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-Bettòlo[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.

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A Potentiometric Study of Some Nitrogen Complexes

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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

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[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.

of the metal and that the concentration of the complex is essentially constant. The last assumption will be true if the complex ion is relatively stable, since, under this condition, virtually all of the reduced metal ion will be in the form of complex ions. The assumption that a stable complex is formed with only the reduced form of the metal was made since, in practically all cases,[1,2] the stable complexes isolated have been complexes of the reduced form of the metal.

Titanium Chloride System.—Figure 1 shows the results of a typical run obtained in dimethyl sulfoxide solutions for the titanium(III) chloride–titanium(IV) chloride system. As can be seen, the slope of the graph is 0.058 which indicates that r/q is equal to 1 or that there is one metal atom for each nitrogen molecule in the complex. This indicates that the formula of the complex in this solvent is probably similar to the formulas of known nitrogen complexes with rhodium, iridium, ruthenium, cobalt, and osmium.

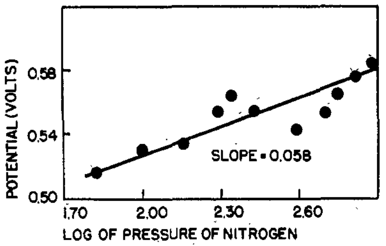

Figure 1.—The relationship between potential (compared to the saturated calomel electrode) and nitrogen pressure in the dimethyl sulfoxide–titanium(III) chloride–titanium(IV) chloride system.

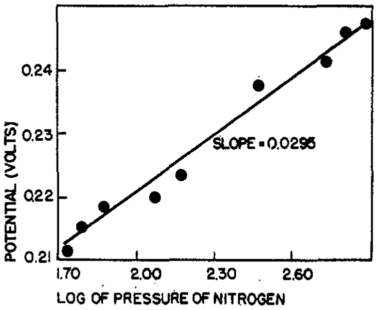

Figure 2.—The relationship between potential (compared to the saturated calomel electrode) and nitrogen pressure in the propylene carbonate–titanium(III) chloride–titanium(IV) chloride system.

Figure 2 shows typical results obtained in propylene carbonate solutions. The slope in this case (0.0295) corresponds to an r/q value of $^1/_2$ which corresponds to a ratio of two metal atoms to one nitrogen molecule. This indicates that the formula of the complex in this solvent is similar to that of the ruthenium complex identified by Taube,[5] in that the nitrogen acts as a bridge between two metal atoms. In both of these experiments, the data shown on the graph were obtained in a random fashion in that some measurements were made as the pressure was increased and others were made as the pressure was decreased.

In summary, the potentiometric study has indicated that in dimethyl sulfoxide titanium(III) chloride forms a 1:1 complex with nitrogen. On the other hand, in propylene carbonate titanium(III) chloride forms a complex in which one nitrogen molecule acts as a bridge between two titanium atoms.

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The Preparation of N-Fluoroformyliminotrifluoromethylsulfur Fluoride, $CF_3SF{=}NCFO$

BY L. C. DUNCAN

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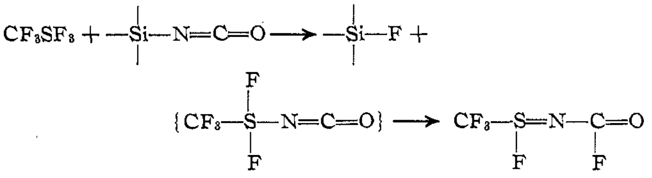
Trifluoromethylsulfur trifluoride[1] reacts with silicon tetraisocyanate forming the colorless liquid N-fluoroformyliminotrifluoromethylsulfur fluoride ($CF_3SF{=}NCFO$) and silicon tetrafluoride: $4CF_3SF_3 + Si(NCO)_4 \rightarrow 4CF_3SFNCFO + SiF_4$. This reaction is analogous to that of sulfur tetrafluoride and silicon tetraisocyanate reported by Clifford and Kobayashi[2] and to the reaction of thionyl tetrafluoride and silicon tetraisocyanate reported by Ruff.[3] A plausible route to the product involves CF_3SF_3 addition with silicon–nitrogen cleavage and then rearrangement of the resulting species to product



$$CF_3SF_3 + {-}\overset{|}{\underset{|}{Si}}{-}N{=}C{=}O \longrightarrow {-}\overset{|}{\underset{|}{Si}}{-}F +$$

$$\{CF_3{-}\overset{F}{\underset{F}{S}}{-}N{=}C{=}O\} \longrightarrow CF_3{-}\underset{F}{S}{=}N{-}\underset{F}{C}{=}O$$

Experimental Section

Materials.—Silicon tetraisocyanate[4] was prepared through the reaction of silver cyanate with silicon tetrachloride. Trifluoromethylsulfur trifluoride was obtained using a modification of the procedure suggested by Lawless and Harman.[1c] Bistrifluoromethyl disulfide (Peninsular ChemResearch, 20 mmol) was condensed into a 100-ml Monel cylinder which had previously been charged with 28.9 g (194 mmol) of AgF_2 (Harshaw). The cylinder was rapidly warmed to 0° and then was allowed to warm to room temperature overnight. An infrared spectrum of the gaseous product mixture after this reaction indicated the presence of CF_3SF_3, CF_3SF_5, and CF_3SSCF_3. The desired trifluoromethylsulfur trifluoride was then isolated as a solid $CF_3SF_3 \cdot BF_3$ ad-

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