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Structure of Tetramethylammonium Tetrachloroferrate(II), [N(CH₃)₄]₂[FeCl₄]. Comparison of Iron(II) and Iron(III) Bond Lengths in High-Spin Tetrahedral Environments

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The structure of tetramethylammonium tetrachloroferrate(II), [(CH₃)₄N]₂[FeCl₄] has been determined from three-dimensional X-ray data collected by counter techniques. The material crystallizes in the orthorhombic space group D_{2h}^{16} - $Pnma$ with $a = 12.312$ (2) Å, $b = 9.033$ (2) Å, $c = 15.580$ (3) Å, $Z = 4$, $\rho_{\text{meas}} = 1.32$ (1) g/cm³, and $\rho_{\text{calcd}} = 1.326$ g/cm³. The structure has been refined by a full-matrix least-squares procedure to a conventional R index (on F) of 0.053 for 1149 observations having $F_o^2 > 3\sigma(F_o^2)$. The iron atom has a crystallographically imposed mirror plane and has a slightly distorted tetrahedral geometry. The Fe(II)-Cl bond distances are 2.2902 (23), 2.2958 (16), and 2.2891 (23) Å and average 2.292 (2) Å. Previous studies have shown that in the FeCl₄⁻ anion Fe(III)-Cl bond distances average 2.185 Å. The FeCl₄²⁻ anion (high-spin Fe(II)) thus has bond lengths 0.11 Å longer than those found in the FeCl₄⁻ anion (high-spin Fe(III)). This expansion of the coordination sphere upon reduction is larger than is found in octahedral complexes. Similar changes in bond lengths are to be expected in some of the iron-sulfur proteins.

Introduction

Chemical, spectroscopic, and structural studies of iron-sulfur proteins have revealed that most of these complex species contain iron coordinated in a tetrahedral manner to four sulfur ligands.¹ Depending upon the state of the protein the iron can be in either the Fe(II) or the Fe(III) state. Since certain individual proteins are known to contain Fe(II) in their reduced state and Fe(III) in their oxidized state,² a detailed understanding of the stereochemical differences between Fe(II) and Fe(III) tetrahedral complexes would be useful.

For such a study we have chosen the high-spin FeCl₄²⁻ and FeCl₄⁻ anions. The FeCl₄⁻ anion, Fe(III), has been well-characterized structurally,³⁻⁶ the most precise structure determination being that of Kistenmacher and Stucky.⁶ The previous structure determinations of the Fe(II) anion, FeCl₄²⁻, are complicated by intermolecular interactions.⁷⁻⁹ Thus in the structure of the charge-transfer complex bis(3,5-dimethyl-1,2-dithiolium) tetrachloroferrate(II), (C₅H₅S₂)₂-FeCl₄, close interactions are found between each chlorine atom of the anion and the sulfur atoms of the cations.^{7,8} The structure of an iron-antimony cluster complex⁹ {[Fe(η^5 -C₅H₅)(CO)₂]₃SbCl₂}[FeCl₄].CH₂Cl₂ contains a close interaction between FeCl₄²⁻ and the solvent molecule, CH₂Cl₂, which is ascribed to hydrogen bonding. This interaction is said to cause two of the Fe-Cl bond lengths to be significantly longer than the remaining two.

Here we report the structure of the tetramethylammonium salt of the tetrachloroferrate(II) anion. This salt crystallizes isomorphously with the analogous nickel(II), cobalt(II), and zinc(II) salts which have been shown^{10,11} to contain no close intermolecular interactions.

Experimental Section

Crystals of [N(CH₃)₄]₂[FeCl₄] were prepared under dinitrogen by slow cooling of a hot aqueous solution of stoichiometric amounts of [N(CH₃)₄]Cl and FeCl₂·6H₂O. Crystals selected for X-ray work were sealed in nitrogen-filled glass capillaries. Preliminary film work indicated that the crystals were probably isomorphous with the analogous cobalt(II), nickel(II), and zinc(II) salts.¹¹ Possible space groups are $Pn2_1a$ or $Pnma$. The density determined by flotation methods was 1.32 (1) g/cm³ and the value calculated for $Z = 4$ is 1.326 g/cm³. The crystal selected for data collection was a prism with the approximate dimensions 0.48 × 0.41 × 0.22 mm. The crystal was mounted on a Picker four-circle diffractometer and the lattice parameters were obtained as previously described.¹² Careful hand centering of 16 reflections with Mo K α_1 radiation (λ 0.70930 Å) in the range 24° < 2θ < 27° yielded the cell parameters $a = 12.312$ (2) Å, $b = 9.033$ (2) Å, and $c = 15.580$ (3) Å. Data were collected

in shells of 2θ by the θ - 2θ scan method using Mo K α radiation. The scan range was from 1° below the Mo K α_1 peak to 1° above the Mo K α_2 peak and the rate of scan was 1°/min. The takeoff angle was 3.3° and the counter was positioned 31 cm from the crystal with an aperture 3.5 mm high by 5.0 mm wide. Data were collected in the range 3° ≤ 2θ ≤ 55° with backgrounds of 10 sec for 2θ ≤ 35° and of 20 sec for 2θ ≥ 35°. The intensities of 6 standard reflections, which were monitored every 100 reflections, showed only statistical variations. Data collection was terminated at 55° owing to a lack of a significant number of reflections above background.

The data were processed in the usual manner^{12,13} using a value of 0.04 for p . The data were corrected for absorption, the transmission coefficients ranging from 0.68 to 0.73 ($\mu = 14.7$ cm⁻¹). Data with $h, k, l \geq 0$ were collected at all angles and in addition reflections for which $h, k, l < 0$ were collected in the range 3° ≤ 2θ ≤ 25°. The resulting 280 Friedel pairs were compared and found to deviate an average of only 0.7% from their average values. This is a good indication that the correct space group is the centric one, D_{2h}^{16} - $Pnma$. With four molecules in $Pnma$ both the anion and cations have a crystallographically imposed mirror plane by analogy with the structures of the related Ni(II), Co(II), and Zn(II) salts.^{10,11} The averaged data were combined with the high-angle data to yield 1149 unique reflections with $F^2 > 3\sigma(F^2)$. These were used in subsequent refinements.

The structure was refined by full-matrix least-squares techniques. The quantity minimized is $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$. Values of the atomic scattering factors and the anomalous terms were taken from the usual sources.¹⁴

Initial refinement,¹³ which was begun using isotropic temperature factors and positional parameters reported for the zinc(II) isomorph,¹⁰ led to values of R and R_w of 0.196 and 0.261. Anisotropic thermal parameters were then introduced and R and R_w were reduced to 0.066 and 0.097, respectively. At this point a difference Fourier map was calculated. The hydrogen atoms of four of the six independent methyl groups could be found. As expected, each of the hydrogen atoms was staggered with respect to those on the other three methyl groups. These hydrogen atoms were idealized and ideal positions were calculated for the remaining hydrogen atoms not found assuming a staggered configuration (C-H = 1.0 Å, \angle 's = 109.5°, $B(H) = B(C) + 1.0$ Å²) and added as fixed contributions to final refinements. Refinement was terminated with R and R_w of 0.053 and 0.069 since in the final cycle the parameter shifts were less than 0.2 σ .

An analysis of $|F_o|$ and $|F_c|$ as a function of setting angles, $|F_o|$, and Miller indices showed no unusual trends. The standard deviation of an observation of unit weight is 2.42 electrons based on the 69 variables and 1149 observations. A structure factor calculation for the 640 reflections having $F_o^2 < 3\sigma(F_o^2)$, which were omitted from the refinement, showed only six reflections having $|F_o^2 - F_c^2| >$

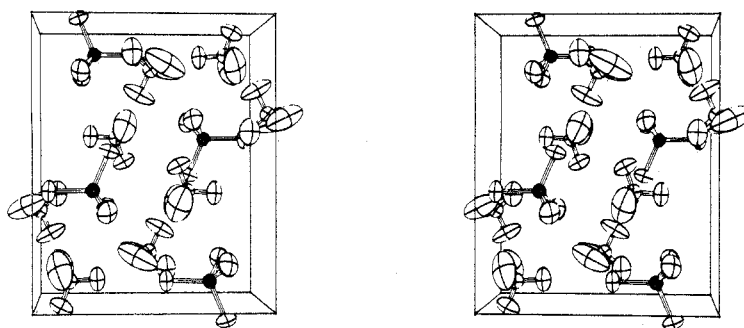


Figure 1. Stereoscopic view of the unit cell of $[N(CH_3)_4]_2[FeCl_4]$. The x axis is horizontal, the y axis points out of the paper, and the z axis is vertical. The shapes of the atoms in this and the following drawing represent 50% probability contours of thermal motion. The Fe atoms have been darkened and the H atoms omitted for the sake of clarity.

Table II. Positional and Thermal Parameters for the Atoms of $[(CH_3)_4N]_2[FeCl_4]$

| Atom | x^a | y | z | β_{11}^b | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|--------------|--------------|--------------|----------------|--------------|--------------|--------------|--------------|--------------|
| Fe | 0.24446 (8) | $1/4$ | 0.40706 (6) | 6.81 (7) | 44.98 (14) | 4.64 (5) | 0 | 0.09 (5) | 0 |
| Cl(1) | 0.05848 (17) | $1/4$ | 0.40429 (17) | 6.84 (15) | 30.4 (5) | 11.51 (17) | 0 | 0.45 (13) | 0 |
| Cl(2) | 0.30435 (17) | 0.04063 (20) | 0.33823 (13) | 14.63 (17) | 22.9 (3) | 12.67 (14) | 4.48 (19) | 1.02 (12) | -6.30 (17) |
| Cl(3) | 0.31572 (25) | $1/4$ | 0.54276 (14) | 15.87 (28) | 53.4 (8) | 5.10 (11) | 0 | -2.44 (14) | 0 |
| N(1) | 0.1481 (5) | $1/4$ | 0.0954 (4) | 7.6 (4) | 16.3 (9) | 5.9 (3) | 0 | 0.2 (3) | 0 |
| N(2) | 0.4932 (5) | $1/4$ | 0.8257 (4) | 8.0 (4) | 14.4 (8) | 5.39 (28) | 0 | -0.8 (3) | 0 |
| C(1) | 0.2638 (8) | $1/4$ | 0.1020 (9) | 8.5 (9) | 68 (5) | 13.9 (10) | 0 | -0.5 (8) | 0 |
| C(2) | 0.1118 (12) | $1/4$ | 0.0080 (8) | 19.6 (15) | 89 (6) | 7.4 (6) | 0 | -4.6 (8) | 0 |
| C(3) | 0.1079 (11) | 0.3722 (17) | 0.1383 (10) | 24.7 (14) | 67 (4) | 32.6 (15) | 17.0 (18) | -5.6 (12) | -31.3 (20) |
| C(4) | 0.4462 (15) | $1/4$ | 0.7409 (8) | 35.3 (23) | 34.8 (25) | 10.4 (8) | 0 | -12.2 (11) | 0 |
| C(5) | 0.4163 (12) | $1/4$ | 0.8882 (13) | 15.4 (13) | 143 (13) | 17.7 (15) | 0 | -0.4 (13) | 0 |
| C(6) | 0.5522 (15) | 0.3702 (16) | 0.8422 (7) | 65 (4) | 75 (4) | 17.6 (9) | -57 (3) | -17.5 (15) | 21.2 (16) |

^a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. ^b The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. The quantities given in the table are the thermal coefficients $\times 10^3$.

Table III. Calculated Hydrogen Atom Parameters for $[(CH_3)_4N]_2[FeCl_4]$

| Atom | x | y | z | $B, \text{\AA}^2$ |
|------|-------|-------|--------|-------------------|
| C1H1 | 0.288 | 0.250 | 0.159 | 6.2 |
| C1H2 | 0.292 | 0.160 | 0.068 | 6.4 |
| C1H3 | 0.292 | 0.340 | 0.068 | 6.5 |
| C2H1 | 0.139 | 0.160 | -0.025 | 6.5 |
| C2H2 | 0.139 | 0.340 | -0.025 | 6.5 |
| C2H3 | 0.030 | 0.250 | 0.003 | 6.8 |
| C3H1 | 0.140 | 0.372 | 0.208 | 7.2 |
| C3H2 | 0.144 | 0.476 | 0.122 | 7.3 |
| C3H3 | 0.032 | 0.391 | 0.148 | 7.4 |
| C4H1 | 0.496 | 0.250 | 0.695 | 5.8 |
| C4H2 | 0.394 | 0.160 | 0.735 | 6.0 |
| C4H3 | 0.394 | 0.340 | 0.735 | 6.8 |
| C5H1 | 0.361 | 0.160 | 0.871 | 6.0 |
| C5H2 | 0.433 | 0.250 | 0.941 | 5.9 |
| C5H3 | 0.361 | 0.340 | 0.871 | 6.0 |
| C6H1 | 0.509 | 0.472 | 0.841 | 7.3 |
| C6H2 | 0.590 | 0.375 | 0.901 | 7.0 |
| C6H3 | 0.616 | 0.392 | 0.799 | 7.2 |

$3\sigma(F_o^2)$. These 640 reflections were omitted from Table I where the values of $10|F_o|$ and $10|F_c|$ are given (supplementary material). The final atomic parameters and their errors are listed in Table II and the calculated parameters for the methyl hydrogen atoms are listed in Table III.

Description of Structure

The structure of $[N(CH_3)_4]_2[FeCl_4]$ is isomorphous with the cobalt(II), nickel(II), and zinc(II) salts previously studied.¹¹ The molecules pack in the unit cell as shown in Figure 1. Each of the three independent ions lies on a mirror plane and deviates slightly from ideal tetrahedral geometry. The intramolecular bond distances and angles for the three ions are listed in Table IV. Other than normal H-H interactions, the closest intramolecular distance is 2.71 Å between Cl(2) and C6H3.

Some of the atoms in this structure have very large thermal parameters as can be seen by examination of Table V which lists the root-mean-square amplitudes of vibration for each of

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[N(CH_3)_4]_2[FeCl_4]$

| | | | |
|-----------|-------------|-----------------------------|-------------|
| Fe-Cl(1) | 2.2902 (23) | Cl(1)-Fe-Cl(2) | 108.20 (7) |
| Fe-Cl(2) | 2.2958 (16) | Cl(1)-Fe-Cl(3) | 113.63 (11) |
| Fe-Cl(3) | 2.2891 (23) | Cl(2)-Fe-Cl(2) ^a | 110.94 (12) |
| | | Cl(2)-Fe-Cl(3) | 107.96 (7) |
| N(1)-C(1) | 1.43 (1) | C(1)-N(1)-C(2) | 112.3 (9) |
| N(1)-C(2) | 1.43 (1) | C(1)-N(1)-C(3) | 108.8 (8) |
| N(1)-C(3) | 1.38 (1) | C(2)-N(1)-C(3) | 110.4 (8) |
| | | C(3)-N(1)-C(3)' | 106.0 (17) |
| N(2)-C(4) | 1.44 (1) | C(4)-N(2)-C(5) | 112.1 (4) |
| N(2)-C(5) | 1.36 (2) | C(4)-N(2)-C(6) | 113.3 (6) |
| N(2)-C(6) | 1.33 (1) | C(5)-N(2)-C(6) | 104.1 (9) |
| | | C(6)-N(2)-C(6)' | 109.2 (17) |

^a Primed atoms are related to the corresponding unprimed atoms by a mirror plane.

Table V. Root-Mean-Square Amplitudes of Vibration (Å)

| Atom | Min | Intermed | Max |
|-------|-----------|------------------|-----------|
| Fe | 0.228 (1) | 0.239 (1) | 0.249 (1) |
| Cl(1) | 0.229 (3) | 3.9 ^a | 0.354 (3) |
| Cl(2) | 0.240 (2) | 7.8 | 0.354 (2) |
| Cl(3) | 0.233 (3) | 3.2 | 0.361 (3) |
| N(1) | 0.241 (7) | 0.259 (7) | 0.271 (7) |
| C(1) | 0.25 (1) | 1.6 | 0.41 (2) |
| C(2) | 0.26 (1) | 10.2 | 0.42 (2) |
| C(3) | 0.29 (1) | 6.2 | 0.43 (1) |
| N(2) | 0.236 (7) | 0.244 (7) | 0.269 (7) |
| C(4) | 0.25 (1) | 5.7 | 0.38 (1) |
| C(5) | 0.34 (1) | 8.2 | 0.47 (2) |
| C(6) | 0.25 (1) | 25.1 | 0.37 (1) |

^a Angles in degrees between the given axis of vibration and the respective Fe-Cl or N-C bond. See text.

the nonhydrogen atoms. Also listed are the angles between the principal axes of vibration of a given Cl or C atom and the corresponding Fe-Cl or N-C bond. The shortest axis of vibration is generally nearly parallel to the bond while the two longer axes are roughly perpendicular to the bond. This effect of large thermal motion directed in such a manner was also

Table VI. Bond Distances and Angles Found for FeCl_4^{2-} and FeCl_4^- Anions

| Salt | Fe-Cl, Å | Cl-Fe-Cl, deg | Ref |
|--|-----------------------------|----------------|-----------|
| | Fe(II) | | |
| $[\text{C}_5\text{H}_5\text{S}_2]_2[\text{FeCl}_4]$ | [2] ^a 2.289 (5) | [1] 112 | 7 |
| | [2] 2.335 (5) | [1] 116 | |
| | (av) 2.313 (4) ^b | [2] 106 | |
| $[\text{C}_5\text{H}_5\text{S}_2]_2[\text{FeCl}_4]$ | [2] 2.31 (1) | [2] 108 | 8 |
| | [2] 2.34 (1) | [1] 112 | |
| | (av) 2.33 (2) | [1] 116 | |
| | | [2] 106 | |
| $\{[\text{Fe}(n\text{-C}_5\text{H}_5)(\text{CO})_2]\text{SbCl}_2\}[\text{FeCl}_4]$ | [2] 2.284 (5) | [2] 108 | 9 |
| | [2] 2.320 (5) | [1] 104.2 (3) | |
| | (av) 2.302 (18) | [1] 108.5 (2) | |
| | | [2] 107.2 (2) | |
| $[\text{N}(\text{CH}_3)_4]_2[\text{FeCl}_4]$ | [2] 2.296 (2) | [2] 115.0 (2) | This work |
| | [1] 2.290 (2) | [1] 113.6 (1) | |
| | [1] 2.289 (2) | [1] 110.9 (1) | |
| | (av) 2.292 (2) | [2] 108.2 (1) | |
| | | [2] 108.0 (1) | |
| | Fe(III) | | |
| $[\text{As}(\text{C}_6\text{H}_5)_4][\text{FeCl}_4]$ | [4] 2.19 (3) | [2] 114.5 (15) | 3 |
| | | [4] 107.0 (15) | |
| $[\text{FeCl}_2(\text{DMSO})_4][\text{FeCl}_4]$ | [4] 2.162 (5) | [2] 112.2 (3) | 4 |
| | | [4] 108.1 (3) | |
| $\text{Na}[\text{FeCl}_4]$ | [1] 2.180 (10) | [1] 108.0 (11) | 5 |
| | [1] 2.184 (8) | [1] 111.6 (5) | |
| | [1] 2.200 (8) | [1] 112.7 (5) | |
| | [1] 2.218 (8) | [1] 110.8 (4) | |
| | (av) 2.196 (9) | [1] 108.8 (4) | |
| $[\text{PCl}_4][\text{FeCl}_4]$ | [2] 2.1819 (10) | [1] 104.9 (4) | 6 |
| | [1] 2.1873 (15) | [2] 108.98 (4) | |
| | [1] 2.1869 (14) | [2] 108.20 (4) | |
| | (av) 2.1854 (17) | [1] 108.53 (6) | |
| | | [1] 113.56 (6) | |

^a Number in brackets is the number of equivalent bonds having the given distance. ^b Estimated standard deviation of average.

seen for the isomorphous cobalt(II), nickel(II), and zinc(II) salts¹¹ and most likely results from large librational effects or possible rotational disorder of the tetrahedra. Because of this thermal motion the apparent C-N bond distances vary over a large range (Table IV). The average uncorrected bond distance, 1.39 (3) Å, is shorter than expected. Correction of these bond distances for librational effects leads to 1.58 Å for the average C-N bond length, a value longer than expected.

The FeCl_4^{2-} anion fortunately has much smaller thermal parameters, so that precise bond distances may be obtained. The three unique bond distances listed in Table III are all within 2σ of the average value of 2.292 (2) Å. Correction for librational motion leads to an average value of 2.33 Å. The geometry of the FeCl_4^{2-} anion is that of a slightly flattened tetrahedron with bond angles ranging from a low of 108.20 (7)° to a high of 113.62 (11)°. (See Figure 2.) The individual angles and the distortions of the tetrahedra are very similar for the CoCl_4^{2-} , NiCl_4^{2-} , and ZnCl_4^{2-} anions in the isomorphous structures. Thus it seems likely that these angular deviations from the ideal tetrahedral geometry are the result of crystal packing forces and not a manifestation of the electronic structure of the anions.

Discussion

In a previous study¹⁵ a variety of octahedral metal complexes in the +2 and the +3 oxidation states were examined. It was found that the differences in metal-ligand bond distances between complexes of the two different oxidation states result from two main factors. The first is the electrostatic charge on the central metal atom. The second is the electronic configuration and spin state of the metal atom. If the spin state is the same, an octahedral complex in the +2 oxidation state will have metal-ligand lengths which are about 0.04 Å longer than those found in the corresponding complex in the +3 oxidation state. The low-spin $\text{Ru}(\text{NH}_3)_6^{2+}$ cation has a Ru-N bond distance of 2.144 (4) Å, which is 0.040 (6) Å

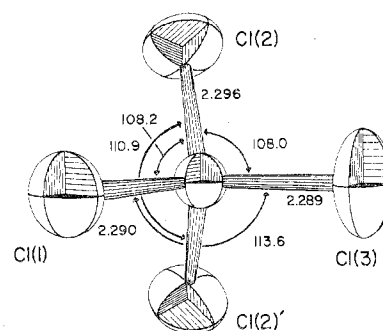


Figure 2. The FeCl_4^{2-} anion. The anion has a crystallographically imposed mirror plane.

longer than the distance of 2.104 (4) Å found for the low-spin $\text{Ru}(\text{NH}_3)_6^{3+}$ cation.¹⁵ A spin change will cause greater differences, as shown by studies¹⁶ of the high- and low-spin forms of $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ (bipy = 2,2'-bipyridine). The low-spin form has a Fe-N bond length of 2.02 Å, which lengthens by 0.12 Å when the complex is converted to its high-spin form. For the cobalt-hexammine complexes the additive effects of both factors are seen.¹⁷ The $\text{Co}(\text{NH}_3)_6^{2+}$ ion is high spin with a Co-N bond length of 2.114 (9) Å, 0.178 (17) Å longer than the $\text{Co}(\text{NH}_3)_6^{3+}$ bond length of 1.936 (15) Å.

Since the present tetrahedral complexes are high spin, the changes in Fe-Cl distances result solely from charge differences. Table VI lists the results of several structure determinations of the FeCl_4^- and FeCl_4^{2-} anions. For the Fe(III) anion the average Fe-Cl bond length found is 2.185 Å in the most precise of the structures,⁶ $[\text{PCl}_4][\text{FeCl}_4]$. If all Fe(III) structures³⁻⁶ are averaged, a value of 2.19 Å is found. The Fe(II) anion reported here has an average Fe-Cl bond length of 2.292 (2) Å. Hence, there is about a 0.11-Å increase in bond distance upon addition of an electron to the FeCl_4^- anion.

Corrections to bond distances because of thermal motion can be large, but if the corrections are applied to both the Fe(II) and the Fe(III) anions, the differences remain about the same. For $[\text{PCl}_4][\text{FeCl}_4]$ the corrected values for Fe-Cl bond lengths average 2.20 Å, while for FeCl_4^{2-} the average is 2.33 (1) Å, which leads to a difference of 0.13 Å.

The difference in tetrahedral bond lengths of Fe(III) and Fe(II) complexes of about 0.11 Å is considerably larger than the 0.04-Å difference found for octahedral complexes.¹⁵ This larger difference is consistent with simple electrostatic arguments. Tetrahedral bond lengths are shorter than octahedral bond lengths¹⁸ and the effect of increased charge should thus be greater. In addition in octahedral complexes the cis ligands are relatively close and can both shield the charge on the metal and cause repulsive interactions between the ligands. The effect of increased charge on the central metal atom is also seen by comparing FeCl_4^- (Fe-Cl = 2.19 (1) Å) with the isoelectronic MnCl_4^{2-} anion¹⁹ (Mn-Cl = 2.324 Å) in $[\text{N}(\text{CH}_3)_4]_2[\text{MnCl}_4]$.

All of the Fe tetrahedra considered have angular distortions from the ideal tetrahedral geometry. The largest angular deviations occur in the structures that have intermolecular interactions.⁷⁻⁹ The remaining tetrahedra have smaller deviations which are perhaps mainly the result of packing forces.

The simplest of the iron-sulfur proteins are the 1-FeS₄ proteins which contain one iron atom coordinated to four cysteine sulfur atoms.¹ In an elegant study²⁰ Watenpaugh, *et al.*, have refined the structure of one such protein, the oxidized form of rubredoxin from *Clostridium pasteurianum*. They found an iron atom coordinated in a tetrahedral manner to four cysteine sulfur atoms. According to magnetic measurements² the iron is in the +3 oxidation state and is high spin. The four independent Fe-S bond distances 2.34 (2), 2.32 (3), 2.24 (3), and 2.05 (3) Å average 2.24 (6) Å. The S-Fe-S angles range from a low of 101° to a high of 115°.

The reduced form of the protein contains tetrahedral high-spin Fe(II).² One would thus expect an expansion of the FeS₄ core upon reduction. The Fe-S bond lengths should increase in length by about 0.11 Å. Since the bond lengths found for the oxidized form do cover a large range, it is difficult to predict actual bond lengths for the reduced form. If the average value of 2.24 (6) Å for Fe(III)-S bond lengths in the protein is a good representation of the range of values, the reduced protein would be expected to have Fe(II)-S bond lengths which average 2.36 Å. Such an expansion could well lead to significant changes in the conformation of the protein. It is interesting to note that for bis(imidotetramethyldithio-diphosphine-S,S)iron(II), a tetrahedral high-spin Fe(II) complex with sulfur ligands, an average value of 2.360 (8) Å is found.²¹

Many iron-sulfur proteins are of the 2-FeS₂S₄ type. On the basis of a variety of experiments on the proteins and on inorganic analogs,²² these proteins are believed to contain a cluster of two iron atoms bridged by two inorganic sulfur ligands as well as two cysteine sulfur ligands bound to each iron. Both iron atoms are in tetrahedral environments. The exact electronic states of the protein are not known, but it has been theorized that the oxidized protein contains two Fe(III) atoms, while the reduced form has one Fe(III) and one Fe(II) atom in localized electronic environments.²³ All species are high spin, but antiferromagnetic coupling reduces the observed spin.

Although no structural studies of such proteins have been reported, the prediction can be made that the oxidized form will have a symmetrical cluster, whereas the reduced form, if it truly has a localized electronic structure, will have an unsymmetrical structure with the Fe(II) atom having longer bond lengths than the Fe(III) atom.

The third major type of iron-sulfur proteins are the 4-

FeS₂S₄ proteins.^{1,24} These contain a cluster of four iron atoms and four inorganic sulfur ligands in a cubane arrangement with each sulfur bridging three iron atoms. Each iron also has one terminal cysteine ligand making its environment a distorted tetrahedron of sulfur ligands. These clusters have delocalized electronic structures.²⁴ They undergo one electron reduction which may cause some expansion of the cluster. The geometric consequences of reduction would be small since the effects are spread out over all four iron atoms.

In summary we have shown that the FeCl_4^{2-} anion, high-spin Fe(II), has bond lengths 0.11 Å longer than those found in the FeCl_4^- anion, high-spin Fe(III). This expansion of the coordination sphere upon reduction is larger than is found in octahedral complexes. Similar changes in bond lengths are to be expected in some of the iron-sulfur proteins.

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Registry No. $[\text{N}(\text{CH}_3)_4]_2[\text{FeCl}_4]$, 14874-07-8.

Supplementary Material Available. A listing of structure amplitudes, Table I, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40485E.

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Coordination of the Aryldiazo Ligand to Transition Metals. Structure of Chloro(bis(3-diphenylphosphinopropyl)phenylphosphine)phenyldiazorhodium Hexafluorophosphate Methylene Chloride Solvate, $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)] [\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$

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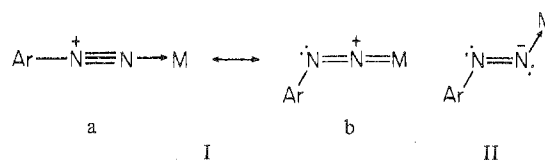
The structure of $[\text{RhLCl}(\text{N}_2\text{C}_6\text{H}_5)] [\text{PF}_6]$ where L = the tridentate phosphine ligand $\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2$ has been determined from three-dimensional X-ray counter data collected on a single crystal of the CH_2Cl_2 solvate. The material crystallizes in space group C_1^1-P1 of the triclinic system with two formula units of the complex and two solvent molecules in a cell of dimensions $a = 12.675$ (7) Å, $b = 13.254$ (7) Å, $c = 15.092$ (10) Å, $\alpha = 94.78$ (5)°, $\beta = 99.47$ (5)°, $\gamma = 112.40$ (8)°, and $V = 2282.3$ Å³. The observed and calculated ($Z = 2$) densities are 1.50 (1) and 1.507 g/cm³, respectively. The structure has been refined (on F) by a full-matrix least-squares procedure to a conventional agreement index of 0.057 for 4031 observations having $F_o^2 > 3\sigma(F_o^2)$. The structural results reveal an ionic complex consisting of $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ cations (Ph = C₆H₅) and PF_6^- anions. The geometry of the cation is distorted tetragonal pyramidal with a basal plane consisting of the chloro ligand and the three P atoms of the tridentate phosphine. The apical coordination site is occupied by a doubly bent aryldiazo ligand and thus affords the first structural example of the aryldiazo analog of NO^- , N_2Ph^- . The doubly bent geometry suggests formulation of the complex as the oxidative adduct of N_2Ph^+ to $\text{Rh}^{\text{I}}\text{LCl}$ yielding $[\text{Rh}^{\text{III}}\text{LCl}(\text{N}_2\text{Ph})]^+$. Distances and angles of interest within the cation are as follows: Rh-P, 2.368 (3), 2.274 (3), 2.352 (3) Å; Rh-Cl, 2.403 (2) Å; Rh-N(1) (α to Rh), 1.961 (7) Å; N(1)-N(2), 1.172 (9) Å; N(2)-C(7) (Ph), 1.445 (11) Å; Rh-N(1)-N(2), 125.1 (6)°; N(1)-N(2)-C(7), 118.9 (8)°. The structural results are compared with those for the corresponding NO complex, $[\text{RhLCl}(\text{NO})]^+$, and with the parent complex, RhLCl . The implications of the nitrosyl-aryldiazo analogy are discussed.

Introduction

The coordination of aryldiazonium cations, ArN_2^+ , to transition metals is a subject of current interest to inorganic chemists. The interest in these systems derives from their employment as model systems for the N_2 -fixing enzyme nitrogenase^{1,2} and because the aryldiazonium cation is formally isoelectronic with the nitrosonium cation, NO^+ .

Recent structural results³ have demonstrated that nitric oxide, NO, can coordinate to a transition metal in a linear fashion formally as NO^+ , where it functions as a two-electron donor (Lewis base), or in a bent ($\text{M}-\text{N}-\text{O}$ angle 120°, M = metal) arrangement formally as NO^- , where it acts as a Lewis acid, accepting an electron pair from the metal center. The last mode of nitrosyl coordination was originally suggested by Owston, *et al.*,⁴ on the basis of an equivocal two-dimensional structure determination of nitrosylbis(dimethylthiocarbamate)cobalt. Later structural work by Hodgson, *et al.*,⁵ firmly established the existence of the bent $\text{M}-\text{N}-\text{O}$ linkage. A number of semiempirical interpretations of the electronic structure underlying this experimentally verified duality of nitrosyl coordination have appeared.⁶⁻⁸ The two distinct modes of nitrosyl coordination have also led to the suggestion^{9,10} that NO may alternately act as an electron source (NO^+) or sink (NO^-), a possibility which has interesting catalytic implications. Indeed, transition metal nitrosyl complexes have been found to act as catalysts for reactions as diverse as hydrogenation,⁹ diene dimerization,¹¹ and isomerization.¹²

The electronic similarity between ArN_2^+ and NO^+ has prompted several authors to speculate that the coordinated aryldiazo group may exhibit a similar duality in bonding and function.¹³⁻¹⁵ The principal canonical forms contributing to the linear (ArN_2^+) and bent (ArN_2^-) forms of the coordinated aryldiazo group may be formulated, by analogy with NO^+ and NO^- , as I and II. Only three structural reports of coordinated



aryldiazo groups have appeared and all involve a linear $\text{M}-\text{N}-\text{N}$ arrangement with Ib clearly predominant.^{13,16,17} Recent work by Bowden, *et al.*,¹⁸ has led these authors to suggest that in the complex $[\text{Ru}(\text{bipy})_2(\text{N}_2\text{Ar}')\text{Cl}] [\text{PF}_6]_2$ (bipy = 2,2'-bipyridine; $\text{Ar}' = p\text{-C}_6\text{H}_4\text{CH}_3$ or $p\text{-C}_6\text{H}_4\text{OCH}_3$) the coordinated aryldiazo group may be of the Ia form. In $\text{Ru}(\text{X})\text{Cl}_3(\text{P})_2$ ($\text{P} = \text{PCH}_3(\text{C}_6\text{H}_5)_2$ or $\text{P}(\text{C}_6\text{H}_5)_3$; X = NO or $p\text{-N}_2\text{C}_6\text{H}_4\text{CH}_3$) both the nitrosyl¹⁹ and aryldiazo¹³ complexes have been characterized and, as expected, an angle of $\sim 180^\circ$ is found at the N atom bound to the metal in both cases.

Recently the synthesis and characterization of a series of Rh(I) complexes of the tridentate chelating ligand $\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2$, hereafter designated L, have been reported.²⁰

The parent complex, RhLCl , has been found to undergo facile addition reactions with a variety of Lewis acids, A ($\text{A} = \text{H}^+, \text{NO}^+, \text{N}_2\text{C}_6\text{H}_5^+, \text{CH}_3\text{CO}^+$), yielding the five-coordinate cationic complexes $[\text{RhLCl}\cdot\text{A}]^+$.²⁰ The structure determination of the nitrosyl complex $[\text{RhLCl}(\text{NO})] [\text{PF}_6]$ ²⁰ revealed a tetragonal-pyramidal cation with the nitrosyl group occupying the apical position of the coordination sphere. The $\text{Rh}-\text{N}-\text{O}$ angle of 131° suggests that the complex may formally be viewed as one of $\text{Rh}(\text{III})$ and NO^- . The corresponding aryldiazo complex $[\text{RhLCl}(\text{N}_2\text{C}_6\text{H}_5)]^+$ ²⁰ is thus a prime candidate for X-ray structural investigation in order to establish that ArN_2^+ is capable of the same duality in bonding as is NO^+ .

In order to provide verification of the aryldiazo analog of