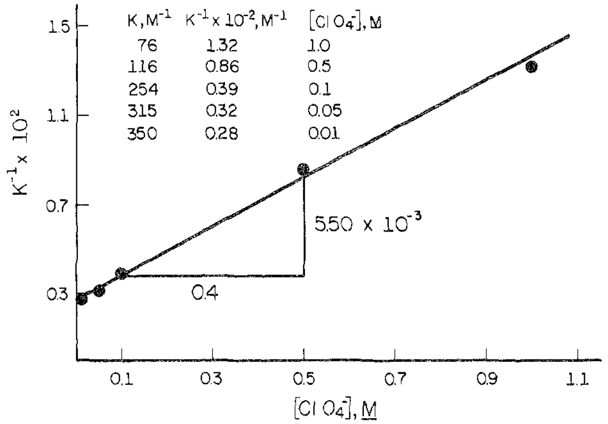

Figure 2. Plots of the reciprocal of the formation constant *K vs.* $[HClO_4] = \mu$.

attributed to K_f' may simply be ionic strength effects, but K_f' is very similar to values reported by Sykes[5a] at low ionic strength.

Ultraviolet Spectra. Yellow octacyanomolybdate(IV) ion exhibits general absorbance in the ultraviolet region of the spectrum, with a peak at 240 nm. This absorbance at the peak is lowered slightly by changing $[H^+]$ from 0.1 to 1.0 M at $\mu = 1.0$. The effect is barely enough to suggest a reaction between $Mo(CN)_8{}^{4-}$ and H^+, but not enough to use to measure an equilibrium constant. The uv absorbances of Fe(III) and Mo(IV) are too great to observe spectral changes at concentrations needed to produce significant formation of the blue complex. $Mo(CN)_8{}^{4-}$ is very susceptible to photochemical decomposition in the presence of either H^+ or Fe^{3+}.

The Insoluble Compound $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$. Various methods were used unsuccessfully in trying to isolate salts of the soluble complex $FeMo(CN)_8{}^-$ from solution. It appears that the interaction between Fe(III) and $Mo(CN)_8{}^{4-}$ is not sufficiently strong to allow isolation by the usual methods. Although the soluble complex could not be isolated from solution, mixing reactant solutions whose concentrations had been increased to 0.05 M produced an insoluble amorphous salt of composition $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$. On mixing the reactant solutions an immediate deep blue precipitate formed which was filtered, washed with water and acetone, and dried under vacuum. *Anal.* Calcd for $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$: C, 21.32; N, 24.87; H, 1.79; Fe, 16.53; Mo, 21.29. Found: C, 21.39; N, 24.50; H, 1.65; Fe, 16.17; Mo, 22.09. An infrared spectrum of the compound, as a Nujol mull, in the cyanide stretching region showed a broad absorption centering at 2135 cm^{-1} with weak shoulder bands at *ca.* 2160 and 2185 cm^{-1}. This spectrum differs greatly from the spectrum of the $K_4Mo(CN)_8 \cdot 2H_2O$ compound which consists of four sharp peaks at 2060, 2103, 2126, and 2136 cm^{-1}, with the main peak appearing at 2103 cm^{-1}. The broadening of the cyanide stretching bands and their shift to higher frequency are of interest in that they indicate bridging of the cyanide ligand as observed by Allen and Lippard[6] in $(UO_2)_2Mo(CN)_8 \cdot (6\text{-}8)H_2O$, by Shriver[7] in the adduct $K_4Mo(CN)_8 \cdot 8BF_3$, and by the present authors in divalent transition metal compounds of the $Mo(CN)_8{}^{4-}$ ion.[8] The same phenomenon is observed with heavy metal ferrocyanides[9] which are known to contain cyanide bridging ligands. Thus it appears likely that $Fe_4[Mo(CN)_8]_3 \cdot 12H_2O$ exists as an amorphous polymer containing bridging cyanide groups.

A halocarbon mull spectrum is very similar to the uv-visible spectrum in solution with the broad band in the near ir shifted to a maximum at 750 nm.

Bonding. Cyanide bridging ligands also can be postulated for the soluble complex $FeMo(CN)_8{}^-$. Precedence for such a conclusion can be found in observations of Haim and Wilmarth,[10] who proposed the existence of a cyanide bridge in the complex ion $[(NC)_5Fe^{II}CNCo^{III}(CN)_5]^{6-}$. Likewise, Burmeister and Sutherland[11] found that when $Co^{III}(NH_3)_5CN^{2+}$ reacts with $Co^{II}(CN)_5{}^{3-}$ to produce $Co^{III}(CN)_6{}^{3-}$, the sixth cyanide group of the product originates from the $Co^{III}(NH_3)_5CN^{2+}$ ion, which indicates that a bridging cyanide ligand occurs in the activated complex for the reaction. Similarly, Cr(III) is found bound to Fe(III) and Mo(V) by CN^- bridges following reduction of Cr(VI) by $Fe(CN)_6{}^{4-}$ [12] and $Mo(CN)_8{}^{4-}$.[13]

Bonding to nitrogen in $Mo(CN)_8{}^{4-}$ is seen to be very weak. No evidence of a protonated form has been found. Its association with triply charged Fe^{3+} is weak. However, it forms strong enough cyanide bridge bonds with metal ions in the solid state to give very insoluble polymers rather than crystalline arrays of simple discrete ions.[8] The blue complex is also produced when Fe^{2+} is mixed with $Mo(CN)_8{}^{3-}$. We are reminded of the $[FeFe(CN)_6{}^-]$ blue complex with mixed iron oxidation states; some delocalization of metal d electrons through the CN^- bridge is probably involved.

Registry No. $[FeMo(CN)_8]^-$, 39993-16-3; $Fe_4[Mo(CN)_8]_3$, 37359-93-6; $[Mo(CN)_8]^{4-}$, 17923-49-8.

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Contribution from the Department of Chemistry,
University of Hawaii, Honolulu, Hawaii 96822

Nature of Iron(III) Chloride in Benzene

R. A. Work, III, and R. L. McDonald*

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During the investigation of the structure of the mixed dimer $[R_3NH^+Cl^-] \cdot [R_3NH^+FeCl_4{}^-]$ in benzene solution[1] differences in the infrared spectra were observed when anhydrous rather than hydrated iron(III) chloride was used in solution

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(1) R. A. Work, III, and R. L. McDonald, *J. Inorg. Nucl. Chem.*, 34, 3123 (1972).

preparation. We found that these differences were due to excess iron(III) chloride dissolved in benzene.

For many years it was believed[2] that iron(III) chloride existed as a solvated monomer in strong donor solvents such as ethers and as a dimer, Fe_2Cl_6, in solvents of weak donor ability such as benzene. Results of experiments conducted over the past decade indicate that this is an oversimplification,[3-7] but the true nature of these solutions is not well established. For example, Carlson[7] used electronic spectral data to argue that Fe_2Cl_6 exists in benzene, but Fajer and Linschitz[6] used similar data to support their claim that the dimer does not exist in benzene. In neither case was any successful attempt to investigate solute-solvent interactions reported. In this report we use infrared evidence to argue that not only is $FeCl_3$ monomeric in benzene but also a benzene adduct of $FeCl_3$ exists in solution.

Experimental Section

Reagents. The iron(III) chloride was sublimed anhydrous reagent grade purchased from Matheson Coleman and Bell. The benzene used was Mallinckrodt NANOGRADE.

Solutions. Solutions of iron(III) chloride in dried benzene were prepared in a nitrogen-purged, controlled-atmosphere drybox by addition of an excess of iron(III) chloride to benzene that had previously been dried over activated Linde 3A molecular sieve. The molecular sieve was activated before using by heating in a vacuum oven at 200° for 48 hr. The solutions are unstable in the presence of moisture; the iron(III) precipitates.

Analysis. The approximate concentration of iron(III) chloride in benzene was determined by quantitative extraction of the iron(III) chloride with water followed by precipitation with ammonium hydroxide and subsequent gravimetric determination as the oxide.[8] The concentrations of the solutions ranged between 0.01 and 0.02 *M*.

Ir Spectra. Spectra in the region 4000–400 cm^{-1} were obtained with a Beckman IR-9 infrared spectrophotometer fitted with KBr optics. Far-infrared spectra in the region 400–40 cm^{-1} were determined with an RIIC Model FS-720 Fourier spectrometer equipped with an FTC 100/7 Fourier transform computer and wave analyzer. In the 4000–600-cm^{-1} region 0.1-mm NaCl cells were used; in the 600–400-cm^{-1} region 1-mm Beckman disposable polyethylene cells were used; below 400 cm^{-1} a Beckman vacuum cell with polyethylene windows and a 2-mm Teflon spacer was used. All band positions are believed accurate within ±3 cm^{-1} unless otherwise stated. The solutions were run *vs.* solvent as a reference.

Results and Discussion

Three infrared maxima were observed for iron(III) chloride in benzene (*ca.* 0.02 *M*) in the region below 600 cm^{-1} (Figure 1). We have assigned these as two stretches and one bend by comparison of their frequencies with those of $FeCl_3$ (see Table I). Fe_2Cl_6 has been examined by infrared techniques in the gas phase[9] and in an argon matrix.[10] In both spectra four intense maxima were observed in the region 550-250 cm^{-1}; all were assigned as stretches. The monomer, $FeCl_3$, was also studied in an argon matrix[10] and found to exhibit three maxima, one stretch and two bends, in agreement with D_{3h} symmetry (Table I). Normal-coordinate calculations were used to confirm the assignments and to obtain the value for the single infrared-inactive mode.

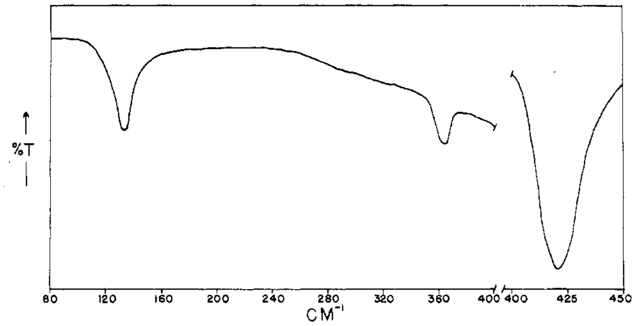

Figure 1. Infrared spectrum of $FeCl_3$ (*ca.* 0.02 *M*) in benzene: 80–400 cm^{-1} in 2-mm cell; 400–450 cm^{-1} in 1-mm cell.

Table I. Infrared Data for Iron(III) Chloride in Benzene and Related Species[a]

Species	Stretches	Bends	Ref
$FeCl_3$ (benzene)	423 vvs, 363 w	132 mw	*g*
$FeCl_3$ (Ar matrix)[b]	465, (332)	116, 102	*h*
$SnCl_3^-$ [c]	295 s, 256 vs, br	129 mw	*i*
$FeCl_3Br^-$ [d]	391 vs, 350 s	135 w, 117 sh	*j*
$FeCl_4^-$ (T_d)[e]	385 vs	133 m	*k*
$FeCl_4^-$ (C_{3v})[f]	396 s, 332 mw	136 m	*l*

[a] Abbreviations: v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder. Parentheses indicate calculated value; all data in cm^{-1}. [b] At 5°K. [c] As "Aliquat 336" salt in benzene solution. [d] Cl–Fe vibrations only (assigned by the authors); as tetrabutylammonium salt. [e] From Raman data of ether extract; ir-active modes only. [f] As trioctylammonium salt. [g] This work. [h] R. A. Trey, R. D. Werder, and Hs. H. Gunthard, *J. Mol. Spectrosc.*, **35**, 260 (1970). [i] R. A. Work, III, Ph.D. Dissertation, Louisiana State University in New Orleans, New Orleans, La., 1971. [j] C. A. Clausen, III, and M. L. Good, *Inorg. Chem.*, 9, 220 (1970). [k] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 4473 (1960). [l] M. L. Good, C. C. Chang, D. W. Wertz, and J. R. Durig, *Spectrochim. Acta, Part A,* **25**, 1303 (1969).

If an XY_3 type molecule is distorted from D_{3h} symmetry (planar) to C_{3v} symmetry (pyramidal), the symmetric stretching mode, $\nu_1(A_1')$, which is inactive in D_{3h} symmetry, becomes infrared active.[11] In C_{3v} symmetry then, all four normal modes are infrared active. These are the symmetric stretching mode, $\nu_1(A_1)$, the asymmetric stretching mode, $\nu_3(E)$, and the two bending modes $\nu_2(A_1)$ and $\nu_4(E)$.[11]

The difference in the number and position of the stretching modes for iron(III) chloride in benzene and for Fe_2Cl_6 suggests that monomeric $FeCl_3$ is present in benzene. The fact that two stretches are observed in the infrared implies that the $FeCl_3$ species in benzene possesses C_{3v} symmetry. The absence of the second bending mode is vexing but not alarming. Comparison of this spectrum with a known C_{3v} complex anion, $SnCl_3^-$, shows that the absence of this band is not inconsistent with the assignment of C_{3v} symmetry. The second bending mode either is not resolved or is too weak to be observable at the concentrations used here.

There is a difference, however, when one compares the relative intensities of the two stretching maxima for $SnCl_3^-$ and $FeCl_3$ in benzene. For the former they have about the same intensities but for the latter the higher frequency band is much more intense. This can be explained if it is assumed that the lower frequency stretching band for $FeCl_3$ is the symmetric stretching mode of a molecule that is only slightly distorted from D_{3h} to C_{3v} symmetry. Because of this slight distortion from planarity, $\nu_1(A_1)$, which is the infrared-forbidden $\nu_1(A_1')$ mode in D_{3h}, is relatively weak.

It is tempting to propose that benzene coordination to

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$FeCl_3$ is the cause of the distortion. In an attempt to confirm this, the infrared spectrum from 4000 to 600 cm^{-1} was observed *vs.* benzene as a reference. Only those bands which possess large intensities and are different from liquid benzene would be expected to appear in this spectrum. Two such bands were observed at 2932 ± 7 and 2864 ± 7 cm^{-1}. These are benzene C–H stretching modes which for unperturbed liquid benzene fall in the region 3062–3048 cm^{-1}.[12] Benzene π complexes often show C–H stretching modes different from liquid benzene. For example, $(C_6H_6)_2W$ shows maxima at 3012 and 2898 cm^{-1}.[12] We conclude that benzene is in fact π bonded to the iron causing a slight displacement of the chlorines away from the benzene, destroying the $FeCl_3$ plane.

Further comparisons are in order. $FeCl_3Br^-$ contains a pyramidal $FeCl_3$ group for which infrared maxima have been assigned.[13] The Fe–Cl bands compare favorably with those of $FeCl_3$ in benzene (see Table I). For completeness the spectral data reported for $FeCl_4^-$ both distorted and regular tetrahedral are also included in the table. Note that the strongest bands in these spectra fall between the two stretching maxima of $FeCl_3$ in benzene; apparently no measurable amount of $FeCl_4^-$ is present in our solutions.

No π-bonded benzene adduct appears to have been reported with more than two benzenes per molecule.[12] If two benzene molecules were coordinated to the iron, one would expect axial coordination and D_{3h} symmetry, by analogy to $FeCl_3$ behavior in water.[14] Two benzenes coordinated so as to destroy the Fe–Cl plane might be expected to give rise to nonequivalent chlorines and to a splitting in the doubly degenerate modes, $\nu_3(E)$ and $\nu_4(E)$. No splitting in $\nu_3(E)$ was detected. All of the evidence is consistent with an $FeCl_3 \cdot C_6H_6$ adduct in solution possessing C_{3v} symmetry.

Registry No. $FeCl_3$, 7705-08-0; $FeCl_3 \cdot C_6H_6$, 40200-01-9; benzene, 71-43-2.

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Contribution from the School of Chemistry, University of Western Australia, Nedlands, Western Australia

Stereochemistry of Five-Coordination.
I. Monodentate Ligands

D. L. Kepert

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Five-coordinate molecules are of considerable interest as they are known with trigonal-bipyramidal (D_{3h} symmetry), square-pyramidal (C_{4v} symmetry), or intermediate (C_{2v} symmetry) stereochemistry. In addition to the comparable stability of these isomers, there is also the possibility of low activation energies leading to rapid intramolecular interconversion.

However there does not appear to have been a completely satisfactory explanation for this variability in stereochemistry or for the detailed stereochemistry of the square pyramidal and intermediate isomers.

Stereochemical calculations based on the minimization of ligand-ligand repulsion energies using an inverse relation between the potential energy and the distance between the donor atoms,[1] and also an inverse square relation,[2] have not been very successful. The predicted bond angles for the square pyramid were not in agreement with those experimentally observed, the calculated displacement of the central metal atom from the basal square plane of donor atoms being much greater than that observed.

These calculations are now extended in more detail for the following reasons: (a) to determine the relative stability of the different isomers, (b) to predict more precisely the geometry of the square pyramid and intermediate isomers, (c) to obtain a precise mapping of the potential energy surface because of the interest in the intramolecular rearrangement of five-coordinate molecules, (d) to examine if this approach to stereochemistry can be extended to cases where all bonds are not equivalent, and (e) to provide a basis enabling a comparison to be made with five-coordinate molecules containing bidentate[3] and polydentate[4] ligands.

Method

The stereochemical arrangement of a number of ligand donor atoms surrounding a central atom may be calculated by the minimization of the total ligand–ligand repulsion energy U obtained by summing over all donor atom–donor atom repulsions. It is assumed that the repulsive energy u_{ij} between any two donor atoms i and j is proportional to some inverse power n of the distance d_{ij} between them. If all bond lengths are equal, that is all donor atoms lie on the surface of a sphere of radius r, then the results can be expressed in the form

$$U = \sum_{ij} u_{ij} = \sum_{ij} ad_{ij} = aXr^{-n}$$

where a is the proportionality constant and X is the repulsive energy coefficient which can be calculated from the value of n and the geometry of the coordination polyhedron.

The most appropriate value of n cannot be known exactly but certainly lies between the limits of 1 (for a purely coulombic interaction) and 12. Fortunately conclusions based on calculations on eight-coordinate[5-7] and six-coordinate[8] complexes have not been very dependent upon the assumed value of n.

Figure 1 defines the general stereochemistry for five-coordination. The twofold axis passes through the central metal atom M and the donor atom E. The angles between this axis and the bonds to each of the pairs of donor atoms A,C and B,D are denoted by ϕ_A and ϕ_B, respectively. The trigonal bipyramid is defined by $\phi_A = 90.0°$ and $\phi_B = 120.0°$ (or $\phi_A = 120.0°$ and $\phi_B = 90.0°$), and the square pyramid is defined by $\phi_A = \phi_B$.

The distances between the donor atoms are given by

$$AB = AD = BC = CD = (2 - 2 \cos \phi_A \cos \phi_B)^{1/2} r$$

$$AC = (2 \sin \phi_A) r$$

$$AE = CE = (2 - 2 \cos \phi_A)^{1/2} r$$

$$BD = (2 \sin \phi_B) r$$

$$BE = DE = (2 - 2 \cos \phi_B)^{1/2} r$$

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