concentrated HCl and adding Cs^+ or $[(C_6H_5)_4As]^+$, the compounds $Cs[ReCl_4(OH)_2]$ and $[(C_6H_5)_4As][ReCl_4(OH)_2]$ can be isolated. The tetraphenylarsonium salt was shown to be essentially diamagnetic and the infrared spectrum of the yellow-orange cesium salt showed a strong band at 960 $cm.^{-1}$. This band was assigned to the Re–O–H group and, in addition, the authors noted the presence of "OH stretching bands at 3500 and 1600 $cm.^{-1}$." Finally, the electronic spectra of these two "$M[ReCl_4(OH)_2]$" compounds were reported as having absorption maxima at 820 mμ (ϵ 23.8), 480 mμ (ϵ 27.3), and 408 mμ (ϵ 33.2).

In view of the results reported in this paper, the formulas and the interpretation of the infrared spectra suggested by Beard, *et al.*,[31] seem to us to be incorrect. First, with regard to the assignment of the infrared spectra of the solid compounds prepared by these authors, we wish to point out that there is no "OH stretching band at 1600 $cm.^{-1}$," while a band at about this frequency is provided by the bending mode of H_2O. In addition, their assignment of the 960 $cm.^{-1}$ band in the cesium salt to an Re–O–H deformation mode, made by analogy to Griffith's work[32] on hydroxy complexes of Os(V) which absorb in the 1050–1090 $cm.^{-1}$ region, is not the only possibility. For, as noted by the authors themselves, the tendency for Re=O bonds to give rise to strong absorptions in the 960 $cm.^{-1}$ region has been well documented.[8] It therefore appears to us that the anionic complex ion in the crystalline compounds is, on the basis of the infrared data alone, probably *trans*-$[ReCl_4O(H_2O)]$. Finally, we wish to point out that the electronic spectra *in concentrated acid solution* of these "$[ReCl_4(OH)_2]$" ions are quite similar to the spectra of the $[ReX_4O]^-$ ions in nonaqueous solvents reported herein. While this is by no means conclusive evidence, we believe that it is very probable that the ion obtained by addition of excess concentrated HCl to $[Re(en)_2O_2]^+$ is $[ReCl_4O(H_2O)]^-$, and not $[ReCl_4(OH)_2]^-$ as reported.

(32) W. P. Griffith, *J. Chem. Soc.*, 245 (1964).

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Raman Study of Complex Cyanides of Copper(I)[1]

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Received August 30, 1965

A Raman study of cyanide complexes of copper(I) in aqueous solution has been carried out. No evidence was found for the formation of mixed complexes of copper(I) cyanides with either halide ions or various organic molecules as potential ligands. The reaction of either cuprous cyanide or the complex cyanides with hydrogen halides leads to the formation of the anion $Cu(CN)_3^{2-}$ and not the mixed complexes. The results are discussed in terms of the stereochemistry of the ions in solution. There is evidence for the importance of π bonding from the abnormal intensity of the C–N vibration frequency.

The interest in ligand–ligand interactions arising from the *trans* effect[2] has led to a number of investigations of bonding in square-planar mixed complexes by vibrational spectroscopy.[3–5] Vibrational frequencies may be particularly informative when polyatomic ligands are studied, as there exists the possibility that ligand–ligand interactions may be observed by changes in the frequencies of the ligands as well as in the metal–ligand frequencies. A study of such interactions in mixed cyanide–halide complexes of trivalent gold has shown that the effect of changing the halide group in these square-planar complexes is observable by a change in the frequency and the intensity of the carbon–nitrogen stretching vibration. Changing the halide atom was found to influence both the metal–carbon σ bond and the metal–carbon π bond from force constant and intensity data.[5] As part of an investigation of ligand–ligand interactions in mixed complexes of different stereochemistries, the formation of mixed cyanide–halide complexes of copper(I) has been investigated to ascertain whether a similar effect was observable in a tetrahedral complex, and the results are presented here.

Copper(I), along with other transition metals, forms complexes with varying numbers of cyanide groups. A number of early studies[6] differ as to the formulation of the species present in solution, but more recent work has clearly demonstrated the value of spectroscopic methods. Both Raman[7] and infrared[8] investigations demonstrated the presence of the ions $Cu(CN)_4^{3-}$ and

(1) This paper was presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965. The work was supported by Grant GP 2643 from the National Science Foundation.

(2) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955); F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958; F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, (1961).

(3) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955); D. B. Powell and N. Sheppard, *ibid.*, 3108 (1956); D. B. Powell, *ibid.*, 4495 (1956).

(4) K. Nakamoto, P. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, **4**, 36 (1965).

(5) L. H. Jones, *ibid.*, **3**, 1581 (1964); S. M. Smith, L. M. Jones, I. K. Kressin, and R. A. Penneman, *ibid.*, **4**, 369 (1965).

(6) C. Calmar and M. Costa, *Compt. rend.*, **243**, 56 (1958); T. F. Young and A. C. Jones, *Ann. Rev. Phys. Chem.*, **3**, 275 (1952).

(7) G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **33**, 736 (1960).

(8) R. A. Penneman and L. H. Jones, *ibid.*, **24**, 293 (1956).

$Cu(CN)_3^{2-}$. An infrared line at 2125 cm.$^{-1}$ was assigned[8] to the species $Cu(CN)_2^-$ and a Raman-active line at 2106 cm.$^{-1}$ was also tentatively assigned to the same species. Recent Raman[9] work has shown, however, that the C–N symmetric stretching frequency is at 2113 cm.$^{-1}$ for this ion and not at 2106 cm.$^{-1}$ as previously suggested; the C–N antisymmetric stretching frequency is apparently not at 2125 cm.$^{-1}$ as reported previously. The Raman-active line at 2106 cm.$^{-1}$ is therefore assigned as the C–N symmetric stretching vibration of the ion $Cu(CN)_3^{2-}$.

Work with labeled cyanide has shown that the exchange of cyanide ions with a copper cyanide complex is extremely rapid.[10,11] The cyano species are clearly in rapid equilibrium in solution as their distribution can be varied simply by the addition of either sodium cyanide or copper(I) cyanide to the solution. The fact that copper(I) cyanide dissolves in strong halogen acids was thought to indicate the formation of mixed cyanide–halide complexes,[12] but attempts to prepare mixed complexes of copper, cyanide, and ethylenediamine are reported to have been unsuccessful.[13] In this work the systems CuCN–NaCN–NaX–H_2O and CuCN–NaX–H_2O (where X is halogen) have been investigated by Raman spectroscopy with a view to studying mixed complex formation between the various copper(I) cyanides and halide ions. The possibility of complex formation between copper(I) cyanides and some N, O, and S donors has also been investigated in an attempt to substantiate the conclusions drawn from the cyanide–halide systems.

Experimental Section

Copper(I) cyanide was prepared by the method of Barber[14] and the solutions of the complex cyano species were prepared by dissolving this in aqueous A.R. sodium cyanide solution. In agreement with a phase study by Bassett and Corbet[15] it was not possible to obtain solutions of sodium dicyanocuprate(I) alone. It was possible, however, to lower the CN/Cu ratio sufficiently (2.76) to permit the observation of the anion $Cu(CN)_3^{2-}$ in the absence of any detectable amount of $Cu(CN)_4^{3-}$. The sodium halides used were all A.R. salts and were used without further purification. Spectra were recorded on a Cary Model 81 Raman spectrophotometer. Both the 4358 and the 4047 Å. lines of the mercury arc were used as exciting lines for the observation of the carbon–nitrogen stretching frequencies. For other ligand frequencies only the 4358 Å. line was used. Solutions were filtered before obtaining their spectra. Intensity measurements were made using an internal standard of perchlorate ion. The absolute intensities for CCl_4, NO_3^-, and ClO_4^- and the determination of the wave length sensitivity of the instrument have been previously described.[16] Attempts to observe the weak metal–carbon lines for the ions $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ were complicated by the close proximity of the C–N stretching frequency excited by the 4047 Å. mercury line. The use of a sufficiently strong filter to remove this line resulted in a reduced intensity of the other Raman shifts and failure to observe the weak Cu–C lines. Attempts to observe the Cu–X (X is halogen) lines in the spectra of CuX–NaX–H_2O and CuCN–NaX–H_2O (following the ether-extraction technique of Creighton and Lippincott[17]) were similarly unsuccessful due to the low intensity of the line. The solutions containing the ion $Cu(CN)_2^-$ were found to be readily oxidized by the air when in the presence of nitrogen donors. In order to avoid this the solutions were mixed under nitrogen and the Raman tubes filled *in vacuo*.

Results

Aqueous solutions of copper(I) cyanide in sodium cyanide exhibit three Raman shifts which are attributed to the C–N stretching frequencies of the ions $Cu(CN)_4^{3-}$ and $Cu(CN)_3^{2-}$. The assignments have been discussed previously[7-9] and are given in Table I along with the corresponding infrared frequencies. Changes in the bond order of the metal–carbon bond as the number of cyanide groups is changed are reflected in the carbon–nitrogen force constant and hence in the C–N stretching frequency. Thus such changes, as well as lower frequency changes, should serve as an indication of any bonding changes. The frequency of the C–N vibration is also dependent on the formal change of the ion and the coordination number of the metal,[18] but regular changes have been reported for a series of mixed cyanide halide complexes of gold(III) in which the charge and coordination number remain the same.[5] It is clear from the work of Jones[5] that the other groups present in gold(III) cyanides influence the cyanide bond in such a way that the effect is observable by both frequency and intensity changes. In the present work it was found that both the CN frequencies and especially intensities were influenced by the presence of other CN^- ligands. Intensity data are given in Table II.

TABLE I

INFRARED AND RAMAN FREQUENCIES OF THE C–N VIBRATIONS IN COPPER(I) CYANIDES IN AQUEOUS SOLUTION

Species	Raman[7,9] spectrum, cm.$^{-1}$	Infrared[8] spectrum, cm.$^{-1}$	Vibrational mode
$Cu(CN)_4^{3-}$	2094	. . .	γ_{sym}
	2079	2076	γ_{asym}
$Cu(CN)_3^{2-}$	2106	. . .	γ_{sym}
	2094	2094	γ_{asym}
$Cu(CN)_2^-$	2113	. . .	γ_{sym}
CN^-	2079	2079	$\gamma_{(CN)}$

TABLE II

RAMAN INTENSITIES OF THE SYMMETRIC C–N STRETCHING FREQUENCIES PER MOLE PER CYANIDE GROUP

Ion Na salt(aq)	Relative molar intensity per CN	Depolarization ratio
CN^-	1.00	0.08
$Cu(CN)_4^{3-}$	2.78	0.00
$Cu(CN)_3^{2-}$	6.6	0.3

The System CuCN–NaCN–NaX–H_2O.—The addition of sodium halide (up to 6 molar excess) to a solu-

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[10] A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **76**, 4222 (1954).

[11] U. Belluco, G. Schiaron, and M. Brono, *Ricerca Sci.*, **27**, 3599 (1957); *Chem. Abstr.*, **52**, 19649 (1958).

[12] M. Ford-Smith, "The Chemistry of Complex Cyanides," H.M.S.O., London, 1964, p. 35.

[13] S. Kida, *Bull. Chem. Soc. Japan*, **32**, 891 (1959).

[14] H. J. Barber, *J. Chem. Soc.*, 79 (1943).

[15] H. Bassett and A. S. Corbet, *ibid.*, 125 (1924).

[16] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

[17] J. A. Creighton and E. R. Lippincott, *J. Chem. Soc.*, 5134 (1963).

[18] M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

tion containing the three-cyano species caused no significant variation in the C–N stretching frequencies. It is possible that the frequency changes are not sufficiently sensitive to bonding changes. However, the derivative of molecular polarizability with respect to lengthening of the various bonds determines the intensity of a Raman line. It may be expected therefore that ligand–ligand interactions in a mixed complex would result in a change in the intensities of the C–N vibrations. For intensity measurements in the system under consideration it is necessary to use a solution containing only $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$ as the complex anions, so that their concentration is known, and to rule out displacement of CN by the added halide. This was done by saturating a solution of 3 *M* sodium cyanide with copper(I) cyanide (CN/Cu ratio of 2.76 and exhibiting lines at 2094 and 2106 cm.$^{-1}$) and noting the absence of the displacement reaction by the failure to observe the line at 2079 cm.$^{-1}$ (due to either free CN^- or $Cu(CN)_4^{3-}$, both of which exhibit a line at 2079 cm.$^{-1}$) on the addition of the halide. Intensity measurements on the lower cyano species showed no significant variation as the concentration of sodium halide was increased.

White solids obtained by slow crystallization from the solutions containing either bromide or iodide were found to consist mainly of sodium dicyanocuprate(I) along with copper(I) cyanides.[19] No halide was detected. An attempt to obtain mixed complexes was made by adding sodium cyanide to both copper(I) bromide and copper(I) bromide–sodium bromide mixtures. Spectra identical with those of the CuCN–NaCN–NaBr–H_2O system were obtained.

These data suggest either that the potential ligands do not coordinate with copper(I) cyanides to form mixed complexes or that if indeed mixed complexes are formed, the cyanide frequency and intensity is not appreciably affected. The fact that the solid cyanides crystallize out of solution without any halide content may support the former suggestion, but is not necessarily an indication of the nature of the solute species.

The System CuCN–NaCN–L–H_2O (L is a Polyatomic Ligand).—It is well known that certain of the vibrational frequencies of some polyatomic ligands are shifted on coordination to a metal atom and that in some cases the strength of the binding is indicated by the extent of the frequency shift.[20] Investigations with some polyatomic ligands which are known to be good complexing agents were carried out. The Raman spectra of copper(I) cyanide solutions (containing $Cu(CN)_3^{2-}$, $Cu(CN)_2^-$) with added urea, glycine, and ethylenediamine showed no new frequencies different from those of aqueous solutions of the potential ligands alone. The solutions in which the added compound was thiourea showed an apparent change in the C–S stretching frequency of the thiourea molecule from 1406.5 to 1404 cm.$^{-1}$. This change is on the border of experimental error and is not considered to be significant in the absence of further data. According to Riley,[21] any factor which increases the localization of negative charge in the coordinating ligand increases its ability to coordinate. This has been confirmed by other workers,[22] and on this basis one would expect methylthiourea and ethylthiourea to coordinate more strongly than thiourea to the copper atom. Polarographic studies have shown that the relative stabilities of copper(I) complexes in water for thiourea, methylthiourea, and ethylthiourea are 9.9, 9.9, and 39, respectively.[23] Strong coordination in the mixed complex with ethylthiourea should be accompanied by a shift in the C–S stretching frequency. Examination of the spectra of free ethylthiourea and an ethylthiourea–copper(I) cyanide mixture (containing $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$) indicated no change in the frequencies of the lines (682, 730, 1125 cm.$^{-1}$ for both cases). In view of this lack of change, the 2 cm.$^{-1}$ shift found for thiourea is apparently not significant. It appears in fact that coordination of these added ligands with the ions $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$ does not occur to any observable extent.

The Systems CuCN–NaX–H_2O and CuCN–HX–H_2O.—Copper(I) cyanide is not soluble in water but is reported to be soluble in strong halogen acids.[12] It was noted during these investigations that copper(I) cyanide is also soluble in aqueous solutions of sodium bromide or sodium iodide. This may be due to mixed complex formation, possibly of the type CuX_3CN^{3-}. In view of the absence of mixed complex formation with the ions $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$ as discussed above the CuCN system was further examined. A solution of copper(I) cyanide in either sodium bromide or sodium iodide solution exhibited Raman lines at 2106 and 2095 cm.$^{-1}$. These are the same as the stretching frequencies for the ion $Cu(CN)_3^{2-}$. A solution of copper(I) cyanide in 12% aqueous hydrogen bromide gave similar results. A probable explanation is the production of the apparently more stable tricyano ions plus bromo complexes with no mixed species formed. A search in the lower frequency region associated with γ_{Cu-Br} failed to produce a line corresponding to the 170 cm.$^{-1}$ line of Creighton and Lippincott.[17] This is probably due to the low intensity of the line and the low concentration of the solutions used (3.0 *M* NaBr, 0.2 *M* CuCN).

Another indication of the stability of $Cu(CN)_3^{2-}$ with respect to addition of further ligands was obtained by studying the reaction of 48% aqueous hydrogen bromide with sodium tetracyanocuprate(I). The concentration of hydrogen bromide in a solution of $Na_3Cu(CN)_4$ was gradually increased and the reaction followed by observation of the γ_{CN} by Raman spectra. The spectra (Figure 1) show the removal of the 2079 cm.$^{-1}$ line of $Cu(CN)_4^{3-}$ and the appearance of the 2106 cm.$^{-1}$ line of $Cu(CN)_3^{2-}$. When the 2079 cm.$^{-1}$

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[19] The other cyanides are supposedly $KCu_2(CN)_3$ and $K_3Cu(CN)_4$,[14] but they were not further investigated.

[20] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1962.

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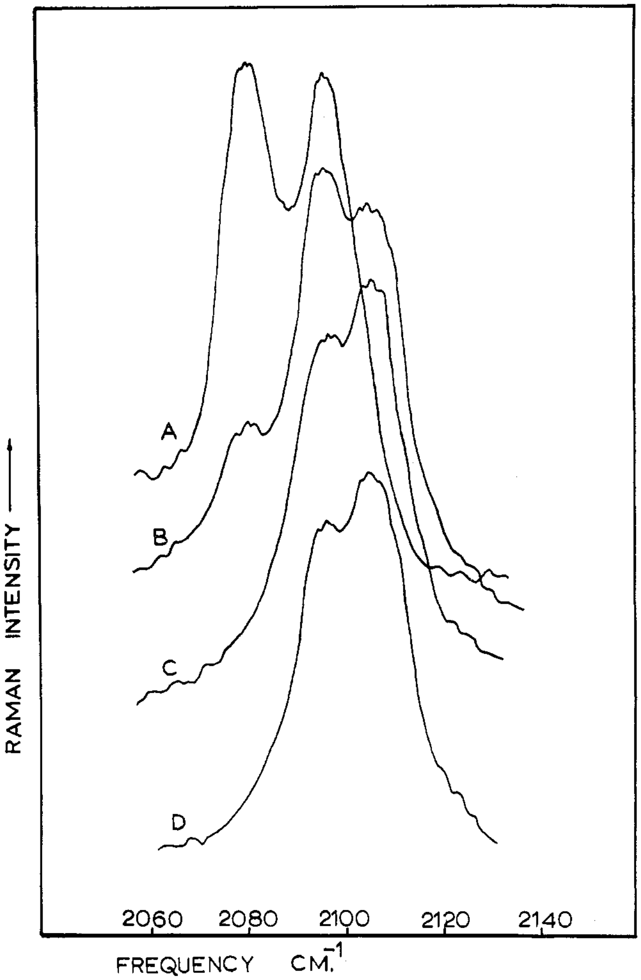

Figure 1.—Raman spectra of complex copper(I) cyanides in the presence of HBr; 1.0 *M* $Na_3Cu(CN)_4$ with increasing HBr concentration. Molarity of HBr: A, 0.0; B, 0.8; C, 1.0; D, 1.6. Maxima are at 2079, 2095–2096, and 2106 cm.$^{-1}$.

line had completely disappeared (at the mole ratio Cu/Br of 1:1), the intensity ratio of the lines at 2094 and 2106 cm.$^{-1}$ remained constant as more hydrogen bromide was added. It is not clear why there should be this difference in stability with respect to hydrogen bromide.[24]

Discussion

It is informative to consider the geometries of the ions in solution in an attempt to understand this apparent absence of complex formation with the various potential ligands. The tetracyanocuprate(I) ion is known to be tetrahedral.[25] For the tricyanocuprate(I) ion, comparison with $Cu(CN)_4^{-3}$ (T_d) would suggest a symmetry of C_{3v}, but one might also expect the symmetry D_{3h} to be favored by the spherical symmetry of the d^{10} copper(I) ion. The question clearly revolves on the presence or absence of coordinated water (or some other coordinated species). It is thought by Griffith[26] that the ion $Cu(CN)_3^{2-}$ will be tetrahedral with a molecule of coordinated water. As it is unlikely that coordinated water would not be displaced by halide ions (particularly by iodide ion) or by ethylenediamine, the lack of coordination of the potential ligands may indicate that there are no coordinated water molecules in the inner sphere. The problem becomes a little clearer when the two symmetries, C_{3v} and D_{3h}, for the tricyanocuprate(I) ion are considered as to vibrational spectra. The D_{3h} species would have seven Raman-active modes of which the three bending vibrations would most probably be too weak to permit observation. The remaining vibrations are two C–N modes (A_1' and E') and two metal–carbon modes (also A_1' and E'). Of these the E' modes are also infrared active, so for C–N and M–C vibrations there should be two Raman-active modes and one infrared-active mode. For C_{3v} symmetry we expect ten vibrations of species $4A_1$, $1A_1$, and 5E. The A_2 is not active and the A_1 and E modes are active in both infrared and Raman spectra. Experimentally Raman lines are observed at 2106 and 2094 cm.$^{-1}$ and only one infrared line is observed at 2094 cm.$^{-1}$ (see Table I). It appears therefore that the molecule has D_{3h} symmetry. Attempts to find the metal–carbon stretching frequencies for the lower cyano species have not been successful. The M–C line for $Cu(CN)_4^{3-}$ has been reported as a weak line at 288 cm.$^{-1}$.[27] The failure to observe the M–C lines for both $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$ is probably due partly to the low intensity of the shift and partly to the coincidence of the C–N frequencies excited by the 4047 Å. mercury line.

The planar molecule with no coordinated water may be favored over the pyramidal form with coordinated water because of the greater importance of π bonding in the planar molecule. In this context it is relevant to consider the data for the trisilylamine and trisilylphosphine molecules. These molecules, which are expected to be pyramidal because of the lone pair, are found to be planar[28] (or "pseudo-planar," *i.e.*, they obey selection rules for a molecule of D_{3h} symmetry). This was thought to be due to the importance of π bond formation utilizing (p → d) π bonding from the nitrogen or the phosphorus to the vacant d orbitals of silicon.[29]

The tricyanocuprate(I) ion is also exceptional in that the Raman intensity of the symmetric C–N stretching mode is abnormally high compared with that of the tetracyanocuprate(I) ion and the cyanide ion (Table II). The high Raman intensity for $Cu(CN)_3^{2-}$ is probably due to greater delocalization of the electron density over the planar system as a result of the increasing π bonding allowed by this configuration.

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(24) The acid $H_3Cu(CN)_4$ is reported to be a strong, extremely unstable acid which decomposes to give CuCN and HCN. It is also claimed by other workers that the acid $HCu(CN)_2$ may be obtained in solution by dissolving CuCN in dilute aqueous HCN,[10] but these reports probably refer to $Cu(CN)_3^{2-}$ for the reasons already discussed.

(25) L. H. Jones, *J. Chem. Phys.*, **29**, 463 (1958).

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(27) P. Chiorboli and C. Testa, *Ann. Chim.* (Rome), **47**, 639 (1957).

(28) (a) E. A. V. Ebsworth, J. R. Hall, M. J. MacKillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, **13**, 202 (1958); (b) E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Chem. Commun.* (London), 122 (1965).

(29) However, $P(CN)_3$ has recently been examined and the spectrum partially assigned on the basis of assumed C_{3v} symmetry: F. A. Miller, S. G. Fromkiss, and O. Sala, *Spectrochim. Acta*, **21**, 775 (1965).

Further evidence for the preference of a planar three coordinate structure for copper(I) comes from X-ray data for the solid dicyanocuprate(I) compound.[30] The configuration of the copper is found to be three-coordinate with the nitrogen of an adjacent cyanide group occupying the third position. The three cyanide ligands are bent only slightly out of plane in the crystal. The present data suggest that M–C π bonding may be sufficiently important to influence the structure of the ions and thus the tendency toward mixed-ligand complex formation. This is in contrast to the analogous mercury(II) compounds, which contain coordinated water in the nonmixed complexes and which form a great number of mixed complexes with a variety of other ligands.[31] Copper(II) also forms mixed-ligand complexes containing cyanide ions.[32] This suggests that the behavior of copper(II) and mercury(II) as compared to copper(I) may be related to a decrease in the π bond character of the M–C bond occurring when the oxidation state of the metal is increased. The difference in the intensities of the A_1 cyanide line for the ions $Hg(CN)_4^{2-}$ and $Cu(CN)_4^{3-}$ is also notable as another point of distinction between Hg(II) and Cu(I).[33] Whereas the mercury complex belongs to a group of ions having "normal" Raman intensities, the intensity of the copper(I) complex was found to be abnormally high and could not be simply treated using bond localized polarizabilities.

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[30] E. Staritzky and D. I. Walker, *Anal. Chem.*, **28**, 419 (1956).

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Contribution from Inorganic Chemistry Research Laboratories,
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Hydrido and Carbonylhydrido Complexes of Iridium Containing Stannous Chloride

By R. Craig Taylor, J. F. Young, and G. Wilkinson

Received August 2, 1965

The preparation of the complexes $IrHClXL_3$, IrH_2XL_3, $IrHClX(CO)L_2$, $IrDClX(CO)L_2$, $IrH_2X(CO)L_2$, and $IrD_2X(CO)L_2$, where $X = SnCl_3^-$ or Cl^- and $L = (C_6H_5)_3P$, are described. The infrared and n.m.r. spectra of these complexes are discussed with regard to possible structures. The results confirm the large *trans* effect of $SnCl_3^-$ as a ligand. A hydride-transfer reaction occurs between $IrCl(CO)L_2$ or $IrHCl_2(CO)L_2$ and H_2O in acetone solutions containing $SnCl_2$. The $IrHClX(CO)L_2 \cdot (CH_3)_2CO$ species initially found in this reaction loses acetone upon recrystallization. A compound corresponding to the formula $IrCl_2X(CO)L$ is also prepared.

Introduction

Hydride complexes of the transition metals have been extensively investigated, and two excellent reviews have appeared in the recent literature.[1,2] In particular, a number of investigations have been reported in which iridium is the central metal atom.[1] In connection with work recently reported in this laboratory on stannous chloride complexes of various transition metals,[3–5] the reaction of $SnCl_2$ with certain Ir(IV), Ir(III), and Ir(I) compounds was investigated. In view of the formation of a rhodium hydride species catalyzed by the presence of $SnCl_2$[6] and the ease with which iridium hydrides are formed by interaction with alcohols in the presence of triphenylphosphine,[7] it was of interest to ascertain whether $SnCl_2$ would catalyze iridium hydride formation. Furthermore, it was also of interest to determine whether $SnCl_2$ would be incorporated in the resulting complex as a trichlorostannate(II) ligand. That $SnCl_2$ promotes the interaction of iridium(III) with solvents is shown by the formation of an anionic iridium carbonyl complex, related to $[Ir_2Cl_6(SnCl_3)_4]^{4-}$,[3,5] which has been prepared in ethanol or 2-methoxyethanol in the absence of triphenylphosphine.

In all of the complexes reported in this paper, $SnCl_2$ appears to be acting as a weak σ-donor ligand, *i.e.*, $SnCl_3^-$, and exhibiting a large *trans* effect as a result of its ability to form d_π–d_π bonds with the central metal atom.[5] Lindsay, *et al.*,[8] have recently reported the characteristics of $SnCl_3^-$ as a ligand, and their results suggest weak σ-donation but a strong $d\pi$–$d\pi$ contribution to the metal–tin bond. Chatt[9,10] has shown that there is a good correlation between *trans*-effect and π-acceptor properties of a ligand in the series *trans*-Pt-

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