written, so that each forward process is favored by an increase of entropy but resisted by an increase of enthalpy. Every K value represents an average of at least two experiments. The datum for 42.23° in Table XI represents an average of log K and $1/T$ at 38.8 and 46.7°.

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Assignment of MC Stretching and MCN Bending Frequencies in Metal Cyanide Complexes[1]

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Infrared spectra of the MC stretching and MCN bending vibrations of $Au(CN)_2Cl_2^-$ and $Au(CN)_2Br_2^-$ and of the ^{13}C and ^{15}N enriched species have been observed in the solid state. By comparing the results with the frequencies calculated for the isotopic species it is shown that the MCN bending frequency is at 456 cm.$^{-1}$ for the chloride and 455 cm.$^{-1}$ for the bromide, while the MC stretching frequency is at 430 and 431 cm.$^{-1}$, respectively. Because this reverses a previous assignment, new sets of force constants are calculated. By analogy the frequencies of $Au(CN)_2I_2^-$ and $Au(CN)_4^-$ are reassigned also, and new force constants are calculated.

Introduction

There are essentially four types of vibrations in metal–cyanide complexes which lie in three spectral regions. The CN stretching frequencies occur in the region 2000–2250 cm.$^{-1}$. The CMC bending frequencies are around 100 cm.$^{-1}$. The MC stretching and MCN bending frequencies are in the 300–600 cm.$^{-1}$ region and are not always in the same order. Thus, it is not always possible to make conclusive assignments of the MC stretching and MCN bending frequencies. For example, the transition metal hexacyanides show two strongly infrared-active frequencies in the region 300–600 cm.$^{-1}$; one in the region 300–420 cm.$^{-1}$ and the other in the region 450–600 cm.$^{-1}$. Nakagawa and Shimanonchi[2] have assigned the higher frequency as MC stretching and the lower as MCN bending. Jones[3] has preferred the opposite assignment.

Another example of ambiguity lies in the assignments of the MC stretching and MCN bending frequencies of the dicyanodihalo complexes of trivalent gold, $Au(CN)_2X_2^-$. For example, solid $KAu(CN)_2Cl_2$ shows strong infrared absorption bands at 456 and 430 cm.$^{-1}$.[4] The *trans*-$Au(CN)_2Cl_2^-$ ion has D_{2h} symmetry and one of these frequencies arises from the B_{2u} MC stretching vibration while the other arises from the B_{3u} MCN bending vibration. The choice between the two possibilities is not conclusive without further data. It was previously postulated[4] that the higher frequency arises from MC stretching because the resulting force constant solution appeared more reasonable. However, careful studies of the frequencies of the material enriched in ^{13}C and in ^{15}N show that the assignment was in error and should be reversed. This paper describes the work which leads to this conclusion.

Results

Calculated Isotopic Shifts for Frequencies of $Au(CN)_2Cl_2^-$.—From a cursory examination of the G matrices[4] one might expect that a change of carbon mass would have a much greater effect on the MC stretching frequency than a change in nitrogen mass. However, this is not the case. The isotopic shifts can be predicted accurately from a computer calculation. The force constants were calculated from the frequencies of the normal species. The G matrix was then changed appropriately for isotopic substitution and the expected frequencies were then calculated from the previously determined force constants (which are assumed invariant to isotopic substitution). Inasmuch as the available ^{13}C and ^{15}N had a considerable amount of the normal isotopic species present, we also calculated frequencies for the mixed ^{12}C–^{13}C and ^{14}N–^{15}N species. This, of course, required a reduction of symmetry from $D_{\infty h}$ to $C_{\infty v}$ and a calculation based on the C_{2v} irreducible representations. The MC stretching vibration falls under the A_1 representation of C_{2v} while the MCN bending vibration falls under B_2 of C_{2v}.

The results of the calculations are given in Table I. The two vibrational frequencies in question are called ν_{11} and ν_{10} in keeping with the nomenclature of ref. 4, even though for the monosubstituted species a different numbering system would be appropriate. From Table I it is apparent that the shifts are quite different for ν_{11} and ν_{14}, and, in fact, it should not be difficult to distinguish ν_{11} from ν_{14} by the pattern of frequencies of the isotopic species.

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **16**, 424 (1960).

[3] L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

[4] L. H. Jones, *ibid.*, **3**, 1581 (1964). In this reference the figures given were 455 and 424 cm.$^{-1}$. More accurate measurements give 430 and 456 cm.$^{-1}$. Also in this reference there are some minor errors. F_{45} should equal $\sqrt{2}(F\alpha\beta' + F\alpha\beta'')$, and $G_{13,14}$ should equal $+2\mu_{m}\rho_2$. The calculated values for unobserved ν_{15} should be about 13% lower.

TABLE I

CALCULATED FREQUENCIES AND ISOTOPIC SHIFTS (CM.$^{-1}$) FOR ν_{11} (ν_{MC}) AND ν_{14} (δ_{MCN}) FOR ^{13}C AND ^{15}N SUBSTITUTED SPECIES OF $KAu(CN)_2Cl_2$

	A[a]		B[a]		A[a]		B[a]	
	ν_{11}[b]	ν_{14}	ν_{11}	ν_{14}	$-\Delta\nu_{11}$	$-\Delta\nu_{14}$	$-\Delta\nu_{11}$	$-\Delta\nu_{14}$
Normal[c]	456	430	430	456				
$(CN)(^{13}CN)$[d]	451.3	424.3	427.0	449.6	4.7	5.7	3.0	6.4
$(CN)(C^{15}N)$	450.0	429.0	426.4	454.7	6.0	1.0	3.6	1.3
$(^{13}CN)_2$	450.0	417.5	424.5	442.2	6.0	12.5	5.5	13.8
$(C^{15}N)_2$	448.7	427.9	423.5	453.5	7.3	2.1	6.5	2.5

[a] A refers to the assignment with $\nu_{11} = 456$ and $\nu_{14} = 430$ cm.$^{-1}$. B refers to the reverse assignment. [b] All frequencies and frequency shifts are in cm.$^{-1}$. [c] These are observed values slightly different from those reported in ref. 4. [d] $(CN)(^{13}CN)$ represents $KAu(^{12}C^{14}N)(^{13}C^{14}N)Cl_2$, etc.

TABLE II

OBSERVED ABSORPTION SPECTRA (CM.$^{-1}$) OF $KAu(CN)_2Cl_2$ ENRICHED IN ^{13}C OR ^{15}N IN THE REGION 400–500 CM.$^{-1}$

	Normal				^{13}C enriched				^{15}N enriched			
	~300°K.		100°K.		~300°K.		100°K.		~300°K.		100°K.	
$Au(CN)_2Cl_2^-$	455.8	(0.09)[a]	457.5	(0.19)	455.5	(0.03)	457.5	(0.07)	455	(0.24)	457	(0.47)
					449.7	(0.075)	450.5	(0.19)			451.5	(0.08)
					440.7	(0.06)	442.7	(0.15)				
	430	(0.14)	434	(0.34)	425.5	(0.32)	428	(0.5)	423	(0.35)	430.5	(0.32)
			429	(0.13)			424	(sh)			425	(0.5)
											422	(0.5)
$Au(CN)_2Br_2^-$	455	(0.06)	457.3	(0.1)	455	(0.01)	458	(0.06)	453	(0.11)	456	(0.25)
					447	(0.07)	450.5	(0.13)			443	(0.02)
					439	(0.08)	442.0	(0.14)				
	430.5	(0.05)	432	(0.08)	425	(0.1)	427.5	(0.14)	424	(0.05)	428	(0.14)
											424.5	(0.16)
											419.5	(0.1)

[a] The number in parentheses is the optical density of the peak at its maximum. Frequencies are in cm.$^{-1}$.

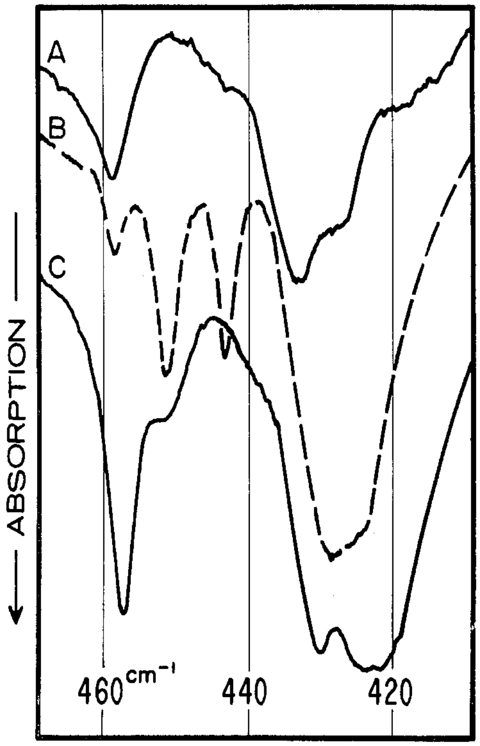

Figure 1.—Absorption by MC stretching and MCN bending vibrations of $Au(CN)_2Cl_2^-$ at 100°K.: A, normal $Au(CN)_2Cl_2^-$; B, $Au(CN)_2Cl_2^-$ enriched in ^{13}C; C, $Au(CN)_2Cl_2^-$ enriched in ^{15}N.

The figures of Table I were calculated with neglect of off-diagonal interaction constants. The calculations were repeated several times with a value of 0.2 mdyne/Å. for the various interaction constants, one by one, and the calculated frequencies differed negligibly from those of Table I.

Experimental Procedure and Observations.—The isotopic species containing about 60 atom % ^{13}C in one case and 70 atom % ^{15}N in the other were available from a previous study.[5] Portions of these samples were dissolved in water and added to a methanol solution of chlorine. Upon evaporation to dryness at room temperature, crystals of $KAu(CN)_2Cl_2 \cdot xH_2O$ were obtained. The infrared absorption of mineral oil mulls was studied in the region 350–500 cm.$^{-1}$. Because the peaks were somewhat broad, the spectrum was observed at about 100°K. also. At the lower temperature the peaks were considerably sharper though somewhat shifted. A similar study was made on $KAu(CN)_2Br_2$ prepared in an analogous fashion. The results are given in Table II. In Figure 1 are shown the spectra of the normal and enriched species of the chloride at 100°K. Assignment of observed peaks is discussed in detail below.

(A) Assignment of Peak at 456 Cm.$^{-1}$.—First, consider the peak observed at 455.8 cm.$^{-1}$ in the normal species. This sharpens and shifts to 457.5 cm.$^{-1}$ at low temperature. The ^{13}C enriched mixture exhibits this peak for the normal species as well as stronger peaks at 449.7 and 440.7 cm.$^{-1}$. The latter two are obviously from $Au(CN)(^{13}CN)Cl_2^-$ and $Au(^{13}CN)_2Cl_2^-$,

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(5) L. H. Jones, *J. Chem. Phys.*, in press.

respectively, and arise primarily from the same internal coordinate type as the 456 cm.$^{-1}$ peak of the normal species. In the ^{15}N enriched mixture we observe only one peak in this region at room temperature, at 455 cm.$^{-1}$. At 100°K. this shifts to 457 cm.$^{-1}$ and a small peak appears at 451.5 cm.$^{-1}$. The latter peak arises from the $^{12}C^{14}N$ stretch of the mixed species, $Au(CN)(C^{15}N)Cl_2^-$. Calculations place it there regardless of the assignments of the peaks at 430 and 456 cm.$^{-1}$ in the normal species. The isotopic shifts of the 456 cm.$^{-1}$ peak are recorded in Table III.

(B) **Assignment of Peak at 430 Cm.$^{-1}$.**—Let us now consider the 430 cm.$^{-1}$ peak. At 100°K. this splits into two peaks at 429 and 434 cm.$^{-1}$. The two peaks no doubt arise from the same vibration of the isolated ion but correspond to two different modes of coupling in the crystal lattice In the ^{13}C enriched species, the room temperature peak drops to 425.5 cm $^{-1}$ and the two peaks at 100°K. decrease to 424 and 428 cm.$^{-1}$. The ^{15}N enriched material shows the 430 cm.$^{-1}$ peak shifted to 423 cm.$^{-1}$ at room temperature. At 100°K. the 430 cm.$^{-1}$ peak splits into three components at 430.5, 424.5, and 422 cm.$^{-1}$. The isotopic shifts are indicated in Table III.

TABLE III

ISOTOPIC SHIFTS (CM.$^{-1}$) OF THE INFRARED-ACTIVE FREQUENCIES OF $Au(CN)_2Cl_2^-$ IN THE 400–500 CM.$^{-1}$ REGION

	Room temp.		100°K.	
	$-\Delta\nu(456)$	$-\Delta\nu(430)$	$-\Delta\nu(458)$	$-\Delta\nu(434, 429)$
$(CN)(^{13}CN)$	6.1	4.5	7.0	6, 5
$(^{13}CN)_2$	14.8		14.8	
$(CN)(C^{15}N)$	0.8	7.0	0.5	3.5, 4
$(C^{15}N)_2$				9, 7.0

As we look at Table III we notice that there is a striking difference in the isotopic shifts of the 456 and 430 cm.$^{-1}$ peaks. The 456 cm.$^{-1}$ peak shifts very considerably for ^{13}C substitution (particularly the disubstituted species), while for ^{15}N substitution the shift is almost negligible. This is exactly as predicted for ν_{14} in Table I On the other hand the 430 cm.$^{-1}$ peak shifts slightly more for ^{15}N substitution than for ^{13}C substitution as predicted for ν_{11} in Table I. The 430 cm.$^{-1}$ peak is quite broad and apparently composed of a doublet resolved only at low temperature. Thus it is not possible to separate the peaks of the mono- and disubstituted species since the shifts are not greatly different. Comparison of these results with Table I shows conclusively that the 456 cm.$^{-1}$ peak of $Au(CN)_2Cl_2^-$ arises from ν_{14}, the B_{3u} MCN bending vibration, while the 430 cm.$^{-1}$ peak is from ν_{11}, the B_{2u} MC stretching vibration. The results on $KAu(CN)_2Br_2$ in Table II indicate an exactly analogous assignment.

Force Constants of $Au(CN)_2X_2^-$.—The conclusions arrived at in the previous section necessitate a change in the assignment preferred in ref. 4. These changes are in the B_{2u} and B_{3u} representations and are given in Table IV. When these new frequency assignments are combined with the A_{1g}, B_{1g}, and B_{3g} frequencies of ref. 4, the valence force constants are calculated[6] to be as given in Table V.

TABLE IV

B_{2u} AND B_{3u} FUNDAMENTALS (CM.$^{-1}$) OF $Au(CN)_2X_2^-$

Representation	Type	$Au(CN)_2Cl_2^-$	$Au(CN)_2Br_2^-$	$Au(CN)_2I_2^-$
B_{2u}	ν_{10} (ν_{CN})	2181	2175	2166
	ν_{11} (ν_{MC})	430	431	430
	ν_{12} (δ_{XMC})	126	[89][a]	[73][a]
B_{3u}	ν_{13} (ν_{MX})	364	258	203
	ν_{14} (δ_{MCN})	456	455	448
	ν_{15} (δ_{XMC})	[97][b]	[89][b]	[81][b]

[a] Not observed. Calculated assuming the same δ_{XMC} force constant for all three complexes. [b] Not observed. Calculated assuming $F_{XMC}^{B_{2u}} = F_{XMC}^{B_{3u}}$.

Comparison of Table V with Table VII of ref. 4 shows that the change in assignment leads to a significant decrease in calculated AuC force constant (from 3.03 to 2.89 mdynes/Å. for the chloride) and increase in AuC, AuC′ interaction constant (from 0.42 to 0.57 mdyne/Å. for the chloride). In fact this interaction constant is larger than in $Au(CN)_2^-$.[3] For $Au(CN)_2X_2^-$ the σ bonding is stronger and π bonding weaker than for $Au(CN)_2^-$. Thus the amount of π bonding is not of sole importance in determining the magnitude of the MC, MC′ interaction constant in metal–cyanide complexes and apparently plays a minor role in this case.[7]

It is to be noted also that the MCN bending force constant and MCN, MC′N′ interaction constant are larger for the corrected frequency assignment.

TABLE V

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

	$Au(CN)_2Cl_2^-$	$Au(CN)_2Br_2^-$	$Au(CN)_2I_2^-$
F_{CN}	17.381	17.275	17.18
F_{AuC}	2.885	2.853	2.8
F_{AuX}	2.223	1.847	1.4
$F_{CN,C'N'}$	−0.025	−0.027	(−0.025)[b]
$F_{AuC,AuC'}$	0.567	0.521	(0.5)[b]
$F_{AuX,AuX'}$	0.219	0.209	(0.2)[b]
F_β (MCN)	0.389	0.38	0.37
$F_{\beta\beta}$	−0.097	(−0.1)[b]	(−0.1)[b]
F_α (CMX)	∼0.6		
F_π (MCN)	∼0.25		

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

Application to $Au(CN)_4^-$.—Force constants were recently calculated for $Au(CN)_4^-$.[8] In this case also there was ambiguity in the assignments of the infrared-active MC stretching and MCN bending frequencies, both of E_u symmetry (under the D_{4h} point group). By analogy with $Au(CN)_2Cl_2^-$ this assignment should probably be reversed. Thus the correct assignment should be ν_9 (MC) = 415 and ν_{10} (MCN) = 462 cm.$^{-1}$. This change in assignment alters the force constant solution and the new values are given in Table VI.

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(6) The symmetrical AuBr stretching frequency was observed in the Raman spectrum at 209 cm.$^{-1}$ on the Cary Model 81 by replacing the filter solution with isopropyl alcohol and using the 5461 Å. Hg line for excitation. This observation, with the data of ref. 3, makes possible the calculation of the A_{1g} force constants which, with the B_{2u} and B_{3u} force constants calculated from Table IV, yield the valence force constants of Table V for the bromide.

(7) The interaction can be explained with a simple electrostatic picture. When one Au–C bond is stretched, the σ-bonding electron pair moves with the carbon atom, leaving the Au atom more positive. The Au atom then pulls tighter on the other carbon atom. The magnitude is no doubt a function of the bond strength. This explanation is, of course, not unique.

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

TABLE VI

VALENCE FORCE CONSTANTS (MDYNES/Å.) OF $Au(CN)_4^-$

F_{CN}	17.51
F_{AuC}	2.782
$F_{CN,C'N'}$ (ad.)[a]	0.026
$F_{CN,C''N''}$ (op.)[a]	−0.060
$F_{AuC,AuC'}$ (ad.)[a]	0.035
$F_{AuC,AuC''}$ (op.)[a]	0.567

[a] The abbreviation ad. stands for adjacent (at 90°) while op. is for opposite (at 180°).

The changes are very similar to the changes for $Au(CN)_2X_2^-$; thus, the comparisons among the different Au(III) complexes in ref. 4 are still valid.

The E_u symmetry force constant for MCN bending is 0.51 mdyne Å. radian^{-2} for the new frequency assignment. With the data of ref. 8 this gives a value of 0.43 mdyne/Å. or more for the MCN valence bending constant. Thus it is still a valid point that the MCN in-plane bending constant is greater for $Au(CN)_4^-$ than for $Au(CN)_2X_2^-$ as discussed in ref. 4.

It would be possible to verify this new assignment for $Au(CN)_4^-$ by observation of the spectra of the isotopically enriched species. However, this would require higher enrichment than we have presently available. If we prepared $KAu(CN)_4$ with 60 atom % ^{13}C we would have a variety of species leading to a rather complex spectrum. Thus if all forms have equal energy, we would expect 13% $Au(^{13}CN)_4^-$, 35% $Au(^{13}CN)_3(CN)^-$, 17% *cis*-$Au(^{13}CN)_2(CN)_2^-$, 17% *trans*-$Au(^{13}CN)_2(CN)_2^-$, 15% $Au(^{13}CN)(CN)_3^-$, and 3% $Au(CN)_4^-$. It would be exceedingly difficult to assign the observed peaks to the various species. Greater than 90 atom % ^{13}C would be highly desirable for such a study.

Off-diagonal Interaction Constants.—Off-diagonal interaction constants such as $F_{MC,CN}$ have been neglected. In a recent study[5] it was shown that for $Au(CN)_2^-$ $F_{MC,CN}$ is about +0.3 mdyne/Å. while $F_{MC,C'N'}$ is about zero. However, it has not yet been shown whether these interaction constants are transferable from one metal–cyanide complex to another. Further studies of isotopic species are necessary to decide this. If the MC, CN interaction constant is positive, as found for $Au(CN)_2^-$, the calculations give a higher CN force constant and a lower AuC force constant.

Summary

By a study of the ^{13}C and ^{15}N enriched species of $Au(CN)_2Cl_2^-$ and $Au(CN)_2Br_2^-$ it has been shown that the assignment of infrared-active MC stretching and MCN bending frequencies can be made unambiguously. The observations presented here show that the previous assignment[4] must be changed. New sets of force constants are given for $Au(CN)_2Cl_2^-$, $Au(CN)_2Br_2^-$, $Au(CN)_2I_2^-$, and $Au(CN)_4^-$. Other ambiguous assignments, such as the MC stretching and MCN bending frequencies of the metal hexacyanides, can be nailed down by similar studies of the isotopically enriched species. However, for species having four or more cyanides per molecule, the enrichment should be above 90 atom % to yield an interpretable spectrum.

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The Charge-Transfer Complex between Triphenylarsine and Iodine

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The 1:1 complex between triphenylarsine and iodine in carbon tetrachloride and dichloromethane solutions has been studied by spectroscopic methods in the ultraviolet, visible, and infrared regions. Formation constants, the thermodynamic functions $-\Delta F°_{298}$, $-\Delta H°$, and $-\Delta S°$, and spectral data have been obtained. Much higher formation constants were observed in the solvent dichloromethane than in carbon tetrachloride. In acetonitrile only I_3^- ions were formed, indicating a complete ionization of the complex. The ultraviolet band at 248 mμ in triphenylarsine, which has been assigned to a transition involving the lone-pair electrons, is not perturbed on complex formation to iodine.

Introduction

The compounds formed between the halogens and alkyl or aryl derivatives of group Va elements have been discussed on the basis of X-ray crystallographic determinations and from dipole and conductometric measurements in solution. X-Ray analysis of the molecules $(CH_3)_3SbX_2$ (X = Cl and Br) showed a bipyramidal configuration with X–Sb–X-type bonding.[1] The zero dipole moments of certain dichlorides support this structure.[2] However, conductometric measurements indicate the existence of ionic species in polar solvents, and the following ionic structures have been proposed: $R_3Y^+X^-$ and $R_3Y^+X_3^-$ (Y = P, As, Sb, and Bi; X = Br and I).[3–5]

The donor properties of the alkyl or aryl derivatives

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(1) A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

(2) K. A. Jensen, *Z. anorg. Chem.*, **250**, 257 (1943).

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(4) G. S. Harris, *Proc. Chem. Soc.*, 65 (1961).

(5) B. J. Pullman and B. O. West, *J. Inorg. Nucl. Chem.*, **19**, 262 (1961).