From the intensity data of Table II is is apparent that there is very little metal–carbon π-bonding in $Hg(CN)_2$ and that it increases in the order $Hg < Ag < Au$. This is the same order as the interaction constants $F_{MC,MC}$. As pointed out for the metal hexacarbonyls[8] the magnitude of the constant $F_{MC,MC}$ depends primarily on the extent of metal–carbon π-bonding. Thus the intensity data and the MC,MC interaction constants corroborate each other.

Note that in spite of the small amount of metal–ligand π-bonding in $Hg(CN)_2$ the HgC force constant is considerably larger than the AgC force constant and almost as large as the AuC force constant. This indicates that the HgC σ-bond is considerably stronger than the AuC σ-bond. Referring to eq. 2 let us compare $Hg(CN)_2$ with $Au(CN)_2^-$.

$$(F_{MC})_{HgC} - (F_{MC})_{AuC} = a[(S\sigma)_{HgC} - (S\sigma)_{AuC}] + b[(S\pi)_{HgC} - (S\pi)_{AuC}]$$

$(S\sigma)_{HgC} - (S\sigma)_{AuC}$ is positive while $(S\pi)_{HgC} - (S\pi)_{AuC}$ is negative so the two terms can compensate each other, leading to nearly equal MC force constants. However, from eq. 3

$$(F_{CN})_{HgC} - (F_{CN})_{AuC} = c[(S\sigma)_{HgC} - (S\sigma)_{AuC}] - d[(S\pi)_{HgC} - (S\pi)_{AuC}]$$

Both terms become positive so we have a considerably higher CN force constant for $Hg(CN)_2$ than for $Au(CN)_2^-$.

Conclusions

This paper shows that the intensities of the infrared-active CN stretching vibrations of metal–cyanide complexes can be correlated with the extent of metal–cyanide π-bonding. Thus an increase in metal–cyanide π-bonding causes an increase in the intensity of the asymmetric CN stretching vibration. This observation corroborates the previous postulation[12] for metal carbonyls that the MC,MC interaction force constants are determined to a large extent by the amount of metal–ligand π-bonding.

In discussing the bonding in metal cyanide complexes it is seen above that consistent results are obtained by treating the metal–cyanide σ-bond strength and the metal–cyanide π-bond strength separately as to their effect on the metal–carbon and carbon–nitrogen force constants. This leads to the following conclusions:

(1) The extent of metal–cyanide π-bonding increases as the number of d_ϵ electrons increases.

(2) The extent of metal–cyanide π-bonding decreases as the effective nuclear kernel charge on the metal increases.

(3) The extent of metal–cyanide σ-bonding increases as the effective nuclear kernel charge on the metal increases.

(4) The carbon–nitrogen force constant decreases as the metal–cyanide π-bonding increases.

(5) The carbon–nitrogen force constant increases as the metal–cyanide σ-bonding increases.

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Contribution from the Department of Chemistry,
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Solvent Extraction Investigation of Anionic Complex Formation in Mercury(II)–Nitrate Systems

By S. S. CHOI and D. G. TUCK

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Solvent extraction experiments using methyldioctylamine (MDOA) in chloroform solution have demonstrated that mercury(II) forms anionic complexes with nitrate ion in aqueous nitric acid solution (0.2–8 *M*). By measuring the distribution coefficient D_{Hg} as a function of MDOA concentration, the extracted species was shown to be $[Hg(NO_3)_4]^{2-}$. This anion appears to protonate readily in aqueous solution.

It is well known that mercury(II) forms strong complexes with halides and pseudo-halides, and that the highest complexes are anionic,[1] but there is little information on corresponding complexes with oxyanions. Salts containing $[Hg(oxalate)_2]^{2-}$ have been prepared,[2] and sulfate complexes have been identified.[3] In nitrate solution, e.m.f. measurements have shown that $[HgNO_3]^+$ and $[Hg(NO_3)_2]^0$ exist.[3] The aim of the present work was to investigate the formation of higher nitrate complexes, $[Hg(NO_3)_3]^-$ and $[Hg(NO_3)_4]^{2-}$, in aqueous solution. We expected these species to have small formation constants and therefore used a sensitive amine solvent extraction method to identify them; the mercury concentration was kept low by the use of radioactive tracer techniques in order to favor formation of the anionic species.

In view of the lack of information on anionic mercury complexes it was decided not to add some foreign

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[1] See "Stability Constants," Chemical Society Special Publication No. 7, London, 1958.

[2] N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, 1950, Vol. I, p. 330.

[3] G. Infeldt and L. G. Sillén, *Svensk Kem. Tidskr.*, **58**, 104 (1946).

anion to maintain constant ionic strength in the aqueous solutions. Uncertainties about possible competition between nitrate and other anions outweighed any advantages accruing from working at constant ionic strength. The lowest nitric acid concentration used was 0.2 *M*, at which strength hydrolysis of Hg(II) is reported to be negligible.[4]

Experimental

Materials.—Methyldioctylamine (MDOA), supplied by British Hydrological Corporation, was found to be sufficiently pure to be used as supplied.[5] Solutions of known strength were made up by weight in chloroform, which was washed with water to remove alcoholic impurities before use. All other reagents were Analytical Reagent grade.

Radioactive Hg^{203} ($t_{1/2}$ 47 days) was obtained by neutron bombardment of 2 g. of mercury metal in the B.E.P.O. reactor at A.E.R.E., Harwell; short-lived isotopes were allowed to decay completely over a period of 2 months before use.

Counting Methods.—Solution samples were counted as liquids with a 1 × 1-in. Tl-activated sodium iodide crystal scintillation counter, coupled through a single-channel pulse height analyzer to the usual scaler, etc., and set to accept only the 279 kev. γ-rays of Hg^{203}. The γ-ray spectrum obtained with this apparatus showed excellent agreement with those reported by other workers.[6,7]

Preparation of Tracer Solution.—About 1.5 g. of the neutron-irradiated mercury was dissolved by adding 9 *M* nitric acid dropwise; when dissolution was complete, the volume was made up to 15 ml. Aliquots (2-ml.) of this solution were evaporated almost to dryness, nitrous fumes were completely removed by air-blowing, and the residue was dissolved in 100 ml. of 1 *M* nitric acid. Fractions of this solution were appropriately diluted with acid to give the solutions used in determining the distribution coefficient. The mercury concentration of the initial aqueous phase in these experiments was approximately 10^{-3} *M*, and the activity $\sim 10^4$ c.p.m./ml.

Experimental Procedure.—About 6 ml. of MDOA in chloroform was first equilibrated with aqueous nitric acid of pre-determined strength to give an equilibrium aqueous phase acid concentration identical with that used in the subsequent experiment. The equilibrated organic phase was separated by centrifuging, re-equilibrated, and again separated, and 5 ml. of the organic solution was removed by pipette. This was then shaken mechanically with an equal volume of tracer solution in nitric acid of known strength in a stoppered tube for 20 min. Check titrations showed that the pre-equilibration prevented any change of nitric acid concentration during this latter operation.

After centrifugation, 2-ml. aliquots of both phases were counted in fixed geometry to the NaI crystal. The distribution coefficient D_{Hg} was evaluated as

$$D_{Hg} = \frac{\text{specific activity (c.p.m./ml.) of organic phase}}{\text{specific activity (c.p.m./ml.) of aqueous phase}}$$

Duplicate determinations, which usually agreed to within 5%, were performed for each experimental point shown.

Results and Discussion

Variation of D_{Hg} with Nitric Acid Concentration.—Figure 1 shows D_{Hg} over the nitric acid concentration range 0.2–8 *M* for three different solutions of MDOA. No extraction could be detected when chloroform alone was used over the same range of acidity. The curves in Fig. 1 are similar in form to that reported by Ichikawa, Uruno, and Imai[8] for an anion-exchange resin.

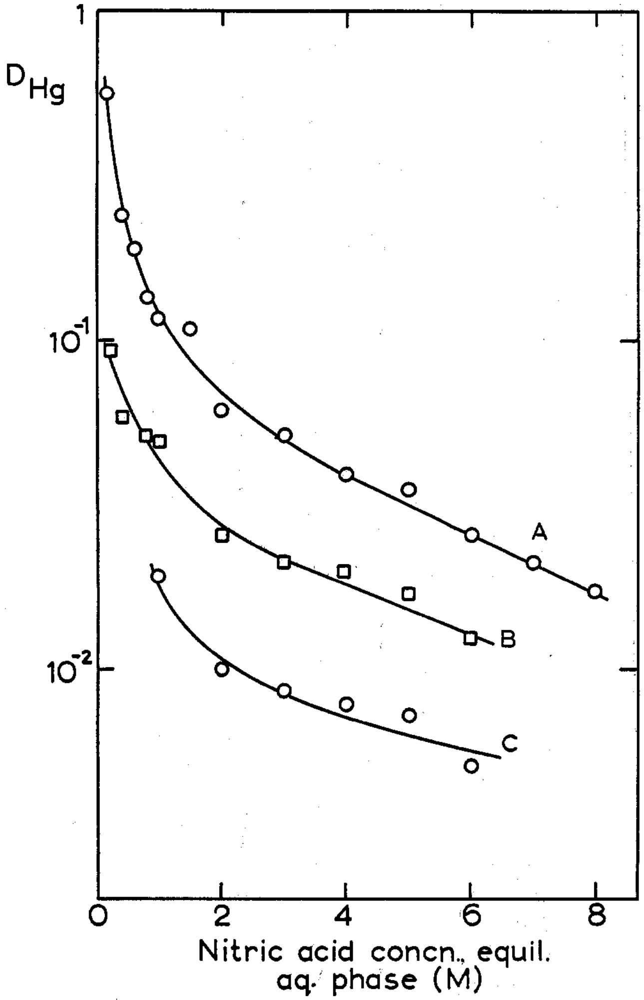

Fig. 1.—D_{Hg} as a function of nitric acid concentration: A, 0.42 *M* MDOA in chloroform; B, 0.31 *M* MDOA; C, 0.21 *M* MDOA.

The formation constant of R_3NHNO_3 (R = *n*-octyl) in the equilibrium

$$R_3N_{(o)} + HNO_{3(aq)} \rightleftharpoons R_3NHNO_{3(o)} \qquad (1)$$

has been shown[9] to be of the order of 10^6 (the exact value depending on the diluent), and similar values have been reported for other long-chain amines.[10] We therefore believe that under the experimental conditions used, the amine is present virtually completely as the ammonium nitrate, and the extraction of mercury into the organic phase can be represented by the general equation

$$nR_3NHNO_{3(o)} + [Hg(NO_3)_{2+n}]^{n-}{}_{(aq)} \rightleftharpoons (R_3NH)_n[Hg(NO_3)_{2+n}]_{(o)} + nNO_3^-{}_{(aq)} \qquad (2)$$

The results in Fig. 1 show clearly that anionic mercury(II) nitrate species must exist.

Charge on the Extracted Species.—It follows from eq. 2 that for constant aqueous phase conditions and low amine concentrations eq. 3 applies.

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(4) B. H. Buttle and J. T. Hewitt, *J. Chem. Soc.*, **93**, 1405 (1908).

(5) S. S. Choi and D. G. Tuck, to be published.

(6) M. K. Ramaswamy and P. S. Justram, *Nucl. Phys.*, **15**, 510 (1960).

(7) C. E. Crouthamel, "Applied Gamma-Ray Spectrometry," Pergamon Press, London, 1960, Appendix II.

(8) F. Ichikawa, S. Uruno, and H. Imai, *Bull. Chem. Soc. Japan*, **34**, 952 (1961).

(9) J. M. P. J. Verstegen, *Trans. Faraday Soc.*, **58**, 1878 (1962).

(10) See Y. Marcus, *Chem. Rev.*, **63**, 139 (1963).

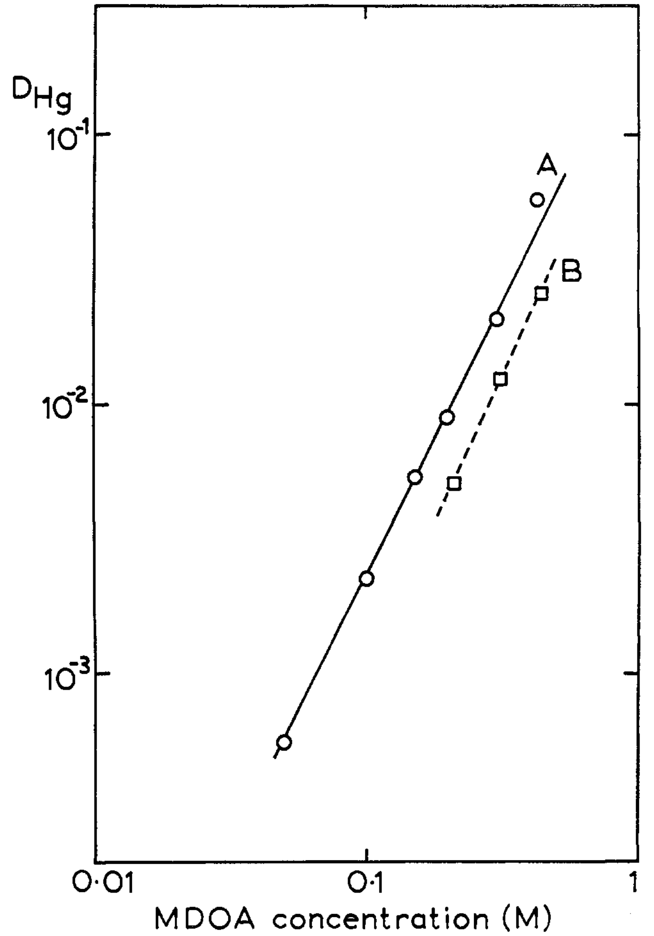

Fig. 2.—D_{Hg} as a function of MDOA concentration in chloroform; A, 2.5 *M* aqueous nitric acid; B, 6 *M* nitric acid.

$$\log D_{Hg} = n \log [\text{MDOA}] + \text{constant} \qquad (3)$$

Figure 2 shows results for two different nitric acid concentrations, both of which give $n = 2.0 \pm 0.1$, so that the species in the organic phase is $(R_3NH)_2[Hg(NO_3)_4]$. This result implies either that $[Hg(NO_3)_3]^-$ does not exist under the conditions studied, or that $[Hg(NO_3)_4]^{2-}$ is more easily extracted than $[Hg(NO_3)_3]^-$. The latter conclusion is apparently ruled out by the Born equation,[11] which predicts that singly charged species should be extracted more easily from aqueous solution than higher charged ions, because of the higher charge density of the latter. This argument, however, takes no account of the effect of hydration of the ions concerned.[12] For the halide complexes of mercury(II), Scaife and Tyrrel[13] and Gallagher and King[14] have suggested that the HgX_3^- ions (X = Cl, Br) in aqueous solution should be written either as the tetrahedral $[HgX_3(H_2O)]^-$ or as the six-coördinate $[HgX_3(H_2O)_3]^-$. If the same situation applies with the nitrate complexes, the trinitrato complex, if it exists in aqueous solution, will be hydrated, and might therefore be more difficult to extract than the tetranitrate. The value $n = 2$ does therefore not rule out the existence of a trinitratomercury(II) anion in aqueous solution. The identification of the $[Hg(NO_3)_4]^{2-}$ anion is clear; in agreement with this, the salt $((CH_3)_4N)_2[Hg(NO_3)_4]$ has now been prepared by reaction of the appropriate salts in ethanol.[15]

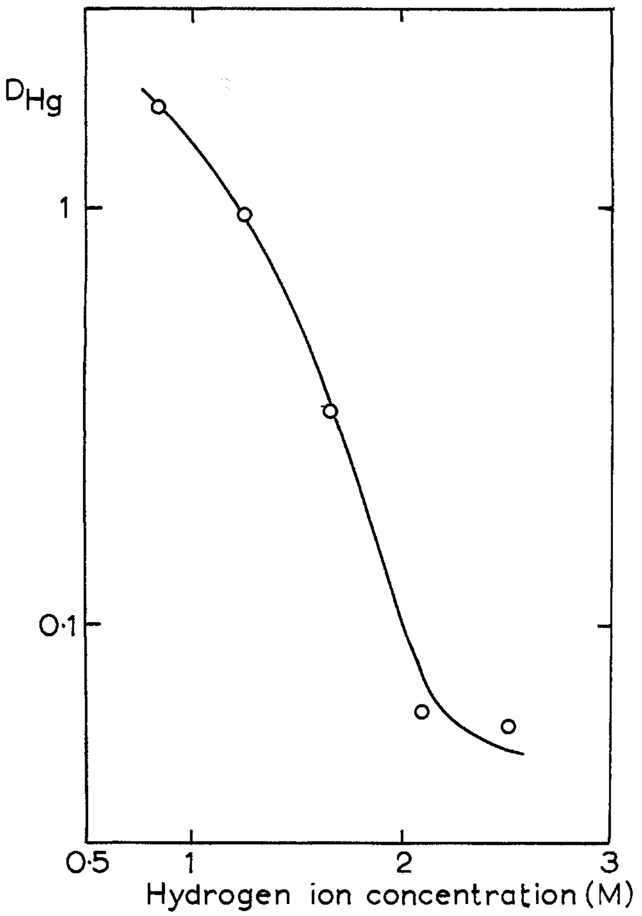

Fig. 3.—D_{Hg} as a function of acidity in nitric acid–potassium nitrate solution.

After the completion of the present work, Waki[16] reported the existence of mercury(II)–nitrate anionic complexes from studies with Dowex 1-X8 resin; both $[Hg(NO_3)_3]^-$ and $[Hg(NO_3)_4]^{2-}$ were found to exist in the resin phase. These conclusions cannot be compared directly with the present work because of the physical differences between the solid resin and a two-phase solution system.

Decrease in D_{Hg} with Increasing Acidity.—All three curves in Fig. 1 show D_{Hg} decreasing with increasing nitric acid concentration. This may be due to increasing nitrate ion concentration forcing eq. 2 to the left, thus reducing the amount of $(R_3NH)_2[Hg(NO_3)_4]$ in the organic phase, and hence lowering D_{Hg}. Similar effects are known in ion exchange with halide and nitrate systems.

An alternative explanation, however, is that the decrease in D_{Hg} is due to processes such as

$$[Hg(NO_3)_4]^{2-} + 2HNO_3 \rightleftharpoons H_2[Hg(NO_3)_4] + 2NO_3^- \qquad (4)$$

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[11] M. Born, *Z. Physik*, **1**, 45 (1920).

[12] See R. M. Diamond and D. G. Tuck, *Progr. Inorg. Chem.*, **2**, 109 (1960).

[13] D. B. Scaife and H. J. V. Tyrrel, *J. Chem. Soc.*, 392 (1958).

[14] P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960).

[15] J. I. Bullock and D. G. Tuck, to be published.

[16] M. Waki, *Bull. Chem. Soc. Japan*, **34**, 829 (1961).

being favored with increasing acidity. This is in agreement with the low ionization constant of nitric acid, which results in increasing concentrations of undissociated acid molecules at high molarities.[17] To investigate the effect of hydrogen ion, extractions were carried out from solutions of nitric acid and potassium nitrate, in which the formal nitrate ion concentration was held constant. The results (Fig. 3) again show D_{Hg} decreasing with increasing acid concentration. This behavior is as predicted from eq. 4, but the results do not rule out some other type of hydrogen ion effect.

Further evidence in favor of the formation of protonated species was, however, obtained from electrical migration experiments in nitric acid–potassium nitrate solutions under standard conditions. After an initial increase, the anionic fraction decreases with increasing acid concentration, as required by eq. 4. It is interesting that the cathode fraction increases smoothly with increasing acid concentration, which suggests that eq. 4 (or some analog) may be followed by eq. 5.

$$H_2[Hg(NO_3)_4] + HNO_3 \rightleftharpoons [H_3Hg(NO_3)_4]^+ + NO_3^- \quad (5)$$

Equations 4 and 5 imply that the mercury(II)–nitrate anionic species are stronger bases than nitrate ion itself; unfortunately there seems to be no data on the base strength of complexes against which to compare this conclusion.

TABLE I

MIGRATION OF TRACER MERCURY(II) IN AQUEOUS NITRIC ACID–POTASSIUM NITRATE SOLUTIONS

HNO_3 concn., *M*	KNO_3 concn., *M*	% Hg activity at anode after 4 hr.	% activity at cathode after 4 hr.
0.41	1.24	5.4	0.3
0.55	1.10	7.6	0.8
0.83	0.82	15.8	1.8
1.10	0.55	7.6	2.8
1.24	0.41	6.6	3.0
1.65	0	1.7	7.7

Acknowledgment.—We wish to thank the University of Nottingham for the award of a Research Studentship (to S. S. C.), and Mr. J. I. Bullock for carrying out the electrical migration experiments.

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[17] See E. Hesford and H. A. C. McKay, *Trans. Faraday Soc.*, **54**, 573 (1958).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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Identification of Complex Ions of Niobium(V) in Hydrofluoric Acid Solutions by Raman and Infrared Spectroscopy

BY O. L. KELLER, JR.

Received October 3, 1962

The Raman spectra of $K_2NbOF_5 \cdot H_2O$ dissolved in water and K_2NbF_7 dissolved in 1 to 50% HF are compared with the Raman spectra of crystalline $K_2NbOF_5 \cdot H_2O$ (which also can be considered as $K_2Nb(OH)_2F_5$), $CsNbF_6$, and K_2NbF_7 to show that the $NbOF_5^{2-}$ (or $Nb(OH)_2F_5^{2-}$) and NbF_6^- ions are present in these solutions. The Raman lines characteristic of the NbF_7^{2-} ion were not seen in any of the solutions. The infrared spectrum of $K_2NbOF_5 \cdot H_2O$ was recorded from 650 to 4000 cm.$^{-1}$ to gain information on whether the $NbOF_5^{2-}$ or $Nb(OH)_2F_5^{2-}$ ion is present in the crystals and the solutions. The infrared and Raman spectra are found to be consistent with the presence of $NbOF_5^{2-}$ ions in the crystals, but they are not found to be consistent with the presence of $Nb(OH)_2F_5^{2-}$ ions.

Introduction

The identification of ionic species in concentrated electrolytes presents a difficult problem. Thermodynamic methods cannot be used in many cases because applicable activity coefficients are not available. Kinetic methods, such as conductance, are less widely applicable than thermodynamic methods. Direct identification of complex ions by molecular spectroscopy often requires a detailed theoretical treatment. If some of the characteristic frequencies of the ion are too weak to be seen, or if there is a mixture of complex ions, such a treatment is difficult. Identification of species in solution can be accomplished simply, however, if direct comparison can be made between spectra of the solutions and spectra of crystals of known composition and structure.

Niobium double fluoride complexes found in 0 to 50% HF are identified in this investigation by comparing the Raman spectra of the solutions with Raman spectra of crystals of $CsNbF_6$, K_2NbF_7, and $K_2NbOF_5 \cdot H_2O$.

Infrared spectra of $K_2NbOF_5 \cdot H_2O$ crystals also were obtained to gain information on whether the $NbOF_5^{2-}$ or $Nb(OH)_2F_5^{2-}$ ion is present in the crystals and the solutions.

Experimental

Raman spectra were obtained with a Cary Model 81 spectrophotometer. The 4358 Å. mercury line was isolated with a filter solution of Cyasorb U.V. 24[2] and ethyl violet in *n*-propyl alcohol solution.

The infrared spectra were obtained with a Perkin-Elmer Model 221 spectrophotometer equipped with the prism grating interchange. A polystyrene film was used for the calibration.

The cells used for the Raman crystal spectra of K_2NbF_7 and

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[1] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[2] American Cyanamid Company.