

Crystal and Molecular Structures of Rinneite, Sodium Tripotassium Hexachloroferrate(II), and Hexaamminecobalt(III) Hexachloroferrate(III). Comparison of Iron-Chloride Distances in Hexachloroferrates(II) and -(III)

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The crystal structures of sodium tripotassium hexachloroferrate(II) (rinneite, $\text{NaK}_3\text{FeCl}_6$, I) and hexaamminecobalt(III) hexachloroferrate(III) ($\text{Co}(\text{NH}_3)_6\text{FeCl}_6$, II) have been determined by X-ray methods using three-dimensional counter data. Crystals of I are trigonal, space group $R\bar{3}c$, with $a = 8.3376$ (7) Å, $\alpha = 92.29$ (1)°, and $Z = 2$. Crystals of II are cubic, space group $Pa\bar{3}$, with $a = 11.2506$ (4) Å and $Z = 4$. The final R factors are 0.022 and 0.025, for 450 and 1328 reflections with $I > 3[\sigma(I)]$, respectively. The $\text{Fe}^{\text{II}}-\text{Cl}$ and $\text{Fe}^{\text{III}}-\text{Cl}$ bond lengths are 2.5100 (5) and 2.3926 (3) Å, respectively. The difference of 0.12 Å is similar to those observed between tetrachloroiron(II) and -iron(III) (0.11 Å), and between hexaquaairon(II) and -iron(III) (0.14 Å). Chloride-chloride repulsion is suggested to affect the $\text{Fe}^{\text{III}}-\text{Cl}$ distance in FeCl_6^{3-} .

Introduction

A recently advanced hypothesis¹ suggests that the difference in metal-ligand distances between $\text{M}^{\text{II}}\text{L}_6$ and $\text{M}^{\text{III}}\text{L}_6$ complexes varies inversely with the strength of the ligand field of L. There appears to be a correlation between the change in bond length upon a change of oxidation state and the position of the ligand in the spectrochemical series. This hypothesis was inferred from comparison of iron(II) and iron(III) structures. Whereas the difference in M-L distances between $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is 0.14 Å, there is no difference between $\text{Fe}(\text{phen})_6^{2+}$ and $\text{Fe}(\text{phen})_6^{3+}$,^{2,3} and between $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ the difference is -0.03 Å; i.e., the $\text{Fe}^{\text{II}}-\text{C}$ distance⁴ is shorter than the $\text{Fe}^{\text{III}}-\text{C}$ distance.⁵

The hypothesis is consistent with recently acquired evidence on cobalt complexes. The difference in M-L distances between $\text{Co}(\text{NH}_3)_6^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ is reported⁶ to be 0.18 Å. With the weaker field H_2O ligand a difference of 0.21 Å is observed between the Co-O distances in $\text{Co}(\text{H}_2\text{O})_6^{3+}$ ⁷ and $\text{Co}(\text{H}_2\text{O})_6^{2+}$.⁸ With the strong-field $-\text{NO}_2$ ligand a redetermination⁹ of a structure containing $\text{Co}(\text{NO}_2)_6^{4-}$ indicates a $\text{Co}^{\text{II}}-\text{N}$ bond only 0.06 Å longer than in $\text{Co}^{\text{III}}(\text{NO}_2)_6^{3-}$.¹⁰

This hypothesis requires that for ligands weaker than water, the bond length differences between iron(II) and iron(III) be greater than the 0.14 Å observed between $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. As a test we have determined structures containing hexachloroferrate in the II and III oxidation states. For FeCl_6^{4-} this involves the redetermination of an earlier inaccurate structure¹¹ of the mineral rinneite, $\text{NaK}_3\text{FeCl}_6$. For FeCl_6^{3-} the structure of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ was determined, taking advantage of the stabilization of this anion by tripositive complexes.¹²

Experimental Section

Data Collection. $\text{NaK}_3\text{FeCl}_6$ (Rinneite). Colorless, rhombohedral crystals of rinneite were prepared by a published method,¹¹ with use of, however, only one-tenth of the reported amount of NaCl. The crystals are very susceptible to atmospheric moisture and oxygen. A crystal with maximum dimensions of 0.25 mm was sealed in a glass capillary and mounted on an Enraf-Nonius CAD4-F diffractometer. Automatic centering and indexing of 12 low-angle reflections confirmed the previously published¹¹ symmetry and cell dimensions. Systematic absences confirmed the previous assignment¹¹ of the space group $R\bar{3}c$. Cell parameters of $a = 8.3376$ (7) Å and $\alpha = 92.29$ (1)° were obtained by least-squares refinement of the 2θ values of 18 reflections measured with graphite-monochromated $\text{Mo K}\alpha_1$ radiation ($\lambda = 0.70926$ Å) in the range of $39 \geq 2\theta \geq 52^\circ$. Profile analyses of a few low-angle reflections indicated that an $\omega-(\lambda/\delta)2\theta$ scan method most closely represented the optimum conditions for data collection.¹³ Scan ranges in ω were calculated from the formula $S = M_s + W_s \tan \theta$, where M is estimated from the mosaic spread of the crystal and W allows for increasing peak width due to wavelength dispersion. The values of M_s and W_s were chosen as 1.0 and 0.35° , respectively. The take-off angle was 4.0° , and the counter was positioned 173 mm from the crystal with a vertical aperture width of 4 mm. The horizontal aperture width was calculated from the formula $A = M_a + W_a \tan \theta$, with M_a and W_a chosen as 1.2 and 0.35 mm, respectively. Each calculated scan range was extended on either side by 25% to accommodate the moving-background determinations (B_1 and B_2). Each reflection was initially measured with use of a rapid (6° min^{-1}) prescan. The net intensity was calculated as $I = P - 2(B_1 + B_2)$ where P is the peak count, with standard deviation $\sigma(I) = [P + 4(B_1 + B_2)]^{1/2}$. A new scan speed was calculated such that the ratio $[\sigma(I)]/I$ was equal to a preset value ($\sigma_F = 0.01$), with the proviso that the total time taken for the final scan should not exceed a preset limit ($T_{\text{max}} = 120$ s). Additionally if $[\sigma(I)]/I$ in the prescan were greater than unity, the final scan was not performed and the reflection was tagged as unobservably weak. A unique set of data (hkl for $0 < h < k$, $0 < k < l$) was measured to a 2θ limit of 70° . Three reference reflections, measured every 5000 s of X-ray exposure, showed a consistent drop in intensity to 85% of their original intensities at the end of the collection of the unique data. The problem of crystal movement was overcome by the reorientation facility on the CAD4, whereby the positions of 3 reference reflections were monitored every 40 reflections. If the position of any of these reference reflections differed from its calculated position by more than $\delta_D = 0.08^\circ$, the orientation matrix was redetermined by centering a number of strong high-angle reflections. Three such reorientation corrections were made according to this rather severe criterion. Visual inspection indicated that the crystal remained centered in the beam. In order to provide a basis for the calculation of standard deviations $\sigma(F)$, we measured 418 equivalent data (hkl for $0 < k < l$, $0 < l < h$) ($2\theta < 70^\circ$). In all,

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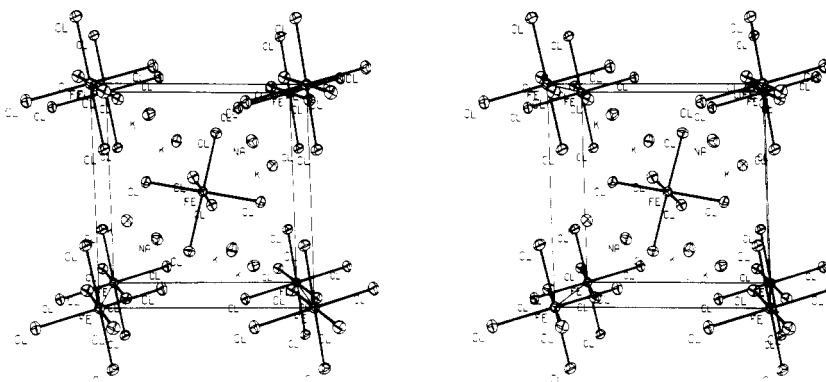


Figure 1. Stereoscopic view of the unit cell of NaK₃FeCl₆.

1075 data were collected. At the end of data collection, the intensities of the standard reflections had fallen to 80% of their initial values.

The data were adjusted to allow for Lorentz, polarization, decomposition, and absorption effects. The polarization correction was based on the assumption that the graphite monochromator was ideally mosaic. The form of the correction term¹⁴ was $1/p = (\cos^2 2\theta + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m)$ where θ is the Bragg angle of the appropriate reflection and θ_m is the Bragg angle of the monochromator, in this case 6.09°. The decomposition correction was based upon the mean intensity of each group of standards relative to the first group. The mean relative intensity of each group was plotted against the accumulated exposure time. The groups of standards were considered six at a time, the correction to be applied for the first time between groups three and four. A straight line $I_c = Rt + C$ was fitted to the six points, where t is the accumulated exposure time, and the correction factor was applied to the data such that $I = I_u/I_c$ where I is the corrected intensity and I_u is the uncorrected intensity. Values of I_c for the first two groups were assigned as 1, i.e., no decomposition. Absorption methods were calculated with use of the Gaussian integration method,¹⁵ in this case with $\mu = 37.55 \text{ cm}^{-1}$ and an $8 \times 8 \times 8$ grid of sampling points. For all reflections with $I > 3[\sigma(I)]$, the weighted and unweighted discrepancy factors defined^{16,17} as

$$R_u = [\sum_h \sum_i (F_h - F_{hi})^2 / \sum_h \sum_i F_{hi}^2]^{1/2}$$

and

$$R_s = [\sum_h \sum_i w_{hi} (F_h - F_{hi})^2 / \sum_h \sum_i w_{hi} F_{hi}^2]^{1/2}$$

where F_h is the weighted mean of the i observations of F_{hi} and w_{hi} is the statistical weight associated with each F_{hi} value, are 0.022 and 0.021, respectively. An estimate of the anisotropic errors in the data was made with use of those reflections measured both in the initial unique data set and in any subsequent equivalent data sets. A curve was fitted to a plot of mean $[\sum_h \sum_i (F_h - F_{hi})^2 - \sigma_{\text{stat}}^2(F_h)]$ values vs. $|F_h|$ for all common reflections with $I > 3[\sigma(I)]$ in ranges of $|F_h|$, where $\sigma_{\text{stat}}^2(F_h)$ is the statistical variance of the weighted mean structure factors, F_h , i.e., $\sigma_{\text{stat}}^2(F_h) = (\sum_h \sum_i w_{hi})^{-1}$. The variance of the weighted mean structure factor was then calculated as the sum of the statistical variance and the value calculated from the above curve.¹⁸ In cases where crystal movement and decomposition were not as severe as in the present case, all equivalent data would be averaged on a weighted basis, i.e., $F = \bar{F}_h$ (e.g., see next section). For rinneite, the equivalent data could be considered unreliable due to the significant decomposition of the crystal prior to this stage of data collection. Therefore, the values of F used in this structure analysis are those of the initially collected unique data set. However, in order to obtain a conservative estimate of errors, the calculated standard deviations $\sigma(F)$ are based on the entire data set. The final data set consisted of 594 unique reflections of which 450 had $I > 3[\sigma(I)]$ and were used in the subsequent analysis.

Table I. Final Fractional Coordinates ($\times 10^5$) for NaK₃FeCl₆

atom	x	y	z
Fe	50 000	50 000	50 000
K	12 598 (5)	37 402 (5)	75 000
Cl	41 962 (6)	21 254 (5)	54 528 (5)
Na	25 000	25 000	25 000

Table II. Final Fractional Coordinates ($\times 10^4$) for Co(NH₃)₆FeCl₆

atom	x	y	z
Fe	0	0	0
Co	5000	5000	5000
Cl	-720.4 (3)	1319.8 (2)	1504.0 (2)
N	5999 (1)	6315 (1)	4430 (1)
H(1)	5770 (24)	7050 (23)	4639 (24)
H(2)	6702 (23)	6246 (23)	4658 (22)
H(3)	6011 (21)	6382 (21)	3675 (23)

Co(NH₃)₆FeCl₆. Multifaceted crystals of Co(NH₃)₆FeCl₆ were prepared by the method of Hatfield et al.¹² A crystal with maximum dimension of 0.25 mm was used for data collection. Crystal orientation, calculation of cell parameters, and collection of data followed the procedure described above. The crystals are cubic, space group $Pa\bar{3}$ with $a = 11.2506$ (4) Å. Unique ($0 < h < k, l$) and equivalent ($0 < k < h, l$) data were measured up to a limit of 100° in 2θ using an ω -($^4/6$) 2θ scan. Values of data constants defined as above were as follows: $M_s = 0.8^\circ$, $W_s = 0.35$, $M_a = 1.5 \text{ mm}$, $W_a = 0.35$, $\sigma_F = 0.01$, $T_{\text{max}} = 120 \text{ s}$. There was no significant crystal decomposition during data collection. In all, 5105 reflections were measured. The data were adjusted for Lorentz, polarization, and absorption ($\mu = 33.0 \text{ cm}^{-1}$, $6 \times 6 \times 6$ grid of sampling points) effects as before. The discrepancy factors R_u and R_s were 0.010 and 0.012, respectively. Calculation of standard deviations, and weighted data averaging were carried out to give a final data set of 2491 unique reflections of which 1328 had $I > 3[\sigma(I)]$ and were used in the subsequent analysis.

Solution and Refinement of the Structure. Both structures were solved by standard heavy-atom methods and refined by full-matrix least squares with use of X-RAY 76.¹⁹ The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms in Co(NH₃)₆FeCl₆ were located from an ($F_o - F_c$) synthesis and refined isotropically. An isotropic extinction parameter was also refined. The final values of R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) and R_w ($= (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$) for observed reflections are as follows: rinneite, 0.022 and 0.035; Co(NH₃)₆FeCl₆, 0.025 and 0.023, respectively. The error in an observation of unit weight is 1.04 for rinneite and 1.24 for Co(NH₃)₆FeCl₆. In each case final ($F_o - F_c$) syntheses were featureless and analysis of $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ and of $\sin \theta$ showed no systematic trends. Final positional parameters are listed in Tables I and II. Lists of thermal parameters and observed and calculated structure factors are available.²⁰ Values of scattering factors for neutral Fe, Co, K, Cl, Na, and N and of bonded H, together with anomalous dispersion terms

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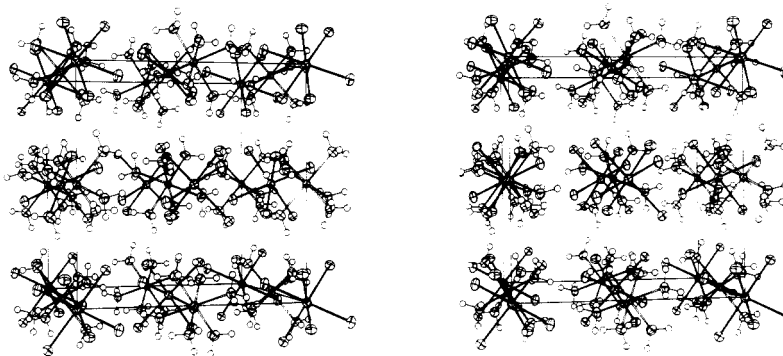


Figure 2. Stereoscopic view of the unit cell of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$. The Fe-Cl bonds are shown as solid lines and the Co-N bonds as open lines.

Table III. Interatomic Distances (Å) and Angles (Deg) for $\text{K}_3\text{NaFeCl}_6^a$

Fe-Cl	2.5100 (5)	Na-Cl	2.8244 (5)
K-Cl	3.3367 (7)	K-Cl ^{iv}	3.2463 (6)
K-Cl ⁱⁱ	3.1752 (6)	K-Cl ^{vi}	3.2137 (7)
Cl-Fe-Cl ^{viii}	180.0	Cl-Na-Cl ⁱ	76.56 (2)
Cl-Fe-Cl ^x	88.39 (2)	Cl-Na-Cl ^{viii}	127.69 (2)
Cl-Fe-Cl ^{xii}	91.61 (2)	Cl-Na-Cl ^{xii}	148.97 (2)
		Cl-Na-Cl ^{xiv}	89.81 (2)
Cl-K-Cl ⁱⁱ	67.06 (2)	Cl ⁱⁱ -K-Cl ^{vi}	130.45 (2)
Cl-K-Cl ^{iv}	64.21 (2)	Cl ⁱⁱ -K-Cl ^{ix}	90.56 (2)
Cl-K-Cl ^{vi}	122.14 (2)	Cl ⁱⁱ -K-Cl ^{xi}	73.42 (2)
Cl-K-Cl ^{vii}	69.82 (2)	Cl ⁱⁱ -K-Cl ^{xiii}	116.39 (2)
Cl-K-Cl ^{ix}	138.97 (2)	Cl ^{iv} -K-Cl ^{vi}	153.21 (2)
Cl-K-Cl ^{xi}	133.82 (2)	Cl ^{iv} -K-Cl ^{ix}	74.17 (2)
Cl-K-Cl ^{xiii}	90.56 (2)	Cl ^{iv} -K-Cl ^{xi}	91.53 (2)
Cl ⁱⁱ -K-Cl ^{iv}	68.17 (2)	Cl ^{vi} -K-Cl ^{ix}	161.95 (2)
K-Cl-Na	91.50 (2)	Na-Cl-Fe	80.73 (2)
K-Cl-K ⁱ	167.45 (2)	K ⁱ -Cl-K ⁱⁱⁱ	105.83 (2)
K-Cl-K ⁱⁱⁱ	85.03 (2)	K ⁱ -Cl-K ^v	87.17 (2)
K-Cl-K ^v	85.64 (2)	K ⁱ -Cl-Fe	85.66 (2)
K-Cl-Fe	83.73 (2)	K ⁱⁱⁱ -Cl-K ^v	94.78 (2)
Na-Cl-K ⁱ	93.40 (2)	K ⁱⁱⁱ -Cl-Fe	168.41 (2)
Na-Cl-K ⁱⁱⁱ	96.75 (2)	K ^v -Cl-Fe	87.21 (2)
Na-Cl-K ^v	167.84 (2)		

^a Superscripts for the distances and angles refer to the following symmetry codes: (i) z, x, y ; (ii) $1-z, 1-x, 1-y$; (iii) $1-z, -x, 1-y$; (iv) y, z, x ; (v) $-y, -z, -x$; (vi) $-y, 1-z, 1-x$; (vii) $1/2-y, 1/2-x, 3/2-z$; (viii) $1/2-y, 1/2-x, 1/2-z$; (ix) $z-1/2, 1/2+y, 1/2+x$; (x) $z-1/2, y-1/2, z-1/2$; (xi) $1/2-z, 1/2-y, 3/2-x$; (xii) $1/2-z, 1/2-y, 1/2-x$; (xiii) $x-1/2, z-1/2, 1/2+y$; (xiv) $1/2-x, 1/2-z, 1/2-y$.

for all nonhydrogen atoms, were taken from ref 21.

Description of the Structures

Rinneite. The structure of rinneite found in this work is illustrated in Figure 1. All atoms other than Cl are situated on positions of special symmetry. The Fe atom has point symmetry $\bar{3}$ and the Na atom point symmetry 3_2 , in opposite positions to those originally proposed,¹¹ as intimated in a subsequent review publication²² and by the proposed structure for the apparently isomorphous K_4CdCl_6 .²³

Each of these two atoms is surrounded by six Cl atoms. All of the Fe-Cl bonds are symmetrically equivalent, as are the Na-Cl contacts. The FeCl_6 coordination polyhedron is very close to octahedral, with no angular deviation from this symmetry greater than 2° (see Table III). The Na octahedron is more distorted. The K atom lies on a 2-fold axis. It is

Table IV. Interatomic Distances (Å) and Angles (Deg) for $\text{Co}(\text{NH}_3)_6\text{FeCl}_6^a$

Bond Distances and Angles			
Fe-Cl	2.3926 (3)	Co-N	1.965 (1)
N-H(1)	0.90 (3)	N-H(3)	0.85 (3)
N-H(2)	0.84 (3)		
Cl-Fe-Cl ⁱ	180.00	N-Co-N ⁱⁱ	180.00
Cl-Fe-Cl ^{iv}	90.62 (1)	N-Co-N ^{vi}	90.12 (4)
Cl-Fe-Cl ^{vii}	89.38 (1)	N-Co-N ^{vii}	89.88 (4)
Co-N-H(1)	116 (2)	H(1)-N-H(2)	106 (3)
Co-N-H(2)	112 (2)	H(1)-N-H(3)	101 (3)
Co-N-H(3)	114 (2)	H(2)-N-H(3)	107 (3)

Hydrogen Bonding

A	B	A...B	H...B	A-H...B
N	Cl ⁱⁱⁱ	3.307 (1)	2.47 (3)	169 (2)
N	Cl ^v	3.555 (1)	2.54 (3)	164 (2)

^a Superscripts refer to the following symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $-x, y, z$; (iv) y, z, x ; (v) $-y, z, -x$; (vi) z, x, y ; (vii) $-z, -x, -y$.

surrounded by eight Cl atoms at distances ranging from 3.1752 (6) to 3.3367 (7) Å. The Cl atom has contacts from Fe, Na, and four K atoms. The arrangement of these atoms about the Cl is reasonably close to octahedral, with maximum angular deviations from this symmetry being about 16° .

$[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$. This compound (Figure 2) is isomorphous with other cubic metal-hexaammine salts of similar trivalent anions such as $[\text{Cr}(\text{NH}_3)_6][\text{FeF}_6]$ ²⁴ and $[\text{Cr}(\text{NH}_3)_6][\text{MnF}_6]$,²⁴ $[\text{Co}(\text{NH}_3)_6][\text{TiCl}_6]$,²⁵ and $[\text{Co}(\text{NH}_3)_6][\text{BiCl}_6]$.²⁶ In addition, $[\text{Co}(\text{NH}_3)_6][\text{SbCl}_6]$ ²⁷ is reported to crystallize in an orthorhombic space group with almost equal unit cell axial lengths. The three independent Cl atoms have positions in the unit cell related by almost perfect cubic symmetry; hence all Sb-Cl bond lengths are equal.

The Co and Fe atoms in $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ have the same $\bar{3}$ point symmetry as the Fe atoms in rinneite. The Cl, N, and H atoms are all situated on positions of general symmetry. All of the Co-N bonds are symmetrically equivalent, as are the Fe-Cl bonds. The Co-N bond length of 1.965 (1) Å is normal. The Co coordination is very close to octahedral with deviations from octahedral symmetry less than 0.2° (see Table IV). The coordination about the Fe atom is very close to octahedral with maximum angular deviation of 0.7° from the ideal. The Cl atom forms two hydrogen bonds to different ammine groups with Cl...H distances of 2.47 (3) and 2.54 (3) Å, Cl...N distances of 3.306 (1) and 3.355 (1) Å, and included angles of 169 (2) and 162 (2) $^\circ$, respectively.

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Discussion

The Fe–Cl distance in the hexachloroferrate(II) atom is 2.5100 (5) Å. This is apparently the first determination of this distance in the FeCl₆⁴⁻ species, but the bond length is nearly identical with that found in *trans*-Fe(H₂O)₄Cl₂: 2.526 (1) Å (X-ray)²⁸ and 2.514 (1) Å (neutron).²⁹ These distances are 0.22–0.23 Å longer than 2.292 (2) Å found in tetrahedral tetrachloroferrate(II).³⁰

The Fe–Cl distance in the hexachloroferrate(III) anion is 2.3926 (3) Å. This is nearly identical with the distance of 2.409 Å in Cs₂NaFeCl₆ quoted²⁹ from unpublished neutron diffraction results.³¹ It is also nearly identical with the average Fe–Cl distance of 2.40 Å found in Fe₂Cl₉³⁻, but in the binuclear complex the Fe^{III}Cl₆ octahedron is significantly distorted, with a terminal Fe–Cl distance of 2.270 (4) Å and a bridge Fe–Cl distance of 2.538 (3) Å.³²

The difference between the Fe^{II}–Cl and Fe^{III}–Cl distances in FeCl₆ octahedra is thus only 0.12 Å. This is remarkably similar to the difference of 0.11 Å found between Fe^{II}–Cl and Fe^{III}–Cl distances in FeCl₄ tetrahedra,³⁰ even though the Fe–Cl bonds are ≈0.2 Å longer in the octahedra in each oxidation state. This similar bond length difference between octahedral and tetrahedral coordinations is unexpected, since the electronic structures and d-electron orbital distribution differ. The bond length difference of 0.12 Å for the FeCl₆ octahedra is less than 0.14 Å found between Fe(H₂O)₆²⁺ and Fe(H₂O)₆³⁺. This contradicts the hypothesis stated in the Introduction, which predicts a larger bond length difference between oxidation states for the weaker field Cl⁻ ligand.

We suggest as an explanation for these observations that a steric effect operates in the hexachloroferrate(III) complex, preventing a shorter Fe^{III}–Cl distance due to anion–anion, i.e., chloride–chloride repulsions. This idea was in fact suggested by Hatfield et al. in the original preparative work¹² to account for the instability of hexachlorometalate(III) complexes of the first transition series.

Two lines of evidence are consistent with this idea. First, there are few M–Cl distances shorter than 2.4 Å found in hexachlorometalate(III) species. A distance of 2.375 (5) Å is reported³³ for RuCl₆³⁻. In the higher M(IV) oxidation state some shorter distances are known, 2.353 (4) Å for ReCl₆²⁻³⁴ and 2.318 (2) Å for RuCl₆²⁻.³⁵

Second, Fe^{III}–Cl distances are considerably shorter in complexes with fewer chloride ligands. Distances as short as 2.236 (4) and 2.251 (4) Å are found in *cis*-[FeCl₂(H₂O)₄]⁺³⁶ and 2.283 and 2.278 Å in *cis*-[FeCl₂(DMF)₄]⁺.³⁷ Somewhat longer distances are observed in *trans* structures, but these are still shorter than found in FeCl₆³⁻. In *trans*-[FeCl₂(H₂O)₄]-Cl·2H₂O the Fe–Cl distance is 2.30 (2) Å;³⁸ in an earlier structure of *trans*-[FeCl₂(H₂O)₄][SbCl₆]·4H₂O it is reported³⁹ to be 2.36 Å. Finally, in *trans*-[FeCl₂(Me₂SO)₄][FeCl₄] it is 2.366 (3) Å.⁴⁰

An alternative inference from the comparison of the *cis*- and *trans*-[FeCl₂(H₂O)₄]⁺ structures just cited is a significant *trans* lengthening effect of the chloride ligand. This, together with an increase in negative charge on the complex, could lead to the longer observed distance in FeCl₆³⁻. If such electronic instead of steric effects are responsible for the longer Fe–Cl distance, they are applicable only in the Fe^{III} oxidation state, since, as described above, the Fe^{II}–Cl distances in *trans*-[FeCl₂(H₂O)₄] and FeCl₆⁴⁻ are nearly identical.

Whatever the reason for the long Fe^{III}–Cl distance in FeCl₆³⁻, it is clear that the choice of hexachloroiron complexes has not provided an unambiguous test of the hypothesis stated in the Introduction. An alternative comparison between *trans*-[FeCl₂(H₂O)₄]^{28,29} and *trans*-[FeCl₂(H₂O)₄]⁺^{38,39} suggests a difference of 0.22 (3) Å between Fe^{II}–Cl and Fe^{III}–Cl. In these complexes, however, the Fe–OH₂ distances are nearly the same, in contrast to the 0.14-Å difference between Fe(H₂O)₆²⁺ and Fe(H₂O)₆³⁺. While these observations can be rationalized by simple ligand field concepts, they indicate that comparison of bond length differences between complexes with different coordination spheres is unreliable.

We conclude that the results of the present work are not inconsistent with the hypothesis stated above¹ and suggest that steric effects may affect the metal–ligand distances in hexachlorometalate(III) complexes.

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Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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