ordination site may inhibit approach of the second ligand. Electronic considerations might also be applicable if one argues that π back-bonding to the cis ligands increases the effective positive charge of the Ru(II) center thus making less favorable a dissociative path for departure of the water molecule. The π-acceptor character of benzonitrile in its interactions with Ru(II) has been reasonably well established,[10,12] while that of pyridine remains somewhat controversial.[6,13]

Perhaps the most important conclusion that can be drawn from the data in Table I is that the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are essentially identical (within experimental uncertainty) for all reactions listed. Furthermore these values are close to those for the substitution reactions of $Ru(NH_3)_5(H_2O)^{2+}$ ($k_L = 0.091\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger} = 15.3 \pm 0.2$ and $\Delta S^{\ddagger} = -13 \pm 1$ for the reaction of pyridine with $Ru(NH_3)_5H_2O^{2+}$ at 25°).[3,14] This implies that the substitution mechanisms for the various systems are similar.

The rates for the reaction of pyridine with *trans*-$Ru(NH_3)_4(H_2O)_2{}^{2+}$ and *trans*-$Ru(NH_3)_4(H_2O)py^{2+}$ are both slower than the analogous reactions with $Ru(NH_3)_5H_2O^{2+}$ or *cis*-$Ru(NH_3)_4(H_2O)_2{}^{2+}$ as substrates. The differences between the trans aquo and the trans pyridyl complexes are relatively small and the activation parameters are comparable, and these differences could be due to minor steric or solvation effects. The activation parameters are comparable to the reactions of the cis isomer and of $Ru(NH_3)_5H_2O^{2+}$; thus mechanistic similarity is inferred. Nonetheless, the reactivity difference between a trans-substituted aquotetraammine and the aquopentaammine ion may also reflect electronic factors. For ruthenium(II)–ammine complexes, it has been observed that a very strong π-acceptor ligand such as SO_2 or NO^+ leads to labilization of the ligand trans to it.[15] This effect is apparently in large part due to weakening of the σ bond between the trans ligand and the Ru(II), as demonstrated by the abnormally long bond (and lability) of the trans NH_3 of $Ru(NH_3)_5NO^{3+}$. Back-bonding alone should strengthen not weaken the metal's σ-bonding ability to the trans ligand. Thus, the σ-bond weakening is likely to be in large part due to the substantial σ overlap between the π-acceptor ligand and the metal owing to the very short bond length. However, in the present case, *trans*-$Ru(NH_3)_4py(H_2O)^{2+}$ is less substitution labile than $Ru(NH_3)_5(H_2O)^{2+}$. Despite the apparent π-acceptor character of pyridine,[6] this result suggests that the interaction is sufficiently weak that other factors are more important in establishing the relative lability of the trans position.

Reaction of *cis*-$Ru(NH_3)_4(H_2O)_2{}^{2+}$ with excess 2-aminomethylpyridine followed simple first-order kinetics indicating that substitution of the first coordination site is rate determining, regardless of whether the pyridine or amine nitrogen coordinates initially. When the product solutions of the rate studies were exposed to air, the originally yellow solution (λ_{max} 414 nm) turned a deep red owing to oxidation of the coordinated ligand to give the complex tetraammine (2-iminomethylpyridine)ruthenium(II). Characterization of this oxidation product was accomplished by spectral and chemical analysis.[16]

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Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (GP-26199) for support of this research.

Registry No. *cis*-$Ru(NH_3)_4(H_2O)_2{}^{2+}$, 29946-00-8; *cis*-$Ru(NH_3)_4(H_2O)py^{2+}$, 26540-33-0; *cis*-$Ru(NH_3)_4(H_2O)bz^{2+}$, 42230-43-3; *trans*-$Ru(NH_3)_4(H_2O)_2{}^{2+}$, 42230-44-4; *trans*-$Ru(NH_3)_4(H_2O)py^{2+}$, 26518-89-8; py, 110-86-1; bz, 100-47-0; AMP, 3731-51-9.

Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Magnetically Perturbed Mossbauer Study of a Distorted Five-Coordinate Iron(II) Complex

W. M. Reiff

Received May 15, 1973

Recent Mossbauer studies of five-coordinate high-spin iron(II) complexes indicate that this coordination environment is often associated with relatively large quadrupole effects. For instance, the monoterpyridyl[1] ferrous halides and pseudohalides whose geometries are believed intermediate[2] between square pyramidal and trigonal bipyramidal show quadrupole splittings (ΔE) ranging from 2.7 to 3.2 mm/sec. Even larger values are found for five-coordinate complexes of Curtis macrocyclic ligands.[3] In this note, we discuss the magnetically perturbed Mossbauer spectra of one such system, Fe(1,7-CTCl)ClO_4 (1,7-CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene), in an attempt to assess bonding and nonbonding electron contributions to the very large electric field gradient in these and similar systems and to ascertain also the nature of the orbital ground state. A schematic of the structure of the cation Fe(1,7-CTCl)$^+$ as well as the ligand is shown in Figure 1. A crystallographic study[4] of [Fe(1,7-CTCl)]I indicates that it possesses at most C_2 symmetry with the C_2 axis corresponding to the Fe–Cl bond and that the coordination environment may be approximated as distorted trigonal bipyramidal. However, for distorted five-coordinate stereochemistry, the question of whether a system is closer to trigonal bipyramidal or square pyramidal is often difficult to decide, if in fact it has any meaning. Previous electronic spectral results as well as those of this investigation favor square-pyramidal symmetry for the ligand field of the [Fe(1,7-CTCl)]$^+$ cation.

Results and Discussion

Figures 2 and 3 show the unperturbed and corresponding magnetically perturbed Mossbauer spectra of Fe(1,7-CTCl)ClO_4 at 300°K. It is evident from the lower energy triplet of the room-temperature spectrum that the principal component of the electric field gradient tensor (V_{zz}) is *positive*[5] and the asymmetry parameter η is small suggesting nearly

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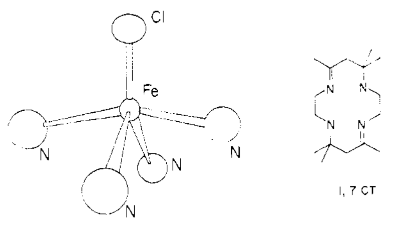

Figure 1. Schematic of the Fe(1,7-CTCl)$^+$ cation and the ligand.

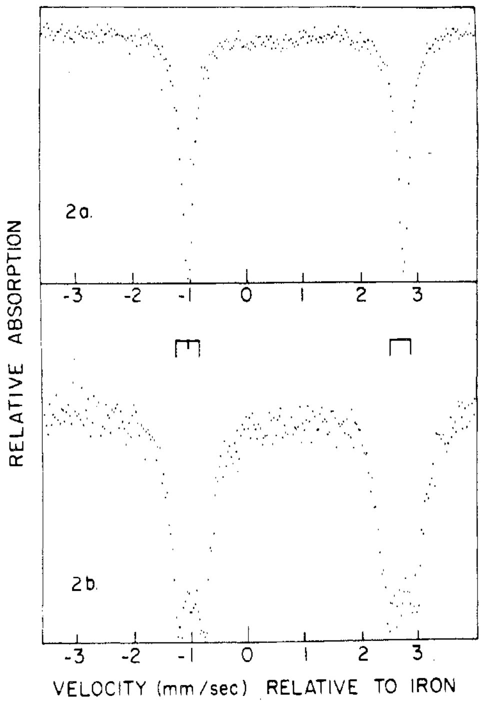

Figure 2. Mossbauer spectra of Fe(1,7-CTCl)ClO$_4$ at 300°K: (a) $H_\perp = 0$; (b) $H_\perp \approx 17$ kG.

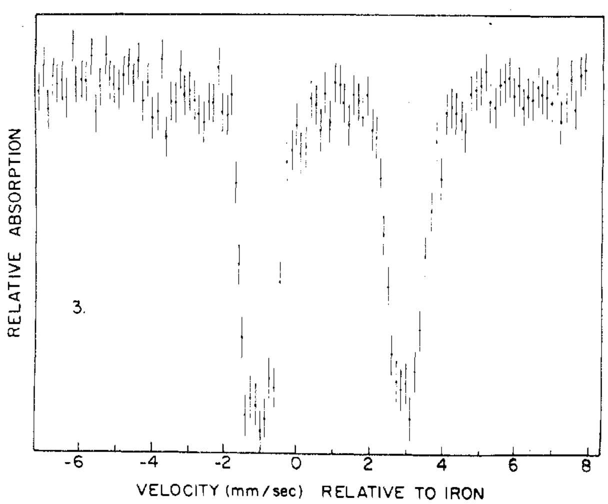

Figure 3. Mossbauer spectrum of Fe(1,7-CTCl)ClO$_4$ at 4.2°K, $H_\parallel \approx 5$ kG.

axial symmetry. The observed doublet-triplet pattern is the typical spectrum expected for a rapidly relaxing paramagnet at high temperatures where its Curie susceptibility is smaller.[6]

For a small applied field (4-5 kG, Figure 3) the spectrum at 4.2°K exhibits some broadening and corresponds to the large quadrupole splitting of 4.0 mm/sec. The only reported high-spin iron II splittings greater than that found here are those[7] of the five-coordinate dimer[8] [Fe(diethyldithiocarbamate)$_2$]$_2$ and the eight-coordinate[9] [Fe(1,8-naphthyridine)$_4$](ClO$_4$)$_2$ whose values of ΔE are 4.16 and 4.54 mm/sec, respectively, at 78°K. Thus it appears however that very large values of the quadrupole splitting are not uniquely[3] characteristic of high-spin *five-coordinate* iron(II) but depend on peculiarities of the particular coordination environment.

From a simple crystal field point of view the order of the one-electron d orbitals for a regular square-pyramidal (SP) complex is $e(d_{xz}, d_{yz}) < b_2(d_{xy}) < a_1(d_{z^2}) \ll b_1(d_{x^2-y^2})$, while the order for a regular trigonal-bipyramidal (TP) complex is $e_1(d_{xz}, d_{yz}) < e_2(d_{x^2-y^2}, d_{xy}) < a_1(d_{z^2})$. Therefore, neglecting covalence anisotropy, the sign of V_{zz} should be *negative* for either the SP or TP limits owing to the single electron in the lowest energy nonbonding e combination or for that matter a single electron in either of the e orbitals through lifting of their degeneracy. The latter situation would however correspond to a nonbonding contribution to $|\Delta E|$ of the order of that for a $^5B_2$ ground term and approximately twice that for ^5E. In any event, the present observation of V_{zz} *positive* is unexpected.

In view of the preceding observations we make the following analysis. If it is assumed that the observed ΔE is due to additive contributions from nonbonding valence electrons and that arising from bonding electrons or covalence anisotropy, then a number of possibilities for the orbital ground state arise. First of all, the contribution to ΔE from covalence anisotropy is expected to be *positive* and relatively large in view of the structure of the complex and difference in the bonding strengths of the ligands involved, *i.e.*, an approximate plane of strongly bonding ligands relative to a single weak axial ligand. The alternative situation of strong axial σ bonding leads to V_{zz} *negative*. Hence if the ground term is the ^5E, its negative contribution to ΔE is expected to reduce that from covalence anisotropy to some extent and even more as the degeneracy of the ^5E is lifted. For a $^5B_2$ ground term the corresponding large *positive* contribution to ΔE will enhance that due to bonding electrons and could very well result in the large and slightly temperature-dependent quadrupole observed. The latter ground state is unexpected but can result from increased metal-ligand σ interaction (destabilization of the e orbitals[10]) as the metal atom moves above the plane of the macrocyclic ligand. The X-ray study[4] confirms such a position for the metal atom. At the same time in-plane π back-donation serves to stabilize[11,12] the $b_2(d_{xy})$. However, these effects will not alter the relative ordering of the a_1 and b_1 levels of a square-pyramidal field. In accord with this there is invariance[3] to the higher energy transition of the near ir-visible spectra of the Fe(1,7-CTX)ClO$_4$ system for the various halogens X.

In conclusion from the discussion presented here, the large positive quadrupole effect (4.0 mm/sec at 4.2°K) appears most consistent with additive contributions from covalence anisotropy and a $^5B_2$ ground term of a square-pyramidal ligand field environment. This is contrary to a previous[3] suggestion of the expected ^5E ground term.

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Registry No. Fe(1,7-CTCl)ClO_4, 31122-42-6.

Contribution from the Department of Chemistry, Northeastern Illinois University, Chicago, Illinois 60625

Hypophosphite in Methanol. A Rapid, Nonaqueous Route to Germanium(II) Compounds[1]

Paul S. Poskozim* and Charles P. Guengerich

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A well-known route[2] to the reduction of germanium(IV) compounds involves the reaction of a 4:1 molar excess of hypophosphorous acid (H_3PO_2) with germanium(IV) chloride ($GeCl_4$) in approximately 3 *M* hydrochloric acid. Reaction times are on the order of 3 hr and temperatures are kept near 95°. Work in our laboratory showed that many of the above parameters could be reduced or excluded without altering the basic nature of the reaction. Specifically, (a) reaction 1 goes essentially to completion at 1:1 molar ratios

$$GeCl_4 + H_3PO_2 + H_2O \xrightarrow[HCl]{3\,M} GeCl_2(aq) + H_3PO_3 + 2HCl \qquad (1)$$

of H_3PO_2:$GeCl_4$, (b) hydrochloric acid is neither essential to the reductive process nor required for the prevention of $GeCl_4$ hydrolysis, and (c) reaction 1 is quite rapid (in the order of several minutes) at temperatures ranging from 65 to 85°.

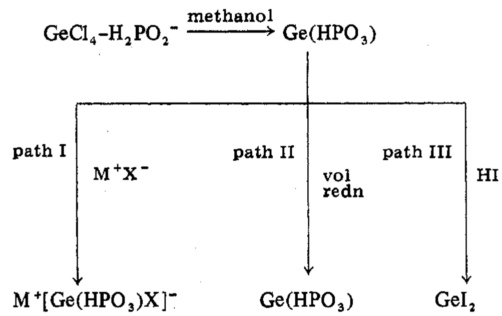
While investigating the implications of points a-c above, it was discovered that hydrated sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$, in methanol solution effectively and almost instantaneously reduces germanium(IV) chloride. To our knowledge, this is the first example of a successful Ge(IV)-Ge(II) reduction reaction in a nonaqueous solvent.

$$GeCl_4 + NaH_2PO_2 \cdot H_2O \xrightarrow{\text{methanol}} Ge(HPO_3) + \underline{NaCl} + 3HCl \qquad (2)$$

Scheme I summarizes data now known about the hypophosphite-germanium(IV) reduction system in solvent methanol. It is possible to isolate and characterize a chloride salt of $Ge(HPO_3)$ by filtering the initial solid sodium chloride from the reaction mixture and then adding a large cation such as trimethylammonium (path I). A white precipitate of $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$ immediately forms. It is a high-melting (>250° with decomposition), highly insoluble, hygroscopic salt. Preliminary evidence indicates that the cesium ion will act in like manner.

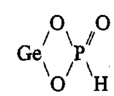
Evaporation under vacuum (path II) causes the eventual precipitation of the $Ge(HPO_3)$ species, a compound first claimed by Everest[3] in the reaction of GeO_2 with H_3PO_2 in

Scheme I. The Hypophosphite-Germanium(IV) Reduction System[a]



[a] M^+ is a large cation such as trimethylammonium, Cs^+, Rb^+, etc.

phosphorous acid solvent. The germanium(II) hydrogen phosphite moiety as obtained herein is either anhydrous or contains one molecule of water. Infrared data (see Experimental Section) seem to indicate the appropriate P–H, P–O, and P=O frequencies consistent with a bidentate structure such as



A proton nmr spectrum taken of the salt dissolved in deuterated methanol showed a sharp, widely spaced doublet (524 Hz) attributable to the P-H linkage and an expectedly large J_{P-H} coupling constant. The J_{P-H} value for $NaH_2PO_2 \cdot H_2O$ in methanol was 500 Hz. No evidence for phosphorous acid (J_{P-H} = 707 Hz)[4] was observed. H_3PO_3 (reaction 1) is formed when germanium tetrachloride is reduced in the aqueous acidic medium. The central germanium(II) atom is no doubt four-coordinated in the solid $Ge(HPO_3)$ structure much like it is in polymeric GeF_2.[5] X-Ray analysis has now been initiated for complete structure elucidation.

Concentrated hydriodic acid (HI) appears to be the only strong acid (path III) capable of completely liberating HPO_3 from $Ge(HPO_3)$ to form the corresponding GeX_2 salt. There is no significant reaction when varying quantities of HBr, HCl, HF, H_2SO_4, and HNO_3 are added. It is probable that an equilibrium exists between GeI_2 and the $Ge(HPO_3)$ species in methanol solution

$$Ge(HPO_3) + 2HI \rightleftarrows GeI_2 + H_3PO_3$$

and that excess HI (about 15:1 molar ratio) is required to effect a significant yield of approximately 60% germanium(II) iodide product. Work is continuing in attempts to maximize yields of GeI_2 and to determine why only HI of all the strong halogen and mineral acids will conveniently precipitate out a GeX_2 salt.

In the course of our studies it was shown that if hexanol and formic acid were used in place of methanol solvent in performing the sodium hypophosphite reduction of germanium tetrachloride, germanium(II) species were indeed produced, but yields were invariably lower and reaction times considerably lengthened. When, however, equimolar quantities of the solid $NaH_2PO_2 \cdot H_2O$ and liquid $GeCl_4$ were mixed neat under an atmosphere of nitrogen, no reaction took place over a period of 5 hr at room temperature. A

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