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Infrared and Raman Studies of Mixed Cyanide–Halide Complexes of Trivalent Gold[1]

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Crystalline dicyanide–dihalide complexes of gold(III) ($KAu(CN)_2X_2$, where X = Cl, Br, or I) are formed on treatment of $KAu(CN)_2$ with the free halogens. Coordinated halide in aqueous $Au(CN)_2X_2^-$ is completely replaced by two equivalents of CN^-; the reverse reaction does not occur in saturated halide solution. The highest cyanide complex of gold observed by means of infrared spectra in saturated KCN solution was $Au(CN)_4^-$. Chlorine treatment of $KAu(CN)_4$ and KBr in methanol yielded $KAu(CN)_3Cl$. Oxidation of $Ag(CN)_2^-$ with Br_2 does not yield a complex of Ag(III) but AgBr and BrCN; iodine and chlorine react similarly. The infrared absorption spectra of $Au(CN)_2Cl_2^-$, $Au(CN)_2Br_2^-$, $Au(CN)_2I_2^-$, $Au(CN)_3Cl^-$, and $HAu(CN)_4 \cdot 2H_2O$ and the Raman spectra of $Au(CN)_3Cl^-$ and $HAu(CN)_4 \cdot 2H_2O$ were recorded. The spectrum of the solid acid, $HAu(CN)_4 \cdot 2H_2O$, shows that the acidic hydrogen is hydrated to form H_3O^+. The Raman and infrared spectra of $Au(CN)_3Cl^-$ suggest the planar configuration of C_{2v} symmetry.

Introduction

Trivalent gold has a d^8 configuration, as do divalent nickel, palladium, and platinum. Characteristic of these four transition element neighbors is the formation of square-planar complexes containing four cyanide groups. It was shown by infrared studies[2,3] that nickel(II) forms the soluble pentacyanide complex ion in concentrated aqueous cyanide although no solid compound containing this ion has been isolated. It was of interest to determine whether the isoelectronic Au(III) would behave similarly. Higher complexes of trivalent gold, $Au(CN)_5^{2-}$ and $Au(CN)_6^{3-}$, have been hypothesized to explain results of measurements of "spontaneous electrolysis."[4] We hoped to verify the existence of these higher complexes by direct observation of their infrared absorption.

Trivalent gold forms an interesting series of water-soluble complexes containing both cyanide and halide: they are of the type $Au(CN)_2X_2^-$ (where X = Cl, Br, or I). The infrared absorption of the $KAu(CN)_2X_2$ solids has been studied by Jones.[5] The infrared absorption spectra of these complexes have not been studied previously in aqueous solution, nor have certain reactions been observed, *e.g.*, the stepwise replacement of halide by cyanide or the reverse reactions, $Au(CN)_{3-n}X_{n+1}^- + CN^- = Au(CN)_{4-n}X_n^- + X^-$.

The infrared study of aqueous cyanide complexes involves measurements of the intensity of absorption due to $C{\equiv}N$ stretching frequencies in the 2100–2200 cm.$^{-1}$ region arising from bound cyanide. A cyanide complex usually has a molar extinction coefficient larger than that of free CN^- and absorbs at a different frequency. Examples of application to aqueous cyanide complexes are: Ni(II)[2,3]; Ag(I) and Au(I)[6]; Cu(I)[7]; Tl(I)[8]; and Zn(II), Cd(II), and Hg(II).[9] Fronaeus and Larsson have studied the infrared absorption spectra of aqueous thiocyanate complexes and were particularly successful in applying it to $NiSCN^+$.[10]

Preparation of the mixed complexes of Au(III) was described in the early literature but they were not further characterized. Gerdy,[11] in 1843, reported the preparation of $KAu(CN)_2I_2 \cdot xH_2O$ by addition of I_2 to $KAu(CN)_2$ solution. Blomstrand[12] and Lindbom[13] prepared $KAu(CN)_2I_2$, $KAu(CN)_2Br_2$, and $KAu(CN)_2Cl_2$ by addition of halogen to $KAu(CN)_2$.

Experimental

Instrumentation and Technique.—A Perkin-Elmer Model 521 double beam recording spectrophotometer was used to obtain infrared data. For solution studies, we used fixed path length cells, modified from Perkin-Elmer "sealed liquid absorption cells" and consisting essentially of two CaF_2 optical flats spaced by 0.002-in. tantalum foil. Solids were examined as mulls in mineral oil or Fluorolube, or were dispersed in polyethylene melts. Raman data were obtained using a Cary Model 81. Solutions were examined in regular tubes; solids were examined using a conical vessel based on a design supplied by R. H. Busey and O. L. Keller,[14] of Oak Ridge National Laboratory.

Compound Preparation. (a) **$KAu(CN)_2Cl_2$, $KAu(CN)_2Br_2$, and $KAu(CN)_2I_2$.**—The three mixed-ligand complexes, $KAu(CN)_2Cl_2$, $KAu(CN)_2Br_2$, and $KAu(CN)_2I_2$, were made by adding a slight excess of the free halogen dissolved in methanol to an aqueous solution of $KAu(CN)_2$. Needle-like hydrate crystals are obtained on evaporation. They are black for the iodide, bright yellow for the bromide, and pale yellow for the chloride. The iodide is the least stable. Clear crystals of the bromide and chloride were found to lose water on standing in dry laboratory air, turning opaque to visible light. Hydrated $KAu(CN)_2Br_2$ can be heated without decomposition at 100° to give the anhydrous salt. Analysis of a typical preparation gave CN/Au = 2.01; Br/Au = 2.05; K/Au = 1.06.

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(1) This work was sponsored by the U. S. Atomic Energy Commission.

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(b) **$KAu(CN)_4$.**—The bromides of $KAu(CN)_2Br_2$ are readily replaced by cyanides and it is thus a useful starting material for the preparation of $KAu(CN)_4$. For this preparation $KAu(CN)_2$ was dissolved in water and a slight excess of bromine was added while stirring; the solution was then heated to 80° until the excess bromine was removed. Evaporation was continued until crystals began to form, then the mixture was cooled to 0° and filtered to remove $KAu(CN)_2Br_2 \cdot 2H_2O$. One mole of KCN was dissolved in methanol (solubility 4.9 g./100 g.) and 0.5 mole of solid $KAu(CN)_2Br_2$ was added with vigorous stirring. After one-half the methanol was evaporated the KBr by-product was filtered off. Evaporation was continued, yielding crude $KAu(CN)_4$ which was then recrystallized from water to remove residual KBr. The product gave a negative test for bromide (oxidation by dichromate and extraction with CCl_4). One molecule of hydrate water was readily lost in dry air, giving $KAu(CN)_4 \cdot 0.5H_2O$.

Anal. Calcd. for $KAu(CN)_4 \cdot 0.5H_2O$: K, 11.2; Au, 56.4; CN, 29.8; H_2O, 2.6, Found: K, 11.4; Au, 55.5; CN, 30.2; H_2O, 2.7.

(c) **$HAu(CN)_4 \cdot 2H_2O$ and $HAu(CN)_2Br_2 \cdot xH_2O$.**—The acid $HAu(CN)_4 \cdot 2H_2O$ was prepared by dissolving 10 g. of $KAu(CN)_4$ in 20 g. of water and passing the solution through the cation exchanger, Dowex 50W X-8, in the H^+ form. Water was removed by evaporation at room temperature in a stream of dry air. The crystalline acid was dried to constant weight in a vacuum desiccator over KOH.

Anal. Calcd. for $HAu(CN)_4 \cdot 2H_2O$: H, 1.5; Au, 58.3; CN, 30.8. Found: H, 1.3; Au, 58.4; CN, 31.2.

Titration of the acid to the phenolphthalein end point with standard potassium hydroxide gave an average equivalent weight of 337.8 (theoretical 338.1). The $HAu(CN)_4 \cdot 2H_2O$ prepared from pure $KAu(CN)_4$ is stable for weeks. However, when KBr impurity was present in the $KAu(CN)_4$, HBr as well as $HAu(CN)_4$ was formed on passage through the ion exchanger, causing decomposition of the $HAu(CN)_4$ and deposition of a yellow solid. Similarly, passage of a $KAu(CN)_2Br_2$ solution through Dowex-50 gave $HAu(CN)_2Br_2 . xH_2O$, but the product was not analyzed chemically.

(d) **$KAu(CN)_3Cl$ and $KAu(CN)_3Br$.**—We prepared $KAu(CN)_3Cl$ by passing chlorine gas through a methanol solution containing KBr and $KAu(CN)_4$ in 1:1 (or greater) mole ratios. After chlorine treatment for 2 hr., the solution was evaporated at 25° leaving a $KAu(CN)_3Cl$–KCl mixture. A test for residual bromide was negative. Analysis of material partially separated from KCl by extraction with methanol gave the following values: CN/Au = 2.99, Cl/Au = 1.78, K/Au = 1.75. These values are consistent with the composition $KAu(CN)_3Cl$ with a residual 0.75 mole of KCl. The mechanism of the reaction is not understood but it was found that chlorine does not replace one of the cyanides on $Au(CN)_4^-$ unless KBr is present initially. Potassium chloride or iodide was not effective. Addition of $KAu(CN)_3Cl$ to saturated KBr yielded $KAu(CN)_3Br$ on crystallization.

(e) **Attempted Preparation of $Au(CN)I^-$.**—Saturated aqueous KI slowly dissolved Au(CN), giving the infrared absorption peak characteristic of $Au(CN)_2^-$. The reaction apparently is

$$2AuCN + \text{excess } I^- = Au(CN)_2^- + AuI$$

(f) **Attempted Preparation of Silver(III) Complexes.**—When a solution of $KAg(CN)_2$ was treated with Cl_2, Br_2, or I_2 a precipitate formed and an infrared absorption different from that of $Ag(CN)_2^-$ was found in the supernatant liquid. However, no silver was found on evaporation of the solution. The infrared absorption was shown in each case to be that of the corresponding cyanogen halide; the initial precipitate was found to be the silver halide. Some cyanate ion was also found when Cl_2 was used as the oxidant.

Measurements.—The molar extinction coefficients of the Au(III) complexes are small, necessitating working with >0.1 *M* concentrations. Solutions were made up by dissolving a weighed amount of complex in water and recording their infrared spectra using cells having a path length of 60.8 μ. The results are given in Table I. The path length of the empty cell was determined by measuring the spacing between 15 or more interference peaks in the infrared. In the case of $Au(CN)_2I_2^-$, slow decomposition with growth of $Au(CN)_2^-$ was noted. Iodide ion also caused some reduction of $Au(CN)_4^-$ when $KAu(CN)_4$ was dissolved in saturated KI solution. As seen from Table I, the extinction coefficient of $KAu(CN)_2$ is large and its absorption position is well resolved from those of the Au(III) complexes. Thus incomplete oxidation of Au(I) to Au(III) [or reduction of Au(III) to Au(I)] was readily detected.

Table I

Infrared Absorptions

	Aqueous solution				
	ν_{max}, cm.$^{-1}$	ϵ_{max}, mole^{-1} l. cm.$^{-1}$	k^a	Solubility, *M*	Solid ν_{max}, cm.$^{-1}$
$KAu(CN)_4$	2189^b	34	320	0.6	2189^b
$HAu(CN)_4 \cdot 2H_2O$	2189	34	320	...	2218, 2204
$KAu(CN)_2Cl_2$	2181	19	180	1.4	2182^c
$KAu(CN)_3Cl$	2186	~15	...	...	2203 w, 2196, 2185
$KAu(CN)_3Br$	...	...	...	...	2201, 2191, 2183, 2175 sh
$KAu(CN)_2Br_2$	2177	48	470	0.6	2175^c
$HAu(CN)_2Br_2$	2177	48	470	...	2231, 2215 sh
$KAu(CN)_2I_2$	2171	94	1140	0.1	2185 w, 2165^c
$KAu(CN)_2$	2147^d	477^d	4980	0.87	2141^e
KCN	2080^d	29^d			

[a] Integrated absorption coefficient, mole^{-1} l. cm.$^{-2}$. [b] Ref. 15. [c] Ref. 5. [d] Ref. 6. [e] Ref. 16. [f] This shoulder is probably from $KAu(CN)_2Br_2$, which absorbs at 2175 cm.$^{-1}$.

Reactions of $KAu(CN)_2X_2$ and Search for $KAu(CN)_3Cl$.—The peak maxima of $Au(CN)_4^-$ and $Au(CN)_2Br_2^-$ are at 2189 and 2177 cm.$^{-1}$, respectively. The effect of adding CN^- in increments to 0.4 *M* $Au(CN)_2Br_2^-$ was studied by dissolving in water weighed amounts of KCN and $KAu(CN)_2Br_2$. The infrared absorption spectra of some of the solutions are shown in Figure 1. At ratios of CN/Au > 4 the infrared spectra showed that $Au(CN)_2Br_2^-$ had

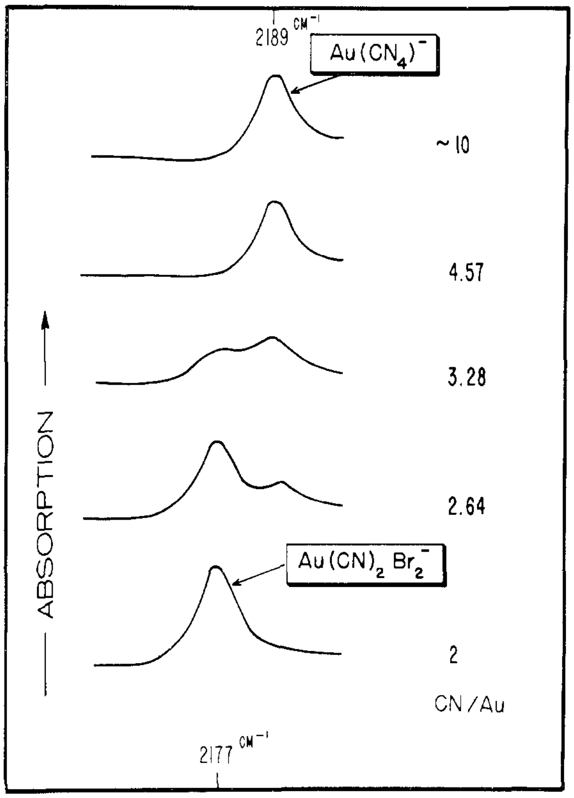

Figure 1.—Infrared spectra of the conversion of $Au(CN)_2Br_2^-$ into $Au(CN)_4^-$ by addition of KCN; Au(III) = 0.4 *M*.

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(15) J. M. Smith and L. H. Jones, *J. Chem. Phys.*, **41**, 2507 (1964).

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been converted completely into $Au(CN)_4^-$. At lower ratios, only $Au(CN)_2Br_2^-$ and $Au(CN)_4^-$ are observed.

When a solution of $KAu(CN)_2Cl_2$ was treated with excess KBr or KI, or when $KAu(CN)_2Br_2$ was treated with excess KI, the corresponding heavier dihalide complex was observed on evaporation of the solution. The heavier halides were not replaced by lighter halide ions. This reaction was not developed as a preparative technique since the dibromide and diiodide complexes were easier to prepare by direct reaction of $KAu(CN)_2$ and the free halogen.

As described in a later section, $KAu(CN)_3Cl$ was prepared by a different technique. Its absorption frequencies in the solid are particularly characteristic since they occur at frequencies higher than those of either $KAu(CN)_2Cl_2$ or $KAu(CN)_4$. It was searched for as an intermediate in the replacement of halide in $Au(CN)_2Cl_2^-$ by cyanide. A solution of $KAu(CN)_2Cl_2$ was divided into two parts; 1 equivalent of KCN was added to the first portion, and 0.5 equivalent of KCN was added to the second. A portion of each solution was dried on a CaF_2 window and the resulting solids were examined in the infrared. Only the absorption peaks of $KAu(CN)_2Cl_2$ and $KAu(CN)_4$ were seen; absorption characteristic of $KAu(CN)_3Cl$ was not observed.

Lack of Formation of $Au(CN)_5^{2-}$ and $Au(CN)_6^{3-}$.—In the above section it was shown (Figure 1) that no absorption other than for $Au(CN)_4^-$ was observed at $CN/Au > 4$. A more careful search was then made for absorption of higher cyanide complexes in the $Au(CN)_4^- + CN^-$ series. Au(III) was maintained at a constant concentration of 0.4 *M* in various concentrations of KCN up to saturation (~10 *M*). The absorption of free CN^- in the Au(III)–KCN solutions was compensated for by the use of the same concentration of KCN in the reference beam. However, high concentrations of KCN did not alter the absorption peak of $Au(CN)_4^-$ nor was any new absorption observed indicative of $Au(CN)_5^{2-}$ or $Au(CN)_6^{3-}$.

Addition of $AuCl_4^-$ to $Au(CN)_4^-$.—The species $Au(CN)_2Cl_2^-$ is stable in aqueous solution for several days, although the solid turns deeper yellow after exposure to air for several weeks. There appears to be no tendency for disproportionation to form $AuCl_4^-$ and $Au(CN)_4^-$. However, when equimolar amounts of $KAuCl_4$ and $KAu(CN)_4$ in aqueous solution were mixed, only the $Au(CN)_4^-$ infrared peak was observed in the solution with no evidence of interaction to form $Au(CN)_2Cl_2^-$ after several hours at 25°.

Infrared and Raman Spectra of Aqueous $Au(CN)_3Cl^-$.—When $KAu(CN)_3Cl$ is dissolved in water, the aqueous solution obtained is stable enough to observe the infrared and Raman spectra, but it decomposes slowly on standing over a period of a few days. $Au(CN)_3Cl^-$ of C_{2v} symmetry will have three CN stretching vibrations, $2A_1 + 1B_1$, which should all be active in both infrared and Raman spectra. The Raman spectrum of aqueous $Au(CN)_3Cl^-$ shows a strong peak at 2202 cm.$^{-1}$ and a weaker peak at 2195 cm.$^{-1}$. The infrared spectrum of the aqueous solution gives a peak at 2186 cm.$^{-1}$ with unresolved absorption on the high-frequency side. The infrared spectrum (Figure 2) of solid $KAu(CN)_3Cl$ shows three peaks: 2186 (strong), 2196 (medium strong), and 2203 (weak). Thus, the spectra are in complete agreement with that expected for $Au(CN)_3Cl^-$. The relative intensities in the Raman and infrared suggest that the symmetrical stretching of the opposite cyanides appears at 2202 cm.$^{-1}$ whereas the vibration at 2196 cm.$^{-1}$ involves primarily stretching of the unique CN group. The vibration at 2186 cm.$^{-1}$ is the asymmetric stretching of opposite CN groups.

In the recently completed study[5] of $KAu(CN)_2Cl_2$, it was shown that the *trans* isomer results when $KAu(CN)_2$ adds Cl_2. *trans*-$Au(CN)_2Cl_2^-$ has but one Raman-active CN vibration at 2199 cm.$^{-1}$ and one infrared-active CN vibration at 2181 cm.$^{-1}$.[5] Thus, the species we here assign as $Au(CN)_3Cl^-$ is definitely distinct from *trans*-$Au(CN)_2Cl_2^-$. This is further borne out by the fact that in aqueous solution $Au(CN)_3Cl^-$ has one Raman-active AuCl stretching frequency at 356 cm.$^{-1}$, compared to 342 cm.$^{-1}$ for *trans*-$Au(CN)_2Cl_2^-$.[5]

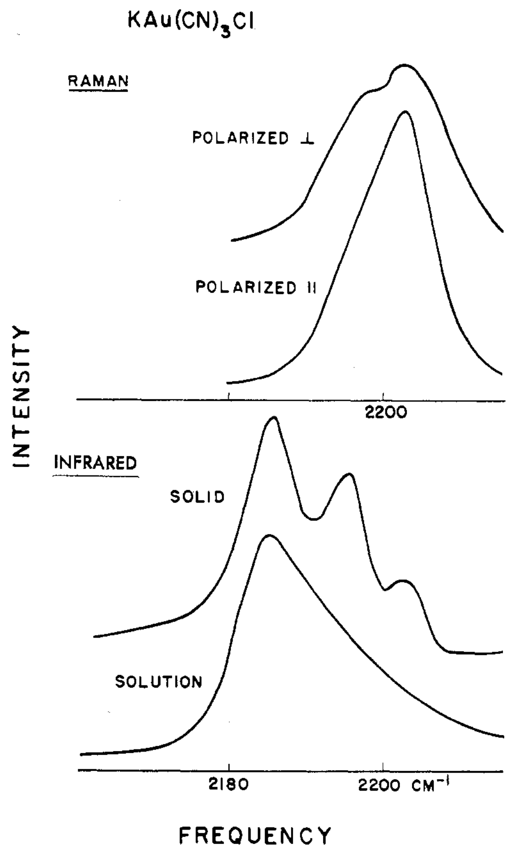

Figure 2.—Infrared and Raman spectra of $KAu(CN)_3Cl$.

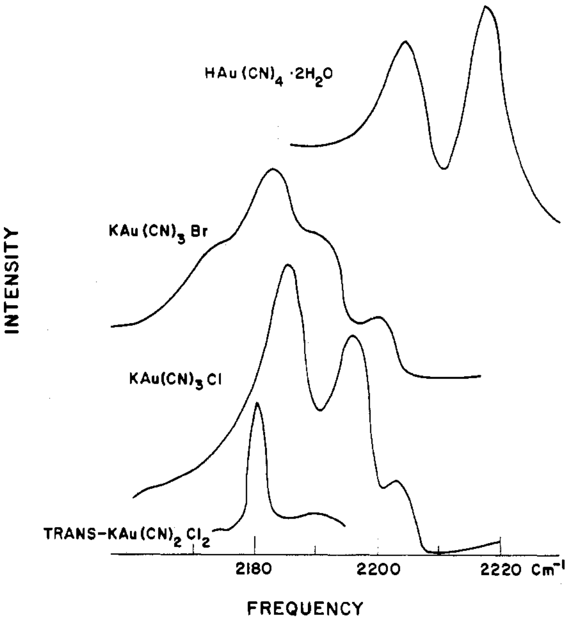

Figure 3.—Infrared absorption of the solids: $HAu(CN)_4 \cdot 2H_2O$, $KAu(CN)_3Br$, $KAu(CN)_3Cl$, and *trans*-$KAu(CN)_2Cl_2$.

Properties of $HAu(CN)_4 \cdot 2H_2O$ and $HAu(CN)_2Br_2 \cdot xH_2O$.—When a $KAu(CN)_4$ solution was passed through H^+ form Dowex-50, the effluent from the ion-exchange column became acid and showed the absorption characteristic of the $Au(CN)_4^-$ ion. The white solid deposited on removal of water over KOH did not show infrared peaks characteristic of residual $KAu(CN)_4$, but two strong new peaks (Figure 3) at 2204 and 2218 cm.$^{-1}$ of approximately equal intensity. Since chemical analysis of the compound showed that it was a hydrate, absorption of H_3O^+ was sought.[17] Peaks characteristic of H_3O^+ were observed at 25° at ~1700, ~2210, and ~3000 cm.$^{-1}$ (the latter two are very broad). The Raman spectrum of the solid gave peaks at 2217 and 2231 cm.$^{-1}$. There are thus three CN stretching vibrations: 2204 cm.$^{-1}$, appearing in the infrared only; 2218 cm.$^{-1}$, appearing in the infrared and Raman; and 2231 cm.$^{-1}$, appearingin the Raman only. These are to be compared with 2189, 2198, and 2207 cm.$^{-1}$ for solid $KAu(CN)_4$.[15] The Au–C stretching frequency appears at 488 cm.$^{-1}$ compared to 461 cm.$^{-1}$ for $KAu(CN)_4$. A solution of $HAu(CN)_4$ containing an equivalent amount of added KBr was allowed to evaporate slowly at 25°. The white solid gave the infrared absorption of $KAu(CN)_4$, showing that HBr had been lost rather than HCN. However, when a Fluorolube mull of $HAu(CN)_4 \cdot 2H_2O$ was placed on a CsBr window in an attempt to observe the low-frequency spectrum, reaction with the CsBr window was observed and an Au–Br frequency appeared.

Passage of a $KAu(CN)_2Br_2$ solution through H^+ form Dowex-50 gave the $Au(CN)_2Br_2^-$ ion in aqueous solution as shown by its infrared absorption. The yellow solid $HAu(CN)_2Br_2 \cdot xH_2O$, obtained on evaporation, showed absorption at 2231 and 2215 cm.$^{-1}$.

Conclusions

Contrary to the behavior found with nickel(II), $Au(CN)_4^-$ does not add cyanide in saturated aqueous cyanide solution to form concentrations of $Au(CN)_5^{2-}$ or $Au(CN)_6^{3-}$ observable by their infrared absorption. Thus, we are faced with a situation similar to that of the reported $Cd(CN)_6^{4-}$ complex[18] which was not confirmed by infrared measurements.[9] We conclude that these higher complexes (if indeed formed) either absorb at the same frequency with the same absorption coefficient as $Au(CN)_4^-$ [or $Cd(CN)_4^{2-}$, respectively] which is unlikely, or are formed in very small concentrations. In this respect, $Au(CN)_4^-$ resembles $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, neither of which forms pentacyanide complexes.[19]

Observation of mixed halide–cyanide complexes of Au(III) is straightforward in the infrared. These compounds react with free cyanide and heavier halides. When $Au(CN)_2X_2^-$ was treated with one equivalent of CN^-, the expected monohalide $Au(CN)_3X^-$ was not observed although the monohalides $Au(CN)_3Cl^-$ and $Au(CN)_3Br^-$ could be prepared by a different method. In aqueous solution, one might have expected $Au(CN)_3Cl^-$ to disproportionate into $Au(CN)_2Cl_2^-$ and $Au(CN)_4^-$, but this was not observed. In solution, $Au(CN)_2Cl_2^-$ is stable, yet it is not formed by the interaction of $AuCl_4^-$ and $Au(CN)_4^-$. On the other hand, metathetical reactions, involving substitution of lighter halides by heavier halides and of any halide by cyanide, occur, showing that the bound halide is somewhat labile.

Reactions followed by infrared solution studies are

$$Au(CN)_2X_2^- \ (X = Cl, Br, \text{ or } I) + 2CN^- = Au(CN)_4^- + 2X^-$$

$$Au(CN)_4^- + \text{saturated KBr} \longrightarrow \text{no reaction}$$

$$Au(CN_2)Cl_2^- + 2X^- \ (X^- = Br \text{ or } I) = Au(CN)_2Br_2 \text{ or } Au(CN)_2I_2$$

$$Au(CN)_2Br_2^- \xrightarrow{HSO_3^-} Au(CN)_2^-$$

$$Au(CN)_3Cl^- + Br^- = Au(CN)_3Br^- + Cl^-$$

The absorption spectrum of $HAu(CN)_4 \cdot 2H_2O$ shows clearly the absorption characteristic of H_3O^+. Thus, at least one of the two H_2O molecules in $HAu(CN)_4 \cdot 2H_2O$ is involved in proton hydration. Further, it appears that in solid $H_3O^+Au(CN)_4^- \cdot H_2O$ both the Au–C and C–N bonds are stronger than in solid $KAu(CN)_4$ or in aqueous $HAu(CN)_4$. The Au–Cl bond in $Au(CN)_3Cl^-$ is apparently slightly stronger than that in *trans*-$Au(CN)_2Cl_2^-$. The Raman and infrared spectra are consistent with a planar configuration of C_{2v} symmetry for $Au(CN)_3Cl^-$.

[17] C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.*, **23**, 1464 (1955).

[18] M. Prytz and T. Osterud, *Acta Chem. Scand.*, **6**, 1534 (1952).

[19] J. M. Smith, L. H. Jones, and R. A. Penneman, unpublished work (1963).

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Substitution Reactions of Iodopentaaquochromium(III) Ion

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Bromide and chloride replace iodide in iodopentaaquochromium(III) ion. The reaction proceeds without intermediate formation of the hexaaquo ion. The rate of decomposition of iodopentaaquochromium(III) ion in the presence of bromide ion was found to be equal to the rate in the presence of perchlorate ion of the same acidity and ionic strength. Bromopentaaquochromium(III) ion is formed along with hexaaquochromium(III) ion at a concentration ratio of 0.127 (in 1 *M* hydrobromic acid). The results are interpreted in terms of an SN1 mechanism. Similar results were obtained in the presence of chloride. The mechanism is confirmed by the observed retardation of the reaction in the presence of iodide which is characteristic for a dissociative mechanism (mass law retardation).

Substitution reactions of octahedral complexes of the type $MA_5X + Y \rightarrow MA_5Y + X$ may be considered to proceed by an SN1 mechanism if the reaction rate is independent of the nature and concentration of the incoming ligand Y (a dependence on Y does not, however, disprove an SN1 mechanism). Another characteristic confined to SN1 reactions is the so-called mass law retardation,[1] *i.e.*, a retardation of the reaction by X which cannot be ascribed to the reversible reaction $MA_5Y + X \rightarrow MA_5X + Y$.

[1] C. K. Ingold, "Structure and Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 362.