faraday method. All measurements were made at three different field strengths (*ca.* 4900, 7350, and 9400 G), and no field dependence was observed, except for one sample as discussed below. The molar susceptibilities were corrected using the following values (in cgsu/mol) for the diamagnetic correction terms: Fe^{2+}, −13; phen, −128; dmph, −152; dipy, −105; ox^{2-}, −25; mal^{2-}, −34; F^-, −11; H_2O, −13. No allowance was made for the temperature-independent paramagnetism of the ferrous ion. The relation $\mu_{eff} = 2.84\sqrt{\chi_m' T}$ was employed to obtain the effective magnetic moment μ_{eff} from the corrected molar susceptibility χ_m' and the temperature (T) in degrees Kelvin.

Magnetic susceptibilities of the complexes in methanolic solution were determined by the Gouy method.

Iron-57 Mössbauer effect measurements were made with a spectrometer of conventional design. Cobalt-57 diffused into palladium was used as source, and both source and absorber were kept at the same temperature. The isomer shifts δ were measured relative to the midpoint of the spectrum of an iron foil absorber at 293°K. Following convention, δ was taken as positive when the source was moved toward the absorber.

Single-crystal X-ray diffraction data for unit cell determinations were recorded photographically with a precession camera, using Cu Kα radiation.

Infrared spectra of solid samples were recorded in Nujol mulls and KBr pellets over the range 4000–250 cm^{-1}. Both a Perkin-Elmer 125 grating spectrophotometer and a Beckman IR 7 instrument equipped with a CsI prism were employed.

Electronic spectra on solutions of the complexes were recorded on a Cary 14 spectrophotometer. A Zeiss PMQ 2 instrument was used to measure reflectance spectra of powdered samples. The wave number range covered is 5000–50,000 cm^{-1}.

Paramagnetic resonance was studied on polycrystalline samples at ~9 Gcps with a Varian V-4502 spectrophotometer using 100-kcps modulation frequency.

Results

Magnetic Data. (i) In the Solid State.—The results of magnetic susceptibility measurements on powder samples of the complexes between 77 and 293°K (or up to 400°K) are listed in Table I. The susceptibilities shown are the average values of five independent measurements for each experimental configuration. The compounds $[Fe(phen)_2ox] \cdot 5H_2O$, $[Fe(phen)_2mal] \cdot 7H_2O$, and $[Fe(phen)_2F_2] \cdot 4H_2O$ have been studied extensively, the susceptibilities being determined every 10°. All the other complexes were measured at four

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TABLE I

MAGNETIC DATA[a] FOR $Fe(phen)_2X_2$, $Fe(dipy)_2X_2$, AND $Fe(dmph)_2X_2$ COMPOUNDS ($X_2^{2-} = ox^{2-}, mal^{2-}, 2F^-$). EACH SET OF THREE NUMBERS GIVES T (°K), χ_m ($10^{-6} \times$ CM^3 MOL^{-1}), AND μ_{eff} (BM)

$[Fe(phen)_2ox]\cdot 5H_2O$

399.4, 5425, 4.32; 379.6, 5491, 4.23; 360.1, 5628, 4.17; 340.2, 5754, 4.10; 319.9, 5981, 4.04; 310.2, 6123, 4.03; 294.2, 6395, 4.00; 280.9, 6558, 3.96; 269.8, 6844, 3.96; 259.7, 7076, 3.95; 250.2, 7357, 3.95; 239.6, 7665, 3.94; 230.0, 8028, 3.94; 220.0, 8323, 3.93; 210.2, 8720, 3.92; 200.2, 9082, 3.90; 189.5, 9568, 3.90; 180.9, 9973, 3.88; 169.5, 10,587, 3.87; 160.0, 11,151, 3.85; 149.6, 12,000, 3.86; 140.4, 12,753, 3.85; 130,7, 13,550, 3.83; 120.8, 14,578, 3.82; 110.6, 15,567, 3.77; 100.2, 16,613, 3.70; 90.3, 18,402, 3.70; 76.8, 21,584, 3.69

$[Fe(phen)_2mal]\cdot 7H_2O$

359.7, 5047, 3.97; 340.1, 5158, 3.90; 330.2, 5279, 3.89; 320.0, 5407, 3.87; 310.4, 5469, 3.83; 293.3, 5834, 3.83; 279.5, 5885, 3.76; 269.8, 6121, 3.77; 259.8, 6337, 3.76; 249.9, 6600, 3.75; 240.0, 6881, 3.75; 229.7, 7126, 3.73; 220.0, 7452, 3.73; 209.7, 7827, 3.73; 200.2, 8187, 3.72; 190.2, 8615, 3.72; 179.9, 9045, 3.70; 170.1, 9530, 3.69; 160.2, 9987, 3.66; 150.2, 10,738, 3.67; 140.2, 11,572, 3.68; 129.5, 12,375, 3.65; 119.9, 13,426, 3.66; 110.1, 14,506, 3.64; 100.7, 16,034, 3.65; 98.4, 17,979, 3.64; 75.7, 21,289, 3.64

$[Fe(phen)_2F_2]\cdot 4H_2O$

336.0, 8113, 4.79; 315.8, 8569, 4.76; 293.4, 9313, 4.78; 259.7, 10,312, 4.72; 239.6, 11,166, 4.72; 218.2, 12,253, 4.71; 199.8, 13,298, 4.69; 179.9, 14,571, 4.65; 160.2, 16,334, 4.64; 140.2, 18,510, 4.62; 120.2, 21,412, 4.59; 100.2, 25,466, 4.57; 76.5, 33,872, 4.59

$[Fe(dipy)_2ox]\cdot 3H_2O$[a]

293, 7040, 4.15; 273, 7500, 4.14; 195, 9930, 4.01; 77, 23,000, 3.80

$[Fe(dipy)_2mal]\cdot 3H_2O$

293, 6140, 3.90; 273, 6590, 3.90; 195, 9110, 3.85; 77, 22,600, 3.77

$[Fe(dmph)_2ox]\cdot 4H_2O$

293, 6760, 4.11; 273, 7395, 4.14; 195, 9500, 3.95; 77, 21,780, 3.71

$[Fe(dmph)_2mal]\cdot 7H_2O$

293, 6960, 4.18; 273, 7650, 4.22; 195, 10,130, 4.08; 77, 24,440, 3.92

[a] Values listed apply to a magnetic field strength corresponding to 2.4 A (*ca.* 7350 G). Slight field dependence of χ_m is observed; *cf.* Table II for values extrapolated to $H = \infty$.

representative temperatures only. In $[Fe(dipy)_2ox]\cdot 3H_2O$, a slight field dependence of the susceptibility was observed. The relevant data in this case are given in Table II which also lists the μ_{eff} obtained on extrapolation to infinite field strength. Within the temperature range from 77 to ~300°K, the susceptibilities of all of these compounds may be approximated by the Curie–Weiss law, $\chi_m = C_m/(T - \Theta)$. The resulting values of the Weiss constant Θ and of μ_{eff} at 293°K are listed in Table III.

(ii) **In Solution.**—The magnetic susceptibilities of those complexes which are sufficiently soluble were measured at 293°K in methanolic solution. The results are reported in Table IV.

Iron-57 Mössbauer Effect.—The ^{57}Fe Mössbauer effect spectra of the complexes were studied on powder samples at 293 and 77°K. Values of the isomer shift δ and the quadrupole splitting ΔE_Q determined from these spectra are collected in Table V.

TABLE II[a]

FIELD DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITY χ_g FOR $[Fe(dipy)_2ox]\cdot 3H_2O$ AND EXTRAPOLATION TO $H = \infty$

Temp, °K	H, A	$10^6\chi_g$, cm^3/g	$10^6\chi_g^\infty$, cm^3/g	$10^6\chi_m^\infty$, cm^3/mol	μ_{eff}^{cor}, BM
293	1.6	14.74			
	2.4	13.78	12.10	6,170	3.90
	3.1	13.52			
273	1.6	15.47			
	2.4	14.70	13.50	6,880	3.97
	3.1	14.50			
195	1.6	20.30			
	2.4	19.48	17.80	9,070	3.83
	3.1	19.10			
77	1.6	45.50			
	2.4	45.10	42.90	21,860	3.71
	3.1	44.10			

[a] The magnetic field strengths corresponding to the electric currents of 1.6, 2.4, and 3.1 A are *ca.* 4900, 7350, and 9400 G, respectively.

TABLE III

APPLICABILITY OF THE CURIE–WEISS LAW FOR THE COMPOUNDS $Fe(diimine)_2X_2$

Compound	Temp range, °K	$\mu_{eff}^{293°}$,[a] BM	Θ, deg
$[Fe(phen)_2ox]\cdot 5H_2O$	77–300	3.98	−20
$[Fe(phen)_2mal]\cdot 7H_2O$	77–300	3.80	−12
$[Fe(phen)_2F_2]\cdot 4H_2O$	77–336	4.78	−15
$[Fe(dipy)_2ox]\cdot 3H_2O$	77–293	3.90	−13
$[Fe(dipy)_2mal]\cdot 3H_2O$	77–293	3.90	−9
$[Fe(dmph)_2ox]\cdot 4H_2O$	77–293	4.11	−51
$[Fe(dmph)_2mal]\cdot 7H_2O$	77–293	4.18	−19

[a] Uncertainty ±0.05 BM.

TABLE IV

MAGNETIC MOMENTS OF $Fe(diimine)_2X_2$ COMPOUNDS IN METHANOLIC SOLUTION

Compound	Temp, °K	Concn, M	$10^6\chi_m$, cm^3 mol^{-1}	μ_{eff},[a] BM
$[Fe(phen)_2ox]\cdot 5H_2O$	293	0.05	5725	3.80
$[Fe(phen)_2mal]\cdot 7H_2O$	293	0.05	5750	3.82
$[Fe(dipy)_2mal]\cdot 3H_2O$	293	0.05	5680	3.76
$[Fe(dmph)_2ox]\cdot 4H_2O$	293	0.05	5900	3.86
$[Fe(dmph)_2mal]\cdot 7H_2O$	293	0.05	6150	3.94

[a] Uncertainty ±0.15 BM.

TABLE V

ISOMER SHIFTS δ AND QUADRUPOLE SPLITTINGS ΔE_Q FROM ^{57}Fe MÖSSBAUER SPECTRA

Compound	Temp, °K	δ,[a] mm/sec	ΔE_Q,[b] mm/sec
$[Fe(phen)_2ox]\cdot 5H_2O$	293	+0.33	0.21
$[Fe(phen)_2mal]\cdot 7H_2O$	293	+0.34	0.18
	77	+0.27	0.18
$[Fe(phen)_2F_2]\cdot 4H_2O$	293	+0.33	0.21
	77	+0.30	0.16
$[Fe(dipy)_2ox]\cdot 3H_2O$	293	+0.34	0.26
	77	+0.27	0.26
$[Fe(dipy)_2mal]\cdot 3H_2O$	293	+0.30	0.31
$[Fe(dmph)_2ox]\cdot 4H_2O$	293	+0.36	0.23
	77	+0.29	0.21
$[Fe(dmph)_2mal]\cdot 7H_2O$	293	+0.33	0.27
	77	+0.27	0.21

[a] Isomer shifts δ are listed relative to the center of the spectrum of a natural iron absorber at 293°K. Movement of the source toward the absorber corresponds to positive velocities. Uncertainty is ±0.04 mm/sec or less. [b] Uncertainty is ±0.03 mm/sec or less.

TABLE VI

INFRARED VIBRATIONAL FREQUENCIES OF OXALATE AND MALONATE LIGANDS IN [Fe(diimine)$_2$X$_2$] COMPLEXES (IN CM^{-1})

Compound	ν_7 ν_{as}(CO)	ν_1 ν_{as}(CO)	ν_2 ν_s(CO) + ν(CC)	ν_8 ν_s(CO) + δ(OCO)	ν_3 ν_s(CO) + δ(OCO)	ν_9 δ(OCO) + ν(FeO)	ν_4 ν(FeO) + ν(CC)	ν_{10} ring def + δ(OCO)	ν_{11} ν(FeO) + ring def	ν_5 δ(OCO)
[Fe(phen)$_2$ox]·5H$_2$O	1707 s	1660 vs, br	1363 vs, br	1260 sh 1252 s, br	887 m, br	789 vs 778 sh	523 s	484 m, br	337 vs, br	321 sh
[Fe(dipy)$_2$ox]·3H$_2$O	1706 s	1660 vs, br	1365 vs, br	1265 sh 1250 s, br	888 s, br	789 vs	522 s	482 s, br	340 vs, br	323 sh
[Fe(dmph)$_2$ox]·4H$_2$O	1706 s	1660 vs, br	1363 vs, br	1258 s, br	885 m, br	789 vs 780 sh	522 s	479 s	338 vs, br	320 sh

	ν_{as}(CO)	CH$_2$ bend + ν_s(CO)	ν_s(CO)	CH$_2$ wag	ν_s(CC)	CH$_2$ rock	δ(OCO)	δ(OCO)	ν(FeO)	ν(FeO)	δ(OCO)	δ(CCC)?
[Fe(phen)$_2$mal]·7H$_2$O	1610 vs, br	~1405 sh	1373 vs, br	1290 m, br	957 s	928 s	778 m, br	710 s	550 m, br	347 vs, br	325 s, sh	292 vs, br
[Fe(dipy)$_2$mal]·3H$_2$O	1610 vs, br	~1395 sh	1375 vs, br	1295 m, br	958 s	927 s	~780 sh	713 s	552 m, br	345 vs, br	325 s, sh	288 vs, br
[Fe(dmph)$_2$mal]·7H$_2$O	1610 vs, br	~1395 sh	1373 vs, br	1290 m, br	958 s	929 s	~790 sh	714 s	555 m, br	...	...	...

Crystal Data.—Single-crystal precession X-ray photographs were used to determine lattice parameters in [Fe(phen)$_2$ox]·5H$_2$O. The crystals are triclinic, space group P$\bar{1}$ or P1, $a = 16.23 \pm 0.05$ Å, $b = 63.2 \pm 0.2$ Å, $c = 10.56 \pm 0.04$ Å, $\alpha = 92° 5' \pm 30'$, $\beta = 102° 21' \pm 30'$, $\gamma = 90° 40' \pm 30'$, $D_m = 1.49 \pm 0.01$ g cm^{-3} (by flotation); with $Z = 16$ molecules per unit cell, $D_c = 1.49 \pm 0.02$ g cm^{-3}. The crystals are red diamond-shaped plates. The plate faces are $\{010\}$, bounded by the faces $\{100\}$ and $\{001\}$.

Infrared Spectra.—The vibrational frequencies due to coordinated oxalate and malonate ions were assigned by comparison with Fe^{II}(diimine)$_2$Cl$_2$ and similar complexes and are listed in Table VI. The notation employed in the case of oxalate complexes is based on a normal-coordinate analysis performed by Fujita, Martell, and Nakamoto.[12,13] No such theoretical treatment is available for malonate complexes. The notation therefore uses empirical assignments proposed by Schmelz, *et al.*[14] However, it is anticipated that, in the malonate complexes, a mixing of normal frequencies should occur which is similar to that found for oxalate complexes. Finally, the infrared frequencies due to the diimine ligands correspond to those of the same ligands within the series Fe^{II}(diimine)$_2$X$_2$ reported previously[5,6] and are not repeated here.

Electronic Spectra.—The wave numbers of the absorption bands observed in the reflectance spectra of two representative complexes and the assignments of these bands are listed in Table VII. Values of the extinction coefficient ϵ and the oscillator strength f have been estimated from the solution spectra in methanol. The electronic spectra of the three phenanthroline compounds are virtually identical. The only difference in the spectra of the two dimethylphenanthroline complexes is a shift of the charge-transfer band to 19,750 cm^{-1} (main peak). The spectra of the dipyridyl compounds are also practically identical.

TABLE VII

ABSORPTION BAND MAXIMA IN THE ELECTRONIC SPECTRA OF Fe(diimine)$_2$X$_2$ COMPLEXES

Wave number, cm^{-1}	ϵ, l. mol^{-1} cm^{-1}		Assignment
		[Fe(phen)$_2$ox]·5H$_2$O	
11,620	~6		d–d
18,850	6,500	6.88 × 10^{-2}	CT (core)π^2t$_2{}^5$e → (core)π^2t$_2{}^4$eπ**
20,800	5,500	4.55 × 10^{-2}	
30,800	1,050	5.30 × 10^{-3}	^{1}L$_b$(phen)
34,200	6,400	3.53 × 10^{-2}	^{1}L$_a$(phen)
36,800	78,000	1.08	^{1}B$_b$(phen)
43,900	43,000	~0.83	^{1}C$_b$(phen)
		[Fe(dipy)$_2$mal]·3H$_2$O[a]	
11,900	~5		d–d
19,200	2,400		CT (core)π^2t$_2{}^5$e → (core)π^2t$_2{}^4$eπ**
20,800	2,100		
29,000	2,800		^{1}L$_b$(dipy)
34,700	38,500		^{1}L$_a$(dipy)
41,000	26,000		^{1}B$_b$(dipy)

[a] Values of ϵ might be affected by partial solvolysis.

Discussion

The compounds of the general types Fe(diimine)$_2$ox and Fe(diimine)$_2$mal studied in the present work were obtained from the corresponding tris complexes as red tabular crystals which, under normal pressure, dehydrated between 100 and 160° and then decomposed, losing the diimine ligand, above 160°. They are usually well soluble in methanol, however only slightly soluble in higher alcohols and water, forming intensely red solutions. These solutions undergo solvolysis, the rate of which is dependent upon the compound and the solvent used. Owing to the long retention time of the only suitable solvents and to the solvolysis thus introduced, molecular weight determinations by the osmometric method were unsuccessful.

The magnetic behavior of the compounds warrants a detailed discussion. In these complexes, intermediate values of the room-temperature magnetic moment were observed (*cf.* Table III) which could arise as a consequence of one of the following: (i) admixture of low-spin iron(III) complex with high-spin iron(II) complex; (ii) ferromagnetic impurity in low-spin iron (II) complex; (iii) antiferromagnetic interaction in high-spin iron(II) complex; (iv) Boltzmann distribution over thermally accessible states of different spin multiplicity; or (v) triplet ground state. These possibilities will be considered in turn and compared with the experimental data.

(i) An admixture of iron(III) would be detected by routine methods of chemical analysis as well as by the other physical measurements performed. For ex-

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[12] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

[13] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[14] M. I. Schmelz, I. Nakagawa, S. I. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 287 (1959).

ample, low-spin iron(III) complexes with phenanthroline ligands are characterized by a $\pi \rightarrow dt_{2g}$ charge-transfer band at 16,890 cm^{-1} with ϵ 780 in the electronic spectra,[15-17] whereas, with dipyridyl ligands, the band is observed at 16,300 cm^{-1} and ϵ 195.[15,17] Obviously, no such absorption band has been detected in the electronic spectra summarized in Table VII. Also any iron(III) impurity would arise as a consequence of air oxidation. Such oxidation is very unlikely on the basis of the analytical data included in this paper and the care taken during preparation and handling of the complexes.

(ii) A ferromagnetic impurity would give rise to a field dependence of the magnetic susceptibility. Within the compounds studied, such dependence has been observed onlyfor $[Fe(dipy)_2ox]\cdot 3H_2O$ and, in this case, the effect of the magnetic field is much too small to account for the intermediate value of the magnetic moment. If the susceptibility of $[Fe(dipy)_2ox]\cdot 3H_2O$ is extrapolated to infinite field strength as shown in Table II, the resulting magnetic moment is, within the experimental uncertainty, equal to the moment values encountered in $[Fe(phen)_2ox]\cdot 5H_2O$. Therefore, the assumption of a ferromagnetic interaction cannot explain the magnitude of the magnetic moment in this series of complexes.

(iii) Antiferromagnetic interaction would result, below the Néel point, in a decrease of the reciprocal susceptibility, $1/\chi_m$, with increasing temperature. In Figure 1 graphs of $1/\chi_m$ *vs.* T are presented for the three phenanthroline complexes of the series. Similar, very nearly linear plots are obtained for the other complexes considered here (*cf.* Table III). Clearly, the curves do not show the behavior expected for antiferromagnetism. In addition, antiferromagnetic interactions may be ruled out on the basis of the identical magnetic moment values determined on the solid substances (*cf.* Table III) and on their diluted (0.05 *M*) solutions (*cf.* Table IV).

(iv) A Boltzmann distribution over different spin states gives rise to a pronounced temperature dependence of the magnetic moment. We have shown previously[4,6] that this is particularly so if the states resulting from the $^5T_2(t_2{}^4e^2)$ and $^1A_1(t_2{}^6)$ terms of the octahedral field are involved. In that case, a transition between the ground states of different multiplicities is observed which virtually assumes cooperative character.[6] Inspection of Figure 1 and Table I shows no indication of such a temperature dependence in the present compounds. A Boltzmann distribution involving a triplet state may be dismissed for the same reason.

(v) Finally, a triplet ground state would be in agreement with the value of $\mu_{eff} \sim 3.9$ BM which is observed for the solid state and which is independent of temperature down to 77°K. This value corresponds to the moment expected for two unpaired electrons (*i.e.*, 2.83 BM) with an additional contribution of about 1.0 BM from the second-order Zeeman effect. The high second-order contribution, although not anticipated on the basis of simple ligand field theory,[18] is commonly observed in d^6 compounds of low-spin type. Also, if the lowest excited levels are properly included, a temperature-independent paramagnetism of ~0.7 BM is calculated.[19] In the case considered here, low-lying excited levels of multiplicities 5 and 1 will be present. Therefore, an increased contribution from the second-order Zeeman effect may not be unexpected. The fact that the susceptibility is not altered in solution demonstrates that the intermediate value of the electron spin, $S = 1$, is a characteristic property of the molecule. This conclusion is, in addition, compatible with the results of various spectroscopic investigations.

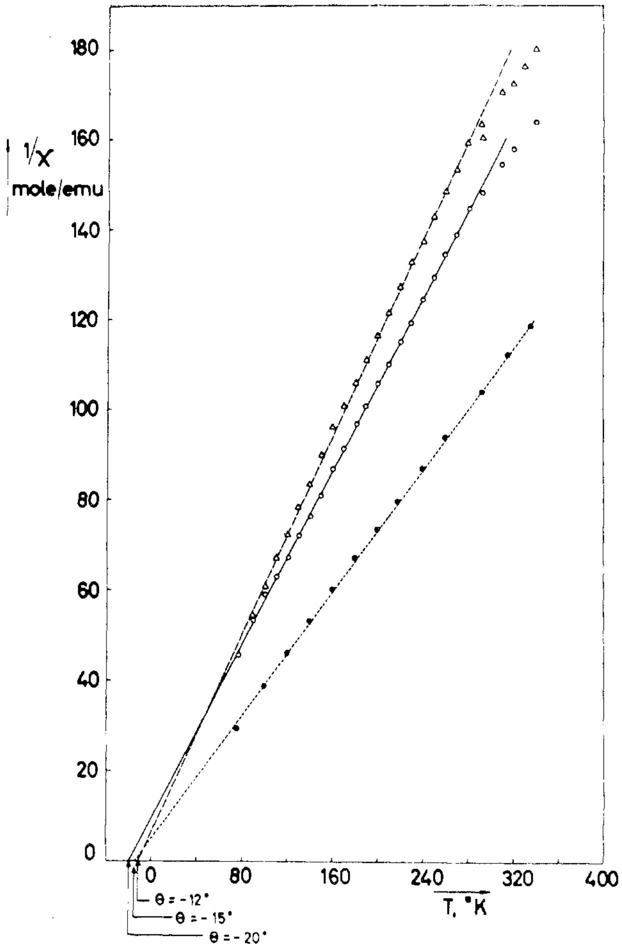

Figure 1.—Plot of the reciprocal molar magnetic susceptibility $1/\chi$ *vs.* T for $[Fe(phen)_2ox]\cdot 5H_2O$ (○), $[Fe(phen)_2mal]\cdot 7H_2O$ (△), and $[Fe(phen)_2F_2]\cdot 4H_2O$ (●).

Thus ^{57}Fe Mössbauer effect studies at 293°K result in isomer shifts, δ, of 0.33 ± 0.04 mm/sec and quadrupole splittings, ΔE_Q, varying between 0.18 and 0.31 mm/sec (*cf.* Table V). At 77°K, essentially the same values are obtained. These results differ distinctly from those measured on $Fe(diimine)_2X_2$ compounds in $^5T_2$ ground states ($S = 2$), where δ is commonly found between 0.96 and 1.09 mm/sec and ΔE_Q between 2.40

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(15) J. Csaszar, *Acta Chim. Acad. Sci. Hung.*, **24**, 55 (1960).

(16) P. Day and N. Sanders, *J. Chem. Soc.*, 1530 (1967).

(17) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

(18) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(19) C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, **11**, 479 (1957).

and 3.04 mm/sec.[20] Also, the spectra bear no resemblance to those of compounds showing a Boltzmann distribution over various spin states.[4,6] The Mössbauer spectral parameters are rather similar to those of $Fe(diimine)_2X_2$ compounds in $^1A_1$ ground states ($S = 0$); *e.g.*, for $[Fe(phen)_2(CN)_2] \cdot H_2O$ $\delta = 0.20$ and $\Delta E_Q = 0.59$ mm/sec, and for $Fe(phen)_2(NO_2)_2$, $\delta = 0.28$ and $\Delta E_Q = 0.38$ mm/sec.[20] On the other hand, the isomer shift values also compare well with $\delta = 0.40$ mm/sec for iron(II) phthalocyanine,[21] the only other iron(II) compound supposed to be in a triplet ground state which, to our knowledge, has been studied by Mössbauer spectroscopy. The value[21] of $\Delta E_Q = 2.62$ mm/sec is of course not comparable owing to the planar geometry of this compound. The low values of ΔE_Q for the oxalate and malonate complexes imply a very small electric field gradient (efg) and thus an almost spherical d-electron distribution. In addition, the almost constant ΔE_Q values suggest *cis* arrangement of the ligating oxygen atoms and thus a monomolecular structure of the compounds.

The infrared spectra contain several features of particular interest. The vibrational frequencies of the oxalate ligand have been assigned as listed in Table VI. Their striking similarity to those of $[Cr(NH_3)_4ox]Cl$, especially with respect to the frequencies ν_4 and ν_{11} at 522 and 340 cm^{-1}, respectively (predominantly Fe–O stretch),[12,13] gives evidence that the compounds considered here include the oxalate ligand in a monomeric *cis* complex. The possibility of a chainlike structure with bridging oxalate groups, where two oxygen atoms of different oxalate ligands would be coordinated *trans* to each other, cannot be supported on the basis of infrared spectra. A similar conclusion may be arrived at for the corresponding malonate complexes (*cf.* Table VI and ref 14).

As far as the diimine ligands are concerned, we have shown previously[5] that there are characteristic differences in the vibrational frequencies between $Fe(diimine)_2X_2$ compounds in $^5T_2$ and $^1A_1$ ground states, particularly if the diimine is phenanthroline. In the compounds studied at present, numerous diimine bands are obscured by the broad bands of the ox^{2-} and mal^{2-} ligand anions. However, confining our attention to, *e.g.*, phenanthroline complexes, comparison of the spectra of, say, $[Fe(phen)_2ox] \cdot 5H_2O$, $[Fe(phen)_3]Cl_2$, and $Fe(phen)_2(NCS)_2$ in both the $^5T_2$ and $^1A_1$ ground states[5] shows that the frequencies of the phen ligand in the present compounds compare well with those of compounds in $^1A_1$ states. In this respect, the following vibrations are particularly significant: the C–C and C–N stretching vibrations of the phen ring system (comparatively weak bands at 1632 (vw), 1600 (w), 1576 (m), 1510 (m), 1491 (w), and 1453 cm^{-1} (w); the strong bands 1423 (vs) and 1408 cm^{-1} (s) are not split), the ring-breathing and in-plane C–H bending vibrations (virtually identical with those of $[Fe(phen)_3]Cl_2$), γ(CH) carbocyclic and γ(CH) heterocyclic (844 (vs) and 722 cm^{-1} (vs), respectively; the weak band at 735 cm^{-1} is also observed for the $^1A_1$ ground state; the satellite 867 cm^{-1}, characteristic of the $^5T_2$ state, has not been detected), the α(CCC) mode (644 (vw), 558 (m), and 530 cm^{-1} (s), coincident with ν_4(ox); *cf.* Table VI), and the absence of the ϕ(CC) mode down to 400 cm^{-1}. Analogous similarities exist between the oxalate and the malonate complexes, with diimine = dipy or dmph, and the corresponding compounds in $^1A_1$ ground states. Thus, within the same series of complexes (diimine = phen, dipy, or dmph), these results suggest a close resemblance of distances and of metal–ligand bonding between compounds in triplet ground states and those in $^1A_1$ ground states. These results are consistent with the close-lying values for the quadrupole splitting, ΔE_Q, in the Mössbauer spectra of compounds having the two different electronic ground states.

The compound $[Fe(phen)_2F_2] \cdot 4H_2O$ obviously belongs to the series of complexes treated in this paper on the basis of Mössbauer effect (*cf.* Table V), electronic spectra (*cf.* Table VII), and electron paramagnetic resonance (*vide infra*). However, its infrared spectrum differs from the spectra discussed above in some of the short-wavelength C–C and C–N ring frequencies (1578 (s), 1515 (vs), and 1492 cm^{-1} (m)), the presence of the γ(CH) satellite at 868 cm^{-1} (m), and the α(CCC) mode at 644 cm^{-1} (m). The Fe–F stretching frequency is observed at 495 cm^{-1} (vs, br) with indications of the presence of two components.

Each of the electronic spectra is dominated by a high-intensity (ϵ up to ~6500) absorption band, the position of which is varying for the different complexes, appearing at 18,850 cm^{-1} for the phen, 19,750 cm^{-1} for the dmph, and 19,200 cm^{-1} for the dipy complexes, respectively. An analogous band has been assigned in the corresponding tris complexes of iron(II) as due to a metal-to-ligand charge-transfer transition.[17,22] On the basis of MO calculations, Day and Sanders have shown recently[16,23] that in the particular case of $Fe(phen)_3^{2+}$, $Fe(dmph)_3^{2+}$, and similar ions, an electron is transferred to the next to lowest antibonding ligand orbital, π^{**}. The transition may thus be written as $(core)\pi^2t_2^6 \rightarrow (core)\pi^2t_2^5\pi^{**}$. We assume, on the basis of similar position, intensity, and band shape, that the band reported here is of similar origin. In the uv region, ligand–ligand bands of the diimine ligand are also observed (*cf.* Table VII).

A notable exception to the bands of high molar absorbance is a single weak band appearing in the 12,000-cm^{-1} region. This band may be supposed to have d–d character. Taking into account possible intensity borrowing from the charge-transfer band at 19,000 cm^{-1}, the intensity of the band (ϵ ~5) indicates that the corresponding transition should be multiplicity forbidden (*cf.* ϵ 4.4 for the $^1A_1 \rightarrow {}^3T_1$ transition in Fe-

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[20] E. König, S. Hüfner, E. Steichele, and K. Madeja, *Z. Naturforsch.*, **22a**, 1543 (1967); *ibid.*, **23a**, 632 (1968).

[21] (a) L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962); (b) the value of δ is listed relative to an absorber of natural iron.

[22] R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

[23] P. Day and N. Sanders, *ibid.*, 1536 (1967).

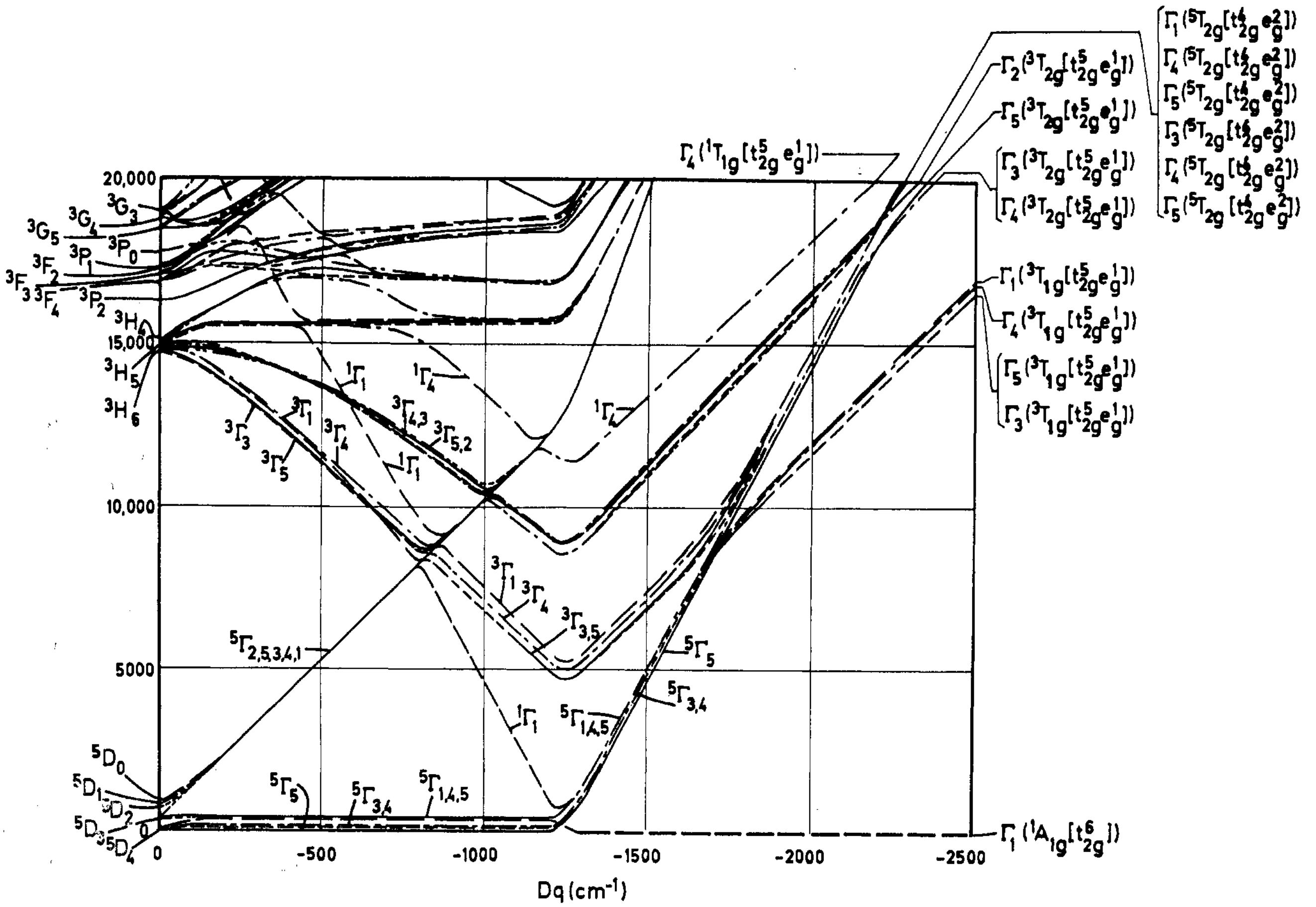

Figure 2.—Part of complete energy level diagram for the octahedral d^6 configuration including spin–orbit coupling (B = 730 cm^{-1}, C = $4B$, ζ = -350 cm^{-1}).

$(phen)_3^{2+}$ [24,25] and ϵ 3.6 in $Fe(dipy)_3^{2+}$ [26]). A definite assignment of it is uncertain, since the exact ordering of the lowest levels is presently unknown.

Paramagnetic resonance absorption has been observed on polycrystalline samples of the compounds at room temperature. In all cases studied, the spectra show two broad lines of different width which probably correspond to two different transitions rather than to a very anisotropic g factor. The high-field line at $g \sim 2.1$ (*viz.*, $g = 2.16$ in $[Fe(phen)_2ox]\cdot 5H_2O$, $g = 2.04$ in $[Fe(phen)_2mal]\cdot 7H_2O$, and $g = 2.17$ in $[Fe(phen)_2F_2]\cdot 4H_2O$) has a half-width of 800–1500 G; the low-field line at $g \sim 4.1$–4.5 (*viz.*, $g = 4.08$, 4.52, and 4.12, respectively) has a half-width of 300–550 G. Although both $\Delta M_s = 2$ and $\Delta M_s = 1$ transitions are expected between the Zeeman levels resulting from an $S = 1$ ground state, the large line width makes a definite assignment somewhat problematic.

Conclusions

The results reported here have to be compared with results of magnetic susceptibility,[3,4,6] Mössbauer effect,[4,6,20] infrared spectral,[4–6,27] and electronic spectral[4,6,24,27] investigations made on a large series of similar $Fe(diimine)_2X_2$ compounds. These exist in either $^5T_2$ or $^1A_1$ ground states or show temperature-dependent $^5T_2$–$^1A_1$ transitions. Such comparison demonstrates that the properties of the compounds studied at present are unique.

The temperature dependence of the magnetism confirms that a triplet state lies lowest for $Fe(diimine)_2ox$ and $Fe(diimine)_2mal$. The states of lowest energy in $Fe(diimine)_3^{2+}$ are those which are denoted as $^1A_1$, $^3T_1$, and $^5T_2$, but $^3T_{1g}$ cannot lie lowest in strict octahedral symmetry.[8] In the C_2 symmetry of the assumed *cis*-octahedral compounds studied here, $^3T_1$ will be split into three orbital singlets, $^3A + {}^3B + {}^3B$, so that a ground state of intermediate spin, $S = 1$, results.

This conclusion is somewhat unexpected at first, since the only better known iron(II) compounds which possibly have a triplet ground state on the basis of magnetic measurements (*viz.*, iron(II phthalocyanine[28] and the diethylphenylphosphine complex of iron(II)[29]) are supposed to be of planar geometry. We, therefore, wish to point out that the d^6 configuration is particularly amenable to the stabilization of states with half-quenched spin. This is clearly shown by Figure 2, which is the relevant part of the complete energy level diagram for a d^6 ion in a ligand field of octahedral sym-

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[24] K. Madeja and E. König, *J. Inorg. Nucl. Chem.*, **25**, 377 (1963).

[25] Compare footnote 48 of ref 4 concerning band assignments listed in ref 24.

[26] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

[27] E. König, *Coord. Chem. Rev.*, in press.

[28] A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

[29] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 285 (1961).

metry including spin–orbit coupling.[30] In this plot, $B = 730\ \mathrm{cm}^{-1}$, $C = 4B$, and $\zeta = -350\ \mathrm{cm}^{-1}$ have been used, where ζ is the one-electron spin–orbit coupling parameter. Also, Bethe's notation is employed for the resulting levels. The notation on the right side of Figure 2, which also lists the initial levels in absence of spin–orbit coupling and the one-electron configurations, is only approximate in that it gives only the largest contribution to the Γ_i levels. Within this approximation, the first excited triplet levels at the crossover point (*i.e.*, at a $Dq \sim 1250\ \mathrm{cm}^{-1}$) which are Γ_3 and Γ_5, with Γ_4 and Γ_1 at slightly higher energy, all originate from ${}^3T_{1g}[t_{2g}{}^5e_g{}^1]$. These levels are not more than $\sim$4500 cm^{-1} above the ground state. In fact, this is the lowest energy assumed by a level of that multiplicity which is not determined by the high-spin or the low-spin ground state of a d^n system in octahedral symmetry (in d^4, ${}^1T_2$ is at least 13,500 cm^{-1} and in d^5, ${}^4T_1$ is at least 8000 cm^{-1}, above the ground state).

These results do not mean that, on application of low symmetry, the lowest split component of ${}^3T_{1g}$ would have to be placed more than 4500 cm^{-1} below the unsplit level for a triplet ground state to be formed. Rather, there is to be expected an extensive interaction between and a mixing of most levels in the close vicinity of the crossover point. In the diagram of Figure 2 already the levels denoted by $\Gamma_4({}^5T_{2g}[t_{2g}{}^4e_g{}^2])$ and $\Gamma_5({}^5T_{2g}[t_{2g}{}^4e_g{}^2])$ are only to $\sim$60% composed of ${}^5T_{2g}$, the residual containing, *e.g.*, ${}^3T_{1g}$ and ${}^3T_{2g}$. The mixing will be dependent on the octahedral as well as the low-symmetry ligand field, the spin–orbit coupling, and the electron repulsion parameters. The formation of a lowest state, which is, to a major part, a spin triplet, may thus occur by a suitable combination of these parameters. Specifically, it may not require large values of the low-symmetry ligand field parameters. For extensive calculations and a detailed discussion of the similar situation in tetragonally distorted d^5 systems, the recently published work of Harris[31] should be consulted.[32] On the basis of these considerations it is quite conceivable that, in d^6 ions, slight deviations from octahedral geometry may result in the stabilization of a component of ${}^3T_{1g}$ as the electronic ground state. The small values of ΔE_Q observed in the Mössbauer spectra seem to be consistent with this assumption.

We wish to point out that several six-coordinated iron(II) compounds have been reported[33–35] which show room-temperature magnetic moments of magnitudes similar to those of the diimine compounds studied in this paper. It is suggested that, in these substances, triplet ground states may be present as well.

Acknowledgments.—The authors appreciate cooperation with Dr. D. H. Christensen and Dr. E. Lindner in measurements of infrared spectra. Thanks are due to Dr. K. J. Watson and Mrs. Sine Larsen for the unit cell determination. Financial support for part of the work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[30] A. D. Liehr, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1964.

[31] G. Harris, *Theoret. Chim. Acta*, **10**, 119, 155 (1968).

[32] Detailed theoretical investigations on the present systems have been initiated.

[33] H. M. Fisher and R. C. Stoufer, *Inorg. Chem.*, **5**, 1172 (1966).

[34] F. P. Dwyer, F. Lions, and D. P. Mellor, *J. Am. Chem. Soc.*, **72**, 5037 (1950).

[35] See also E. König, "Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds," in Landolt-Börnstein, New Series, Vol. II/2, K. H. Hellwege and A. M. Hellwege, Ed., Springer-Verlag, Berlin, 1966.

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The Reactions of Pentacyanonitrosylferrate(III) with Bases. IV. Acetophenone and Substituted Acetophenones

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Received May 17, 1968

An investigation of the reactions between pentacyanonitrosylferrate(III) (nitroprusside), $(NC)_5FeNO^{2-}$, and acetophenone and substituted acetophenones has been carried out. In the case of acetophenone the rate law for the formation of the initial product, $(NC)_5Fe(C_8H_6O_2N)^{4-}$, is $k[(NC)_5FeNO^{2-}][OH^-][\text{acetophenone}]$, where k is 6.6 M^{-2} sec^{-1} at 298°K and $\mu = 1.0$ (NaCl and NaOH). The aquation reaction of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ to yield the $(NC)_5FeH_2O^{3-}$ and the oxime is first order in $(NC)_5Fe(C_8H_6O_2N)^{4-}$. The first-order rate constant for this process is 3.6×10^{-3} sec^{-1} at 298°K and $\mu = 1.0$ (NaCl and NaOH). The enthalpy of activation is 19.4 ± 1.5 kcal/mol. The reactions of substituted acetophenones are compared with that of acetophenone.

Introduction

As part of a continuing study of the kinetics of reactions between bases and pentacyanonitrosylferrate(III) (nitroprusside), $(NC)_5FeNO^{2-}$,[1–3] the reactions of $(NC)_5FeNO^{2-}$ with acetophenone and substituted acetophenone in 17% ethanol–83% water by volume have been investigated.

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[2] P. A. Rock and J. H. Swinehart, *ibid.*, **5**, 1078 (1966).

[3] J. H. Swinehart and W. G. Schmidt, *ibid.*, **6**, 232 (1967).