water, which was removed by passing a stream of dry air through the liquid for 24 hr. The product, a viscous water-white liquid, weighed 38.6 g., corresponding to a yield 77% of theoretical based upon the weight of alcohol consumed. The purity of the product was ascertained by titration and chromatography. *Anal.* Calcd. for $C_8H_{17}H_2PO_4$: P, 14.7; equiv. wt., 210. Found: P, 14.3; equiv. wt., 204; $n^{25}D$ 1.4411.

Preparation of Mono-*n*-decyl Phosphate.—Pyrophosphoric acid (111 g., 0.625 mole), *n*-decyl alcohol (79.0 g., 0.500 mole), and benzene (100 g.) were added to a 500-ml. flask. After stirring until a clear solution formed, the flask was allowed to stand for 4 days. A portion (138 g.) of the viscous liquid produced was dissolved in 300 ml. of ether. In extraction procedures, ether is preferred over benzene since monoalkyl phosphates show a lesser tendency toward emulsification in ether. The ether solution was extracted once with 200 ml. of water. The ether-rich layer then was added dropwise with stirring to a solution prepared from 500 ml. of water and 60 g. of 50% NaOH. During the addition, 100 ml. of ether also was added to reduce viscosity. From the resulting ether-rich layer 4.0 g. of *n*-decanol was recovered. The pH of the aqueous layer was adjusted from an initial 12.4 to a final 0.5 with concentrated HCl. During the acidification the formation and dissolution of both $C_{10}H_{21}NaHPO_4$ and $C_{10}H_{21}NaHPO_4 \cdot C_{10}H_{21}H_2PO_4$ was observed. These salts were not isolated as their preparation by neutralization of alcoholic monoalkyl phosphates has been described previously.[11] At pH 0.5, 300 ml. of ether was added with the formation of two liquid layers. The aqueous layer was discarded. The ether-rich layer was washed with 1 *N* HCl and transferred to an evaporating dish. After evaporation of the ether, the crude product was vacuum desiccated over sulfuric acid. The crude product weighed 47.1 g., 94% of the expected yield based upon the quantity of alcohol consumed. Recrystallization from hexane gave a white, crystalline product containing no other decyl phosphates. *Anal.* Calcd. for $C_{10}H_{21}H_2PO_4$: P, 13.0; equiv. wt., 238. Found: P, 12.9; equiv. wt., 236; m.p. 45°.

The following compounds were prepared in a similar manner: **Mono-*n*-dodecyl phosphate**: yield, 100%. *Anal.* Calcd. for $C_{12}H_{25}H_2PO_4$: P, 11.65; equiv. wt., 266. Found: P, 11.6; equiv. wt., 265; m.p. 58°. **Mono-*n*-tetradecyl phosphate**: yield, 92%. *Anal.* Calcd. for $C_{14}H_{29}H_2PO_4$: P, 10.5; equiv. wt., 294. Found: P, 10.8; equiv. wt., 302; m.p. 68°.

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CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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Nature of Bonding in Metal Cyanide Complexes as Related to Intensity and Frequency of Infrared Absorption Spectra[1]

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The frequencies of the infrared-active CN stretching, MC stretching, and MCN bending vibrations of several metal–hexacyanide complexes have been observed in aqueous solution. The integrated absorption coefficients of the CN stretching vibrations increase regularly with the number of d_ϵ electrons. These intensity and frequency data together show that the extent of metal–cyanide π-bonding increases as the number of d_ϵ electrons increases and as the effective nuclear kernel charge decreases. The carbon–nitrogen force constant is shown to increase with increase in metal–cyanide σ-bonding and decrease in metal–cyanide π-bonding. The linear dicyanides of Ag(I), Au(I), and Hg(II) are shown to fit into this picture also.

Introduction

In the past few years much has been written on the nature of bonding in metal–cyanide complexes, perhaps the most recent being a review by Griffith.[2] Part of his discussion concerns the relation of MC and CN force constants to the nature of σ-bonding and π-bonding in the complex. However, a good share of the reported force constants for the metal–carbon bonds are subject to considerable doubt. For instance, Griffith[2] quotes Pistorius'[3] value for F_{MC} of $Ni(CN)_4^{-2}$ as 3.42 mdynes/Å. while McCullough, *et al.*,[4] in a more detailed study, report F_{MC} as 2.6 mdynes/Å. Also Griffith[2] reports for $Co(CN)_6^{-3}$ Nakagawa's and Shimanouchi's[5] value for F_{CoC} of 2.31 mdynes/Å. whereas Jones[6] gives F_{CoC} equals 1.8 mdynes/Å. Thus it is difficult to base a theory of bonding on this evidence.

Another source of information, too often neglected, on the bonding in complexes, is the observation of intensities of the vibrational absorption bands. From these intensities information can be obtained about the rearrangement of electrons accompanying changes of configuration and thus an insight into the nature of the equilibrium electronic configurations is available. In this paper the intensities of absorption of several metal–cyanide complexes are compared and related to electronic distribution and bonding properties.

Experimental

The absorption bands discussed in this paper were measured in aqueous solution. For the CN stretching region a fixed-thickness cell with 2-mil tantalum spacer and calcium fluoride windows was used with a Perkin-Elmer Model 421 spectrometer. From the spacing of interference peaks in the infrared region, the thickness was determined to be 0.0062 cm. A cell of the same thickness containing water only was used in the reference beam to cancel out the solvent absorption.

The two infrared-active fundamentals in the region 300–600 cm.$^{-1}$ were recorded by a single-beam Perkin-Elmer Model 112 spectrometer with a CsBr prism. The cells used for this region contained KRS5 windows and tantalum spacers of 0.2 mil

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

[3] C. W. F. T. Pistorius, *Z. physik. Chem.* (Leipzig), **23**, 200 (1960).

[4] R. McCullough, L. Jones, and G. A. Crosby, *Spectrochim. Acta*, **16**, 424 (1960).

[5] I. Nakagawa and T. Shimanouchi, *ibid.*, **18**, 101 (1962).

[6] L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

thickness. Because of the strong water absorption, small path lengths are necessary for the CsBr region. Since these path lengths were uncertain, quantitative intensity measurements were attempted only for the asymmetric CN stretching vibration, ν_6, at 2000–2200 cm.$^{-1}$.

When such intensity measurements are made, slit width and concentration effects must be considered carefully. For all the hexacyanides discussed herein, it was found that increasing the slit width resulted in a decrease in the extinction coefficient (measured at the maximum) but that the integrated absorption coefficient remained essentially constant as the band broadened. It was also found that for some of the hexacyanides the extinction coefficient at the maximum increased slightly as the concentration decreased, while the integrated absorption coefficient did not change significantly with concentration. For example, the integrated absorption coefficient for $Ir(CN)_6^{-3}$ is constant for concentrations from 0.004 to 0.067 *f*. Thus, for purposes of comparing intensities among different species, we have measured the integrated absorption coefficients.

Results and Discussion

Intensity and Relation to Metal–Carbon π-Bonding.—The numbering of vibrations is the same as used by the author in a study[6] of the solid state infrared spectrum of $K_3Co(CN)_6$. The infrared-active cyanide stretching vibration is labeled ν_6; ν_7 is primarily an MCN bending vibration, while ν_8 is primarily an MC stretching vibration.[7] The intensity data on ν_6 and the frequencies of ν_6, ν_7, and ν_8 are given in Table I for aqueous solutions of metal hexacyanides ranging from 0.004 to 0.25 *f*.

TABLE I

VIBRATIONAL FREQUENCY AND INTENSITY DATA FOR SOME METAL HEXACYANIDES

Solute	d_ϵ	ν_6, cm.$^{-1}$	ν_7, cm.$^{-1}$	ν_8, cm.$^{-1}$	$k_6{}^a$	$\epsilon_6{}^b$
$K_3Cr(CN)_6$	3	2128	458	339	2,100	232
$K_3Mn(CN)_6$	4	2112	483	361	8,200	584
$K_3Fe(CN)_6$	5	2118	506	389	12,300	1062
$K_3Co(CN)_6$	6	2129	564	416	18,300	1748
$K_3Rh(CN)_6$	6	2133	522	387	17,200	1600
$K_3Ir(CN)_6$	6	2130	521	401	22,100	1920
$K_4Fe(CN)_6$	6	2044	583	416	92,000	4600

[a] k_6 is the integrated absorption coefficient, moles^{-1} l. cm.$^{-2}$. [b] ϵ_6 is measured in moles^{-1} l. cm.$^{-1}$ at the absorption maximum of ν_6. ϵ_6 was measured on a Perkin-Elmer Model 421 spectrometer with double-grating interchange and slit width of 750 μ. It is given merely for the convenience of the reader.

The integrated absorption coefficient, k_6, is given in eq. 1 as a function of the change in dipole moment during the vibration; k is the absorption coefficient,

$$k = \alpha(\partial\mu/\partial Q_i)^2 \qquad (1)$$

α is a proportionality constant, and $\partial\mu/\partial Q_i$ is the change in dipole moment accompanying the characteristic oscillation of normal coördinate Q_i.

From eq. 1 the band intensity, k_6, is proportional to $(\partial\mu/\partial Q_6)^2$. It is apparent from Table I that for the first four complexes k_6, and thus $(\partial\mu/\partial Q_6)^2$, increases markedly from $Cr(CN)_6^{-3}$ to $Co(CN)_6^{-3}$. The main difference in this group of trivalent cyanide complexes is in the number of d_ϵ electrons. Thus, the number of d_ϵ electrons increases from 3 to 6 in the progression from $Cr(CN)_6^{-3}$ to $Co(CN)_6^{-3}$. This intensity variation is readily explained by postulating an oscillation of the d_ϵ electron density due to changes in M–C π-bonding accompanying changes in bond lengths.

For example, the vibration ν_6 of a hexacyanide can be represented by the motion depicted in Fig. 1.

$$\underset{\leftarrow}{N_1} - \underset{\rightarrow}{C_1} - M - \underset{\rightarrow}{C_2} - \underset{\leftarrow}{N_2}$$

Figure 1.

As one CN expands the opposite CN contracts. Also, there are lesser changes in C_1M (contracts) and C_2M (expands). The other four C_iN_i and corresponding C_iM groups can be neglected as they will not change much for this member of the triply degenerate set of ν_6.

As C_1N_1 stretches, the C_1N_1 antibonding $v\pi$-orbitals become more available for accepting the $d\pi$ electrons of the metal in MC_1 π-bond formation.[8] At the same time C_2N_2 is contracting, thus making its antibonding $v\pi$-orbitals less available for electrons, resulting in a decrease of MC_2 π-bonding.[9] Therefore, during the phase of the vibration ν_6 represented by Fig. 1 there is a net flow of d_ϵ electrons from C_2 toward M and from M toward C_1. A half-cycle later there is a flow of these d_ϵ electrons in the opposite direction. This shifting of electrons back and forth during the vibration leads to a change in dipole moment of the ion oscillating with the frequency of the vibration, ν_6. *Thus, the intensity of ν_6 serves as a measure of the extent of metal–cyanide π-bonding.*

Another comparison of interest is that of the isoelectronic series $Co(CN)_6^{-3}$, $Fe(CN)_6^{-4}$, $Cr(CO)_6$ for which the intensity of ν_6 increases as the valence of the metal decreases. Thus, k_6 = 18,300; 92,000; and 199,000 for the Co(III), Fe(II), and Cr(0)[10] complexes, respectively. It is clear that the extent of π-bonding increases markedly as the effective nuclear kernel charge[11] decreases.

Metal–Carbon Force Constant.—With the exception of $Co(CN)_6^{-3,6}$ the force constants of these ions have not been calculated as not enough information is available. However, since the metal masses are not very different, the frequencies of ν_8 (and to some extent ν_7)

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[7] I. Nakagawa and T. Shimanouchi in ref. 5 have assigned the higher frequency, ν_7, to the M–C stretching and ν_8 to MCN bending. However, this leads to a negative MC_i, MC_j interaction constant which is not realistic [see L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962)]. This is the cause of the discrepancy in CoC force constant mentioned in the Introduction. Consequently the author feels that the MC force constants reported in ref. 5 are too high.

[8] This is analogous to a similar discussion of metal hexacarbonyls: L. H. Jones, *J. Mol. Spectry.*, **9**, 130 (1962).

[9] A. D. Liehr [*J. Chem. Educ.*, **39**, 135 (1962), and private communication] presents another scheme which rejects the primary use of the CN antibonding π-orbitals because of their high energy. Instead, he invokes the explanation that the CN π-electrons form π-bonds with the metal d_ϵ orbitals. The CN π-electrons then fill up these bonding π-orbitals so that any d_ϵ electrons of the metal are placed in the corresponding metal–ligand *antibonding* π-orbital. Such a scheme of molecular orbitals leads to a prediction of decreasing metal–ligand bond strength with increasing number of d_ϵ electrons. This is contrary to experimental observations and thus the author prefers the explanation presented in the text.

[10] The value for $Cr(CO)_6$ was measured in the gas phase; however, the difference in intensity from that of $Fe(CN)_6^{-4}$ is large enough to be meaningful. The units are the same for all three.

[11] By nuclear kernel the author means the nucleus plus the inner electrons; the outer d electrons are neglected as they are not expected to screen the nucleus very efficiently.

are determined primarily by the MC force constant. Therefore, we can obtain an approximation to the relative values of the MC force constants by comparing the values of ν_8 in Table I.

The metal–carbon force constant is determined by the strength of the metal–carbon σ-bond as well as that of the metal–carbon π-bond. For the four trivalent hexacyanides, from $Cr(CN)_6^{-3}$ to $Co(CN)_6^{-3}$ the σ-bond strength should increase with atomic number as the d_ϵ electrons will not screen the metal from the ligand groups very well and the effective nuclear kernel charge of the metal atom will increase in the order Cr < Mn < Fe < Co. Also the π-bond strength increases in the same order, as noted from the intensity data, due to the increase in number of d_ϵ electrons. Thus, we expect a considerable increase in metal–carbon force constant in the order CrC < MnC < FeC < CoC. This is, in fact, observed as noted in Table I by the definite increase in frequency ν_8 in the series from $Cr(CN)_6^{-3}$ to $Co(CN)_6^{-3}$.

From Table I it is apparent that Co–C in $Co(CN)_6^{-3}$ has about the same metal–carbon force constant as Fe–C in $Fe(CN)_6^{-4}$. The cobalt species has a higher effective charge on the metal and thus we should expect a stronger σ-bond. However, due to the lower nuclear kernel charge of Fe(II), as discussed above, we expect stronger metal–ligand π-bonding for Fe(II)–CN than for Co(III)–CN. Thus, in going from $Co(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$ we expect weaker σ-bonding and stronger π-bonding, resulting in the observed near equivalence of metal–carbon force constants.

Carbon–Nitrogen Force Constant.—For free CN^- ion the force constant is 16.9 mdynes/Å. while for HCN it is 18.7. There is certainly no HC π-bonding so we have the observation that formation of a σ-bond by CN to another atom through the carbon atom results in an increase in the CN force constant. This suggests the conclusion that a stronger metal–carbon σ-bond leads to a stronger CN bond. On the other hand the formation of a metal–ligand π-bond using an antibonding $v\pi$-orbital of CN should weaken the CN bond. In the series of trivalent hexacyanides, from $Cr(CN)_6^{-3}$ to $Co(CN)_6^{-3}$, as discussed above, we expect a stronger metal–carbon σ-bond and a stronger metal–carbon π-bond. These apparently result in compensating effects on the CN bond strength leading to the observed nearly equivalent CN stretching frequencies.

On the other hand, from $Co(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$ there is decreased metal–carbon σ-bonding and increased metal–carbon π-bonding, both effects tending to decrease the CN bond strength. Thus, we observe the decrease in ν_6 (2129 for $Co(CN)_6^{-3}$ and 2044 for $Fe(CN)_6^{-4}$).

We can set down the above ideas in the form of two simple relations

$$F_{MC} = a(S\sigma)_{MC} + b(S\pi)_{MC} \qquad (2)$$

$$F_{CN} = c(S\sigma)_{MC} - d(S\pi)_{MC} \qquad (3)$$

F_{MC} = metal–carbon force constant
F_{CN} = carbon–nitrogen force constant
a, b, c, d are arbitrary constants
$(S\sigma)_{MC}$ = metal–carbon σ-bond strength
$(S\pi)_{MC}$ = metal–ligand π-bond strength

Interaction Constants.—The constant representing interaction of a metal–carbon bond with another metal–carbon bond is quite appreciable for most cyanide complexes.[6] This is to be expected from the considerable changes in π-bonding occurring during the vibration ν_6. What this means is that stretching C_1M results in a contraction of C_2M of Fig. 1.

On the other hand, the interaction of one CN bond with another is in general very small as the symmetric and asymmetric CN stretching frequencies are not greatly different (see, for example, ref. 6). The intensity data of Table I serve as strong evidence that there is a considerable change in metal–ligand π-bonding during the vibration ν_6. Increased metal–cyanide π-bonding will tend to weaken the CN bond. However, apparently there is a compensating effect (such as increased CN σ-bond strength) which tends to strengthen the CN bond. Thus, stretching C_1N_1, though it apparently leads to an increase in $M–C_1N_1$ π-bonding and a decrease in $M–C_2N_2$ π-bonding, does not affect the C_2N_2 bond distance appreciably. This is in accord with the observed constancy of CN force constant among the $M(CN)_6^{-3}$ ions even though the M–CN π-bonding changes considerably.

Other Systems.—It is of interest to compare the three species $Co(CN)_6^{-3}$, $Rh(CN)_6^{-3}$, and $Ir(CN)_6^{-3}$ having the same number of d_ϵ electrons and about the same effective charge on the metal nuclear kernel. Note that from the intensity data of Table I the degree of metal–ligand π-bonding decreases in the irregular order Ir > Co > Rh. If one allows for the effect of mass on the frequency (using the rough approximation that $F_{MC} = \lambda_{MC}/G_{MC}$), it is found that the force constants progress in the same order (IrC > CoC > RhC). It is perhaps somewhat surprising that the heaviest atom gives the strongest bond and the intermediate atom the weakest bond. However, it is interesting to note that the same order is observed[12] for the hexacarbonyls of Cr, Mo, and W; that is, $F_{WC} > F_{CrC} > F_{MoC}$. Also, the same order is observed[13] for the metal–carbon force constants of the tetracyanides of Zn, Cd, and Hg; thus, $F_{HgC} > F_{ZnC} > F_{CdC}$.

Another interesting group is made up of the linear dicyanides of Ag(I), Au(I), and Hg(II). The force constant[14] and intensity data are given in Table II.

TABLE II

FORCE CONSTANTS AND INTENSITIES IN AQUEOUS SOLUTION FOR ν_{CN} OF SOME LINEAR DICYANIDES

	F_{CN}, mdynes/Å.	F_{MC}, mdynes/Å.	$F_{MC,MC}$ mdynes/Å.	k_6, mole^{-1} l. cm.$^{-2}$
$Ag(CN)_2^-$	17.04	1.83	0.22	3100
$Au(CN)_2^-$	16.75	2.81	.51	4980
$Hg(CN)_2$	17.62	2.61	.14	71

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(12) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

(13) L. H. Jones, *ibid.*, **17**, 188 (1961).

(14) The force constants are calculated from the data of ref. 15–17 assuming $F_{CN,MC} = 0$.

(15) $KAg(CN)_2$, L. H. Jones, *J. Chem. Phys.*, **26**, 1578 (1957).

(16) $KAu(CN)_2$, L. H. Jones, *ibid.*, **27**, 468 (1957).

(17) $Hg(CN)_2$, L. H. Jones, *ibid.*, **27**, 665 (1957).

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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Solvent Extraction Investigation of Anionic Complex Formation in Mercury(II)–Nitrate Systems

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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).