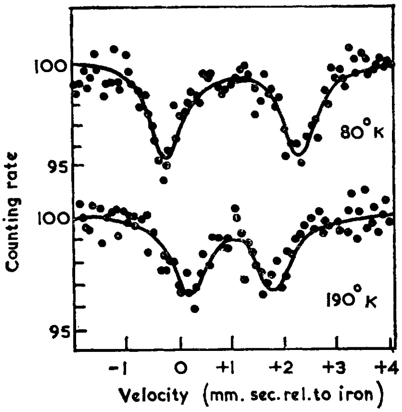
1290. *The Mössbauer Spectrum of the Tetrachloroferrate*(II) *Ion*

By T. C. GIBB and N. N. GREENWOOD

The Mössbauer spectrum of tetraethylammonium tetrachloroferrate(II) shows a temperature-dependent quadrupole splitting which is interpreted in terms of a distortion which lifts the degeneracy of the Fe^{II} e_g levels by 185 cm.$^{-1}$.

THE Mössbauer spectrum of iron(II) in a discrete tetrahedral environment has not previously been reported. Published accounts of the Mössbauer effect in high-spin iron(II) compounds have dealt almost exclusively with an octahedral environment of six ligands bonding through oxygen,[1-3] although Fe^{2+} has been observed in tetrahedral sites in spinels and other oxides.[4] This Paper describes measurements on a compound containing the tetrahedral ion $FeCl_4^{2-}$; these are of additional interest because of the anomalous magnetic moment of this ion.[5]

The Mössbauer spectrometer has been described elsewhere.[6] Samples of various tetrahalogenoferrates were kindly supplied by Professor R. S. Nyholm and Dr. B. Taylor of University College, London. Powdered samples were pressed between aluminium foil in a copper mount, and cooled to various temperatures in a glass cryostat insulated with foam plastic. Typical spectra for tetraethylammonium tetrachloroferrate(II) at 80°K and 190°K are shown in the Figure. Spectra could not be obtained at room temperature because of the low recoil-free fraction. Nor could the Mössbauer effect be observed in tetraethylammonium tetrabromoferrate(II) or cæsium tetrachloroferrate(II) even at 80°K because of the larger mass absorption coefficient associated with the heavier elements in these compounds.



Mössbauer spectra of $(Et_4N)_2FeCl_4$

The chemical shifts, δ, relative to metallic iron, the quadrupole splittings, Δ, and the γ-ray resonance line widths at half-height, Γ, for tetraethylammonium tetrachloroferrate(II) are given in the Table (±0·10 mm./sec.).

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[2] V. I. Goldanskii, "The Mössbauer Effect and its Application in Chemistry," New York Consultants Bureau, 1964.

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[4] T. Mizoguchi and M. Tanaka, *J. Phys. Soc., Japan*, 1963, **18**, 1301.

[5] N. S. Gill, *J.*, 1961, 3512.

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Mössbauer parameters * for $(Et_4N)_2FeCl_4$

Temp. (°K)	δ (mm./sec.)	Δ (mm./sec.)	Γ (mm./sec.)
80	1·00	2·49	0·79
190	0·93	1·63	0·75

* For ^{57}Fe, 1 mm./sec. = $4{\cdot}80 \times 10^{-8}$ ev.

These spectra show that, at the temperatures used, the compound gives a symmetrical doublet typical of high-spin Fe^{2+}, $e_g^3t_{2g}^3$. There is no indication of a six-line spectrum due to a hyperfine magnetic field resulting from ferro- or antiferro-magnetic interactions. This is consistent with the known temperature dependence of the magnetic susceptibility of this compound down to 95°K.[5] The quadrupole splitting is caused by the odd electron outside the half-filled *d* shell in the lower e_g levels. If these levels were in completely degenerate groups, it can be shown, in an analogous way to the octahedral case,[7] that there would be no quadrupole splitting. The temperature dependence of the quadrupole splitting results from a small splitting of the e_g energy levels. A full interpretation of this dependence would follow the approach of Ingalls [8] and would include the e_g splitting, Δ_1, the effect of covalency on the radial dependence function of the sixth *d* electron, and the spin-orbit coupling effect. This is impracticable with the data obtainable from the present system. However, a simple treatment of the temperature dependence, neglecting covalency and spin–orbit coupling has been given for the octahedral case.[7] Recalculating this for a tetrahedral environment gives the following relation between the quadrupole splitting, Δ, and the temperature, *T*:

$$\Delta = \Delta_0[1 - \exp(-\Delta_1/\boldsymbol{k}T)]/[1 + \exp(-\Delta_1/\boldsymbol{k}T)]$$

where Δ_0 is the low-temperature limit of Δ as *T* approaches absolute zero, Δ_1 is the energy difference between the two e_g levels, and $\boldsymbol{k}$ is Boltzmann's constant. At high temperatures Δ approaches zero, *i.e.*, the two e_g levels have equal electron population when $\boldsymbol{k}T \gg \Delta_1$. The two values of the quadrupole splitting in the Table lead to a value of ~2·7 mm./sec. for Δ_0 and an approximate value of 185 ± 50 cm.$^{-1}$ for the e_g energy difference Δ_1. This is smaller than the resolution of normal ultraviolet and visible spectrometers, but might be observable directly in the infrared region at low temperatures. It is unlikely that the implied minute distortion of the four chlorine atoms from perfect tetrahedral symmetry about the iron atom could be detected by *X*-ray diffraction techniques. The results constitute the first evidence for such a distortion in an ion of this type.

The chemical shifts in the Table are smaller than those normally observed for hydrated high-spin iron(II); [1-3] this indicates that replacement of six oxygen ligands by four chloride ligands causes an overall increase in the *s* electron density at the iron nucleus.[9] This, in turn, implies an increase in covalency, that is, an increased involvement of the iron 4*s* and $3d(t_{2g})$ orbitals in the bonding. The precise magnitude of the chemical shift of $FeCl_4^{2-}$ compared with Fe^{2+} in an oxide lattice cannot be calculated quantitatively, but qualitatively it can be seen to depend on the interplay of several factors. Thus there is the increase in 4*s* electron density at the iron nucleus as a result of the increased covalency. This is counteracted slightly by the increased shielding of the nucleus which arises from the increased 3*d* occupation. A further auxilliary effect is the expansion of the outer orbitals of the iron atom by the nephelauxetic effect which diminishes the 3*d* shielding, thus again increasing the total *s* electron density and reducing the chemical shift. In this connection it is relevant to note that for the ion $FeCl_4^-$ (where there is one less electron than in $FeCl_4^{2-}$) the chemical shift [10] is about 0·7 mm./sec. less than for $FeCl_4^{2-}$. There is also the possibility of configuration interaction between $Fe^{2+}(3d^6)$ and $Fe^{2+}(3d^54s^1)$.

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[8] R. Ingalls, *Phys. Rev.*, 1964, **133**, A, 787.
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In summary this Paper reports the first Mössbauer spectrum of a discrete, tetrahedral, high-spin iron(II) complex. The magnitude of the chemical shift in $FeCl_4^{2-}$ is consistent with an increase in covalency compared with Fe^{2+} in hydrated compounds, and the existence of a temperature dependent quadrupole split is consistent with a distortion which lifts the degeneracy of the lower e_g levels by about 185 cm.$^{-1}$. This is the first reported evidence for the distortion expected in a tetrahedral d^1 or high-spin d^6 complex. There is no indication of ferro- or antiferro-magnetic exchange down to 80°K; the enhanced magnetic moment above the spin-only value is thus still not satisfactorily explained.

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DEPARTMENT OF INORGANIC CHEMISTRY,
THE UNIVERSITY, NEWCASTLE UPON TYNE 1.

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