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.

Received October 17, 1969

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).

TABLE I

^{35}Cl AND ^{37}Cl NQR DATA FOR OXYGEN DONOR–MERCURIC CHLORIDE ACCEPTOR COMPLEXES

Complex	$\nu(^{35}Cl)$, MHz	Signal:noise	$\nu(^{37}Cl)$, MHz	Signal:noise
$HgCl_2$[a]	22.251 ± 0.005	90:1	17.530 ± 0.005	40:1
	22.064 ± 0.005	50:1	17.390 ± 0.005	15:1
$HgCl_2$·diox	20.454 ± 0.005	12:1	16.126 ± 0.005	6:1
$HgCl_2$·BZQ	20.540 ± 0.005	4:1	16.193 ± 0.005	2:1
$HgCl_2$·DMP	19.155 ± 0.005	3:1	15.089 ± 0.005	2:1
$HgCl_2$·THF	21.019 ± 0.005	25:1	16.550 ± 0.005	8:1
	19.628 ± 0.005	20:1	15.471 ± 0.005	8:1
$HgCl_2$·APH	20.872 ± 0.005	5:1	16.436 ± 0.005	3:1
	19.396 ± 0.005	3:1	15.275 ± 0.005	2:1
$HgCl_2$·BPH	21.685 ± 0.005	18:1	17.075 ± 0.005	6:1
	20.742 ± 0.005	13:1	16.330 ± 0.005	4:1
$HgCl_2$·DMSO	21.184 ± 0.005	8:1	16.680 ± 0.005	4:1
	20.075 ± 0.005	4:1	15.810 ± 0.005	2:1

[a] Two crystallographically different chlorine atoms exist.

The fact that the compounds are not simply mixtures is evident because definite nqr signals well shifted from pure $HgCl_2$ were recorded. Nqr signals are generally destroyed by random crystal lattice impurities.[12]

Nqr Spectrometer.—The nqr results reported in Table I were recorded using a Wilks Scientific NQR-1A spectrometer. A Hewlett-Packard 5245L electronic counter was used for frequency measurements. All resonances were recorded at 23°.

Results and Discussion

$HgCl_2$ and $HgCl_2$·diox.—Several nqr[13,14] and X-ray crystallographic studies[15,16] are available for $HgCl_2$. For $HgCl_2$·diox, a room-temperature X-ray structure study[17] and a 77°K nqr result[18] have been published. $HgCl_2$·diox crystallizes in a triclinic cell containing one formula unit and consists of infinite chains of alternating $HgCl_2$ and dioxane molecules. The Hg, Cl, and O atoms and the center of the dioxane molecules lie in the same plane and the mercury atom attains four-coordination as shown in Figure 1. Far-ir[19] and Raman[20] studies of both $HgCl_2$ and $HgCl_2$·diox are available and indicate that $HgCl_2$ and dioxane form such a weak complex that its spectrum is almost superimposable on the pure substituents.[19]

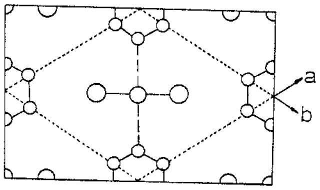


Figure 1.—The unit cell of $HgCl_2$·diox as viewed along the *c* axis.[17]

In Table II pertinent experimental information for $HgCl_2$ and $HgCl_2$·diox is compared and indicates that definite donation of electron density from the dioxane molecule into the $HgCl_2$ system has occurred. The nqr result is in accordance with the X-ray data since only one resonance was found.

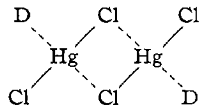
TABLE II

EXPERIMENTAL DATA FOR $HgCl_2$ AND $HgCl_2$·diox

Compound	Hg–Cl bond distance, Å	Hg–Cl str freq,[a] cm^{-1}	$\nu(Cl^{35})$, MHz
$HgCl_2$ [Cl(1)]	2.23	342	22.251[b]
[Cl(2)]	2.27		22.064[b]
$HgCl_2$·diox	2.34	321	20.454

[a] Degeneracy-weighted average. [b] Reference 14.

$HgCl_2$ Addition Complexes with THF, DMSO, Acetophenone, and Benzophenone.—The presence of two rather widely separated ^{35}Cl resonances in these compounds suggests that two chemically inequivalent chlorine atoms exist. It is unlikely that a three-coordinate mercury atom could be present in such a way that the chlorine atoms are markedly different. More feasible explanations based on a closer examination of the nqr data may be made. First, the lattice may be thought of as containing free $HgCl_2$ and four-coordinate $HgCl_2\cdot(D)_2$ (I), or, second, the lattice may contain dimeric units (II) as



where D is the donor. Both I and II would account for the presence of two chlorine signals. A closer look at the two resonance frequencies reveals, however, that both resonances are affected by the nature of D in roughly the same way; *i.e.*, for a given D, both resonances shift to higher or lower frequencies with respect to the other D's. II accounts for this fact but no conclusion could be drawn using I. II would indicate that one of the resonances should be more sensitive to the nature of D than the other since the bridge halogen is simultaneously affected by two donors compared to the terminal halogen which is affected by just one. The nqr data are consistent with this. Bridged halogens have been found to have lower nqr frequencies[21] than terminal ones. The lower frequency resonance is the one most affected by D. Thus,

---

(12) T. P. Das and E. L. Hahn, *Solid State Phys. Suppl.*, **1**, 205 (1958).

(13) H. G. Dehmelt, H. G. Robinson, and W. Gordy, *Phys. Rev.*, **93**, 408 (1954).

(14) H. Negita, T. Tanaka, T. Okuda, and H. Shimada, *Inorg. Chem.*, **5**, 2196 (1966).

(15) H. Braekken and W. Scholten, *Z. Krist.*, **89**, 484 (1934).

(16) D. Grdenić, *Arhiv Kem.*, **22**, 14 (1950).

(17) O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **8**, 1953 (1954).

(18) D. Biedenkapp and A. Weiss, *Z. Naturforsch.*, **19a**, 1518 (1964).

(19) Y. Mikawa, R. J. Jacobsen, and J. W. Brasch, *J. Chem. Phys.*, **45**, 4528 (1966).

(20) P. Tarte and P. A. Laurent, *Bull. Soc. Chim. France*, **24**, 402, (1957).

(21) J. C. Evans and G. Y-S. Lo, *Inorg. Chem.*, **6**, 836 (1967).

three pieces of nqr data are consistent with structure II. Similar dimeric units are also known for Au, Pt, Pd, etc.[22]

It is difficult to evaluate the relative basicities of D in these weak complexes by the variation in the chlorine nqr frequencies since crystal effects may be important. However, some comment should be made. THF might be expected to be a better donor than dioxane since only one oxygen atom competes for localization of the electron density. This is in accordance with the nqr data. Concerning acetophenone *vs.* benzophenone, Susz and Chalandon[23] reasoned that the carbonyl donor strength increases as the number of aromatic groups attached to it increases. Their reasoning was based on the relative shift of the carbonyl ir stretching frequency. Paoloni and Marini-Bettólo[24] found the carbonyl frequency shift was about the same for both acetophenone and benzophenone in the $HgCl_2$ complexes. Table III shows that the ir and nqr data for these compounds do not concur. Both studies may be complicated somewhat by crystal lattice effects. The nqr results for the DMSO complex indicate that the donor strength of the C=O and S=O groups is similar.

TABLE III

A COMPARISON OF IR AND NQR DATA FOR SEVERAL CARBONYL DONOR MOLECULES WITH $HgCl_2$ AS THE ACCEPTOR

Compound	$\nu_{C=O}$ shift from the pure donor, cm^{-1}	$\nu(^{35}Cl)$, MHz
$HgCl_2 \cdot BZP$	-33^a	20.742
$HgCl_2 \cdot APH$	-34^a	19.396
$HgCl_2 \cdot DMP$	-41^b	19.155

[a] Reference 24. [b] Reference 11.

$HgCl_2$ Addition Complexes with Benzoquinone and 2,6-Dimethyl-γ-pyrone.—Like the dioxane complex, only one resonance was recorded for these two compounds. With benzoquinone the Hg–O interaction is probably similar to that in the dioxane and the 1,4-cyclohexanedione[25] complexes.

Only one resonance was found in $HgCl_2 \cdot DMP$. Since γ-pyrone has an ether oxygen *para* to the carbonyl group, it is possible that end-to-end linkage similar to the dioxane complex could form. The mercury atom would simultaneously interact with both a carbonyl and an ether oxygen atom to attain four-coordination. The largest shift in the chlorine resonance frequency from pure $HgCl_2$ was observed in this compound. Table III shows that a large shift in the carbonyl stretching frequency also occurs—at least greater than in the benzophenone and acetophenone complexes.

Acknowledgment.—We wish to thank the North Carolina Board of Science and Technology for support toward the purchase of the nqr spectrometer.

[22] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962.

[23] B. P. Susz and P. Chalandon, *Helv. Chim. Acta*, **41**, 1332 (1958).

[24] L. Paoloni and G. B. Marini-Bettólo, *Gazz. Chim. Ital.*, **89**, 1972 (1959).

[25] P. Groth and O. Hassel, *Acta Chem. Scand.*, **18**, 1327 (1964).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
BAYLOR UNIVERSITY, WACO, TEXAS 76703

A Potentiometric Study of Some Nitrogen Complexes

BY THOMAS C. FRANKLIN AND RANDOLPH C. BYRD

Received October 20, 1969

The fact that the fixation of nitrogen can occur quite rapidly in the presence of enzyme systems containing transition elements has, in recent years, led to a number of studies of complexes between nitrogen and transition metals and the fixation of nitrogen using these complexes. This work has been the subject of two recent reviews.[1,2] The recent work on the electrolytic fixation of nitrogen utilizing these complexes as catalysts[3] indicates that useful information could be obtained from a simple potentiometric study of the system.

Experimental Section

The solvents used were dimethyl sulfoxide and propylene carbonate. The purest grade commercially available was used and no attempt was made to dry them. The titanium(IV) chloride–titanium(III) chloride system was chosen for study. The titanium solutions were prepared by electrolytically reducing a solution of titanium(IV) chloride externally under a helium atmosphere in a cell with the anode and cathode compartments separated by a porous cup.

The potential was measured as a function of nitrogen pressure using a Fluke Model 801 differential voltmeter. The nitrogen pressure was controlled by a Cartesian manostat.

The indicator electrode in all cases was a platinum wire. The reference electrode was a Beckman saturated calomel electrode separated from the nonaqueous system by an asbestos fiber.

The cell (a 300-ml beaker) was mounted in a 2-l. resin reaction kettle in a nitrogen atmosphere with nitrogen slowly bubbling through the solution.

Results and Conclusions

The potentiometric data were interpreted in terms of the reactions

$$TiCl_4 + e^- \longrightarrow TiCl_3 + Cl^-$$

$$rN_2 + qTiCl_3 \longrightarrow [TiCl_3]_q(N_2)_r$$

where $TiCl_4$ and $TiCl_3$ refer to the solvated forms of the compounds, and $[TiCl_3]_q(N_2)_r$ refers to the nitrogen complex of the reduced compound.

From these reactions, one can derive that the potential at different pressures of nitrogen and constant concentrations of the oxidized and reduced forms of the metal and the chloride ion is given by the following equation[4] at 25.0°

$$E = K + 0.059\frac{r}{q}\log P_{N_2}$$

In this derivation, it was assumed that the nitrogen forms a stable complex only with the reduced form

---

[1] R. Murry and D. C. Smith, *Coord. Chem. Rev.*, **3**, 453 (1968).

[2] A. D. Allen and F. Bottomley, *Accounts Chem. Res.*, **1**, 360 (1968).

[3] E. E. van Tamelen and B. Akermark, *J. Am. Chem. Soc.*, **90**, 4492 (1968).

[4] S. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1949.