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)SO$_4$.—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$)$_2$O 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

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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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plexes of iron, nitric oxide, and several proteins which give electron spin resonance spectra. As mentioned by Woolum,[2] esr signals related to the Fe–NO group have been observed also in carcinogen-induced rat liver tissue.

With the purpose of further elucidating the nature of this class of compounds, we present the results of our investigations on halide–Fe–NO and some other anionic Fe–NO complexes formed in water–ethanol solution. Free-radical species which exhibit intense esr spectra have been observed and the nature of these complexes, the number of ligand ions, and the equilibrium processes involved have been studied.

Experimental Section

Solutions of Fe–NO complexes were prepared as follows. Water–ethanol solutions of from 5×10^{-4} to 5×10^{-3} M $FeSO_4$ or $FeCl_2$ were deoxygenated by stirring under a nitrogen stream. After addition of the proper amount of ligand, solutions were saturated with gaseous NO, which reacts almost instantly to form the Fe(II) complexes. The colors of the solutions ranged from brown to reddish brown, depending on the nature of the ligand. Anionic ligands were added as sodium or potassium salts. Gaseous nitric oxide was obtained from ferrous sulfate, sulfuric acid, and sodium nitrite, following the method described by Blanchard, *et al.*[5] The pH of the solutions was adjusted by adding small amounts of NaOH, HCl, or $HClO_4$. The sample was kept under nitrogen when transferred to the quartz flat sample cell and examined in the esr spectrometer. All chemicals were reagent grade.

Spectra were registered with a Varian V-4502 X-band spectrometer with 100-kc field modulation, equipped with a dual sample cavity and with a temperature controller. The nitrosyldisulfonate ion was used as standard reference for g factor and hyperfine coupling constant measurements. The Klystron frequency was measured with a Hewlett-Packard Model X532B frequency meter.

Results and Discussion

When a neutral solution of $FeSO_4$ is saturated with NO, the well-known "brown-ring compound" is formed. Infrared studies and magnetic susceptibility measurements have shown the compound to be a high-spin d^7 octahedral complex $Fe^{I}NO(H_2O)_5{}^{2+}$ with the NO molecule donating three electrons to form the nitrosonium NO^+ group.[6] Such compounds are not usually expected to exhibit detectable paramagnetic resonance. However, a weak absorption has been observed in neutral or slightly acidic solutions (pH >4). The spectrum consists of a single peak about 8 G wide at a g factor 2.033 and was attributed to a solvated iron–dinitrosyl compound.[1] The same spectrum is observed when NO is obtained in $FeSO_4$ solution by adding $NaNO_2$ and a reducing agent, for instance, neutralized ascorbic acid.[2]

Indications about the nature of this compound may be obtained by observing the time and temperature dependence of esr signal height. At room temperature, immediately after addition of the reagents, the signal increases rapidly for about 0.5 min and then decreases quickly toward a value about two orders of magnitude less than the maximum value observed. Addition of ethanol to the aqueous solution enhances the signal intensity and seems to retard significantly both the formation and the decomposition of the paramagnetic species. Some typical results are shown in Figure 1, in which the signal height at constant field is registered as a function of time at different ethanol concentrations. In all cases the kinetics of the decomposition appear to be first order with respect to complex concentration in the first stage of the reaction. Changes of temperature cause reversible changes of the signal intensity, which decreases with increasing temperature. It is therefore evident that the free-radical complex is an unstable species which transforms itself into the "brown-ring compound" and that an equilibrium exists between the free radical exhibiting the esr spectrum and a more stable compound, probably again the $FeNO(H_2O)_5{}^{2+}$ complex. Solvent changes seem to affect mainly the kinetic steps by changing the rates of free-radical reactions and the equilibrium constants. Similar solvent effects have been observed for other free-radical reactions,[7] but a complete analysis of this subject requires a more detailed knowledge of the entire process.

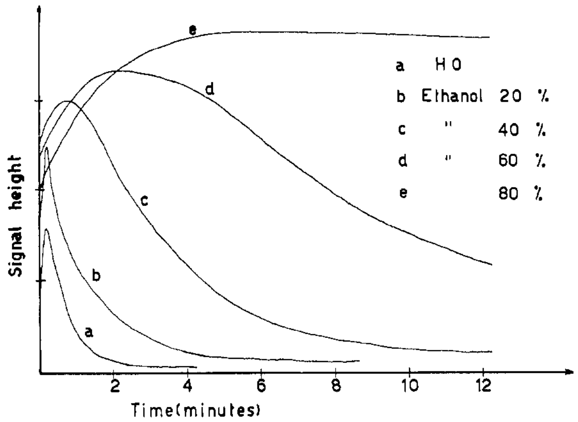

Figure 1.—Esr signal intensity of the solvated iron–nitrosyl complex *vs.* time as a function of per cent ethanol.

When $FeSO_4$ is allowed to react with NO in 80% alcohol, the equilibrium is shifted toward the free-radical species so that, after a few minutes, an intense spectrum almost stable at room temperature, may be observed (see Figure 1).

Unfortunately the hyperfine structure due to the nitrogen atoms in the NO groups is not resolved and does not allow the determination of the number of nitrosyl groups bonded in the complex. However the mononitrosyl form has been observed by esr only in the octahedral $FeNO(CN)_5{}^{3-}$ complex[8] or when $FeSO_4$ and NO react with bidentate ligands, such as dithiols,[1] dithiolenes,[9] and some other sulfurated compounds[10] to form free-radical complexes with the NO group occupying a pyramidal position. All of these complexes give a triplet spectrum with N^{14} isotropic hyperfine constant of

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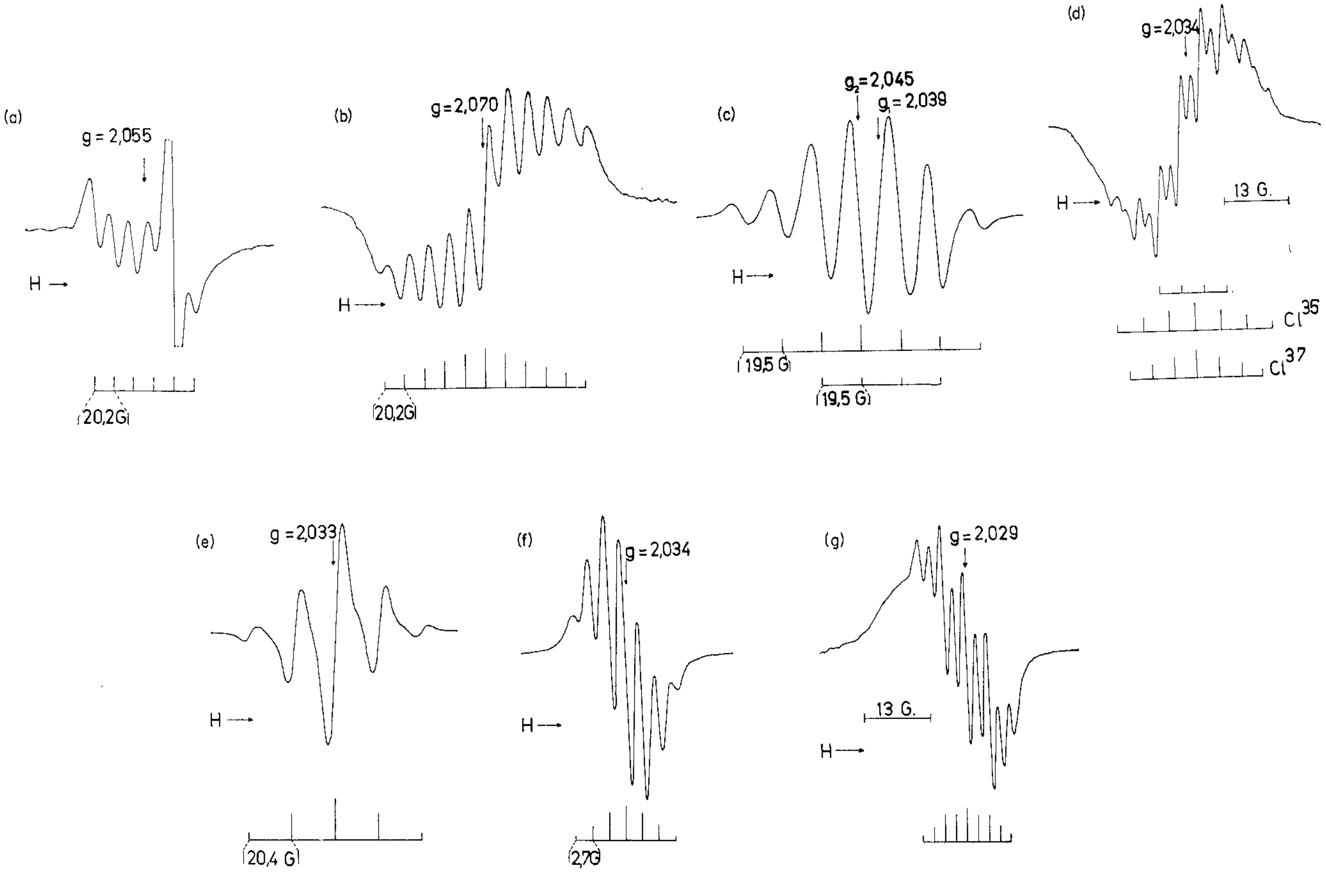
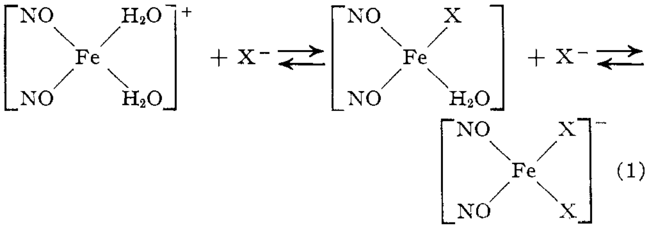


Figure 2.—Esr spectra of: (a) 5×10^{-3} *M* $FeSO_4$ and 0.1 *M* KI saturated with NO at 0° in 80% alcohol at pH 4.5; (b) 5×10^{-3} *M* $FeSO_4$ and 5×10^{-1} *M* KI saturated with NO at 0° in 80% alcohol at pH 4.5; (c) 5×10^{-3} *M* Fe–NO complex in the presence of 0.7 *M* KBr in 80% alcohol at −10° and pH 4.5; (d) iron–nitrosyl–chloride compounds: the three superimposed spectra are attributed to $Fe(NO)_2Cl^{35}(H_2O)$, $Fe(NO)_2Cl^{35}{}_2{}^-$, and $Fe(NO)_2Cl^{37}{}_2{}^-$; the spectrum was registered at −13° in 80% alcohol at pH 4.5; (e) 5×10^{-4} *M* $FeSO_4$ with added 1 *M* F^- in 80% alcohol at 5° and pH 4.5; (f) complex formed from Fe^{2+}, $N^{15}O$, and NCS^- in 80% alcohol at pH 5 and −5°; the thiocyanate concentration was 0.5 *M;* (g) complex formed from Fe^{2+}, $N^{14}O$, and NCS^- in 80% alcohol at pH 10 and −5°; the thiocyanate concentration was 0.5 *M*.

12–20 G. This is certainly not the case here. In most cases, the iron–nitrosyl free-radical complexes exhibit a resolved hyperfine structure which demonstrates the presence of two equivalent nitrosyl groups. Comparison with these results strongly suggests the dinitrosyl form $Fe^{I}(NO)_2(H_2O)_2{}^+$ to be present, in which the expected N^{14} hyperfine structure is not resolved because of higher line width. We will make the assumption in the following description that in these species only one unpaired electron is present, delocalized over the NO–Fe–NO group with a predominant spin density over the iron atom, which appears to be in the d^7 state.

Iron–Nitrosyl–Halide Complexes.—A number of iron nitrosyl halides are known which are generally reported as trinitrosyl[11] and dinitrosyl[12] compounds. The dinitrosyl[11,12] compounds are the more stable and are thought to be in the dimeric form $[Fe(NO)_2X]_2$ with the odd electrons in the metal atoms shared to form a metal–metal antiferromagnetic bond. The trinitrosyl compounds $Fe(NO)_3X$ are monomeric and of the nitrosonium type.[11-13] None of these models is paramagnetic and accounts for the observed esr spectrum.

(a) Iodine, Bromine, and Chlorine Compounds.—Water solutions of Fe–NO complexes in the presence of I^-, Br^-, and Cl^- ions do not exhibit paramagnetic resonance other than the weak signal described above for the solvated Fe–NO complex. In 80% alcohol solution at pH 4–8, an intense spectrum is observed, whose hyperfine structure clearly indicates that two species, a monohalogenated and a dihalogenated complex, are formed. When the temperature is raised, the halide complex concentration is greatly reduced and the structureless spectrum at $g = 2.033$ increases significantly. This process is completely reversible and indicates that a two-step equilibrium association is present which may be represented by



(1)

Figures 2a and 2b show spectra of the Fe–NO complex when different amounts of KI are added. At lower I^-

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concentration ($<10^{-1}$ M), a clear sextet of 20.2-G spacing (Figure 2a) indicates an isotropic hyperfine interaction with one iodine nucleus ($I_{\text{I}^{127}} = {}^5/_2$). The structureless spectrum at $g = 2.033$ is still present. With increasing I^- concentration, the spectrum converts to 11 lines (Figure 2b), due clearly to two equivalent iodine nuclei. The hyperfine splitting constant is again 20.2 G and the g gactors of the two spectra are 2.055 and 2.070, respectively. The line width of the individual components is about 9 G and no N^{14} splitting of the NO group is resolved. Similar results are obtained with Br^- and Cl^- ions, but in this case it is impossible to obtain separate spectra of mono- and dihalogenated species. However the mono- and dihalogenated forms are easily observable in the esr spectra. Bromine–iron–nitrosyl complexes exhibit a superimposed spectrum (Figure 2c) in which a quartet and a septet are observable, due, respectively, to one and two equivalent Br nuclei ($I_{\text{Br}^{79}} = I_{\text{Br}^{81}} = {}^3/_2$). According to the stepwise equilibrium of eq 1, the relative intensity of the quartet and the septet spectra changes with anion concentration. At a Br^- concentration above 0.5 M the septet spectrum begins to be predominant. The g factors are 2.039 and 2.045, respectively, while the hyperfine splitting constant is 19.5 G in both spectra. Neither the N^{14} splitting nor the individual spectra from Br^{79} and almost equally abundant Br^{81} is resolved.

Chlorine complexes have much smaller hyperfine coupling constants and their spectra are much less resolved (Figure 2d) but the quartet and septet spectra expected from the interaction of the electronic spin with one and two chlorine nuclei ($I_{\text{Cl}^{35}} = {}^3/_2$) are still detectable. Opposite to that observed with Br^- and I^-, the g factor of the mono- and of the dihalogenated forms has the same value ($g = 2.034$) but the hyperfine splitting constants differ significantly (4.7 and 5.3 G, respectively). No resolved hyperfine structure from NO groups is present. An additional septet due to naturally abundant (24.6%) Cl^{37} ($I_{\text{Cl}^{37}} = {}^3/_2$) is also detectable. The ratio of the isotropic splitting constants is that expected from the ratio of the nuclear moments of the two isotopes ($\mu_{\text{Cl}^{35}}/\mu_{\text{Cl}^{37}} = 1.2$). In the quartet spectrum the Cl^{37} structure is not resolved. Hyperfine splitting constants and g values for the various species are summarized in Table I.

TABLE I

HYPERFINE COUPLING CONSTANTS DUE TO LIGAND NUCLEI (a_L) AND TO THE NITROSYL GROUPS (a_{NO}) AND LINE WIDTH OF Fe–NO COMPLEXES

Complex	pH	g	a_L, G	a_{NO}, G	Line width, G
$Fe(NO)_2(H_2O)_2^+$	4.5	2.033	...	...	8
$Fe(NO)_2(OH)_2^-$	11	2.027	...	2.2	...
$Fe(NO)_2F_2(H_2O)_2^-$	4.5	2.033	20.4	...	7.2
$Fe(NO)_2F_4^{3-}$	4.5	2.033	20.4	...	7.2
$Fe(NO)_2Cl^{35}(H_2O)$	4.5	2.034	4.7	...	1.5
$Fe(NO)_2Cl^{35}{}_2^-$	4.5	2.034	5.3	...	1.5
$Fe(NO)_2Cl^{37}{}_2^-$	4.5	2.034	4.4	...	1.5
$Fe(NO)_2Br(H_2O)$	4.5	2.039	19.5	...	10
$Fe(NO)_2Br_2^-$	4.5	2.045	19.5	...	10
$Fe(NO)_2I(H_2O)$	4.5	2.055	20.2	...	9
$Fe(NO)_2I_2^-$	4.5	2.070	20.2	...	9
$Fe(N^{14}O)_2(NCS)_2^-$	5	2.034	(2.7)	(2.0)	...
$Fe(N^{14}O)_2(NCS)OH^-$	10	2.029	4.3	2.15	...
$Fe(N^{15}O)_2(NCS)_2^-$	5	2.034	2.7	2.7	...
$Fe(N^{15}O)_2(NCS)OH^-$	10	2.029	4.3	2.9	...

(b) **Fluorine Compounds.**—The fluorine ion as a ligand in the Fe–NO complexes in 80% alcohol solution at pH 4–7 shows somewhat different behavior with respect to the other halide ions. By increasing ligand concentration, the single peak at $g = 2.033$ converts to a well-resolved triplet and subsequently to a quintet spectrum with a 1:4:6:4:1 intensity relationship. At a F^- concentration of about 1 M only the quintet spectrum is observed (Figure 2e). At room temperature, the stability of these compounds is very low and a green precipitate forms in a few minutes, probably due to $FeF_2(H_2O)_4$. A better stability is obtained at lower temperatures. Both spectra have a g factor of 2.033 essentially identical with the single peak of the solvated Fe–NO complex and a hyperfine coupling constant of 20.4 G. These results are consistent with hyperfine splitting due, respectively, to two and four equivalent fluorine nuclei ($I_{\text{F}^{19}} = {}^1/_2$). Again no hyperfine structure due to N^{14} is resolved.

It is evident that the structure of these complexes differs from that of the chlorine, bromine, and iodine compounds. Also in this case it is difficult to determine whether one or two NO groups are linked in the complex. Spectra obtained by substituting N^{14} with N^{15} ($I_{\text{N}^{15}} = {}^1/_2$) using $NaN^{15}O_2$ are substantially identical with those obtained with N^{14} and give no further indication. We suggest however that an octahedral symmetry, rather than a tetrahedral, is present, according to which the two complexes should be of the form $Fe(NO)_2F_2(H_2O)_2^-$ and $Fe(NO)_2F_4^{3-}$.

Thiocyanate–Iron–Nitrosyl Complexes.—When NO is allowed to react with $FeSO_4$ in the presence of KSCN in 80% ethanol solution at pH 4–7, a reddish brown complex is formed. The esr spectrum produced by this compound consists of nine hyperfine components spaced about 2.3 G apart, at a g factor of 2.034. This spectrum accounts for a paramagnetic species possessing two equivalent N^{14} nuclei from the NO groups and two equivalent N^{14} nuclei from the NCS^- ligands with almost the same hyperfine coupling constant. Resolution of this spectrum is very poor. Better results are obtained using $N^{15}O$, in which case the increase of the hyperfine splitting allows the resolution of a septet spectrum corresponding to a 1:4:8:10:8:4:1 intensity relationship, due clearly to two equivalent N^{15} and two equivalent N^{14} nuclei from the NCS group (Figure 2f). Both N^{14} from NCS and N^{15} from NO show the same splitting constants of 2.7 G. The monothiocyanate complex has not been observed.

We believe that the structure of the thiocyanate complex corresponds closely to the iodine–, bromine–, and chlorine–iron–nitrosyl complexes. In addition, with increasing pH of the solution, the signal intensity decreases slightly, until, at pH $\simeq 8$, it disappears and another spectrum appears at a g factor of 2.029. This new spectrum has its maximum intensity at pH 9.5. It consists of nine lines (Figure 2g) whose spacing and intensity relationship speak for a complex formed by two equivalent N^{14} nuclei (the NO groups) and one N^{14} nucleus (NCS group) with almost a double hyperfine constant. Nitrogen-15 experiments confirm these results, exhibiting a nine-line spectrum due to a 1:2:1 triplet from two $N^{15}O$ groups separated into a 1:1:1 triplet by one thiocyanate group. At even higher pH (>11) a quintet spectrum becomes predominant at $g = 2.027$. This corresponds to the one reported by McDonald,[1] *et al.*, in a water solution of $FeSO_4$ in the presence of NO which was attributed to $Fe(NO)_2(OH)_2^-$. It is then evident that at pH 9.5 one thiocyanate group has been replaced by an OH group to form the $Fe(NO)_2NCS(OH)^-$ complex. No such observations are made with the iron–nitrosyl–halide complexes, which give no detectable esr signals above pH 7.

Other spectra can be obtained in ethanol–water solution with a variety of inorganic and organic ligands. Cyanate ion gives results close to the thiocyanate ion. Intense spectra were observed with sulfite, hyposulfite, carbonate, dithionite, and a number of other ligands.

However we wish to emphasize here that these Fe–NO complexes, which give easily detectable esr spectra also in pure water solution in the presence of excess ligand concentration, arise from monomerization of a dimeric structure related to the red Roussin's salt.[1] With the exception of some organic complexes, which show better solubility, no advantages are obtained in the presence of ethanol. Nitrate, nitrite, and sulfate ions seem to give no detectable spectra in water or in alcoholic solutions.

Esr Line Width.—In addition to the above-mentioned variation of the relative intensities of the various species, changes of temperature influence the line width of esr signals significantly. In all cases the best resolution of the hyperfine splitting was obtained at a temperature in the range between −15 and 5° depending on the ligand ion, while an increase of line width was observed above and below this temperature. This means that at least two mechanisms of relaxation are effective with opposite temperature coefficients. At lower temperature, the most probable line-broadening source is motional modulation of the anisotropic g and hyperfine tensors. The increase of line width above the point of maximum resolution may well be attributed to ligand exchange, the lifetime of the radical thus determining the electron spin relaxation time T_2. It is noteworthy that the line width does not depend on ligand concentration and on the number of ions coordinated in the complex (Table I). This would be accounted for only by an S_N1 exchange mechanism; that is, a process in which the rate-determining step corresponds to the loss of a ligand ion from the complex which is almost instantly replaced with a new ligand. However, spin rotational relaxation may also account for the observed positive temperature dependence of the line width[14] and more detailed data would be necessary to make an unequivocal attribution. In the present work all spectra were registered at the temperature of maximum resolution.

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Preparation and Kinetics of Hydrolysis of Trifluoroacetatopentaamminechromium(III)

BY R. DAVIES, G. B. EVANS, AND R. B. JORDAN

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Although the kinetics of the hydrolysis in alkaline and acid solutions of carboxylatopentaammine complexes of Co(III), Rh(III), and Ir(III)[1-3] have already been reported, the Cr(III) analogs have only recently been prepared.[4] The complexes are usually prepared in aqueous solution by heating the aquopentaammine complex with the required carboxylic acid. In the case of chromium(III), however, this procedure is not possible owing to the rapid loss of ammonia from the metal ion and subsequent formation of a complex mixture of products. Recently preparative procedures involving much less vigorous conditions have been developed in the pentaamminecobalt(III) system.[5,6] These methods have now been applied with some success to the preparation of the carboxylatopentaamminechromium(III) complexes.

The complex $((NH_3)_5CrO_2C_2F_3)(ClO_4)_2$ has been obtained by two different preparative routes. In the first method $((NH_3)_5CrCl)(ClO_4)_2$ was mixed with an equivalent amount of $AgO_2C_2F_3$ dissolved in N,N-dimethylformamide (DMF). The second method[6] also carried out in DMF used the reaction of $((NH_3)_5CrOH_2)(ClO_4)_3$ with trifluoroacetic anhydride in the presence of a base, N,N-dimethylbenzylamine. A third method,[5] not reported in detail, involves the reaction of $((NH_3)_5CrN_3)(ClO_4)_2$ with isoamyl nitrite and trifluoroacetic acid, also in DMF. The main disadvantage of the latter method is the difficulty in preparing pure $((NH_3)_5CrN_3)(ClO_4)_2$.

The kinetics of the hydrolysis of $(NH_3)_5CrO_2C_2F_3^{2+}$ have been studied in acid and alkaline solution, and the

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