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


Keywords: Iron / Thiocyanate / X-ray diffraction / Magnetic properties / IR spectroscopy / Moessbauer spectroscopy / Coordination modes / Isomers

(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.

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 Morath[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 (μ = 5.92 μB). 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 intermolecular redox process (presumably corresponding to hyperbaric stabilisation of the LMCT excited state FeII–NCS·–; cf. ref.[10]) and also to the linkage isomerisation Fe–NCS ↔ Fe–SCN. The assignment of this remarkable isomerisation was based on the shifting of νFe–NCS and νC–N[6,11] to frequencies traditionally associated with M–SCN 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 counterion, 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] crystallizes from ethanol as unsolvated monoclinic crystals belonging to the space group C2/c.
The Hexakis(thiocyanato)ferrate(III) Ion

One of the tetramethylammonium ions is disordered.

Table 1. Crystal Data for (Me₄N)₃[Fe(NCS)₆] (CCDC-252536).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula:</td>
<td>C₁₈H₃₆FeN₉S₆</td>
</tr>
<tr>
<td>Formular mass:</td>
<td>626.77</td>
</tr>
<tr>
<td>a</td>
<td>24.9838(16) Å</td>
</tr>
<tr>
<td>b</td>
<td>9.3117(7) Å</td>
</tr>
<tr>
<td>c</td>
<td>28.624(2) Å</td>
</tr>
<tr>
<td>β</td>
<td>100.245(1)°</td>
</tr>
<tr>
<td>V</td>
<td>6553.0(8) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Crystal dimensions</td>
<td>0.4×0.18×0.1 mm</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.865 mm⁻¹</td>
</tr>
<tr>
<td>ρcalcd.</td>
<td>1.271</td>
</tr>
<tr>
<td>T</td>
<td>295(2) K</td>
</tr>
<tr>
<td>R(all)</td>
<td>0.107</td>
</tr>
<tr>
<td>Rₑ(all)</td>
<td>0.147</td>
</tr>
<tr>
<td>Final R</td>
<td>0.0548</td>
</tr>
<tr>
<td>Final Rₑ</td>
<td>0.127</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.032</td>
</tr>
</tbody>
</table>

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 [Fe(NCS)₆]³⁻ population (anions A, possessing C₃ symmetry), a mutually cis pair of the NCS⁻ ligands are in a “bent” mode, with the Fe–N–C angle at 146.5(4)°. Such structural diversity within the unit cell is reminiscent of previously reported instances, such as [Cu(Dipica)₂](BF₄)₂,[15] and [Ni(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 = Cd),[20] and a difference 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±0.01 Å vs. 1.62±0.01 Å, 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 (Me₄N)₃[Fe(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.](image-url)
symmetric B anions, the FeN₆ moiety is not homometric, the thioocyanate 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 thioocyanate ligands are 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 thioocyanate ligands are

![Image](https://example.com/image.png)

Figure 2. Plot of $\chi T$ vs. $T$ for (Me₄N)$_3[Fe(NCS)₆]$. 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 $\chi T$) = $\Sigma (\chi T_{\text{obd.}} - \chi T_{\text{calc.}})^2/\Sigma (\chi T_{\text{obd.}})^2 = 4 \times 10^{-4}$.

Below 15 K, $\chi T$ decreases noticeably, reaching 4.19 cm$^3$K·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 $\chi T$ at very low temperature could be attributed to the onset of weak intermolecular antiferromagnetic ordering (cf. $\theta$ 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]

$Z_m = \frac{Ng^2\beta^2}{12kT} \left[ \frac{75e^{-10g\beta I_{3z}}}{e^{-2g\beta I_{3z}}} + \frac{7e^{-2g\beta I_{3z}}}{e^{-2g\beta I_{3z}}} + \frac{3e^{g\beta I_{3z}}}{e^{g\beta I_{3z}}} \right]$

Although the ambient-temperature data could be fitted with a non-zero quadrupole splitting (0.45 mm$^{-1}$), 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 $\gamma$-absorption recoil energy. This is especially so at room
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 [Fe(NCS)6]3– salts,[6,11,24] the infrared spectrum of (Me₄N)₃[Fe(NCS)₆] displayed very strong absorption in the νCN 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 observed effects of applied pressure – i.e., the lattice is mechanically “soft”.

In (Me₄N)₃[Fe(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±4°, 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

(ΝMe₂)₃[Fe(NCS)₆] was prepared according to Forster and Goodgame[6] using tetramethylethylthiocyante obtained by metathesis between KCNS and Me₂NCl 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 MPMSSS 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 ⁵⁷Co(Rh) sample was used as the γ-ray source, while isomer shifts are referred to a-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.

Conclusions

In (Me₄N)₃[Fe(NCS)₆], the CN bands’ frequencies and relative intensities are actually countercation-dependent, opening the way for validation of further studies on a variety of [Fe(NCS)₆]³⁻ salts.

In acetonitrile solution at the 1 mm level, a quasi-reversible Fe³⁺/Fe²⁺ redox couple was observed at +0.11 V vs. the nonaqueous Ag⁺/Ag electrode (+0.41 V vs. SCE[26]).

Scheme 1.

Figure 3. Mössbauer spectrum of (Me₄N)₃[Fe(NCS)₆] at 80 K. The abscissa is the isomer shift, relative to α-Fe.
Solution, refinement and outputting were performed using the SHELX suite of programmes. 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 placed geometrically and then included in subsequent cycles of refinement.

Acknowledgments

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