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# The Ferric Chloride α-Di-imine System.
# Part IV. X-ray Structure Determination of Trichloro(N,N-dimethyl-formamide)(1,10-phenanthroline)Iron(III), a Meridional Monomer

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The title compound, $Fe(phen)Cl_3 \cdot DMF$, is to our knowledge one of the few examples of a *neutral monomeric* high-spin ferric species containing coordinated α-di-imine ligands to be characterized by X-rays. This compound is of interest in that it exhibits novel slow paramagnetic relaxation in iron-57 Mössbauer spectra for large external magnetic fields. Its structure is presented in this note.

## Experimental

The crystal data for the yellow-orange complex, trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III) are collected in Table I. Three-dimensional intensity data were collected with a Syntex $P_2$ automated diffractometer using Mo(Kα) monochromatized radiation. Lorentz and polarization corrections were applied to the data. Absorption corrections were not made. Anomalous dispersion corrections for the iron and chlorine ions were included in both structure refinements.

### *Solution and Refinement of Structure*

#### *Trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III)*

The three-dimensional Patterson map revealed the iron(III) position. The remaining chlorine atoms and the atoms of the phenanthroline and dimethylformamide groups were found in subsequent Fourier synthesis maps. Least-squares refinement using anisotropic temperature factors and $1/\sigma^2_{F_o}$ weighting resulted in a weighted R-value of 0.043. All hydrogen atoms were found in a difference Fourier map and least-squares refinement including the hydrogens resulted in a final weighted R-value of 0.034. The inversion-related coordinates resulted in a structure refinement that converged to a weighted R-value of 0.037. Application of Hamilton's R-tests [1] indicated the initial structure was the correct structure (99.5% confidence).

TABLE I. Crystal Data for the Yellow-Orange Complex, Trichloro(N,N-dimethylformamide)(1,10-phenanthroline)-iron(III).

| | Yellow-orange complex |
|---|---|
| Space group | $P2_1$ |
| cell dimensions | $a$ = 6.698(1) A |
| | $b$ = 13.271(2) A |
| | $c$ = 9.787(2) A |
| | $\beta$ = 105.10(2) Å° |
| | $V$ = 870.0(2) Å$^3$ |
| Calculated density | 1.64 g/cc |
| Observed density (floatation) | 1.62 g/cc |
| Range of data | $2\theta$max = 65° |
| Total reflections | 3160 |
| Observed reflections$^a$ | 2102 |

$^a I \geq 1.5\sigma(I)$.

The atomic scattering factors for iron, chlorine, nitrogen, carbon and oxygen were taken from Cromer and Mann [2] and those for hydrogen from Stewart *et al.* [3]. The X-RAY 76 [4] computer program system was used throughout for data processing, structure determination, and least-squares refinement. All drawings were made using the ORTEP [5] program. The observed and calculated structure factors are given in supplementary Table A.

## Description of Structure and Discussion

The local coordination of the yellow-orange *mer*-trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III) is similar to that of the chromium(III) analog [6] and is shown in Fig. 1. The packing diagram for the complex is shown in Fig. 2. Postional and thermal parameters for nonhydrogen atoms are given in Table II, while the refined hydrogen atom positions are listed in Table III. Bond distances and angles with corresponding standard deviations are

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TABLE II. Positional and Thermal Parameters[a] of Non-Hydrogen Atoms of Trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III).

| *Atom* | *X* | *Y* | *Z* | $U_{11}$[b] | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Fe^{3+}$ | -0.4624(1) | -0.2500 | -0.3488(1) | 2.72(5) | 2.10(4) | 3.52(5) | -0.01(4) | 1.44(3) | -0.20(4) |
| Cl(1) | -0.2139(2) | -0.2861(1) | -0.1292(1) | 3.31(8) | 3.55(8) | 4.34(9) | -0.12(6) | 1.12(7) | 1.21(7) |
| Cl(2) | -0.2972(2) | -0.3388(1) | -0.4831(2) | 4.71(9) | 3.89(9) | 5.15(11) | 0.97(7) | 2.57(8) | -0.73(8) |
| Cl(3) | -0.7187(2) | -0.1843(1) | -0.5402(2) | 3.49(8) | 3.99(9) | 3.85(9) | 0.68(7) | 0.77(7) | -0.26(7) |
| *Phenanthroline* | | | | | | | | | |
| N(1) | -0.2938(6) | -0.1117(3) | -0.3431(4) | 2.2(2) | 2.5(2) | 2.6(2) | 0.2(2) | 0.9(2) | 0.4(2) |
| C(2) | -0.1399(8) | -0.0951(4) | -0.4041(6) | 2.9(3) | 3.1(3) | 3.1(3) | 0.2(2) | 1.2(2) | 0.6(2) |
| C(3) | -0.431(8) | -0.0006(5) | -0.3979(6) | 2.8(3) | 4.2(3) | 3.6(3) | 0.0(3) | 1.4(2) | 1.5(3) |
| C(4) | -0.0998(8) | 0.0754(4) | -0.3241(6) | 3.0(3) | 3.0(3) | 4.5(4) | -0.7(2) | 0.4(3) | 0.7(3) |
| C(5) | -0.3242(9) | 0.1342(4) | -0.1707(7) | 4.5(4) | 1.9(3) | 5.0(4) | -0.7(3) | 1.1(3) | -0.4(3) |
| C(6) | -0.4746(9) | 0.1135(4) | -0.1037(6) | 4.5(4) | 2.6(3) | 4.3(4) | -0.3(3) | 0.8(3) | 1.4(3) |
| C(7) | -0.7251(8) | -0.0102(5) | -0.479(6) | 3.7(3) | 3.2(3) | 2.8(3) | 0.7(3) | 0.8(2) | -0.7(3) |
| C(8) | -0.8093(8) | -0.1057(4) | -0.676(6) | 3.0(3) | 3.9(3) | 3.5(3) | -0.7(3) | 1.4(3) | -0.5(3) |
| C(9) | -0.7407(8) | -0.1738(4) | -0.1532(6) | 3.3(3) | 2.6(3) | 3.6(3) | -0.2(2) | 1.5(3) | 0.4(3) |
| N(10) | -0.5944(6) | -0.1518(3) | -0.2188(4) | 2.3(2) | 2.2(2) | 2.9(2) | 0.0(2) | 0.7(2) | 0.0(2) |
| C(11) | -0.5092(8) | -0.0579(4) | -0.1993(6) | 2.4(3) | 2.5(3) | 2.8(3) | 0.0(2) | 0.5(2) | 0.2(2) |
| C(12) | -0.3479(7) | -0.360(4) | -0.2677(5) | 2.3(2) | 2.6(3) | 2.4(3) | 0.1(2) | 0.2(2) | 0.4(2) |
| C(13) | -0.2557(8) | 0.0592(4) | -0.2531(6) | 2.8(3) | 2.2(3) | 3.1(3) | -0.2(2) | 0.3(2) | 0.6(2) |
| C(14) | -0.5700(7) | 0.0159(4) | -0.1156(6) | 2.6(3) | 2.4(3) | 3.2(3) | 0.4(2) | 0.5(2) | -0.1(2) |
| *DMF* | | | | | | | | | |
| O | -0.6439(6) | -0.3628(3) | -0.3091(4) | 3.5(2) | 2.2(2) | 5.0(3) | -0.4(2) | 1.5(2) | -0.3(2) |
| C(15) | -0.6010(8) | -0.4548(4) | -0.2960(6) | 3.4(3) | 3.1(3) | 3.0(3) | -0.7(3) | 0.3(3) | -0.4(3) |
| N | -0.7168(7) | -0.5209(3) | -0.2507(5) | 3.7(3) | 2.6(3) | 3.7(3) | -0.2(2) | 0.9(2) | -0.2(2) |
| C(16) | -0.9033(8) | -0.4897(4) | -0.2106(7) | 3.7(3) | 4.0(4) | 5.6(4) | -0.5(3) | 1.6(3) | 0.1(3) |
| C(17) | -0.6616(10) | -0.6276(4) | -0.2346(7) | 7.5(5) | 2.3(3) | 6.1(5) | 0.4(3) | 1.7(4) | 0.7(3) |

[a] Estimated standard deviations are given in parentheses and refer to the least significant digits. [b] The anisotropic temperature factors are multiplied by 100 and are of the form $T = \exp[-2\pi^2(U_{11}(ha^*)^2 + \ldots + 2U_{12}(hka^*b^*) + \ldots]$.

TABLE III. Refined Hydrogen Positions[a] for Trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III).

| *Atom* | *X* | *Y* | *Z* | $U$[b] |
|---|---|---|---|---|
| *Phenanthroline* | | | | |
| H(2) | -0.106(7) | -0.150(4) | -0.446(5) | 3(1) |
| H(3) | 0.062(6) | 0.005(4) | -0.442(5) | 2(1) |
| H(4) | -0.028(7) | 0.141(4) | -0.311(5) | 2(1) |
| H(5) | -0.267(7) | 0.196(4) | -0.162(5) | 2(1) |
| H(6) | -0.518(8) | 0.164(4) | -0.058(5) | 3(2) |
| H(7) | -0.768(7) | 0.032(4) | -0.009(5) | 4(2) |
| H(8) | -0.918(7) | -0.131(4) | -0.028(5) | 4(2) |
| H(9) | -0.777(8) | -0.236(5) | -0.160(6) | 6(2) |
| *DMF* | | | | |
| H(15) | -0.466(8) | -0.478(5) | -0.313(6) | 6(2) |
| H(16A) | -0.878(9) | -0.481(6) | -0.114(8) | 8(2) |
| H(16B) | -0.978(11) | -0.446(6) | -0.264(8) | 10(3) |
| H(16C) | -1.006(14) | -0.550(8) | -0.233(10) | 13(4) |
| H(17A) | -0.584(15) | -0.653(8) | -0.290(11) | 14(4) |
| H(17B) | -0.621(17) | -0.657(9) | -0.155(12) | 18(4) |
| H(17C) | -0.808(18) | -0.669(9) | -0.262(11) | 18(4) |

[a] Estimated standard deviations are given in parentheses and refer to the least significant digits. [b] Temperature factors are multiplied by 100.

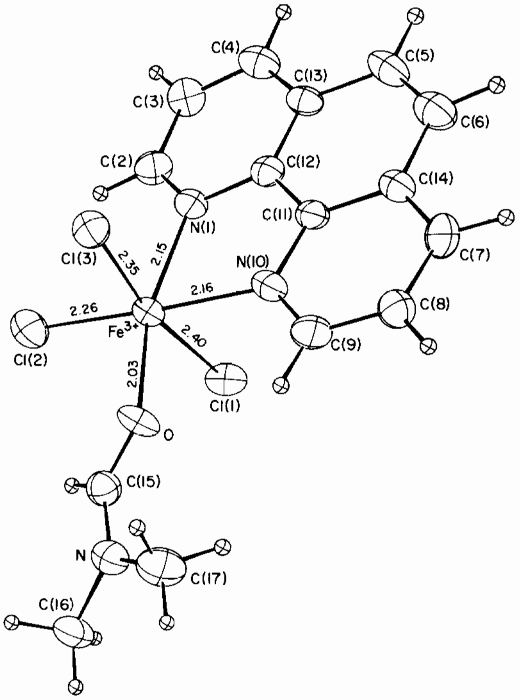

Fig. 1. View of the local coordination environment of trichloro(N,N-dimethylformamide) (1,10-phenanthroline)iron(III).

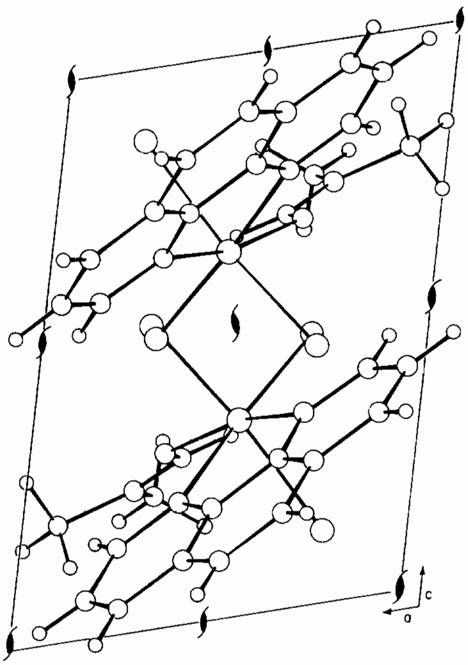

Fig. 2. Packing diagram for trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III).

TABLE IV. Bond Lengths and Angles for Non-Hydrogen Atoms[a] of Trichloro(N,N-dimethylformamide)(1,10-phenanthroline)iron(III).

| | | | |
|---|---|---|---|
| *Lengths* (Å) | | | |
| Fe–Cl(1) | 2.40(3) | C(6)–C(14) | 1.436(8) |
| Fe–Cl(2) | 2.26(1) | C(14)–C(7) | 1.41(1) |
| Fe–Cl(3) | 2.35(3) | C(7)–C(8) | 1.381(8) |
| Fe–N(1) | 2.15(1) | C(8)–C(9) | 1.39(1) |
| Fe–N(10) | 2.16(1) | C(9)–N(10) | 1.34(1) |
| Fe–O | 2.03(1) | N(10)–C(11) | 1.364(7) |
| N(1)–C(2) | 1.34(1) | C(11)–C(14) | 1.403(9) |
| C(2)–C(3) | 1.406(8) | C(11)–C(12) | 1.44(1) |
| C(3)–C(4) | 1.35(1) | C(12)–N(1) | 1.254(7) |
| C(4)–C(13) | 1.41(1) | O–C(15) | 1.322(9) |
| C(13)–C(5) | 1.43(1) | C(15)–N | 1.46(1) |
| C(5)–C(6) | 1.36(1) | N–C(16) | 1.462(8) |
| C(13)–C(12) | 1.397(7) | N–C(17) | 1.351(8) |
| Angles (°) | | | |
| Cl(1)–Fe–Cl(2) | 95.0(1) | C(5)–C(6)–C(14) | 120.7(6) |
| Cl(1)–Fe–Cl(3) | 168.2(1) | C(6)–C(14)–C(7) | 123.2(5) |
| Cl(1)–Fe–N(1) | 84.8(1) | C(6)–C(14)–C(11) | 119.1(5) |
| Cl(1)–Fe–N(10) | 83.6(1) | C(11)–C(14)–C(7) | 117.6(5) |
| Cl(1)–Fe–O | 89.5(1) | N(1)–C(12)–C(13) | 123.6(5) |
| Cl(2)–Fe–Cl(3) | 95.5(1) | N(1)–C(12)–C(11) | 116.3(4) |
| Cl(2)–Fe–N(1) | 97.2(1) | C(13)–C(12)–C(11) | 120.0(5) |
| Cl(2)–Fe–N(10) | 173.5(1) | C(12)–C(11)–C(14) | 119.8(5) |
| Cl(2)–Fe–O | 97.8(1) | C(12)–C(11)–N(10) | 117.2(5) |

(continued overleaf)

TABLE IV. *(continued)*

| | | | |
|---|---|---|---|
| Cl(3)–Fe–N(1) | 88.5(1) | N(10)–C(11)–C(14) | 123.0(5) |
| Cl(3)–Fe–N(10) | 85.4(1) | C(14)–C(7)–C(8) | 118.8(5) |
| Cl(3)–Fe–O | 94.4(1) | C(7)–C(8)–C(9) | 119.6(5) |
| N(1)–Fe–N(10) | 76.3(2) | C(8)–C(9)–N(10) | 123.2(5) |
| N(1)–Fe–O | 164.3(2) | C(9)–N(10)–C(11) | 117.8(5) |
| N(10)–Fe–O | 88.5(2) | Fe–N(1)–C(2) | 126.2(4) |
| C(2)–N(1)–C(12) | 118.0(4) | Fe–N(1)–C(12) | 115.8(3) |
| N(1)–C(2)–C(3) | 121.9(5) | Fe–N(10)–C(11) | 114.3(4) |
| C(2)–C(3)–C(4) | 119.9(6) | Fe–N(10)–C(9) | 127.9(3) |
| C(3)–C(4)–C(13) | 119.7(5) | O–C(15)–N | 122.8(5) |
| C(4)–C(13)–C(5) | 123.9(5) | C(15)–N–C(16) | 121.3(5) |
| C(4)–C(13)–C(12) | 116.8(5) | C(16)–N–C(17) | 117.1(5) |
| C(5)–C(13)–C(12) | 119.3(5) | C(15)–N–C(17) | 121.7(5) |
| C(13)–C(5)–C(6) | 121.0(5) | Fe–O–C(15) | 127.3(4) |

[a] Estimated standard deviations are given in parentheses and refer to the least significant digits.

given in Table IV. The distribution of ligands about the central iron is a distorted octahedron due to the constraints imposed by the rigid phenanthroline system on the N1–Fe$^{3+}$–N10 angle. The phenanthroline ligand is essentially planar with a maximum deviation from the plane of 0.02 Å.

As in the chromium analog, the Fe$^{3+}$–Cl(2) bond is significantly shorter than other, typical [7] Fe$^{3+}$–Cl octahedral bonds. This may be accounted for by examination of $\pi$-backbonding interactions. Filled p or empty d orbitals of Cl(2) can interact with one of the iron $t_{2g}$ orbitals. It is interesting to note that the comparatively short Fe–Cl(2) bond distance (2.26 Å) in *mer*-trichloro(N,N-dimethylformamide)-(1,10-phenanthroline)iron(III) is quite similar to both cationic Fe–Cl bond distances (2.24 and 2.25 Å) in dichlorobis(1,10-phenanthroline)iron(III) tetrachloroferrate(III) studied by Goodwin and McPartlin [8]. In the preceding high-spin cation, each Cl$^-$ has access to noncompetitive interactions with iron $t_{2g}$ orbitals. The Fe–N bond distances in the yellow-orange compound are close to those found in Goodwin's complex and 0.05 Å longer than those found for the chromium analog [6]. This latter difference is likely the result of occupancy of antibonding $e_g$ orbitals in the iron(III) complex. The Fe–O bond distance of 2.03 Å is somewhat shorter than Fe$^{III}$–OH$_2$ and may be attributed to the use of sp$^2$ hybridized orbitals of the DMF oxygen compared to sp$^3$ hybridized orbitals of the water oxygen. In passing, we point out that there have been relatively few X-ray crystallographic studies of *high-spin Fe(III)* with *coordinated* $\alpha$-di-imine ligands. In addition to the present system and that of reference 8, [Fe(phen)$_2$Cl$_2^+$][FeCl$_4^-$], as well as the bipyridine analog [9], we know of [phenH$^+$][Fe(phen)Cl$_4^-$]. The only other *neutral monomeric species* that we know of and which has been characterized in single crystal X-ray studies are [Fe(phen)Cl$_3$H$_2$O] and [Fe(phen)Cl$_3$CH$_3$OH] [11]. Interestingly, the latter complexes are *facial* with respect to the chlorine atoms as compared to the present *meridianal* [Fe(phen)Cl$_3$DMF]. A full understanding of the factors controlling the choice of one or the other of these structural variants should prove to be the subject of interesting future research.

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