Experimental Section

A solution of iron pentacarbonyl (2.5 ml) (Alfa Inorganics) in 1-methylnaphthalene (50 ml) was slowly added in small portions over a period of 1 hr to a refluxing solution of tetrafluorophthalonitrile (Fluochem, Glossop, England) (12.5 g) in 150 ml of 1-methylnaphthalene. This was performed under an atmosphere of nitrogen; the solution became green-blue and a quantity of lustrous microcrystals was produced, after refluxing for 1 hr further.

After cooling, the mixture was diluted with 100 ml of benzene and filtered, and the solid was washed with the following solvents: benzene (five 60-ml portions) (dark washings), acetone (two 60-ml portions) (dark blue washings), and diethyl ether (50 ml) (blue washings); 8.6 g of a purple-blue microcrystalline powder resulted. It is soluble in simple alcohols, ketones, and donor solvents but insoluble in hydrocarbon solvents. Analysis gives good results for hexadecafluorophthalocyaninatoiron(II). *Anal.* Calcd for $FeC_{32}F_{16}N_8$: Fe, 6.52; C, 44.89; F, 35.50; N, 13.09. Found: Fe, 6.61; C, 44.80; F, 35.27; N, 12.92.

The infrared spectrum shows a series of very intense peaks reminiscent of ferrous phthalocyanine. The C–N stretch, at 1620 cm^{-1}, is much more intense than the corresponding one at 1610 cm^{-1} in ferrous phthalocyanine. Further assignments have not been made.

Properties.—Like ferrous phthalocyanine, it can be degraded with concentrated nitric acid to a phthalimide, in this case fully fluorinated. *Anal.* Calcd for $C_8HF_4NO_2$: C, 43.85; H, 0.46; F, 34.69; N, 6.9. Found: C, 43.68; H, 0.30; F, 34.95; N, 6.43. Boiling with concentrated aqueous ammonia, on the other hand, results in no adduct formation and no hydrolysis; N and F analytical figures and ir spectra of the fluorinated phthalocyanine are identical before and after boiling. Like ferrous phthalocyanine, it produces a green diamagnetic bis-pyridine adduct. *Anal.* Calcd for $FeC_{42}H_{10}F_{16}N_{10}$: Fe, 5.51; C, 49.73; H, 0.99; F, 29.97; N, 13.81. Found: Fe, 5.42; C, 49.68; H, 1.42; F, 29.90; N, 13.73. The ^{19}F nmr spectrum of this adduct in pyridine confirms its diamagnetism and structure, with just two ^{19}F environments (ϕ +126.5 and 141.5 ppm as compared with tetrafluorophthalodinitrile with ϕ values of +128.5 and +144.4 ppm). (Small particles of "unpyridinated" iron complex, being paramagnetic, can "wash out" the nmr spectrum.)

A Perkin-Elmer Hitachi 124 vapor pressure machine was used to measure the molecular weight of a 6.2×10^{-4} *M* solution of the fluorinated iron phthalocyanine, and this averaged at 905, as compared with a formula weight of 856. Thus acetone solutions are essentially monomeric at the concentrations used. Acetone solutions have a single broad peak in the visible spectrum, at 620 nm; accurate determination of the extinction coefficient was made difficult by "fading" which is being further investigated. Preliminary magnetic measurements on acetone solutions (5×10^{-3} *M*) by Evans' method[4] indicate paramagnetism, μ_{eff} at 33° being 3.3 ± 0.2 BM, which may be compared with a value of 3.0 ± 0.2 BM from preliminary measurements on the solid using a simple Gouy balance at 20°. These measurements tend to support a triplet ground state for iron in our fluorinated complex, confirming designation of the complex as an iron(II) compound.

In contrast to the measurements in acetone, a weak donor, measurements by Evans' method in dimethyl sulfoxide and pyridine solutions indicate diamagnetism for our complex, which would agree with it being low-spin iron(II) in an octahedral environment. The visible spectrum of such solutions is different from that of the acetone solutions; in dimethyl sulfoxide there are twin maxima of equal intensity at 630 and 660 nm; in pyridine there are virtually the same maxima, with a pronounced shoulder at 600 nm, too.

Preliminary kinetic measurements support the magnetic assignments; reaction of pyridine with our complex in acetone solution is slow, a spin change being involved; reaction in dimethyl

sulfoxide is much faster, no spin change being involved; these interesting reactions are being investigated more closely.
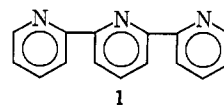
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Mono(2,2',2''-terpyridine) Complexes of Iron(II)

By W. M. REIFF,[1] N. E. ERICKSON, AND W. A. BAKER, JR.[2]

The terdentate ligand 2,2',2''-terpyridine (terpy), **1**,

1

is well known to form both mono and bis complexes[3–9] with divalent transition metal ions. The bis complexes are presumed to have distorted octahedral structures. A single-crystal X-ray analysis has been carried out on Zn(terpy)Cl$_2$ and the structure was shown[10,11] to be five-coordinate. On the basis of a comparison of X-ray powder data it was suggested[9] that the mono(terpyridine) chloride, bromide, and iodide of Zn(II), Co(II), Ni(II), and Mn(II) (and the bromide and iodide of Fe(II)) all have a five-coordinate structure similar to that of Zn(terpy)Cl$_2$. The chloride of Fe(II) appears to be different. We have previously[7,8] reported magnetic and spectral data on the Ni(II) and Co(II) systems. It is the purpose of this note to present data on a series of compounds having the empirical formula Fe(terpy)X$_2$ (X = Cl$^-$, Br$^-$, I$^-$, SCN$^-$, 0.5SO$_4^{2-}$).

Experimental Section

Preparations.—The substance having the empirical formula Fe(terpy)Cl$_2$ was prepared by three methods. All gave the same product as evidenced by X-ray powder data. Method a was the procedure used by Broomhead and Dwyer.[12] In method b, 1.5 mmol of terpyridine and 1.9 mmol of FeCl$_2$·4H$_2$O were dissolved in 30 ml of a 60:40 water–methanol solution. The solution was concentrated to a volume of 15 ml and 70 ml of acetone was added A precipitate formed which was removed, washed with water, and dried under vacuum. Method c involved the heating

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TABLE I
ANALYTICAL DATA

	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%F Calcd	%F Found
Fe(terpy)Cl₂ (a)	50.00	49.70	3.09	3.18	11.67	11.48	15.51	15.04
(b)		50.03		3.09		11.67		15.15
(c)		51.48		3.13		11.53		15.32
Fe(terpy)Br₂	40.10	40.40	2.47	2.38	9.36	9.50		
Fe(terpy)I₂	33.20	32.85	2.05	1.80	7.74	7.57		
Fe(terpy)(NCS)₂	50.40	50.40	2.74	2.67	17.28	17.42		
Fe(terpy)SO₄	46.77	46.59	2.88	3.28	10.91	10.85		

TABLE II
MÖSSBAUER DATA

	Isomer shift, δ^a Room temp	Isomer shift, δ^a 78°K	Quadrupole splitting, $\Delta E_Q{}^a$ Room temp	Quadrupole splitting, $\Delta E_Q{}^a$ 78°K
Fe(terpy)Br₂	0.89	1.01	2.76	3.16
Fe(terpy)I₂	0.83	0.98	2.51	3.18
Fe(terpy)(NCS)₂	0.88	1.03	2.46	2.78
[Fe(terpy)₂][FeCl₄]	0.21, 0.91	0.27, 1.06	0.98, 1.69	0.99, 3.05

a In mm/sec relative to iron foil.

of the bis complex Fe(terpy)₂Cl₂·3.5H₂O at a pressure of 1 μ and a temperature of 200° for 12 hr.

The other mono(terpyridine) complexes were prepared by heating the corresponding bis complexes under vacuum. The approximate times and temperatures used were: bromide, 24 hr at 180°; iodide, 24 hr at 230°; thiocyanate, 12 hr at 210°. Analytical data which were obtained by Galbraith Laboratories are given in Table I.

Physical Measurements.—Magnetic data were obtained using both Faraday[6] and Gouy[13] balances. Diamagnetic corrections used are given in ref 6. Spectra were obtained using instrumentation as previously described.[14]

Results and Discussion

Five-Coordinate Complexes.—X-Ray powder data suggest that Fe(terpy)Br₂ and Fe(terpy)I₂ are five-coordinate.[9] The corresponding thiocyanate is, on the basis of other data, probably of a similar structure. The most convincing evidence is in the Mössbauer data. The isomer shifts and quadrupole splittings for the Br⁻, I⁻, and NCS⁻ are given in Table III. The similarity as well as the low values of the isomer shifts suggest coordination numbers of 5. The magnetic data in Table III show that they are high spin with very little temperature dependence to the moment. Infrared data for the thiocyanate show bands at 2059 (s), 852 (m), and 476 cm⁻¹ (w). These values are normal for the C–N stretch, C–S stretch, and N–C–S bending modes, respectively, in N-coordinated thiocyanates.[15]

The electronic spectra for all three show a band near 10,000 cm⁻¹ which is presumably a d–d transition. In addition, the thiocyanate shows another d–d band with a maximum at 4100 cm⁻¹. This band in the Cl⁻ and Br⁻ is presumably at too low an energy to be observed. There are intense absorptions beginning around 16,000 cm⁻¹ which are probably charge-transfer bands. Unfortunately, these data are not sufficient to allow us to say anything about the d-orbital splittings in the complexes. The d–d spectra are essentially identical, par-

TABLE III
MAGNETIC DATA

Compound	Temp, °K	$10^6 \chi_M{}'$, cgsu	μ_{eff}, BM
[Fe(terpy)₂][FeCl₄]*a*	310	6,150	3.92
	80	22,860	3.84
Fe(terpy)Br₂	288	12,490	5.39
	80	45,120	5.34
Fe(terpy)I₂	296	12,470	5.45
	80	46,440	5.43
Fe(terpy)(NCS)₂	291	11,610	5.22
	80	42,480	5.18
Fe(terpy)SO₄	300	3,620	2.95
	21	30,100	2.25

a Preparation (a).

ticularly for the thiocyanate, to those of two other five-coordinate complexes of saturated amines[16,17] which have been shown to be basically trigonal bipyramidal.

Fe(terpy)Cl₂.—A compound having the empirical formula Fe(terpy)Cl₂ was previously reported by Broomhead and Dwyer[12] and by Robinson and Kennard.[18] The former authors suggested that the compound was five-coordinate similar to the corresponding Zn complex, although they did no X-ray work and in spite of the fact that their reported magnetic moment was 4.60 BM, well below the spin-only value. The latter authors present X-ray powder data for the compound and claim that it is isomorphous with the Zn complex, but a very strong line corresponding to a d spacing of 3.27 Å which appears in the data for Zn-(terpy)Cl₂ was not reported in their iron data.

We have prepared a compound with the empirical formula Fe(terpy)Cl₂ by three methods and the evidence clearly indicates the compound to be [Fe(terpy)₂]-[FeCl₄]. All three preparations give essentially identical results.

The magnetic data are given in Table III. Assuming a $\chi_M{}'$ value for Fe(terpy)₂²⁺ of 300 × 10⁻⁶ cgsu as reported by Hogg and Wilkins,[4] we calculate a moment

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of 5.48 BM for the anion, in excellent agreement with that reported by Clark, *et al.*[19] The Mössbauer spectra present even more conclusive evidence. As indicated in Table II, the spectra consist of two quadrupole split transitions. One has a δ value of $\sim$0.2 mm/sec and a ΔE_Q value of $\sim$1.0 mm/sec, both of which are essentially temperature independent. This pair of lines is attributable[20,21] to the cation $Fe(terpy)_2{}^{2+}$. The other quadrupole split pair has a δ of $\sim$0.9 mm/sec and a markedly temperature-dependent ΔE_Q ranging from 1.23 mm/sec at 418°K to 3.05 mm/sec at 80°K. The large temperature dependence is presumably due to a splitting of the e_g orbitals of the order of kT by a low symmetry field component. It is possible to evaluate[22,23] this splitting from the temperature dependence of ΔE_Q. We get excellent agreement between experimental values measured from 412 to 80°K and calculated values obtained assuming a ΔE_Q at 0°K of 3.27 mm/sec and an e_g splitting of 235 cm^{-1}. The latter value is in the range observed by Edwards, *et al.*,[24] for $FeCl_4{}^{2-}$ in a variety of salts.

The ratio of intensities, I_a/I_c, of the lines for the anion and cation is markedly temperature dependent. At room temperature $I_a/I_c \approx 0.2$ while at 80°K, it is $\sim$1.0. This large difference in intensities of the two ions makes the high-temperature spectrum appear to be due to $Fe(terpy)_2{}^{2+}$ plus a small amount of an impurity. The near equality of intensities at 78° combined with the magnetic data rule out this possibility. Differences in recoil-free fractions for different types of ions in the same compound have been noted before, but this is one of the largest differences noted and implies that successfully to use Mössbauer intensity data for determing the relative numbers of different types of irons in a compound, the intensities should be compared at the lowest temperature possible.

The electronic spectrum of the chloride supports the cation–anion structure. The 10,000-cm^{-1} band found in the other complexes is missing but there is a band at 4400 cm^{-1}, in the region expected[25] for $FeCl_4{}^{2-}$.

Fe(terpy)SO₄.—We have reproducibly prepared a compound which from elemental analysis is indicated to be $Fe(terpy)SO_4$. The magnetic moment at 300°K is 2.95 BM. This drops in an almost linear fashion to 2.25 BM at 21°K. The Mössbauer spectrum is complicated, showing probably four lines, but we have been unable to resolve them sufficiently to obtain the parameters. The infrared spectrum suggests that the sulfate is coordinated and the electronic spectrum shows no transitions below the charge-transfer region ($\sim$16,000 cm^{-1}). An oxygen-bridged species such as $(Fe(terpy)SO_4)_2O$ would give an analysis close to that observed and would explain the magnetic behavior,[14] but

we are unable to find the infrared band near 800 cm^{-1} which is characteristic of such systems.[14] Work is continuing on this compound.

Bis(terpyridine) Complexes.—Finally, we wish to mention that we have obtained the Mössbauer spectra of $Fe(terpy)_2{}^{2+}$ in salts with ten different anions. Since the corresponding Co(II) complexes exhibit anomalous magnetic behavior[6] which is dependent on the anion, we thought the Mössbauer spectra might also show an anion dependence. Although the corresponding Fe(II) and Co(II) complexes are isomorphous, no such anion dependence was observed in the spectra, all being identical within experimental error.

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Electron Spin Resonance of Iron–Nitric Oxide Complexes. Iron–Nitrosyl–Halide Compounds

By L. Burlamacchi, G. Martini, and E. Tiezzi

Nitric oxide compounds of transition metals exhibit properties of general interest in the field of inorganic chemistry. The outstanding versatility of nitric oxide as a ligand arises from its unusual electronic structure and from its free-radical nature. In most cases the M–NO bond involves transfer of the odd electron of the NO group to the metal ion or its pairing with an electron accepted from the metal. Electron spin resonance (esr) experiments have shown that an intermediate situation exists in which the unpaired electron is either retained in the NO group or delocalized on a molecular orbital extending over the entire complex which then behaves like a free-radical species.

A number of iron–nitrosyl complexes formed in water solution with a variety of organic and inorganic ligands have been reported recently by McDonald, *et al.*,[1] and by Woolum, *et al.*,[2] and their structures have been considerably elucidated in terms of electron–nuclear hyperfine interactions.

In the past few years, this kind of nitric oxide complexes has received increasing attention for its biological implications. Complexes of nitric oxide with hemoglobin and other heme-containing substances have been reported by Azhipa, *et al.*[3] Vanin[4] has studied com-

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