CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CLIPPINGER LABORATORIES, OHIO UNIVERSITY,
ATHENS, OHIO   45701

Dependence of the Proton Resonance Shifts in Aqueous Solutions of Chromium(II) on the Perchlorate Ion Concentration

BY F. W. BREIVOGEL, JR.

The purpose of the present study was to measure the unpaired spin density in the hydrogen 1s orbitals in the $Cr(H_2O)_6^{2+}$ ion and to elucidate the mechanism for the electron delocalization. It was possible to obtain this information by studying the proton resonance shifts in aqueous solutions of Cr^{2+} at different perchlorate ion concentrations and comparing these with the results of Jackson, *et al.*,[1] who studied the ^{17}O resonance shifts of similar solutions.

Experimental Section

Solutions were prepared by dissolving weighed quantities of $Cr(ClO_4)_3 \cdot 6H_2O$ in solutions containing known amounts of $NaClO_4$ and $HClO_4$. Reduction to Cr^{2+} was carried out in a nitrogen atmosphere by adding amalgamated zinc to the solutions. A small amount of amalgamated zinc was placed in the nmr sample tubes to ensure that no oxidation of the Cr^{2+} occurred.

Nmr spectra were obtained on a Varian A-60 spectrometer equipped with a variable-temperature controller. The temperature was determined by measuring the peak separation in ethylene glycol. Most measurements were made at the ambient probe temperature of 31°. Dioxane was used as an internal standard. The chemical shifts of the Cr^{2+} solutions were determined by comparing with solutions containing identical concentrations of $HClO_4$ and $NaClO_4$.

Results and Discussion

When a solution containing Cr^{3+} ion was reduced, the proton nmr line width decreased by a factor of 10 and there was a large increase in the observed chemical shift. The line width of the Cr^{3+} solutions increased with temperature while the line width of the Cr^{2+} solutions decreased with temperature. These observations show that the amount of Cr^{3+} remaining in our solutions was too small to have an appreciable effect on the chemical shift measurements.

Previous studies have shown that at room temperature the exchange of water molecules between the first coordination sphere of Cr^{2+} and the bulk solution is very fast.[1,2] In this case the equation

$$\Delta\nu = P_M \Delta\nu_M \tag{1}$$

is applicable where P_M is the fraction of protons in water molecules complexed to the metal ion, $\Delta\nu$ is the observed chemical shift of the solution with respect to a similar solution not containing Cr^{2+} ions, and $\Delta\nu_M$ is the chemical shift of a proton in the first coordination sphere of the metal ion with respect to one in the bulk solution. The applicability of this equation was confirmed by

(1) A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **38**, 836 (1962).

(2) C. W. Merideth, Ph.D. Thesis, University of California, Berkeley, Jan 1965. Lawrence Radiation Laboratory Report UCRL-11704.

TABLE I

PROTON CONTACT SHIFTS FOR AQUEOUS SOLUTIONS OF Cr^{2+} AT VARIOUS PERCHLORATE ION CONCENTRATIONS AT 31°

M_{H^+}	$M_{ClO_4^-}$	$10^3 P_M$	$-\Delta\nu_M$, Hz
1.0	1.2	7.08	12,100
1.0	1.2	8.74	12,000
0.9	4.3	6.25	11,000
0.9	4.3	8.75	10,800
4.4	4.6	6.00	10,800
4.4	4.6	7.45	10,700
4.0	6.6	7.05	10,500
4.0	6.6	7.41	10,400
3.3	8.7	7.12	8,700
3.3	8.7	6.05	9,000

observing that $\Delta\nu$ was directly proportional to $1/T$ from 0 to 100°. A coordination number of 6 was assumed in calculating P_M.

Table I gives the results. All shifts are to lower fields. Assuming that the shifts are due to the Fermi contact interaction the results indicate a positive spin density on the protons. The addition of perchlorate ion has a relatively small effect on the proton resonance. In contrast, Jackson, *et al.*,[1] found that the perchlorate ion concentration had a great effect on the ^{17}O resonance of aqueous solutions of Cr^{2+}. For example, in a solution 0.40 M in Cr^{2+} and 1.3 M in chloride ion the ^{17}O chemical shift was -0.55 part in 10^4 with respect to pure water. In a solution 0.57 M in Cr^{2+}, 1.9 M in chloride ion, and 8.5 M in perchlorate ion the shift was $+0.33$ part in 10^4. The results were explained by assuming that complexes were formed between Cr^{2+} and perchlorate ions. Further evidence for the existence of these complexes was the large shift in and broadening of the resonance of the ^{17}O atoms in the perchlorate ions at high perchlorate ion concentrations.

The model proposed by Jackson, *et al.*, is the following. The $Cr(H_2O)_6^{2+}$ complex is assumed to be a distorted octahedron with perchlorate ions perferentially replacing the axial water molecules. Electron spin transfer to the oxygen occurs by a σ interaction. Oxygen atoms in the axial positions transfer electrons to the half-filled d_{z^2} orbital leaving a positive spin on the oxygen and producing a downfield shift. When the oxygen atoms in the planar positions transfer electrons to the empty $d_{x^2-y^2}$ orbital, the transferred electrons preferentially line up with the spin of the Cr^{2+} ion leaving negative spin on the oxygen atoms. This gives rise to an upfield shift. In the absence of complex formation the downfield shift dominates, but if the axial waters are replaced by perchlorate ions, the shift changes to an upfield shift.

The present proton magnetic resonance results are consistent with the assumption that spin transfer to the water *protons* occurs primarily through π interactions. All three d orbitals capable of forming π bonds with the ligands are half-filled in Cr^{2+} and π bonding would place positive spin density on both axial and planar protons. (It is possible to place negative spin on the protons *via* π bonding, but in similar studies on other ions,[3,4] π bonding always produces positive spin

(3) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(4) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966).

on the protons.) Replacement of the axial waters by perchlorate ions would not change the sign of the observed shift but would reduce the magnitude of the shift. This mechanism involves transfer of spin to the protons through the oxygen p orbitals and, therefore, would not place spin at the oxygen nucleus. This mechanism has been proposed previously as the predominant electron delocalization mechanism to explain the observed spin densities on the protons in the hydrated Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} ions.[3,4]

From the value of the chemical shift at low perchlorate ion concentrations the fraction of an unpaired 1s electron on the hydrogen atom was calculated to be 0.0026. (This represents an average value since the spin densities on the axial and planar protons would undoubtedly be different.) The corresponding value[3] for $Mn(H_2O)_6{}^{2+}$, which also has three unpaired d electrons capable of π bonding, is 0.0022.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTH CAROLINA STATE UNIVERSITY,
RALEIGH, NORTH CAROLINA 27607

A Nuclear Quadrupole Resonance Study of Oxygen Donor–Mercuric Chloride Acceptor Complexes[1a]

BY T. B. BRILL[1b] AND Z Z. HUGUS, JR.

Three-coordinate Hg(II) appears to be relatively rare. It has been found in $(CH_3)_4N^+$ salts[2,3] of $HgCl_3{}^-$, $HgBr_3{}^-$, and $HgI_3{}^-$. The coordination about the mercury atom approaches trigonal but, as a result of lattice interactions, is slightly pyramidally distorted. Na^+, $NH_4{}^+$, and Cs^+ salts of $HgCl_3{}^-$ do not contain three-coordinate Hg(II) at all.[4–6] There exist a large number of donor–acceptor complexes of $HgCl_2$ whose 1:1 stoichiometry suggests three-coordination about the mercury atom.[7] In fact $HgCl_2 \cdot DMSO$ has been proposed to be just this.[8]

Clearly it would be interesting to investigate oxygen donor–$HgCl_2$ acceptor complexes with 1:1 stoichiometry in detail. Nuclear quadrupole resonance spectroscopy is a particularly attractive technique for studying such weak complexes since the electric field gradient at a quadrupole nucleus is very sensitive to small changes in the surrounding valence electrons.

The ^{35}Cl and ^{37}Cl nqr signals in complexes of $HgCl_2$ and seven organic oxygen-donor compounds have been recorded. Interpretation of the results strongly suggests that in the compounds studied, three-coordinate $HgCl_2$ with the oxygen atom does not exist.

Experimental Section

Materials.—Mercuric chloride (B.A. reagent) was recrystallized from water to remove the small amount of insoluble matter. Tetrahydrofuran (THF) (Fisher reagent), *p*-dioxane (diox) (Matheson Coleman and Bell), and dimethyl sulfoxide (DMSO) (Fisher reagent) were dried over molecular sieves and used without further purification. Benzophenone (BPH) (Matheson Coleman and Bell), acetophenone (APH) (Fisher reagent), and 2,6-dimethyl-γ-pyrone (DMP) (Aldrich Chemical Co.) were used without further purification. Benzoquinone (BZQ) (Eastman Kodak Co.) was carefully sublimed twice and the yellow crystals were used immediately.

Dioxane–Mercuric Chloride.—This compound was prepared by the method of Husemann.[9] The long colorless needles are unstable with respect to the loss of dioxane so for the nqr measurements the crystals were placed in a sealed vial containing excess dioxane. The instability of the complex provides an easy method for analysis. The crystals were rapidly weighed and then exposed to the air for several days. All the dioxane evaporated leaving only the mercuric chloride. *Anal.* Calcd for $HgCl_2 \cdot C_4H_8O_2$: $HgCl_2$, 75.5. Found: $HgCl_2$, 75.4.

Acetophenone–Mercuric Chloride.—This compound was prepared using the method of Volhard.[10] Analysis was carried out by adding KOH to a water solution of the complex. The resulting HgO was washed, dried, and weighed. *Anal.* Calcd for $HgCl_2 \cdot C_8H_8O$: Hg, 51.2. Found: Hg, 51.0.

Dimethyl Sulfoxide–Mercuric Chloride.—This compound was prepared using the method of Selbin, Bull, and Holmes.[8] For nqr measurements the crystals were placed in a vial with excess DMSO. Initially no resonance could be found, but after the compound stood for about 5 months the resonances were recorded. Analysis was carried out by converting the complex to HgO. *Anal.* Calcd for $HgCl_2 \cdot C_2H_6SO$: Hg, 57.4. Found: Hg, 57.2.

Benzophenone–Mercuric Chloride.—This compound was prepared using the method of Volhard.[10] Analysis was carried out by converting the complex to HgO. *Anal.* Calcd for $HgCl_2 \cdot C_{13}H_{10}O$: Hg, 44.2. Found: Hg, 44.2.

2,6-Dimethyl-γ-pyrone–Mercuric Chloride.—This compound was prepared using the method of Cook[11] and analyzed by converting it to HgO. *Anal.* Calcd for $HgCl_2 \cdot C_7H_{10}O_2$: Hg, 50.4. Found: Hg, 50.5.

Tetrahydrofuran–Mercuric Chloride.—This previously unreported compound is unstable with respect to the loss of THF. It was prepared by dissolving $HgCl_2$ (5.0 g) in THF (40 ml). Upon evaporation of the THF to about 15 ml, long, colorless needles formed. For the nqr measurements the crystals were kept in a sealed vial under excess THF. Conventional analysis is not possible so it was analyzed in the same way as the $HgCl_2 \cdot$ diox complex. *Anal.* Calcd for $HgCl_2 \cdot C_4H_8O$: $HgCl_2$, Found: $HgCl_2$, 79.1.

Benzoquinone–Mercuric Chloride.—This compound appears not to have been reported in the past. It was prepared by dissolving $HgCl_2$ (5.00 g, 0.018 mol) in ethanol and adding it to benzoquinone (1.95 g, 0.018 mol) dissolved in ethanol. After several days, long (2 cm × 1 mm) yellow needles formed. The nqr study was carried out immediately since the compound tends to turn black after several weeks. Analysis was carried out on freshly prepared sample by warming a known amount in a vacuum desiccator for several days. The benzoquinone sublimed leaving the $HgCl_2$. *Anal.* Calcd for $HgCl_2 \cdot C_6H_4O_2$: $HgCl_2$, 71.5. Found: $HgCl_2$, 71.7.

(1) (a) Abstracted from the Ph.D. dissertation of T. B. B., University of Minnesota. (b) NDEA fellow at the University of Minnesota, 1966–1969.

(2) J. C. White, *Acta Cryst.*, **16**, 397 (1963).

(3) E. Fattuzo, R. Nitsche, H. Roetschi, and S. Zingg, *Phys. Rev.*, **125**, 514 (1962).

(4) A. Weiss and K. Damm, *Z. Naturforsch.*, **9b**, 82 (1954).

(5) E. J. Harmsen, *Z. Krist.*, **100**, 208 (1938).

(6) Z. V. Zvonkova, V. V. Samodurov, and L. G. Vorontsova, *Dokl. Akad. Nauk SSSR*, **102**, 1115 (1955).

(7) I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, Inc., Berlin, 1963.

(8) J. Selbin, W. E. Bull, and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **16**, 219 (1961).

(9) J. Husemann, *Ann.*, **126**, 281 (1862).

(10) J. Volhard, *ibid.*, **267**, 172 (1892).

(11) D. Cook, *Can. J. Chem.*, **39**, 1184 (1961).