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Vibrational Spectra, Force Constants, and Bonding in Mixed Cyanide–Halide Complexes of Gold[1]

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Infrared spectra of solid $KAu(CN)_2Cl_2$, $KAu(CN)_2Br_2$, and $KAu(CN)_2I_2$ have been observed from 100 to 4500 cm.$^{-1}$. The Raman spectrum of aqueous $KAu(CN)_2Cl_2$ has also been observed. The results have been combined to calculate valence force constants for the $Au(CN)_2X_2^-$ ions. It is found that substitution of halides for two of the cyanides in $Au(CN)_4^-$ results in a slight lowering of the CN stretching force constant, iodide having the greatest effect and chloride the least. This is explained as arising from a slight decrease in metal–carbon σ-bond strength with perhaps a little increase in metal–ligand π-bonding. The metal–halide force constants decrease considerably in the order $F_{AuCl} > F_{AuBr} > F_{AuI}$ as expected from the increasing size of the halide ions. Nevertheless the iodide ion has the greatest effect on the Au–C–N bond structure, indicating that the Au–I bond is more covalent than the others.

Introduction

Vibrational spectra of complex ions have been shown to enhance our understanding of the nature of bonding. From the spectra, if sufficiently complete, many of the bond stretching force constants can be calculated. Such a force constant is an evaluation of the force necessary to stretch the bond and thus can be considered a direct measure of the strength of the bond. Comparison of force constants among a group of similar complexes gives valuable clues as to the nature of bonding. The interaction constants, informing us how much distortion of one bond or bond angle affects another bond or bond angle, are often quite enlightening about the identification and characteristics of the bonding electrons.

Much has been learned about the bonding in metal–cyanide complexes from their vibrational spectra.[2] To further this knowledge it is of interest to study the effect caused by replacing some of the cyanides by halides. Thus does the replacement of a cyanide by a halide cause the remaining cyanide to be held more or less tightly? How does it affect the σ- and π-bond structure of the other cyanides? Which halides should have the biggest effect? Many such questions may be answered by infrared and Raman studies of suitable complexes. Trivalent gold which is isoelectronic with divalent platinum and thus forms square-planar complexes displays an interesting group of complexes containing cyanides and halides. Because of the high "effective nuclear kernel charge" on Au(III) we expect[2] strong gold–ligand σ-bonding and weak gold–ligand π-bonding. This has been shown to be true[3] for $KAu(CN)_4$. It is of interest to determine the changes accompanying partial replacement of cyanides by halides. For this purpose we have studied the vibrational spectra and determined the force constants of some gold–cyanide–halide complexes, namely $KAu(CN)_2Cl_2$, $KAu(CN)_2Br_2$, and $KAu(CN)_2I_2$.

Experimental

Preparation of the salts $KAu(CN)_2Cl_2$, $KAu(CN)_2Br_2$, and $KAu(CN)_2I_2$ from $KAu(CN)_2$ will be described in a future publication.[4] Crystallization from methanol yielded long thin needles of all three compounds.

Recording of Infrared Spectra.—For recording the frequencies of the CN stretching vibrations single crystals were used in an infrared microscope. For weaker absorption bands, pressed disks of the pure material gave the best results. For low-frequency fundamentals (<500 cm.$^{-1}$) mineral oil mulls and dispersions in polyethylene were quite satisfactory. We covered the region from 100 to 4500 cm.$^{-1}$ using several medium resolution spectrometers. The primary absorption bands for the dichloride are shown in Fig. 1 and 2. The dibromide and diiodide spectra are similar. The observed absorption bands are given in Table I.

Recording of Raman Spectra.—A saturated aqueous solution of $KAu(CN)_2Cl_2$ is pale yellow and gave quite good Raman spectra using a Cary Model 81 Raman spectrometer. The low-frequency Raman peaks are shown in Fig. 3 and recorded in Table II. $KAu(CN)_2Br_2$ is too highly colored for Raman studies using the 4358 Å. line of Hg for excitation. Probably it is quite satisfactory for excitation by 5461 Å. of Hg or longer wave length lines of He, etc.; however, we are not set up for this region as yet. Solutions of $KAu(CN)_2I_2$ are definitely too dark and probably too unstable for any hope of Raman studies.

Symmetry and Selection Rules.—The complex $Au(CN)_2X_2^-$ will undoubtedly be planar, as is $Au(CN)_4^-$, using dsp^2 orbitals for the four σ-bonds. The question arises, will it be the *cis* or the *trans* form? The preparation involves adding the free halogen in methanol to the linear $NCAuCN^-$ ion in aqueous solution. The most likely path is for the halide atom to form bonds perpendicular to the linear NCAuCN axis yielding the *trans* species.[5]

From the infrared and Raman spectra of $KAu(CN)_2Cl_2$ it is quite clear that we do indeed have the *trans* structure. There is one infrared-active CN stretching frequency at 2180 cm.$^{-1}$ (ν_{10}) and one Raman-active CN stretching frequency at 2199 cm.$^{-1}$ (ν_1). The *cis* form should have two CN stretching frequencies active in both infrared and Raman. Furthermore, the only infrared-active combination of CN stretching frequencies observed is $\nu_1 + \nu_{10}$, whereas for the *cis* form we should expect to see $\nu_1 + \nu_{10}$, $2\nu_1$, and $2\nu_{10}$. $KAu(CN)_2Br_2$ follows the pattern of the dichloride. $KAu(CN)_2I_2$ is somewhat different. Two infrared-active CN stretching frequencies appear, at 2186 and 2166

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963), and references therein.

[3] L. H. Jones and J. M. Smith, *J. Chem. Phys.*, in press.

[4] J. M. Smith, L. H. Jones, and R. A. Penneman, to be submitted to *Inorg. Chem.*

[5] If we could replace two cyanides of $Au(CN)_4^-$ by halides, we would expect to produce the *cis* form because of the strong *trans*-directing influence of the CN^- ions.

TABLE I

INFRARED ABSORPTION BANDS OF $KAu(CN)_2X_2$

$Au(CN)_2Cl_2^-$		$Au(CN)_2Br_2^-$		$Au(CN)_2I_2^-$		
ν, cm.$^{-1}$	α^a	ν, cm.$^{-1}$	α^a	ν, cm.$^{-1}$	α^a	Assignment
4354	1.0	4342	0.9	4330	0.4	$\nu_1 + \nu_{10}$
				4303	0.4	$2\nu_{10}$
2681	0.08					
2650	0.1	2633	1.5	2622	1.3	$\nu_1 + \nu_{11}$
2629	1.5	2621	1.5			$\nu_2 + \nu_{10}$
2565	0.08					$\nu_1 + \nu_{13}$
2548	0.1	2543	0.3	2530	0.4	$\nu_4 + \nu_{10}$
		2477	0.15			$\nu_6 + \nu_{10}$
2236	0.2					
2210	0.2					
				2185	5.3	ν_1
2182	16	2175	30	2165	50	ν_{10}
2159	0.2	2151	0.4			$\nu_{CN^{15}}$
2140	0.8	2134	0.9	2121	1.5	$\nu_{C^{13}N}$
818	0.4	820	0.15			$\nu_4 + \nu_{11}$
790	0.6	798	0.1	792	0.5	$\nu_4 + \nu_{14}$
730	0.6	730	0.15	728	0.3	
705	1.8					$\nu_3 + \nu_{13}$
598	0.6					$\nu_6 + \nu_7$
		580	0.1			
565	0.7					$\nu_2 + \nu_{15}$
509	1.5			481	1	
455	43	454	60	447	5	ν_{11}
424	59	425	66	424	4	ν_{14}
362	105	258	30	203	3	ν_{13}
338	7?					ν_3
		330	1?			
126	37					

[a] α is an approximate absorption coefficient in mM^{-1} cm.^{2} for the solid state.

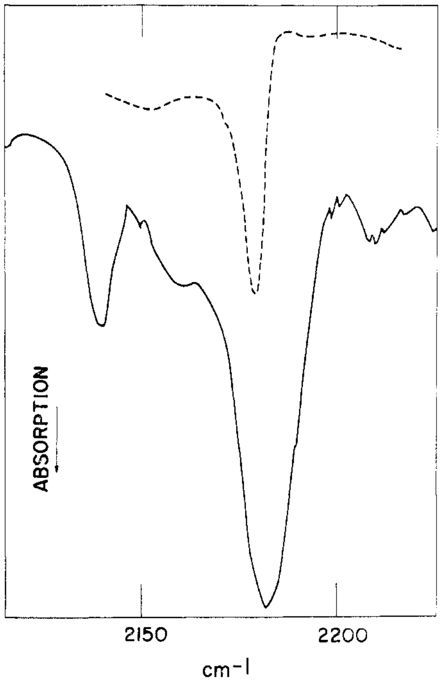

Fig. 1.—Infrared-active CN stretching fundamental of $KAu(CN)_2Cl_2$: ———, single crystal; - - - - - dispersion in polyethylene.

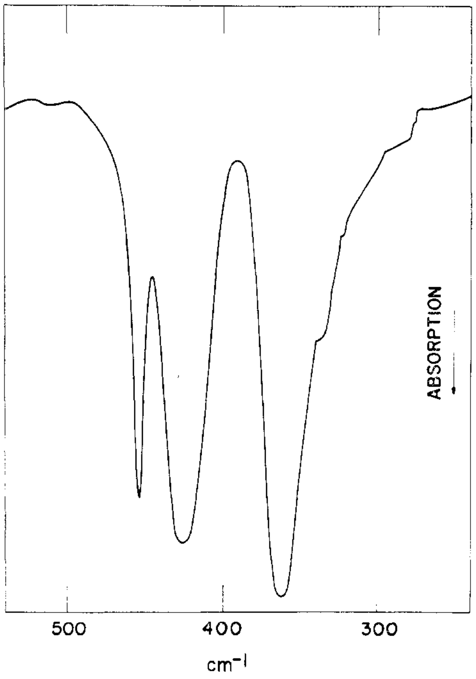

Fig. 2.—Infrared spectrum of medium frequency fundamentals of $KAu(CN)_2Cl_2$ as dispersion in polyethylene.

cm.$^{-1}$. There are two reasonable explanations for this; either we are dealing with the *cis* form or the D_{2h} symmetry of the *trans* species is reduced by the crystal symmetry making both ν_1 and ν_{10} active in the infrared. We obtained polarized spectra of a single crystal of $KAu(CN)_2I_2$ and observed that ν_1 and ν_{10} are polarized in the same general direction. This shows that we have the *trans* form for $KAu(CN)_2I_2$ also. In support of this is the fact that the peak at 2186 cm.$^{-1}$ is much weaker than that at 2166 cm.$^{-1}$ in the solid. For the *cis* form the two peaks should show similar absorption intensity. We shall treat all three complexes as the *trans* species of D_{2h} symmetry.

Ions of the type $M(CN)_2X_2$ with D_{2h} point group[6] will have 15

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[6] We do not know the crystal structures and thus cannot give the precise selection rules for the solid state. However, we can be confident that the selection rules will not be greatly altered from those of D_{2h} symmetry.

TABLE II

RAMAN SPECTRUM OF AQUEOUS $KAu(CN)_2Cl_2$

ν,[a] cm.$^{-1}$		I[b]
2199	P(0.4)	5
461	P (0.24)	0.8
342	P (0.18)	6.5
294	D	0.2
126	D	0.4

[a] Frequencies labeled P are highly polarized. The depolarization ratios, given after P, are arrived at using the corrections of Koningstein and Bernstein [J. A. Koningstein and H. J. Bernstein, *Spectrochim. Acta*, **18**, 1249 (1962)]. They are very approximate. [b] These intensities are for a molar solution. They are to be compared with 100 for pure CCl_4 at 458 cm.$^{-1}$ using a 4 cm.$^{-1}$ slit.

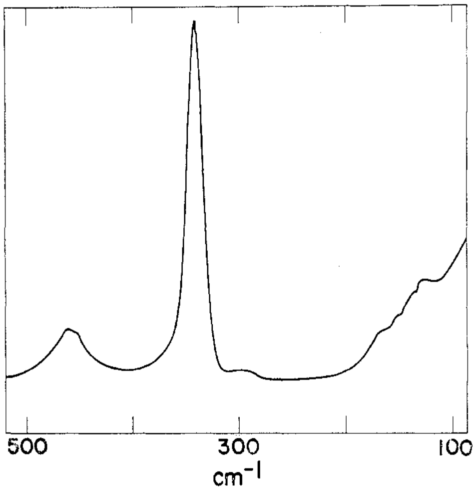

Fig. 3.—Raman spectrum of 1.4 *M* aqueous $KAu(CN)_2Cl_2$.

TABLE III

FUNDAMENTAL FREQUENCIES OF THE IONS $Au(CN)_2X_2^-$

Representation[a]	Type[b]	$Au(CN)_2Cl_2^-$	$Au(CN)_2Br_2^-$	$Au(CN)_2I_2^-$
A_{1g}	ν_1 (ν_{CN})	2199	[2191][c]	2186
	ν_2 (ν_{MC})	461	[456][c]	
	ν_3 (ν_{MX})	342		
B_{1g}	ν_4 (δ_{MCN})	[368][c]	[368][c]	[364][c]
	ν_5 (δ_{XMC})	126		
B_{3g}	ν_6 (π_{MCN})	297	[302][c]	
B_{1u}	ν_7 (π_{MCN})	[301][c]		
	ν_8 (π_{CMC})			
	ν_9 (π_{XMX})			
B_{2u}	ν_{10} (ν_{CN})	2181	2175	2166
	ν_{11} (ν_{MC})	455	454	447
	ν_{12} (δ_{XMC})	126	[89][d]	[73][d]
B_{3u}	ν_{13} (ν_{MX})	362	258	203
	ν_{14} (δ_{MCN})	424	425	424
	ν_{15} (δ_{XMC})	[109][e]	[101][e]	[94][e]

[a] All g vibrations are Raman-active only while u vibrations are infrared-active only. [b] ν refers to stretching, δ to "in-plane" bending, π to "out-of-plane" bending. [c] From combination band. [d] Not observed. Calculated assuming same δ_{XMC} force constant for Br and I compounds as for Cl compound. [e] Not observed. Calculated assuming $F_{XMC}^{B2u} = F_{XMC}^{B3u}$.

fundamental vibrations; $3A_{1g}$, $2B_{1g}$, $1B_{3g}$, $3B_{1u}$, $3B_{2u}$, and $3B_{3u}$. Table III gives a rough characterization of the various vibrations and assignments for some of the fundamental frequencies as discussed below. All the g frequencies are Raman-active only while the u frequencies are infrared-active only. The $3A_{1g}$ vibrations should be polarized in the Raman spectrum, and indeed we find three polarized Raman shifts (see Table II). The *cis* form would have C_{2v} symmetry with six A_1 vibrations, all of which could be polarized in the Raman. This offers further evidence favoring the *trans* form.

Frequency Assignments

We shall first discuss the frequency assignments for $Au(CN)_2Cl_2^-$. The value for ν_{10} is 2180.5 cm.$^{-1}$ in aqueous solution and about 2182 cm.$^{-1}$ in the solid. Also ν_1 and ν_3 are observed in the Raman spectrum of the solid at the same frequency as in solution (2199 and 342 cm.$^{-1}$, respectively). Thus we can feel confident in using aqueous solution frequencies where available and solid state frequencies otherwise.

A_{1g} Vibrations.—From the polarization data of Table II it is obvious that $\nu_1 = 2199$ cm.$^{-1}$ and ν_2 and ν_3 are at 461 and 342 cm.$^{-1}$. By analogy with $KAu(CN)_4$[3] the 461 cm.$^{-1}$ peak must arise from Au–C stretching, leaving the 342 cm.$^{-1}$ peak for Au–Cl stretching.

B_{1g}.—The Raman shift at 126 cm.$^{-1}$ must arise from ν_5 as it is too low for either ν_4 or ν_6. The peak at 297 cm.$^{-1}$ is quite low for an in-plane MCN bending vibration so we do not assign it to ν_4 but to the out-of-plane Raman active bending, ν_6, similar to the analogous vibration in $KAu(CN)_4$.[3] There is an infrared active combination band at 2548 cm.$^{-1}$ which is perhaps best explained as $\nu_4 + \nu_{10}$, placing ν_4 at 368 cm.$^{-1}$. This must be considered uncertain.

B_{3g}.—As discussed above ν_6 appears at 297 cm.$^{-1}$.

B_{1u}.—These are infrared active out-of-plane bending vibrations. We have no real evidence as to their value. Most likely ν_7 is around 300 cm.$^{-1}$ and ν_8 and ν_9 below 100 cm.$^{-1}$.

B_{2u} and B_{3u}.—ν_{10} is readily assigned as 2181 cm.$^{-1}$ from an average of aqueous and solid state spectra. The strong band at 362 cm.$^{-1}$ is shifted considerably downward for the bromide and iodide so it is readily assigned as ν_{13}, the Au–Cl stretching vibration of B_{3u} symmetry. This leaves 455 and 424 cm.$^{-1}$ for the ν_{11} and ν_{14} vibrations; 455 cm.$^{-1}$ is assigned as ν_{11}, otherwise, the AuC, AuC interaction force constant as calculated below is too large.

The frequency 126 cm.$^{-1}$ is assigned as the B_{2u} XMC

TABLE IV

F AND *G* MATRICES OF $M(CN)_2X_2$ OF D_{2h} SYMMETRY[a]

Representation	*F* Matrix	*G* Matrix
A_g	$F_{11} = F_r + F_r'$	$G_{11} = \mu_C + \mu_N$
	$F_{22} = F_R + F_{RR}'$	$G_{22} = \mu_C$
	$F_{33} = F_D + F_{DD}'$	$G_{33} = \mu_X$
	$F_{12} = F_{rR}' + F_{rR}''$	$G_{12} = -\mu_C$
	$F_{13} = 2F_{rD}'$	$G_{13} = 0$
	$F_{23} = 2F_{RD}'$	$G_{23} = 0$
B_{1g}	$F_{44} = F_\beta + F_{\beta\beta}'$	$G_{44} = \mu_N\rho_1^2 + \mu_C(\rho_1 + \rho_2)^2$
	$F_{55} = F_\alpha + F_{\alpha\alpha}'' - F_{\alpha\alpha}' - F_{\alpha\alpha}'''$	$G_{55} = 2\mu_C\rho_2^2 + 2\mu_X\rho_3^2$
	$F_{45} = F_{\alpha\beta}' + F_{\alpha\beta}''$	$G_{45} = -\sqrt{2}\mu_C\rho_2(\rho_1 + \rho_2)$
B_{3g}	$F_{66} = F_\pi + F_{\pi\pi}'$	$G_{66} = G_{44}$
B_{1u}	$F_{77} = F_\pi - F_{\pi\pi}'$	$G_{77} = G_{44} + 2\mu_M\rho_2^2$
	$F_{88} = F_\delta$	$G_{88} = (2\mu_C + 4\mu_M)\rho_2^2$
	$F_{99} = F_\epsilon$	$G_{99} = (2\mu_X + 4\mu_M)\rho_3^2$
	$F_{78} = \sqrt{2}F_{\delta\pi}'$	$G_{78} = -\sqrt{2}\mu_C\rho_2(\rho_1 + \rho_2) - 2\sqrt{2}\mu_M\rho_2^2$
	$F_{79} = \sqrt{2}F_{\epsilon\pi}'$	$G_{79} = -2\sqrt{2}\mu_M\rho_2\rho_3$
	$F_{89} = F_{\delta\epsilon}'$	$G_{89} = 4\mu_M\rho_2\rho_3$
B_{2u}	$F_{10,10} = F_r - F_{rr}'$	$G_{10,10} = \mu_C + \mu_N$
	$F_{11,11} = F_R - F_{RR}'$	$G_{11,11} = \mu_C + 2\mu_M$
	$F_{12,12} = F_\alpha - F_{\alpha\alpha}'' + F_{\alpha\alpha}' - F_{\alpha\alpha}'''$	$G_{12,12} = G_{99}$
	$F_{10,11} = F_{rR}' - F_{rR}''$	$G_{10,11} = -\mu_C$
	$F_{10,12} = \sqrt{2}(F_{r\alpha}' - F_{r\alpha}'')$	$G_{10,12} = 0$
	$F_{11,12} = \sqrt{2}(F_{R\alpha}' - F_{R\alpha}'')$	$G_{11,12} = -2\sqrt{2}\mu_M\rho_3$
B_{3u}	$F_{13,13} = F_D - F_{DD}'$	$G_{13,13} = \mu_X + 2\mu_M$
	$F_{14,14} = F_\beta - F_{\beta\beta}'$	$G_{14,14} = G_{77}$
	$F_{15,15} = F_\alpha - F_{\alpha\alpha}'' - F_{\alpha\alpha}' + F_{\alpha\alpha}'''$	$G_{15,15} = G_{88}$
	$F_{13,14} = 2F_{D\beta}'$	$G_{13,14} = -2\mu_M\rho_2$
	$F_{13,15} = 2\sqrt{2}F_{D\alpha}'$	$G_{13,15} = -2\sqrt{2}\mu_M\rho_2$
	$F_{14,15} = \sqrt{2}(F_{\alpha\beta}' - F_{\alpha\beta}'')$	$G_{14,15} = G_{78}$

[a] μ_i = reciprocal of mass of atom i. $\rho_1 = 1/R_{CN}$; $\rho_2 = 1/R_{MC}$; $\rho_3 = 1/R_{MX}$.

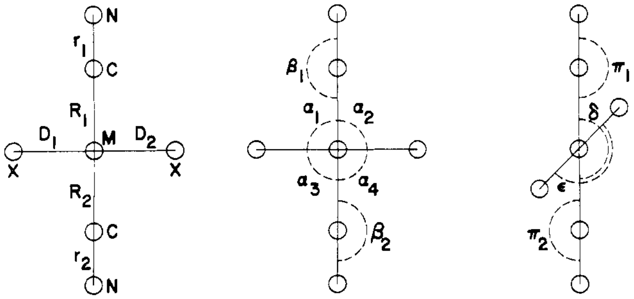

Fig. 4.—Internal coordinates of $M(CN)_2X_2$ of D_{2h} symmetry.

bending vibration, ν_{12}. This should be higher than ν_{15} and since 126 cm.$^{-1}$ is quite high for such a bending frequency we shall assign it as ν_{12}. ν_{15} is not observed but is calculated to be about 109 cm.$^{-1}$ from the normal coordinate treatment which follows, by assuming $F_{XMC}^{B_{2u}} = F_{XMC}^{B_{3u}}$.

For $KAu(CN)_2Br_2$ and $KAu(CN)_2I_2$ the Raman spectrum was not observed as the salts are too highly colored. The symmetric stretching vibration, ν_1, was observed at 2186 cm.$^{-1}$ for $KAu(CN)_2I_2$ because of breakdown of the D_{2h} selection rules by the crystal lattice interactions. This was discussed above. For $KAu(CN)_2Br_2$ the ν_1 frequency is estimated to be at about 2191 cm.$^{-1}$ from the value of ν_{10} and $\nu_1 + \nu_{10}$ and application of an anharmonic correction of $X_{1,10} = -24$ cm.$^{-1}$, which is an average of that for $Au(CN)_2Cl_2^-$ (-26 cm.$^{-1}$) and that for $Au(CN)_2I_2^-$ (-22 cm.$^{-1}$).

The other Raman active frequencies assigned for the bromide and iodide in Table III are estimated from combination bands and cannot be considered conclusive.

Calculation of Force Constants

***F* and *G* Matrices.**—The *F* and *G* matrices were derived by the method of Wilson, Decius, and Cross.[7a] They are given in Table IV.

The various internal coordinates are given in Fig. 4. The interaction force constants as given in Table IV are then as defined in Table V.

In order to proceed with the calculations we must have the bond lengths. For the AuC bond we shall

TABLE V

DEFINITION OF INTERACTION CONSTANTS FOR $M(CN)_2X_2$

F_{rR}'	R_1 with r_1
F_{rR}''	R_1 with r_2
$F_{\beta\beta}'$	β_1 with β_2
$F_{\alpha\alpha}'$	α_1 with α_2
$F_{\alpha\alpha}''$	α_1 with α_4
$F_{\alpha\alpha}'''$	α_1 with α_3
$F_{\alpha\beta}'$	α_1 with β_1
$F_{\alpha\beta}''$	α_1 with β_2
$F_{\pi\pi}'$	π_1 with π_2
$F_{\delta\pi}'$	δ with π_1
$F_{\epsilon\pi}'$	ϵ with π_1
$F_{r\alpha}'$	r_1 with α_1
$F_{r\alpha}''$	r_2 with α_1
$F_{R\alpha}'$	R_1 with α_1
$F_{R\alpha}''$	R_2 with α_1
$F_{D\beta}'$	D_1 with β_1
$F_{D\alpha}'$	D_1 with α_1

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(7) (a) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955; (b) A. Rosenzweig and D. T. Cromer, *Acta Cryst.*, **12**, 709 (1959).

TABLE VI

SYMMETRY FORCE CONSTANTS OF $Au(CN)_2X_2^-$

		$Au(CN)_2Cl_2^-$	$Au(CN)_2Br_2^-$	$Au(CN)_2I_2^-$	
A_{1g}	F_{11}	17.356	(17.230)[a]	(17.151)[a]	mdynes Å.$^{-1}$
	F_{22}	3.452			mdynes Å.$^{-1}$
	F_{33}	2.442			mdynes Å.$^{-1}$
B_{1g}	F_{44}	0.292			mdynes Å. radian^{-2}
	F_{55}	0.583			mdynes Å. radian^{-2}
B_{3g}	F_{66}	0.252			mdynes Å. radian^{-2}
B_{2u}	$F_{10,10}$	17.312	17.216	17.095	mdynes Å.$^{-1}$
	$F_{11,11}$	2.611	2.602	2.518	mdynes Å.$^{-1}$
	$F_{12,12}$	0.652	0.652[b]	0.652[b]	mdynes Å. radian^{-2}
B_{3u}	$F_{13,13}$	1.983	1.636	1.185	mdynes Å.$^{-1}$
	$F_{14,14}$	0.375	0.378	0.376	mdynes Å. radian^{-2}
	$F_{15,15}$	0.650[b]	0.650[b]	0.650[b]	mdynes Å. radian^{-2}

[a] Approximate values estimated from ratio of ν_1 frequencies to that of $Au(CN)_2Cl_2^-$. [b] These values were assumed to be about the same as $F_{12,12}$ of the dichloride.

use 2.1 Å. as in $KAu(CN)_2$.[7b] The CN bond length is chosen as 1.15 Å. by analogy with other CN complexes. The AuCl bond length is assumed to be 2.24 Å., that found[8] for the terminal AuCl bonds in Au_2Cl_6. The AuBr and AuI distances were then estimated by adding on the differences in single bond radii (0.99, 1.14, and 1.33 for Cl, Br, and I, respectively).[9]

Symmetry Force Constants.—From the observed frequencies of Table III for $Au(CN)_2Cl_2^-$ all but the B_{1u} symmetry force constants have been calculated. For the B_{3u} block ν_{15} was not observed, so for the calculation we have assumed $F_\alpha^{B_{2u}} = F_\alpha^{B_{3u}}$ which is equivalent to assuming $F_{\alpha\alpha}' = F_{\alpha\alpha}'''$. All off-diagonal force constants have been neglected. It has been shown previously[3,10,11] that neglect of MC, CN interactions is a good approximation for most cyanide complexes. The other off-diagonal interaction constants have only a small effect on the stretching force constants. Their effect on the bending constants will be considered below.

The symmetry force constants thus calculated are given in Table VI.

Valence Force Constants.—From the symmetry force constants of Table VI and the F matrix of Table IV the valence force constants are calculated. They are given in Table VII along with corresponding values of $Au(CN)_4^-$ for comparison. For F_{CN} an average of F_{11} and $F_{10,10}$ is given. For F_{AuC}, F_{AuX}, and the corresponding interaction constants of the dibromide and diiodide the calculations were made assuming $F_{AuC',AuC}$ is proportional to F_{AuC} and $F_{AuX',AuX}$ is proportional to F_{AuX}; thus, $F_{AuC',AuC}(Br) = F_{AuC',AuC}(Cl) \cdot F_{AuC}(Br)/F_{AuC}(Cl)$.

Discussion of Force Constants and Bonding

F_{CN} and F_{MC}.—In view of its high AuC and CN force constants it was concluded[3] that $Au(CN)_4^-$ has strong Au–C σ-bonds and negligible Au–CN π-bonding. This conclusion follows from a recent discussion[2] in which it was shown that for cyanide complexes strong metal–carbon σ-bonding leads to a relatively high CN force constant, while metal–cyanide π-bonding depresses the CN force constant. We now ask what effects can be expected upon replacement of two CN groups by halide ions, *trans* to each other? From the data of Table VII it is evident that the effect is not large. For clarity we shall first discuss the series of dihalides.

In all of the $Au(CN)_2X_2^-$ ions the AuC and CN constants are relatively high, indicating, as with $Au(CN)_4^-$, that the AuC bonds are primarily quite strong σ-bonds with very little π-bonding. However, the AuC force constant and CN force constant both decrease monotonically with heavier halogen substitution; that is, $(F_{AuC})_{Cl} > (F_{AuC})_{Br} > (F_{AuC})_I$ and $(F_{CN})_{Cl} > (F_{CN})_{Br} > (F_{CN})_I$. The differences are small but significant and indicate that the AuC σ-bond strength decreases in the order $(\sigma_{AuC})_{Cl} > (\sigma_{AuC})_{Br} > (\sigma_{AuC})_I$. This indicates that the heavier halogens donate their σ-bonding electrons more to the gold atom because of their smaller electronegativity. A further discussion of the metal–halogen bonding is presented in the following section on AuX force constants.

With such an increase in electron density around the gold atom we might expect greater tendency for it to π-bond to the cyanide ligands. Indeed there is a considerable increase in the intensity of the CN stretching vibration[4] in the order Cl < Br < I which suggests[2] an increase in Au–CN π-bonding in the same order. It is surprising that there is not observed a greater effect of this π-bonding on the AuC and CN force constant, in particular an increase in F_{AuC}. Apparently the increase in π-bonding is sufficient to increase the intensity of ν_{CN} but insufficient to affect the force constants appreciably in the presence of the strong gold–carbon σ-bond.[12]

Now we should consider what is the effect of replacing two cyanides of $Au(CN)_4^-$ by chlorides. We would

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(8) E. S. Clark, D. H. Templeton, and C. H. MacGillavry, *Acta Cryst.*, **11**, 284 (1958).

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 224.

(10) L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

(11) L. H. Jones, *ibid.*, **41**, 856 (1964).

(12) Another force constant solution is arrived at if we exchange assignments of ν_{11} and ν_{14}. However, this would have the effect of decreasing F_{AuC} considerably and increasing $F_{AuC',AuC}$. Since F_{CN} for $Au(CN)_2Cl_2^-$ is slightly lower than F_{CN} for $Au(CN)_4^-$ we expect F_{AuC} to be slightly lower if π-bonding is not important, or higher if π-bonding is important. Therefore, it is not reasonable to choose the solution which makes F_{AuC} even lower. Furthermore, the value for $F_{AuC',AuC}$ becomes even larger, which is not reasonable for σ-bond–σ-bond interaction.

TABLE VII

VALENCE FORCE CONSTANTS OF $Au(CN)_2X_2^-$

	$Au(CN)_4^-$	$Au(CN)_2Cl_2^-$	$Au(CN)_2Br_2^-$	$Au(CN)_2I_2^-$
F_{CN}	17.44	17.33	17.22	17.12
F_{AuC}	2.995	3.032	3.022	2.925
F_{AuX}	...	2.213	1.826	1.323
$F_{AuC', AuC}$	0.354	0.421	0.420	0.407
$F_{AuX', AuX}$	...	0.230	0.190	0.138
F_{β}	~0.4	0.334		
$F_{\beta\beta'}$		−0.042		
F_{α}	~0.5	~0.6		
F_{π}	~0.25	~0.25		

[a] Units for stretching constants are mdynes $Å.^{-1}$. Units for bending constants are mdynes $Å.$ radian^{-2}.

expect the chlorides to be held less tightly than the cyanides, leading to a greater positive charge on the gold and stronger AuC σ-bonding. As a matter of fact the AuC bond for $Au(CN)_2Cl_2^-$ is slightly stronger than for $Au(CN)_4^-$, though the difference is small. Actually we can say that the bonding has not changed greatly and the effect noticed may arise from change in overlap accompanying change in hybridization of the metal–carbon orbital from dsp^2 to sp or dp. It is of interest that the AuC, AuC interaction constant for the dihalides is about the same[3] as the sum of the AuC, AuC interaction constants of $Au(CN)_4^-$, also indicating little change in MCN bonding.

F_{AuX}.—There is little to compare with the metal–halide force constants. The AuCl and AuBr force constants are considerably higher than the ZnCl and ZnBr force constants[13] in $ZnCl_4^{2-}$ and $ZnBr_4^{2-}$.

The fact that iodide has a greater effect on the N–C–Au–C–N bond system than bromide indicates that the AuI σ-electron pair is somewhat more associated with the gold than is the AuBr σ-electron pair. Thus the evidence indicates greater association with the metal for the metal–halide σ-bond electron pair in the order $I > Br > Cl$. This is in the order predicted[14] for stability of Au(III)–halide complexes. Also this order is shown by the fact that a heavier halide readily replaces a lighter halide in the complex.[4]

This leaves us in an apparent dilemma as the AuX force constants decrease in the order $Cl > Br > I$. Thus the Au–I bond is the weakest, yet its σ-electrons are more tightly associated with the Au atom. Since the iodide ion is largest, it cannot reside as close to the metal in forming a strong σ-bond. This leads to a lower force constant. Nevertheless the iodide is a better electron donor than bromide or chloride (it is less electronegative) and, therefore, forms a more covalent bond with the gold. The same situation exists for the gaseous hydrogen halides, the force constants being 5.16, 4.12, and 3.14 mdynes/Å., respectively, for HCl, HBr, and HI, while the HI bond is the most covalent and HCl the most ionic.[15]

It is of interest to note that the chloride is pale yellow, the bromide is deep yellow, and the iodide is black, paralleling somewhat the colors of the free halogens but not of the colorless halide ions. This in itself points to strong covalent bond formation, making the electronic energy levels similar to those in the free halogens.

Bending Force Constants.—The bending force constants are less well determined than the stretching constants; however, it is apparent that the in-plane MCN bending constant is lower than that in $Au(CN)_4^-$.[3] This indicates that it is easier for a CN group to bend against a halide ion than against another CN group. Even in $Au(CN)_4^-$ the MCN bending constant is significantly lower than it is in the hexacyanides of Co, Rh, and Ir.[11] This indicates that the metal–cyanide π-bonding in the latter gives increased rigidity to the MCN bond system.

The in-plane CMCl bending force constant is somewhat higher than the CMC bending constant of $Au(CN)_4^-$, probably because of the larger radius of the Cl ion. More striking is the fact that the CMC bending constant of the tetracyanide is very much larger than that of the hexacyanides determined[11] so far. Thus the strong metal–ligand σ-bonds of trivalent gold have strong directional character.

Summary

From the infrared spectra of the complex ions $Au(CN)_2Cl_2^-$, $Au(CN)_2Br_2^-$, and $Au(CN)_2I_2^-$ and the Raman spectrum of $Au(CN)_2Cl_2^-$ many of the fundamental vibrational frequencies have been assigned. Force constants have been calculated. It is found that both the CN and AuC stretching force constants show a slight, regular decrease in the order dichloride > dibromide > diiodide. This is explained as arising from a slight decrease in gold–carbon σ-bond strength in the same order. Intensity data suggest that there is an increase in Au–CN π-bonding in the same order. Iodide forms the weakest bond with Au(III), yet it has the greatest effect in lowering the strength of the Au–C bond, probably because it donates its electrons more fully to the gold atom in covalent bond formation.

The changes in Au–C–N bonding in going from $Au(CN)_4^-$ to the dihalides is small and may arise primarily from changes in symmetry of the metal–carbon orbitals causing changes in orbital overlap.

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(13) Calculated from data of A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964), as 1.0 and 0.8 mdynes/Å. for $ZnCl_4^{2-}$ and $ZnBr_4^{2-}$, respectively.

(14) S. Ahrland and R. Larsson, *Acta Chem. Scand.*, **8**, 354 (1954); S. Ahrland, *ibid.*, **10**, 723 (1956).

(15) Reference 9, p. 81.