805. *Some Nitric Oxide Complexes of Iron and Copper.*

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The magnetic suceptibilities and absorption spectra of the complex ions $[Fe(H_2O)_5NO]^{2+}$, $[Fe(NH_3)_5NO]^{2+}$, and $[Fe(C_2H_5{\cdot}OH)_5NO]^{3+}$ have been measured. It is concluded that these paramagnetic species have sp^3d^2-outer-orbital bonding involving co-ordination of the nitrosyl (NO^+) ion to the metal atom. $[Fe(CN)_5NO]^{3-}$, which involves co-ordination of nitric oxide to the metal atom by two electrons only, $[Cu(C_2H_5{\cdot}OH)_3NO]^{2+}$, and $Fe(NO)_4$ have also been studied.

The Penta-aquonitrosyliron(I) *Ion,* $[Fe(H_2O)_5NO]^{2+}$; "*Brown-ring*" *Compounds.*—Aqueous solutions of ferrous salts absorb nitric oxide [1] to give dark brown, unstable substances, sometimes known as the "brown-ring" compounds since they are also formed in the familiar qualitative tests for nitrates. The first quantitative studies on these compounds were made by Manchot and his co-workers,[2-5] who studied the equilibrium

$$Fe_{aq}^{2+} + NO \rightleftharpoons Fe(NO)_{aq}^{2+}$$

in chloride and sulphate solutions [2,3,4] over a range of temperatures and evaluated [3] the heats of reaction in aqueous solution (11·9 kcal./mole). Electrolysis of the solutions showed that nitric oxide was bound in a cationic complex.[5] Measurements of the absorption spectra of solutions [6] gave results independent of the nature of the anion and in addition, since we find that brown-ring compounds can be prepared in perchlorate solution, it seems unlikely that the cation is other than an octahedral penta-aquonitrosyliron(I) ion, $[Fe(H_2O)_5NO]^{2+}$.

Manchot isolated some of the nitrosyl compounds as rather ill-defined solids: the sulphate as $Fe(NO)SO_4$ and $2Fe(NO)SO_4,13H_2O$,[7] the selenate as $Fe(NO)SeO_4,4H_2O$,[5] and the phosphate as $Fe(NO)HPO_4$.[8] Much work has been done on the decomposition products in acidic, neutral, and alkaline solutions of the brown-ring compounds; [9-13] this

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[1] Priestley, "Experiments and Observations on Different Kinds of Air," Thomas Pearson, Birmingham, 1790, Vol. I, p. 328.

[2] Manchot, *Annalen*, 1910, **372**, 179.

[3] Manchot and Haunschild, *Z. anorg. Chem.*, 1924, **140**, 22.

[4] Manchot and Zechentmayer, *Annalen*, 1906, **350**, 368.

[5] Manchot and Linckh, *Z. anorg. Chem.*, 1924, **140**, 37.

[6] (*a*) Schlesinger and Van Volkenburgh, *J. Amer. Chem. Soc.*, 1929, **51**, 1323; (*b*) Schlesinger and Salathe, *ibid.*, 1923, **45**, 1863.

[7] Manchot and Huttner, *Annalen*, 1910, **372**, 153.

[8] Manchot, *Annalen*, 1910, **375**, 308.

[9] (*a*) Dunstan and Dymond, *J.*, 1887, **51**, 646; (*b*) Usher, *Z. phys. Chem.*, 1908, **62**, 622.

[10] (*a*) Divers and Haga, *J.*, 1885, **47**, 361; (*b*) Huffner, *Z. phys. Chem.*, 1907, **59**, 416.

[11] (*a*) Kohlschutter and Sazanoff, *Ber.*, 1911, **44**, 1423; (*b*) Cambi and Clerici, *Atti R. Accad. Lincei*, 1929, **9**, 519.

[12] (*a*) Manchot, *Ber.*, 1914, **47**, 1614; (*b*) Cambi and Gagnasso, *Atti R. Accad. Lincei*, 1930, **11**, 133.

[13] Tarte, *Ind. chim. Belg.*, 1952, **17**, 42.

was briefly reviewed by Tarte,[13] who also carefully and thoroughly investigated the decomposition products of slightly acidic ferrous sulphate–nitric oxide complexes. Tarte found that little or no oxidation of the ferrous ion had taken place after removal of nitric oxide from the solutions under reduced pressure; all of the ferrous sulphate was regenerated. It must therefore be assumed that previous workers who claimed that oxidation did take place must have used nitric oxide containing traces of nitrogen dioxide. In alkaline or neutral solution the ferrous is readily oxidised to the ferric state, and it is not surprising that such partial oxidation occurred, with reduction of nitric oxide to nitrogen and nitrous oxide; according to Cambi,[14] some hyponitrite occurs in the residual alkaline liquors, but this could not be confirmed.[13]

We measured the magnetic susceptibility of aqueous solutions of the ferrous sulphate–nitric oxide complex over a wide range of concentrations. By using Manchot and Haunschild's values [3] of the equilibrium constant for the reaction, which we now write as

$$[Fe(H_2O)_6]^{2+} + NO \rightleftharpoons [Fe(H_2O)_5NO]^{2+} + H_2O$$

we obtained the values given in the last column of Table 1. These show that the complex has three unpaired electrons. The infrared spectra in the N–O stretching region of the brown-ring compounds both in the solid state and in aqueous solutions (Table 2) show frequencies in the region 1730—1850 cm.$^{-1}$, which is characteristic of nitric oxide in complexes derived by co-ordination from NO^+.[15] Ferrous nitrosyl selenate absorbs at 1853 cm.$^{-1}$.[16]

The brown-ring complex being assumed octahedral with only water and nitric oxide as ligands, the above facts conclusively eliminate the formulations as (*a*) an inner-orbital complex (d^2sp^3) with nitric oxide donating three electrons to the metal, since here the complex would be diamagnetic and of the form $[Fe^{II}(H_2O)_5NO]^{3+}$ and would give a ferric salt on decomposition, which does not occur;[13] (*b*) an inner-orbital complex with nitric oxide donating two electrons, since such a complex $[Fe^{II}(H_2O)_5NO]^{2+}$ would have one unpaired electron and should react with potassium cyanide to give $K_3[Fe^{II}(CN)_5NO]$ (see below), which it does not; (*c*) an inner- or outer-orbital complex involving hyponitrite bridging, since no absorption is found in the region ~1200 cm.$^{-1}$ (cf. ref. 17); (*d*) an outer-orbital complex (sp^3d^2) with nitric oxide donating two electrons to the metal, since in this case, $[Fe^{II}(H_2O)_5NO]^{2+}$, the magnetic susceptibility would be the same as that of the ferrous ion.

TABLE 1. *Magnetic measurements on aqueous solution of* $[Fe(H_2O)_5NO]SO_4$ *at* 293° K.

Susceptibility values (χ) are in c.g.s. units × 10^6.

$[Fe^{2+}]$ (moles/l.)	0·91	0·78	0·53	0·42	0·25	0·19
$\chi_g\{[Fe(H_2O)_5NO]SO_4\}$ *	24·7	24·7	22·8	24·1	24·9	23·7
χ_M †	6700	6700	6200	6550	6770	6440
$\mu_{eff.}$ (B.M.)	3·97	3·97	3·80	3·90	3·99	3·88

* Assuming $\chi_g(FeSO_4,7H_2O) = 41·5 \times 10^{-6}$ c.g.s. units.

† For Fe atom fully corrected for diamagnetism of ligands and anion.

TABLE 2. *Infrared spectra of iron and copper nitrosyl compounds in* N–O *region* (cm.$^{-1}$)

Where no solvent is given the value refers to the solid state.

$[Fe(H_2O)_5NO]SO_4$	1765(s) (3% H_2SO_4)	$[Fe(NH_3)_5NO]SO_4$	1745(m)
$[Fe(H_2O)_5NO]Cl_2$	1795(s) (3% HCl)	$[Fe(C_2H_5{\cdot}OH)_5NO]Cl_3$	1775(s) ($C_2H_5{\cdot}OH$)
$[Fe(H_2O)_5]SeO_4$	1815(s) (3% H_2SeO_4)	$Fe(NO)_3NO$	1810(vs), 1730(s), 1140(m)
$2FeSO_4{\cdot}NO,13H_2O$	1845(s)		
$FeHPO_4NO,xH_2O$	1738(s) (CCl_4)	$[Cu(C_2H_5{\cdot}OH)_3NO]Cl_2$	1854 ($C_2H_5{\cdot}OH$)
$[Fe(NH_3)_5NO]Cl_2$	1754(s)	$[Cu(C_2H_5{\cdot}OH)_3NO]Br_2$	1848 ($C_2H_5{\cdot}OH$)

[14] Cambi, *Z. anorg. Chem.*, 1941, **247**, 22.

[15] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[16] Hieber and Jahn, *Z. Naturforsch.*, 1958, **13b**, 196.

[17] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

The only acceptable formulation is that of an outer-orbital complex (sp^3d^2), $[Fe^I(H_2O)_5NO]^{2+}$ with the nitric oxide donating three electrons to the ferrous ion. The N–O stretching frequency in such a complex might well be expected to lie in the region 1730—1850 cm.$^{-1}$ (where inner-orbital nitric oxide complexes absorb) as, although no π-bonding in the metal–NO bond is possible, the outer-orbital bonding will be more polar in character than the inner-orbital bonding which occurs in the diamagnetic nitric oxide complexes. In addition, this formulation indicates a magnetic moment corresponding to three unpaired electrons and would be in keeping with the regeneration of the ferrous ion on removal of nitric oxide, in accordance with the observations.

The brown colour of the complexes is attributable to charge-transfer spectra; since the iron atom is formally in the +1 oxidation state a comparison of ligand-field bands with those in other iron complexes is not possible. Table 3 contains values of the extinction coefficient at the various maxima for the solution of the iron and copper complexes. The absorption spectrum of $[Fe(EtOH)_5NO]Cl_3$ in the region 500—800 mμ is similar to that of $[Fe(EtOH)_6]Cl_2$, as expected from the above considerations.

TABLE 3. *Absorption spectra in the near infrared and visible regions.*

Complex	ε	Wavelength		Complex	ε	Wavelength	
$[Fe(H_2O)_5NO]SO_4$ ...	38	385 mμ	17,100 cm.$^{-1}$	$[Cu(C_2H_5{\cdot}OH)_3NO]Cl_2$	51·1	805 mμ	12,450 cm.$^{-1}$
$[Fe(C_2H_5{\cdot}OH)_5NO]Cl_3$	15·7	810 ,,	12,400 ,,		309·1	565 ,,	17,700 ,,

The Pentamminonitrosyliron(I) *Ion*, $[Fe(NH_3)_5NO]^{2+}$.—The very unstable chloride and sulphate of this ion were made by Weitz and Muller.[18] The infrared spectra, measured in solution, are similar to those of the brown-ring compounds. The determination of the magnetic moment was not possible owing to the presence of a trace of a ferromagnetic impurity, which proved impossible to eliminate. It seems reasonable to assume, however, that the ion is similar to the above aquo-species and that it is $[Fe^I(NH_3)_5NO]^{2+}$ and not, as may have been expected, similar to the red salt $[Co(NH_3)_5NO]SO_4$.[17]

The Pentacyanonitrosyliron(II) *Ion*, $[Fe(CN)_5NO]^{3-}$.—Aqueous solutions of $Na_3[Fe(CN)_5NH_3]$ in the presence of a slight excess of acetic acid (to absorb ammonia) absorb either carbon monoxide or nitric oxide to give $Na_3[Fe(CN)_5CO]$ and the ion $[Fe(CN)_5NO]^{3-}$ respectively.[19] The latter cannot be isolated as a salt, but the ratio Fe : NO is unity. Sidgwick [20] suggested that the nitric oxide is bound to the metal by two electrons only, just as the carbon monoxide is bound in the diamagnetic carbonyl cyanide. It is not true, however, that the complex exists in a violet and a yellow form as stated by Sidgwick.

Magnetic-susceptibility measurements at three concentrations in aqueous solution show that the complex has a moment corresponding to slightly less than one unpaired electron (Table 4). Addition of aqueous sodium hydroxide to solutions of the complex in absence of air leads to the ferrous aquo-complex $Na_3[Fe^{II}(CN)_5H_2O]$, while in the presence of air the ferric compound $Na_2[Fe^{III}(CN)_5H_2O]$ is obtained. The action of potassium cyanide in absence of air produces the ferrocyanide. These chemical reactions show clearly that in the nitric oxide complex the iron is ferrous. Although formally the complex could be considered the equivalent of the ions $[Fe(H_2O)_5NO]^{2+}$ and $[Fe(NH_3)_5NO]^{2+}$, it cannot be formed from them by the action of cyanide, differing in this regard from the complex $[Fe(C_2H_5{\cdot}OH)_5NO]^{3+}$ (see below), which produces the nitroprusside ion. This difference is in keeping with Sidgwick's formulation $[Fe^{II}(CN)_5NO]$, the odd electron remaining localised on the ligand in this case, with inner-orbital d^2sp^3 bonding due to the strong ligand-field effect of the cyanide ion.

The Pentaethanolnitrosyliron(III) *Ion*, $[Fe(C_2H_5{\cdot}OH)_5NO]^{3+}$.—This new complex ion is

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[18] Weitz and Muller, *Angew. Chem.*, 1950, **62**, 221.

[19] Manchot, Merry, and Worringer, *Ber.*, 1912, **45**, 2869.

[20] Sidgwick, " The Chemical Elements and their Compounds," Oxford University Press, 1950, p. 1360.

obtained by passing dry nitric oxide into anhydrous ethanolic solutions of anhydrous ferric chloride. It is dark green in solution and, like the cupric–nitric oxide complexes discussed below, cannot be isolated as a solid salt. Measurement of the absorption of nitric oxide by ferric chloride solutions of different concentrations shows that the ratio NO : Fe is somewhat less than unity, and that in solution there is an equilibrium

TABLE 4. *Magnetic measurements on aqueous solutions of* $Na_3[Fe(CN)_5NO]$ *at* 295·4° K.

$[Fe(CN)_5NO]^{3-}$ (moles/l.)	$\chi_g(Na_3[Fe(CN)_5NO])$	χ_M *	$\mu_{eff.}$ (B.M.)
0·44	2·66	826	1·41
0·34	2·58	803	1·38
0·20	3·40	1036	1·56

TABLE 5. *Magnetic measurements on ethanolic solutions of* $[Fe(C_2H_5{\cdot}OH)_5NO]Cl_3$ *at* 295·4° K.

$[Fe^{3+}]$ (moles/l.)	$\chi_g\{[Fe(C_2H_5{\cdot}OH)_5NO]Cl_3\}$ †	χ_M *	$\mu_{eff.}$ (B.M.)
0·314	52·6	10,100	4·89
0·135	54·4	10,500	4·98
0·132	55·3	10,600	5·01
0·076	56·7	10,900	5·10
0·065	56·3	10,900	5·08

For Tables 4 and 5, susceptibilities are in c.g.s. units × 10^6.
* For Fe atom, fully corrected for diamagnetism of ligands and cation.
† χ_g for $FeCl_3$ is taken as $86{\cdot}2 \times 10^{-6}$ c.g.s. units.

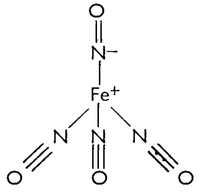
$$[Fe(C_2H_5{\cdot}OH)_6]^{3+} + NO \rightleftharpoons [Fe(C_2H_5{\cdot}OH)_5NO]^{3+} + C_2H_5{\cdot}OH.$$

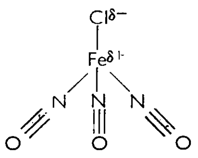
The equilibrium constant and heat of reaction were determined; magnetic measurements over a concentration range indicate a moment corresponding to four unpaired electrons (Table 5). An absorption band at 1775 cm.$^{-1}$ in ethanolic solution is attributed to nitric oxide's donating as NO^+. The compound is decomposed by water; with potassium cyanide traces of $K_2[Fe^{II}(CN)_5NO]$ are formed.

The only structure in keeping with the results is $[Fe^{II}(C_2H_5{\cdot}OH)_5NO]^{3+}$ involving sp^3d^2 outer-orbital bonding. The complex is thus the ferric analogue of the brown-ring compound. The fact that water decomposes the complex, and that aqueous ferric solutions do not absorb nitric oxide, seems to indicate that the ion $[Fe^{II}(H_2O)_5NO]^{3+}$ does not exist in detectable concentration; solutions of the hexammine–iron(III) ion [21] also do not absorb nitric oxide.

Iron Tetranitrosyl, $Fe(NO)_4$.—This compound was made by Manchot and Enk [22] by treating iron pentacarbonyl with nitric oxide under pressure. It is very reactive, forming compounds such as $Fe(NO)SO_4$ with sulphuric acid, $Fe(NO)_2S{\cdot}C_2H_5$ with ethanethiol, etc. Sidgwick suggested (ref. 20, pp. 1373, 1485) that the compound had the structure $[Fe(NO)_3]^-NO^+$; this would account for its non-volatility and would give an inert-gas structure to the metal atom.

Unfortunately the compound is so unstable (it decomposes slowly above 0° even in nitrogen) that it is impossible to measure its magnetism reliably. Infrared spectra of several different preparations of the substance have been obtained, however (Table 2). These show two frequencies in the NO^+ region and one near 1150 cm.$^{-1}$ in the region assigned to nitric oxide donating in complexes as NO^-.[17] This suggests that the compound has the structure (I), with three nitric oxide molecules donating as NO^+ and one as NO^-.


(I)


(II)

The two higher frequencies are similar to those observed (at 1826 cm.$^{-1}$ and 1763 cm.$^{-1}$) for $Fe(NO)_3Cl$,[16] with which $[Fe^+(NO)_3]NO^-$ is clearly analogous.

[21] Biltz and Birk, *Z. anorg. Chem.*, 1923, **134**, 125.

The tetranitrosyl does not decompose to give a dimer $[Fe(NO)_3]_2$ as might be expected by analogy with the decomposition of $Fe(NO)_3Br$;[23] this must be because nitric oxide has less tendency to act as a bridge group.

The Triethanolnitrosylcopper(I) *Ion*, $[Cu(C_2H_5{\cdot}OH)_3NO]^{2+}$.—Cupric salts in non-aqueous solvents absorb nitric oxide to give violet complexes[4, 8, 24] which are considerably weaker than those of ferrous iron. Electrolysis shows that the nitric oxide is associated with a copper cation of +2 charge.[25] According to Kohlschutter and Kutscheroff,[24] the ratio NO : Cu in ethanol is 3·6 : 1. Later experiments by Manchot[8] showed that this value was in error and that the ratio NO : Cu was in fact less than unity. We confirmed this observation and determined the equilibrium constant (Table 6) of the reaction which we now write as

$$[Cu(C_2H_5{\cdot}OH)_4]^{2+} + NO \rightleftharpoons [Cu(C_2H_5{\cdot}OH)_3NO]^{2+} + C_2H_5{\cdot}OH.$$

Magnetic measurements on the ethanolic solutions show that the complex is diamagnetic and the infrared spectrum (Table 2) shows that the complex must be formulated with donation by NO^+.

TABLE 6. *Equilibrium constants and heats of reaction in ethanolic solutions.*

$[Fe^{3+}]$ (moles/l.)	Temp. (°K)	p_{NO} (mm.)	V *	K' †	$[Cu^{2+}]$ (moles/l.)	Temp. (°K)	p_{NO} (mm.)	V *	K' ‡
0·034	282·4	740·0	21·3	—	0·05	273·4	742·9	19·1	—
0·017	282·4	740·0	21·0	43·8	0·025	273·4	742·9	20·1	115·0
0·034	294·4	724·1	18·0	—	0·05	283·0	731·9	17·3	—
0·017	294·4	724·1	17·4	196·0	0·025	283·0	731·9	17·0	226·4
0·034	298	705·0	15·2	—	0·05	297·6	696·9	15·6	340·8
0·017	298	705·0	16·1	305·0	0·025	304·4	686·0	12·2	568·0
Heat of reaction 20·4 *kcal./mole*					*Heat of reaction* 7·3 *kcal/mole*				

* Vol. of NO absorbed per mole at N.T.P.

† Mean value of $(p_{NO}[FeCl_3])/[FeCl_3NO]$.

‡ Mean value of $(p_{NO}[CuCl_2])/[CuCl_2NO]$.

On decomposition of the nitric oxide complex, the cupric ion is regenerated. This fact, together with the infrared and magnetic data, indicates that the complex must be formulated as $[Cu^I(C_2H_5{\cdot}OH)_3NO]^{2+}$, where the number of solvate molecules is most likely three, by analogy with the cupric aquo-complex ion.[26]

EXPERIMENTAL

Preparations.—Compounds were made and purified according to the following references: $2FeSO_4{\cdot}NO,13H_2O$,[7] $[Fe(NH_3)_5NO]Cl_2SO_4$,[17] and $Na_3[Fe(CN)_5NO]$[18] from $Na_3[Fe(CN)_5NH_3]$.[27]

The brown-ring compounds were made from aqueous ferrous solutions containing a 3% excess of sulphuric, hydrochloric, or perchloric acid. Nitric oxide was obtained from a sodium nitrite–ferrous sulphate generator and any nitrogen dioxide was removed with concentrated potassium hydroxide.

Iron tetranitrosyl was made by Manchot and Enk's method,[22] slightly modified as follows. Iron pentacarbonyl (1·5 g.) was placed in a 20-ml. stainless-steel bomb (Baskerville and Lindsay Ltd., Manchester) in nitrogen. Nitric oxide was introduced from a cylinder at about 100 atm. and the bomb was then closed and held at room temperature for 3 days. It was then cooled to −70° and the tetranitrosyl removed and centrifuged at −40° in sodium-dried ether. The product shows no infrared carbonyl frequencies; it consists of a fine mass of long, dark brown-black needles which decompose on standing even at 0° [Found: Fe, 33·08. Calc. for $Fe(NO)_4$: Fe, 31·75].

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[22] Manchot and Enk, *Annalen*, 1929, **470**, 275.

[23] Hieber and Beck, *Z. Naturforsch.*, 1958, **13***b*, 194.

[24] Kohlschutter and Kutscheroff, *Ber.*, 1904, **37**, 3044.

[25] Manchot, *Ber.*, 1914, **47**, 1601.

[26] O'Brien, " Chemistry of Co-ordination Compounds," J. C. Bailar (Editor), Reinhold, New York, 1956.

[27] Hofmann, *Z. anorg. Chem.*, 1896, **12**, 146.

Physical Measurements.—The compounds were handled in a nitrogen atmosphere throughout. Magnetic measurements were made in sealed 5-ml. Gouy solution tubes at fields of 8000 gauss. Infrared measurements were made on a Perkin-Elmer Model 21 instrument with sodium chloride optics. Solids were examined as Nujol mulls and aqueous solutions as films between arsenic sulphide plates, which were made airtight with an **O**-ring of grease. The near infrared and visible spectra were taken on a Perkin-Elmer "Spectracord" double-beam recording spectrophotometer. Gas absorption was measured in a conventional Warburg-type apparatus.

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