

The Hexakis(thiocyanato)ferrate(III) Ion: a Coordination Chemistry Classic Reveals an Interesting Geometry Pattern for the Thiocyanate Ligands

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(NMe₄)₃[Fe(NCS)₆] crystallizes from ethanol in the monoclinic space group C2/c. Two different types of complex ions are contained in the unit cell, though both possess exclusively *N*-coordination of the thiocyanate ligands. In one ion, the thiocyanate ligands are all essentially linearly bound, with an Fe–N–C angle of 174 ± 4°, while in the other, there are two *cis*-thiocyanate ligands with a notably small Fe–N–C angle of 146.5°. The EPR and Mössbauer results show that

all the iron(III) centers maintain the high-spin state down to 80 K, while the magnetic susceptibility confirms this to 2 K. Infrared and Mössbauer spectra provide evidence for an unusually “soft” lattice. Traditional criteria for interpretation of the infrared frequencies are not strictly applicable for this compound.

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Introduction

Given that the [Fe(NCS)₆]³⁻ [“iron(III) rhodanide”] ion is a classical Werner complex of fundamental significance, there has hardly been an overwhelming number of studies of it since Krüsz and Moraht^[1] first described its isolation as (the apparently double) salt Na₃[Fe(NCS)₆]·6NaNCS·4H₂O over a century ago. Other cations’ [Fe(NCS)₆]³⁻ salts were subsequently prepared by Rosenheim and Cohen,^[2] while spectrophotometric studies, originated in 1931,^[3] moved forward to define the d-d (940 nm, 570 nm) and LMCT (480, 320, 250 nm) bands.^[4–9] Forster and Goodgame^[6] also demonstrated the high-spin nature of (NMe₄)₃[Fe(NCS)₆] at ambient temperature ($\mu = 5.92 \mu_B$). From the LMCT spectroscopy of the Fe(NCS)₆³⁻ ion doped into the analogous lanthanide lattices (R₄E)₃–[Ln(NCS)₆], Walker and McCarthy^[10] noted a photosensitivity which they ascribed to NCS⁻ dissociation, yielding [Fe(NCS)₅]²⁻. In hyperbaric studies of [Me₄N]₃[Fe(NCS)₆]^[11] and K₃[Fe(NCS)₆]^[12] by infrared and Mössbauer spectroscopy, respectively, Hellner et al.^[11] and Fung and Drickamer^[12] detected responses which they attributed to an in-

tramolecular redox process (presumably corresponding to hyperbaric stabilisation of the LMCT excited state Fe^{II}–NCS⁻; cf. ref.^[10]) and also to the linkage isomerisation Fe–NCS \rightleftharpoons Fe–SCN. The assignment of this remarkable isomerisation was based on the shifting of $\nu_{\text{Fe–NCS}}$ and $\nu_{\text{C–N}}$ ^[6,11] to frequencies traditionally associated with M–SCN rather than M–NCS bonding.^[13]

Thiocyanatometallates are capable of acting as ligands (i.e., thiocyanato-bridged Fe–M systems), in this regard bearing an analogy to hexacyanoferrates, which have been used extensively in supramolecular lattice construction.^[14] In connection with our interest in the potential of [Fe(NCS)₆]³⁻ as a building block for supramolecular lattices, we present here the results of a crystallographic characterisation of a salt of this anion.

Questions which we anticipated might thus be addressed included: (1) is any *S*-thiocyanato coordination present under ambient conditions, or is coordination exclusively via the nitrogen atoms? and (2) if the latter is the case, does spin-crossover occur for [Fe(NCS)₆]³⁻ at sub-ambient temperatures?

As we considered it important to avoid coordinative interactions between [Fe(NCS)₆]³⁻ and any metal counteranion, we sought tetraalkylammonium salts of [Fe(NCS)₆]³⁻, of which the tetramethylammonium one, (Me₄N)₃[Fe(NCS)₆], indeed proved amenable to crystallography.

Results and Discussion

(Me₄N)₃[Fe(NCS)₆] crystallises from ethanol as unsolvated monoclinic crystals belonging to the space group C2/c

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(Table 1). One of the tetramethylammonium ions is disordered.

Table 1. Crystal Data for $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ (CCDC-252536).

Empirical formula: $\text{C}_{18}\text{H}_{36}\text{FeN}_9\text{S}_6$
Formular mass: 626.77
$a = 24.9838(18) \text{ \AA}$
$b = 9.3117(7) \text{ \AA}$
$c = 28.624(2) \text{ \AA}$
$\beta = 100.245(1)^\circ$
$V = 6553.0(8) \text{ \AA}^3$
$Z = 8$
Crystal dimensions: $0.4 \times 0.18 \times 0.1 \text{ mm}$
Absorption coefficient = 0.865 mm^{-1}
$\rho_{\text{calcd.}} = 1.271$
$T = 295(2) \text{ K}$
$R(\text{all}) = 0.107$
$R_w(\text{all}) = 0.147$
Final $R = 0.0548$
Final $R_w = 0.127$
Goodness-of-fit = 1.032

The most notable feature of the Fe coordination is that there are two types of anions present in the unit cell. In one set of anions (*B*, Fe[1]; Figure 1, Table 2), the thiocyanate ligands are all essentially “linearly” coordinated to iron(III), with Fe–N–C angles ranging from 170 to 179°.

In the other half of the $[\text{Fe}(\text{NCS})_6]^{3-}$ population (anions *A*, possessing C_2 symmetry), a mutually *cis* pair of the NCS^- ligands are in a “bent” mode, with the Fe–N–C angle at $146.5(4)^\circ$. Such structural diversity within the unit cell is reminiscent of previously reported instances, such as $[\text{Cu}(\text{Dipica})_2](\text{BF}_4)_2$,^[15] and $[\text{Ni}(\text{CN})_5]^{2-}$.^[16] M–N–C angles of 160–175° are common in the literature,^[17,18] including cases^[19] where different thiocyanate ligands in the same complex display significantly different angles. On the other hand, M–N–C angles of 130–150° are encountered less frequently (almost exclusively for $M = \text{Cd}$),^[20] and a difference

Table 2. Selected bond lengths [\AA] and angles ($^\circ$) in $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$.

<i>A</i> anions			
Fe(1)–N(13)	2.046(4)	C(13)–N(13)–Fe(1)	173.9(4)
Fe(1)–N(11)	2.050(4)	N(13)–Fe(1)–N(13')	179.4(2)
Fe(1)–N(12)	2.061(4)	N(13)–Fe(1)–N(11)	88.81(16)
S(11)–C(11)	1.611(5)	N(13)–Fe(1)–N(11')	91.58(16)
S(12)–C(12)	1.605(5)	N(11)–Fe(1)–N(11')	92.7(2)
S(13)–C(13)	1.604(5)	N(13)–Fe(1)–N(12)	89.66(16)
N(11)–C(11)	1.125(5)	N(11)–Fe(1)–N(12')	177.84(16)
N(12)–C(12)	1.147(5)	N(11)–Fe(1)–N(12)	88.87(16)
N(13)–C(13)	1.130(5)	N(11)–C(11)–S(11)	178.2(5)
C(11)–N(11)–Fe(1)	146.5(4)	N(12)–C(12)–S(12)	177.6(4)
C(12)–N(12)–Fe(1)	175.4(4)	N(13)–C(13)–S(13)	177.8(5)
<i>B</i> anions ^[a]			
Fe(2)–N(21)	2.045(4)	C(23)–N(23)–Fe(2)	178.4(4)
Fe(2)–N(23)	2.052(4)	N(21)–Fe(2)–N(23)	91.33(15)
Fe(2)–N(22)	2.057(4)	N(21)–Fe(2)–N(23)	88.67(15)
S(21)–C(21)	1.611(5)	N(21)–Fe(2)–N(22)	89.09(14)
S(22)–C(22)	1.627(5)	N(23)–Fe(2)–N(22)	89.58(15)
S(23)–C(23)	1.629(5)	N(21)–Fe(2)–N(22)	90.91(14)
N(21)–C(21)	1.152(5)	N(23)–Fe(2)–N(22)	90.42(15)
N(22)–C(22)	1.142(5)	N(21)–C(21)–S(21)	179.1(4)
N(23)–C(23)	1.148(5)	N(22)–C(22)–S(22)	178.1(4)
C(21)–N(21)–Fe(2)	169.9(4)	N(23)–C(23)–S(23)	179.0(5)
C(22)–N(22)–Fe(2)	175.2(4)		

[a] The *trans*-N–Fe–N angles are obligatorily 180°.

of 30° in M–N–C angles within the same molecule, as observed in the present case, is unusual, if not unique.

Sulfur coordination is not seen in either complex anion, any ligand N/S-orientation ambiguity in this regard being mitigated by the clear differentiation between N–C and C–S bonds in the lattice ($1.14 \pm 0.01 \text{ \AA}$ vs. $1.62 \pm 0.01 \text{ \AA}$, respectively) The thiocyanate ligands (particularly the sulfur atoms) show some librational mobility, principally in one of the local (coordination octahedron) Cartesian directions. For the bent thiocyanate ligands, this occurs at right-angles to the Fe–N–C angle, so is not connected with any intrinsic variation in the Fe–N–C angle. Even in the more

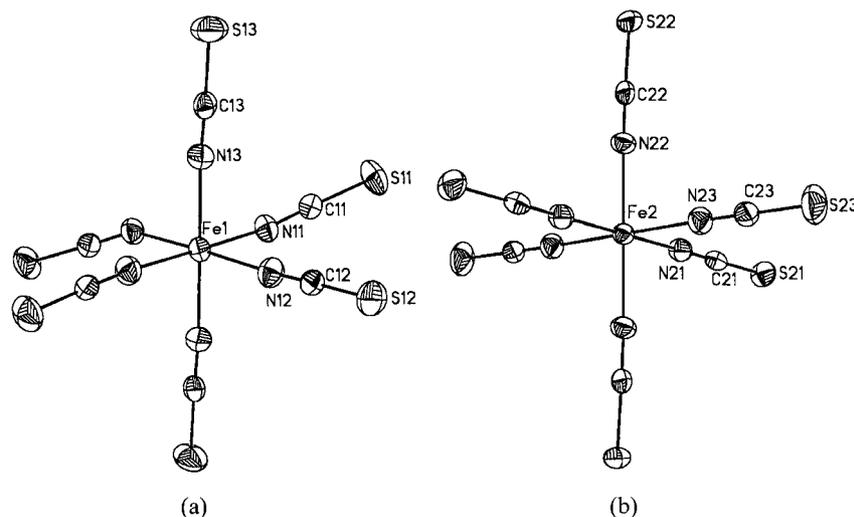


Figure 1. ORTEP diagrams of (a) the “*A*” anion in $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$, displaying the four “linear” and the two “bent” *cis*-Fe–N–CS linkages, and (b) the “*B*” anion, displaying the six linear Fe–N–CS linkages. In each ion, there is a unique facial set of NCS^- ligands with the opposite set symmetry-related to them. The ellipsoids are displayed at the 20% level.

symmetric *B* anions, the FeN_6 moiety is not homometric, the thiocyanate ligands being arranged (via their local inversion symmetry) as *trans* pairs, with the intermediate Fe–N distance (2.052 Å) being the mean of the shorter (2.045 Å) and longer (2.059 Å) values. Although static Jahn–Teller distortion is not expected (depending on the spin state, *vide infra*), the possibility of lattice dynamism should not be ruled out, and may be a factor relevant to the various spectroscopic results.^[11,12] We do not consider the difference (0.004 Å) between the average Fe–N distances in the *A* anions vs. the *B* anions to be chemically significant. Perhaps unexpectedly, the mutually *trans*-linear Fe–NCS in the *A* anion display the shortest (2.040 Å) Fe–N linkages, the Fe–N (bent) distances (2.046 Å) being hardly unique, but close to the average (2.050 ± 0.007 Å) of the six discrete Fe–N values in the unit cell. All the thiocyanate ligands are linear within 2° (N–C–S).

Magnetic susceptometry of $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ yielded a susceptibility ($\chi_{m,c} = 14.5 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$) at ambient temperature, corresponding closely to the high-spin moment reported previously.^[6] The variable-temperature results are shown in Figure 2; the value of χT (4.37 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) is essentially constant from ambient temperature down to 15 K, and may be compared with the value (4.375 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) expected for a $g = 2.0$, $S = 5/2$ ion.

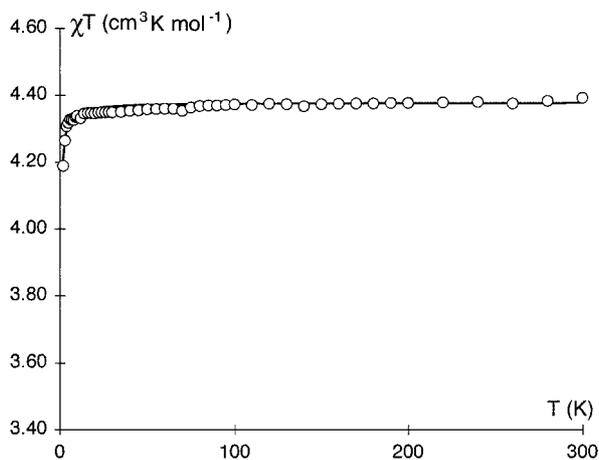


Figure 2. Plot of χT vs. T for $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$. The solid line is the fit computed with $g = 2.00(5)$, the circles being the experimental data. The goodness-of-fit index used was R^2 (on χT) = $\Sigma(\chi T_{\text{obsd.}} - \chi T_{\text{calcd.}})^2 / \Sigma(\chi T_{\text{obsd.}})^2 = 4 \times 10^{-6}$.

Below 15 K, χT decreases noticeably, reaching 4.19 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K. The data accede to a Curie–Weiss law, with $C = 4.375$ and $\theta = +0.07$ K. The downturn in χT at very low temperature could be attributed to the onset of weak intermolecular antiferromagnetic ordering (cf. θ value). However, we advocate a more informative interpretation, in which the departure from simple paramagnetism is due to zero-field splitting of the $S = 5/2$ state:^[21]

$$\chi_m = \frac{Ng^2\beta^2}{12kT} \cdot \frac{75e^{-10D/3kT} + 27e^{2D/3kT} + 3e^{8D/3kT}}{e^{-10D/3kT} + e^{2D/3kT} + e^{8D/3kT}}$$

Polycrystalline $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ at 77 K yielded a powder ESR spectrum with broad resonances ($\Delta H_{\text{p-p}}$ of 25–70 mT) typical of iron(III). An intense bisignate resonance at $g = 2.08$ is assigned to the (M_s) $-1/2 \rightarrow +1/2$ transition of $S = 5/2$ Fe^{III} , for which the ZFS parameter D is expected to be small ($D < hv$) when the ion is close to O_h symmetry.^[22] A band at $g = 5.68$ and shoulder near $g = 3.2$ are indicative of a non- O_h component, the g values for Fe^{III} being highly sensitive to D .^[23] If the D value for the *A* anions, for instance, dominates that from the more symmetric *B* anions, then attribution of the low- T downturn in the χT value to the ZFS of the *A* anions yields $D = +0.051(2) \text{ cm}^{-1}$. A first-order estimate of the resonance fields (Table 3) reveals that the observed EPR spectrum is in turn consistent with this interpretation, when the more anisotropic component has $D \approx 0.05 \text{ cm}^{-1}$. (There is no unique solution yielding values for both D_A and D_B ; the solution yields only that $D_A + D_B \approx 0.05 \text{ cm}^{-1}$.)

Table 3. Resonance fields with $D > 0$.

Transition	Energy	$g_{\text{app./calcd.}}$ ^[a]	$g_{\text{obsd.}}$
$-1/2 \rightarrow +1/2$	$g\beta H$	2.08	2.08
$-1/2 \leftrightarrow -3/2$	$\pm(2D - g\beta H)$	3.05	3.17
$-3/2 \leftrightarrow -5/2$	$\pm(4D - g\beta H)$	5.69	5.68
$+3/2 \leftrightarrow +5/2$	$4D + g\beta H$	1.27	^[b]

[a] Using $g = 2.08$, $D = 0.0485 \text{ cm}^{-1}$ at $\nu = 9.15 \text{ GHz}$. [b] Not observed.

The data thus confirm a high-spin state for iron(III) at all temperatures, so that it is clear that there is no spin-cross-over. The results also militate against any static Jahn–Teller distortion, which would require an inhomogeneous spin population in the e_g or t_{2g} subshell ($S = 1/2$, t_{2g}^5).

The Mössbauer spectroscopic results for $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ displayed in Table 4 and Figure 3 are in consonance with the bulk magnetochemical results. Data were obtained at both 300 K and 80 K, and the isomer shift is characteristic of iron(III).

Table 4. Mössbauer results.

Temp.	Isomer shift [$\text{mm} \cdot \text{s}^{-1}$]	Line width [$\text{mm} \cdot \text{s}^{-1}$]	Relative mössbauer effect (area/baseline)
300 K	+0.46	1.54	0.6%
80 K	+0.57	1.66	3.4%

Although the ambient-temperature data could be fitted with a non-zero quadrupole splitting (0.45 $\text{mm} \cdot \text{s}^{-1}$), its difference from zero was not of great statistical significance, and the quadrupole splitting actually diminished to essentially zero for the 80 K spectrum. Thus, the electronic field symmetry of the iron center is close to spherical, which matches its homoleptic, high-spin d^5 situation. However, the linewidths are unusually large, and there is a notable difference in sensitivity (amplitude response) between 80 K (higher) and 300 K (lower). This indicates a very low Debye temperature and the presence of numerous low-energy lattice phonon modes which serve as relaxation pathways for the γ -absorption recoil energy. This is especially so at room

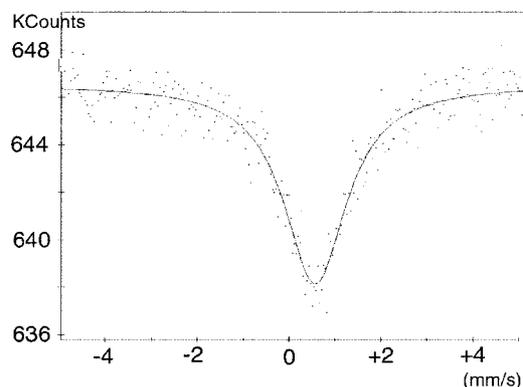
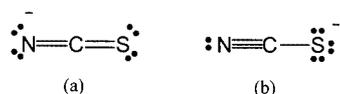


Figure 3. Mössbauer spectrum of $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ at 80 K. The abscissa is the isomer shift, relative to $\alpha\text{-Fe}$.

temperature, though the large linewidth would also require that the consequent polarisability be transmitted to the metal ion itself. This observation is consistent with the hypothesis of lattice dynamism (*vide supra*) – and the previously observed effects of applied pressure – i.e., the lattice is mechanically “soft”.

Similarly to prior reports for $[\text{Fe}(\text{NCS})_6]^{3-}$ salts,^[6,11,24] the infrared spectrum of $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ displayed very strong absorption in the ν_{CN} region, consisting of a band at 2060 cm^{-1} , along with a well-defined but lesser intensity absorption at 2012 cm^{-1} . Frequencies near 2050 cm^{-1} are traditionally considered typical of *N*-coordinated thiocyanate, while *S*-coordination shifts the frequency to near 2100 cm^{-1} , the ν_{CN} pattern in any case being much more dependent on the NCS^- binding mode than on molecular symmetry considerations.^[13] From an orbital hybridisation viewpoint (as implied by the resonance structures in Scheme 1), the higher C–N bond order can be associated with the more intense band assigned to the majority of the thiocyanate ligands coordinated in the linear mode [Scheme 1(b)], which, by requiring *sp* hybridisation at the nitrogen atom, elevates the C–N bond order. Thus, the two ν_{CN} bands' frequencies and relative intensities are actually quite consistent with the difference in ligand electronic structure between linear and bent NCS^- coordination. A similar correlation, between spin state and ν_{CN} (with $\nu_{\text{CN}} = 2110\text{ cm}^{-1}$), was seen for some (triaryltriazole)iron(II) *N*-thiocyanates.^[18] Inasmuch as the molar volume of an $[\text{M}(\text{NCS})_6]^{3-}$ anion should decrease when ligands transform from the linear to the bent coordination mode, such a transformation may well contribute to any hyperbaric reorganisation pathway. However, the facts that (a) these frequencies are slightly different from those reported previously for the tetraethylammonium salt,^[24] and (b) the previous Mössbauer study^[12] was performed on the *potassium* salt brings forward the likelihood that the precise coordination geome-



Scheme 1.

try in $[\text{Fe}(\text{NCS})_6]^{3-}$ is actually counteraction-dependent, opening the way for validation of further studies on a variety of $[\text{Fe}(\text{NCS})_6]^{3-}$ salts.

In acetonitrile solution at the 1 mM level, a quasireversible $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox couple was observed at $+0.11\text{ V}$ vs. the nonaqueous Ag^+/Ag electrode ($+0.41\text{ V}$ vs. SCE^[26]).

Conclusions

In $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$, two different types of complex ions are contained in the unit cell, though both possess exclusively *N*-coordination of the thiocyanate ligands. In one ion, the thiocyanate ligands are all essentially linearly bound, with an Fe-N-C angle of $174 \pm 4^\circ$, while in the other, two of the thiocyanate ligands are *cis*, with an Fe-N-C angle of 146.5° . The EPR, magnetic susceptibility and Mössbauer results show that all the iron(III) centers maintain the high-spin state down to 2 K. Infrared and Mössbauer spectra provide evidence for a lattice of unusual mechanical softness. Traditional criteria for interpretation of the infrared frequencies are not strictly applicable for this compound.

Experimental Section

$(\text{NMe}_4)_3[\text{Fe}(\text{NCS})_6]$ was prepared according to Forster and Goodgame,^[6] using tetramethylammonium thiocyanate obtained by metathesis between KNCS and Me_4NCl in ethanol. The product was recrystallised from ethanol, yielding crystals which indeed in reflected light appear olive-green, with a metallic lustre. Infrared spectra were obtained from powdered crystals and nujol oil mulls (to minimise pressurization) with a Thermo Nicolet Avatar 360 FT-IR equipped also with a Nicolet Smart MIRacle ATR diamond crystal accessory. Magnetic susceptibilities were measured with a Pd-standard-calibrated Quantum Design MPMS5S SQUID magnetometer, at a field of 0.1 T. EPR spectra were obtained with a Varian E-12 X-band instrument, calibrated with diphenylpicrylhydrazyl radical and chloropentaamminechromium(III) chloride. Mössbauer spectra were obtained in the transmission mode with a constant-acceleration-type spectrometer (Wissel), a liquid nitrogen cooled, bath-type cryostat being used for low-temperature spectra. An 800 MBq $^{57}\text{Co}(\text{Rh})$ sample was used as the γ -ray source, while isomer shifts are referred to α -iron at room temperature. The sample was measured in the form of a fine powder in order to avoid texture effects in the spectra. Spectra were deconvoluted using the MossWin 3.0 code,^[25] applying Lorentzian lineshape. Cyclic voltammetry was performed at 25°C in deoxygenated CH_3CN solution with $0.1\text{--}0.2\text{ M}$ Et_4NClO_4 as supporting electrolyte using a Bioanalytical Systems BAS 100A electrochemical analyzer. The three-electrode assembly comprised a Pt-wire working electrode, an Ag^+ (0.01 M , 0.1 M Et_4NClO_4 , CH_3CN)/Ag reference electrode (“APE”)^[26] and a Pt auxiliary electrode. For X-ray diffraction, a suitable crystal was mounted on a glass fiber with epoxy cement and attached to a goniometer head of a Siemens P4S diffractometer utilising a CCD area detector and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073\text{ \AA}$). Cell constants and orientation matrices were obtained by least-squares procedures using φ and ω scans, the data collection and reduction being controlled by Bruker SMART software. Absorption corrections ($\mu = 0.865\text{ mm}^{-1}$) were obtained with SHELXA.^[27] A total of 28471 reflections were collected (-29

$\leq h \leq 29$, $-10 \leq k \leq 10$, $-33 \leq l \leq 33$) in the θ range 1.45–24.71°. Solution, refinement and outputting were performed using the SHELX suite of programmes.^[27] The structure was refined with direct methods using full-matrix least-squares procedures, on F^2 against 5576 independent reflections with $F^2 > 2\sigma(F^2)$. H atoms were initially emplaced geometrically and then included in subsequent cycles of refinement.

Acknowledgments

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- $$\chi_m = \frac{Ng^2\beta^2}{12kT} \frac{\sum a_i e^{-E_i/kT}}{\sum b_j e^{-E_j/kT}}$$
- where the exponential terms represent the Boltzmann distribution over the M_s states of the Fe^{III} center, at $-8D/3$ ($M_s = \pm 1/2$), $-2D/3$ ($M_s = \pm 3/2$) and $+10D/3$ ($M_s = \pm 5/2$). The TIP was taken to be zero for this ⁶A_{1g} term: A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London, New York, **1968**, p. 67.
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