are bonded to one metal ion and the carboxylate group is bonded to a second metal ion.[44] In the complex [Cu(GlyGlyGly)Cl]$\cdot$1.5H_2O, where the peptide nitrogens of triglycine are protonated, the amino nitrogen and the carbonyl oxygen of the β-peptide linkage are bonded to one copper ion while the terminal carboxyl group is coordinated to a second copper ion, so that the structure consists of –Cu–peptide–Cu–peptide– chains.[47]

The α-methylene protons of diglycine, however, undergo a downfield shift upon coordination of the amino group which could be due either to binding to the adjacent peptide linkage or to increased coordination at the carboxylate end. Thus no information about the structures of the amino-coordinated complexes can be obtained from the chemical shift data.

Complexation Effects on the Reactivity of the Peptide Linkages of Triglycine.—The reactivity of the peptide linkages of triglycine is affected by coordination to cadmium, zinc, and lead as evidenced by the increased peptide proton exchange rates (Tables V and VI).

Pagenkopf and Margerum[34] observed that coordination of the carbonyl group of the α-peptide linkage of Cu($H_{-1}L$), where $H_{-1}L$ is triglycine with the β-peptide nitrogen deprotonated and copper coordinated, labilizes the α-peptide proton. The peptide proton of acetylglycine is also labilized upon coordination to cadmium, zinc, and lead.[17b] In the case of the cadmium complex, the proton exchange rate is 53 times faster than that of free acetylglycine. In the present work, it was not possible to resolve rate constants for specific complexes from the data in Tables V and VI due to uncertainties in the species present. The data indicate, however, that both the α- and β-peptide protons are labilized by coordination to these metal ions, with the apparent degree of labilization being greater for the α-peptide protons over the pH ranges where the kinetics are accessible by nmr. This is likely due to the fact that over these pH ranges coordination to the C-terminal carboxylate group is at a maximum while there is much less coordination at the amino end. Considering only the changes in charge, coordination of a dipositive metal ion to the ionized C-terminal carboxylate group is also predicted to enhance the rate of exchange of the adjacent α-peptide proton more than replacement of the amino proton by a dipositive metal ion is predicted to enhance the rate of exchange of the β-peptide proton.

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Coordination Compounds of Indium. XVII. Force Constant Calculations for Anionic Indium(I) and -(III) Halide Complexes

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Received June 2, 1972

A simplified GQVFF model has been used to calculate force constants for the anionic indium(III) halide complexes InX_4^- (X = Cl, Br, or I), $InCl_5^{2-}$, and $InCl_6^{3-}$ and for the recently prepared indium(I) species InX_3^{2-} (X = Cl, Br, or I). The primary stretching force constants for the indium(III) chloro anions decrease linearly with increasing coordination number. The results for the indium(I) complexes are compared with those in the literature for isoelectronic tin(II) and antimony(III) species.

Introduction

One of the interesting features of the coordination chemistry of indium is that three-, four-, five-, and six-coordinate complexes can be prepared, in some cases with the same ligand. In particular, recent preparative work has shown that for anionic halide complexes, coordination numbers four, five, or six can be obtained with chloride, four or six with bromide, and four with iodide. Slight changes in experimental conditions may bring about changes in the coordination number; for example, both the four- and five-coordinate chloride species are stabilized by the tetraethylammonium cation, depending on the solvent from which the complex is recrystallized.[1,2]

A discussion of these phenomena is hampered both by the lack of a reliable model of the bonding involved and by the absence of appropriate energetic data, in particular of bond strengths. As part of a general investigation of these problems, we have now carried out force constant calculations for all those anionic indium(III) halide complexes for which complete vibrational spectra are available. We also report the results of similar calculations for the halide complexes of indium(I) recently prepared by us,[3] and the values obtained are compared with those for some isoelectronic species. In general, the results reveal some interesting empirical relationships among the force constants and the oxidation state of the metal, the nature of the ligand, and the coordination number. These relationships are discussed in terms of the indium–halide bonding interactions.

The calculations were based on a simplified general quadratic valence force field model (GQVFF), which has generally been accepted as a good approximation for expressing the potential energy of small molecules.

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Force field models do not lead to a unique expression of the potential energy, but this approximation does allow meaningful comparisons to be made with previous results and isostructural molecules. Raman and infrared vibrational spectra from the literature have been used in normal-coordinate analyses for the indium(III) species InX_4^- (X = Cl, Br, and I), $InCl_5^{2-}$, and $InCl_6^{3-}$ and for the indium(I) anions InX_3^{2-} (X = Cl, Br, or I). In all cases Wilson's F and G matrix method was used, and the force constants were fitted to the observed frequencies by an iterative procedure. Computations were performed on the IBM 360/60 computer of the Simon Fraser Computing Centre, whose assistance is acknowledged with thanks.

Results

Tetrahaloindate(III) Anions, InX_4^-.—A number of salts containing the tetrahaloindate(III) anions (X = Cl, Br, and I) have been prepared.[1,2] The infrared and Raman results on the crystalline solids are in good agreement with the Raman spectra reported by Woodward and his coworkers[4-6] for extract solutions of these species. The solution spectra of the anions were assigned on the assumption of T_d symmetry, with four molecular vibrations ($A_1 + E + 2F_2$); some splitting of the F modes in the solid state was observed. The tetrahedral symmetry has been confirmed by X-ray crystallographic studies for the $InCl_4^-$ anion,[7] and more recently, for InI_4^-, both in simple salts[8] and in the ionic dimer $[InI_2(DMSO)_4][InI_4]$ (DMSO = dimethyl sulfoxide).[9] The spectral data used in our calculations (see Table I) are those reported by Woodward, *et al.*, for the solution species. Table I also gives the relevant In–X bond lengths in the solid state; since no experimental values are available for In(III)–Br, the mean of the lengths of the In(III)–Cl and In(III)–I bonds was used.

TABLE I

VIBRATIONAL SPECTRA, STRUCTURAL PARAMETERS, AND FORCE CONSTANTS FOR TETRAHEDRAL InX_4^- ANIONS

A. Vibrational Spectra (cm^{-1}) and Bond Length (10^{-8} cm)

Species	Condition	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	In–X bond length
$InCl_4^-$	Ether extract	321	89	337	112	2.33
$InBr_4^-$	Isobutyl methyl ketone	197	55	239	79	2.47
InI_4^-	Aqueous solution	139	42	185	58	2.70

B. Force Constants (10^{-5} dyn/cm)

						Calcd frequencies			
Species	f_r	f_{rr}	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$	ν_1	ν_2	ν_3	ν_4
$InCl_4^-$	1.865	0.095	0.086	0.086	0.015	321	89	336	112
$InBr_4^-$	1.598	0.067	0.076	0.076	0.013	196	56	239	79
InI_4^-	1.199	0.079	0.058	0.058	0.007	139	42	183	58

The potential function for these tetrahedral species is

$$2V = 4f_r(\Delta r_i)^2 + 6r^2f_\alpha(\Delta\alpha)^2 + 12f_{rr}(\Delta r_i)(\Delta r_j) + 24rf_{r\alpha}(\Delta r)(\Delta\alpha) + 12r^2f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j)$$

Following the usual practice, the force constants associated with the stretching–bending interactions and bending–bending interactions were assumed to be zero when no common bond is involved. The term $f_{r\alpha}$ refers to the interaction involving one bond and the angle, and all the other terms have their usual meaning. The G-matrix elements were constructed from the structural parameters given in Table I.

Examination of the potential function reveals that the number of force constants to be calculated is greater than the number of vibrational frequencies available. Following Donalson, *et al.*,[10] we used the approximation $f_{r\alpha} = f_\alpha$, an assumption which was also found to be necessary in calculations on $InCl_6^{3-}$ and InX_3^{2-} (see below). Table IB shows the derived force constants for the InX_4^- species and the calculated frequencies, which are in good agreement with the experimental results in Table IA.

Woodward, *et al.*,[4-6] used an approximate method to obtain values of 2.16, 1.83, and 1.44 × 10^{-5} for the primary stretching force constants for $InCl_4^-$, $InBr_4^-$, and InI_4^-, respectively. These values differ considerably from those calculated in the present work, mainly because the authors assumed that all other force constants could be neglected. More recently, Muller and Krebs have also calculated force constants for these species, using a modified valence force field, and assuming that $F_{34} = 0$, which leads to the unrealistic conclusion that $f_{r\alpha}$ is zero.[11] Their values for the primary stretching force constants are about 0.1–0.2 unit lower than those given in Table IB, but the agreement between the two calculations for the bending force constants is reasonably good, with differences of less than 0.05 unit. In related work based on a general valence force field approach, Krebs, Muller, and Fadini[12] obtained the primary stretching force constants and the stretching–stretching interaction force constants for the InX_4^- species, but did not calculate any bending force constants. These calculations gave values close to, but still different from, those in Table IB. It is worth pointing out that Krebs, *et al.*, only obtained the difference $f_\alpha - f_{\alpha\alpha}$ for the bending interactions, with values of 0.7, 0.6, and 0.5 × 10^{-5} for the chloride, bromide, and iodide respectively, surprisingly similar to those which can be derived from our calculations.

The calculated eigenvectors and potential energy distribution for the F_2 vibrations show that the eigenvectors S_3 and S_4 in ν_3 undergo slightly increased coupling along the series $InCl_4^-$, $InBr_4^-$, and InI_4^-; ν_3 contains less than 0.5% of S_4 in $InCl_4^-$, 4% in $InBr_4^-$, and 7% in InI_4^-. The opposite situation is found for ν_4, where S_3 is present to about 4% in the chloride and 2% in the bromide, with the vibration 100% pure in InI_4^-.

The Pentachloroindate(III) Anion, $InCl_5^{2-}$.—Raman,[13] polarized single-crystal Raman,[14,15] and polarized far-infrared[15] spectra of the $InCl_5^{2-}$ anion have been reported. The spectra reported by Adams and Smardzewski[15] were used in our calculations, and Table II shows their assignments, the derived force constants,

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TABLE II

FORCE CONSTANTS (10^{-5} DYN CM^{-1}) AND OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) FOR $InCl_5{}^{2-}$

Obsd[a] freq	Assignment[a]	Force constant	Calcd freq
294	$\nu_1(A_1)$	$f_R = 1.378$	239
283	$\nu_2(A_1)$	$f_r = 1.305$	283
140	$\nu_3(A_1)$	$f_{rr'} = -0.039$	140
287	$\nu_4(B_1)$	$f_{rr} = 0.335$	286
183	$\nu_5(B_1)$	$f_\alpha = 0.016$	183
165	$\nu_6(B_2)$	$f_{\alpha\alpha} = -0.010$	164
274	$\nu_7(E)$	$f_\beta = 0.033$	274
143	$\nu_8(E)$	$f_{\beta\beta} = 0.009$	143
108	$\nu_9(E)$		108

[a] From ref 15.

and the observed and calculated frequencies for $InCl_5{}^{2-}$.

The single-crystal X-ray structure[16] of $((C_2H_5)_4N)_2[InCl_5]$ shows that the anion has C_{4v} symmetry in this salt. The unique apical In–Cl bond is slightly shorter (2.415 ± 0.012 Å) than the four basal bonds (2.456 ± 0.007 Å), and an average bond length of 2.45 Å was used in the present calculations. The error involved in this assumption is negligible. The Cl–In–Cl bond angle in the basal plane is 86.70°, and the Cl_{base}–In–Cl_{axial} angle 103.87°. No $InBr_5{}^{2-}$ species have been isolated in the crystalline state, so that the comparisons possible for $InX_4{}^-$ anions could not be repeated in this symmetry.

In the calculation of the force constants the potential function for the C_{4v} $InCl_5{}^{2-}$ was

$$2V = f_r(\Delta r_5) + 4f_r(\Delta r)^2 + 4_r{}^2f_\alpha(\Delta\alpha)^2 + 4r^2f_\beta(\Delta\beta)^2 + 8f_{rr}(\Delta r_i)(\Delta r_j) + 8f_{rr'}(\Delta r_i)(\Delta r_j) + 8r^2f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 8r^2f_{\beta\beta}(\Delta\beta_i)(\Delta\beta_j)$$

where f_{rr} refers to the interaction force constant of a bond in the plane and the axial bond, f_β is the primary bending force constant of the axial ligand, and $f_{\beta\beta}$ refers to the bending interaction for the same ligand. The symmetry coordinates listed by Begun and Fletcher[17] were used. The various internal coordinates are defined as follows: r_i (i = 1, 2, 3, 4) = In–Cl_{basal}, r_5 = In–Cl_{axial}, α_{ij} is the angle between bonds in the basal plane, and β_{ij} the angle between the axial bond r_5 and any of the bonds in the basal plane. The G-matrix elements were calculated from the formulas of Wilson, *et al.*,[18] using the structural parameters quoted above.

Examination of Table II shows that f_R, the primary stretching force constant for the axial ligand, is slightly greater than the corresponding force constant for the basal chlorides, which is readily explained by the fact that $InCl_5{}^{2-}$ is a very slightly distorted C_{4v} species in which the indium atom is a little above the basal plane of the four chlorides.

TABLE III

FORCE CONSTANTS (10^{-5} DYN CM^{-1}) AND OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) FOR $InCl_6{}^{3-}$

Obsd freq	Assignment	Force constant	Calcd freq
275, R	$\nu_1(A_{1g})$	$f_r = 0.949$	275
175, R	$\nu_2(E_g)$	$f_{rr} = 0.154$	176
245, ir	$\nu_3(F_{1u})$	$f_{rr'} = 0.010$	245
150, ir	$\nu_4(F_{1u})$	$f_{r\alpha} = 0.089$	151
130, R	ν_5 (F_{2g})	$f_\alpha = 0.089$	130
		$f_{\alpha\alpha} = 0.028$	

The Hexachloroindate(III) Anion, $InCl_6{}^{3-}$.—The vibrational spectrum of the $InCl_6{}^{3-}$ anion has been recorded for salts with both organic[2] and inorganic cations.[19] There is reasonable agreement between these two sets of results, leading to the assignments shown in Table III. No crystal structure determinations have been reported, but the number of bands in the vibrational spectrum confirms the expected O_h symmetry. For the In–Cl bond in this anion we have taken a bond length of 2.61 Å, based on the data[20] for $[InCl_5\cdot H_2O]^{2-}$ and on the discussion of In–Cl bond lengths given previously.[16]

The potential function has the form

$$2V = 6f_r(\Delta r)^2 + 12r^2f_\alpha(\Delta\alpha)^2 + 24f_{rr}(\Delta r_i)(\Delta r_j) + 6f_{rr'}(\Delta r_i)(\Delta r_j) + 24rf_{r\alpha}(\Delta r)(\Delta\alpha) + 24r^2f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j)$$

where $f_{rr'}$ refers to the interaction force constant of two mutually perpendicular bonds, and the other terms have the usual meaning. Table III shows the derived force constants, the calculated and observed frequencies, and the vibrational assignments. Taking into account the change in the mass of the central atom and the oxidation state, the f_r value for $InCl_6{}^{3-}$ is in reasonable agreement with that reported by Wharf and Shriver[21] for $SnCl_6{}^{2-}$ (1.435×10^{-5}).

The eigenvectors and potential energy distribution calculations for the F_{1u} vibrations show that ν_3 is quite pure, whereas ν_4 contains about 10% of the S_3 eigenvector.

No salts of the corresponding $InI_6{}^{3-}$ anion have been reported, but the $InBr_6{}^{3-}$ complex has been identified in the crystalline lattice of $(CH_3NH_3)_4InBr_7$ and $((CH_3)_2NH_2)_4InBr_7$ ($4R_4N^+ + InBr_6{}^{3-} + Br^-$). The ν_1 and ν_3 absorptions of this presumably O_h anion are at 170 and 179 cm^{-1}, respectively;[2] unfortunately these results do not constitute a sufficient basis for calculation of the force constants for this anion.

Trihaloindate(I) Anions, $InX_3{}^{2-}$.—The vibrational spectra of the $InX_3{}^{2-}$ species (X = Cl, Br, or I) have been shown to be consistent with C_{3v} molecular symmetry.[3,13] The two higher frequency bands were assigned, by comparison with other known C_{3v} species, as the symmetric and asymmetric stretching modes, and the two lower frequencies as the symmetric and asymmetric bending modes respectively.

The potential function for the $InX_3{}^{2-}$ species has the form

$$2V = 3f_r(\Delta r)^2 + 3r^2f_\alpha(\Delta\alpha)^2 + 6f_{rr}(\Delta r_i)(\Delta r_j) + 12rf_{r\alpha}(\Delta r)(\Delta\alpha) + 6r^2f_{\alpha\alpha}(\Delta a_i)(\Delta\alpha_j)$$

It is clear that the number of force constants to be calculated is greater than the number of frequencies available, and the approximation $f_{r\alpha} = f_\alpha$ used for $InX_4{}^-$ and $InCl_6{}^{3-}$ was again applied for the $InX_3{}^{2-}$ anions. Values of bond lengths and bond angles are not available, so that in constructing the G-matrix elements we used the bond angles found for the isoelectronic SbX_3 species[22] and bond lengths from ref 20. Table IV

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(16) D. W. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, **8**, 14 (1969).

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TABLE IV

FORCE CONSTANTS (10^{-5} DYN CM^{-1}) AND OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) FOR InX_3^{2-} ANIONS

Species	r, Å	α, deg	f_r	f_{rr}	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$	ν_1	ν_2	ν_3	ν_4	
$InCl_3^{2-}$	2.42	99	0.760	0.205	0.101	0.101	0.006	251	103	185	98	Calcd
								252	102	185	97	Obsd
$InBr_3^{2-}$	2.54	97	0.750	0.160	0.050	0.050	0.012	177	73	145	45	Calcd
								177	74	149	46	Obsd
InI_3^{2-}	2.86	99	0.625	0.170	0.071	0.071	0.026	137	80	108	40	Calcd
								136	78	110	40	Obsd

shows the derived force constants, the observed and calculated frequencies, and the structural parameters used in constructing the G matrices.

The calculated eigenvectors and potential energy distribution for the InX_3^{2-} species indicate that the vibrations are fairly pure, although there is some change in the $\nu_1(A_1)$ vibration from $InCl_3^{2-}$ (100% S_1) to InI_3^{2-} (90% S_1 + 10% S_2). The opposite situation is found for the $\nu_2(A_1)$ vibration, which in $InCl_3^{2-}$ contains about 23% of S_1, whereas in InI_3^{2-}, ν_2 is almost 100% S_2. The E vibrational modes are less coupled, so that in $InCl_3^{2-}$ ν_3 contains no S_4 eigenvector; in InI_3^{2-}, ν_3 contains only 3% of S_4. For $InCl_3^{2-}$, ν_4 contains about 17% of S_3, compared with 5% of S_3 in $InBr_3^{2-}$ and 12% in InI_3^{2-}.

Discussion

The results of the force constant calculations reveal a number of interesting relationships between these constants for the various indium complexes, and in some cases between the values for complexes of indium and related elements.

As noted in the Introduction, direct evidence on the type of bonding in anionic indium halide complexes is lacking, but two nuclear quadrupole resonance (nqr) studies strongly imply that the bonding is in fact ionic in character. The nqr spectra (^{115}In and ^{31}Cl) of $[InCl_5 \cdot H_2O]^{2-}$ have been interpreted in terms of ionic In–Cl bonds,[23] and similar studies[24] of SnX_6^{2-} anions (X = Cl, Br, I) lead to the conclusion that the percentage ionic character varies from 60% in $SnCl_6^{2-}$ to 55% in SnI_6^{2-}, with a linear dependence on the difference in the electronegativities ($X_{hal} - X_{Sn}$). Finally, and of more immediate relevance, Wharf and Shriver[21] showed that calculations based on ionic models gave the correct ratio of stretching force constants for $SnCl_4$ and $SnCl_6^{2-}$. It therefore seems a reasonable working hypothesis that the bonding in the isoelectronic indium(III)-halide complexes is significantly ionic.

We first consider the primary stretching force constants (f_r) for the tetrahaloindate(III) anions (Table I), for which f_r decreases smoothly from $InCl_4^-$ to InI_4^-. It seems likely that these changes in f_r arise from concomitant (but not necessarily proportional) changes in bond strength and, in the light of the above discussion, changes in f_r might be related to changes in the electronegativity difference ΔX ($= X_{halogen} - X_{In}$). In fact, if one takes the Pauling electronegativities used in establishing the relationship between percentage ionic character and ΔX in the nqr studies,[24] f_r is linearly dependent on ΔX (=1.38, 1.18, and 0.88 for Cl, Br, and I, respectively). In order to put such a relationship in its proper context, it must be pointed out that with either the Sanderson or Allred–Rochow values for ΔX, a plot of f_r against ΔX is markedly curved (and presumably this also applies to the nqr results). The general conclusion, however, seems valid, namely, that with such ionic-bonded species the stretching force constant, and hence presumably the bond strength, depends on the electronegativity of the ligand.

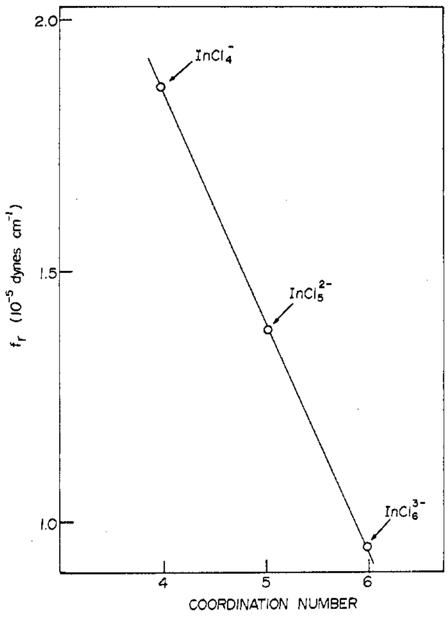

Figure 1.—The dependence of the primary stretching force constant (f_r) on the coordination number in some halide complexes of indium(III).

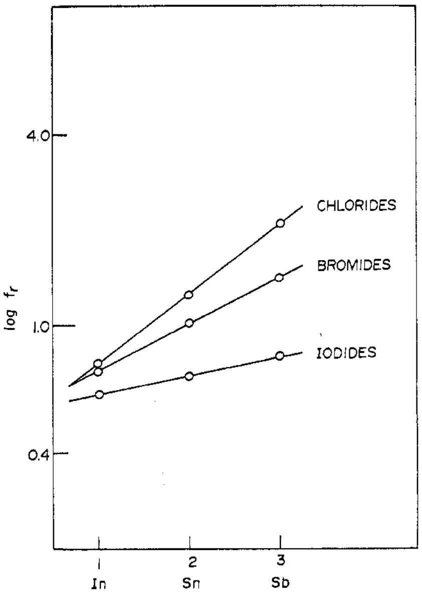

Figure 2.—The dependence of log f_r on the oxidation state of the metal for MX_3 halides of some main group metals.

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[23] S. L. Carr, B. B. Garrett, and W. G. Moulton, *J. Chem. Phys.*, **47**, 1170 (1967).

[24] See M. Kubo and D. Nakamura, *Advan. Inorg. Chem. Radiochem.*, **8**, 257 (1966).

Recent work[25] has shown that a similar relationship exists for the stretching modes of MCl_4 and MBr_4 molecules (M = C, Si, Ge, or Sn). For these species, ν_1 and ν_3 are found to be dependent upon the ionic character of the M–X bond, but here again the nature of the relationship depends on the set of electronegativity values which are used. There seems to be little profit in discussing the detailed nature of such dependences at this point.

Wharf and Shriver[21] noted an interesting effect of oxidation state in their work, which covered both tin(II) and -(IV) halide complexes. They defined a parameter Ω = oxidation state/coordination number and showed that Ω is proportional to f_r in tin–chloride complexes, in which the ratio of the stretching force constants for SnX_3^- to SnX_4 varies from 0.48 to 0.59, with an average value of 0.54 which is in good agreement with the ratio $\Omega(SnX_3^-)/\Omega(SnX_4) = 0.67$. We have tested this suggestion for our compounds and find that the ratio of the stretching force constants for pairs of InX_3^{2-} and InX_4^- anions varies from 0.41 to 0.52, with an average value of 0.46, which is somewhat closer to the ratio $\Omega(InX_3^{2-})/\Omega(InX_4^-) = 0.44$ than is the case for the analogous ratios for the tin compounds. Unfortunately the dependence of f_r on Ω does not hold within the group of indium(III) halide complexes, in which the coordination number varies from four to six. The relevant values are

	Ω	$10^5 f_r$, dyn cm^{-1}
$InCl_4^-$	0.75	1.865
$InCl_5^{2-}$	0.60	1.378, 1.305
$InCl_6^{3-}$	0.50	0.949

Despite this absence of a proportionality between Ω and f_r for these three species, a relatively simple relationship does exist, as is shown by the plot of f_r against coordination number (Figure 1). Again it is difficult to place any detailed interpretation on these relationships, except that an ionic model would require a gradual weakening of bonds with increasing coordination number.

Figure 2 shows another relationship between the log of the primary stretching force constants for the isoelectronic species InX_3^{2-}, SnX_3^-, and SbX_3[26,27] and the oxidation state of the central element. There is some uncertainty in the point for $SbBr_3$, arising from the range of values reported[25] for f_r (1.338–1.686×10^{-5} dyn cm^{-1}). Relationships between stretching frequencies and oxidation state are well-known (see, for example, Adams[28]), but Figure 2 implies the existence of a more precise dependence than is usually acknowledged.

In summary, then, the primary stretching frequencies of the indium(I) and -(III) anionic halide complexes depend on ligand electronegativity, coordination state, and oxidation state in a manner which is qualitatively in keeping with a model of significantly ionic In–X bonding, the details of which remain to be elucidated.

Acknowledgment.—This work was supported by Operating Grants from the National Research Council of Canada. One of us (J. G. C.) is grateful for leave of absence from the University of Concepción, Chile.

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Reactions of Halocarbonyls of Group VIb Elements. I. Complexes of Tervalent Molybdenum with Nitrogen, Oxygen, and Sulfur Donors

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Received March 27, 1972

Preparation of complexes of the type MoX_3L_3 [X = Cl, Br; L = pyridine, nitrile, tetrahydrofuran, tetrahydrothiophene] from the reaction of $Mo(CO)_4X_2$ with the pure liquid donor is described. The results indicate that donor ligands which do not have a special ability to stabilize low oxidation states cause a disproportionation of Mo(II) into Mo(0) and Mo(III). Magnetic properties and infrared and electronic spectral data of the complexes are discussed.

When $Mo(CO)_4Cl_2$ and $Mo(CO)_4Br_2$ are treated with substances containing N, P, As, and Sb as donor atoms, products of the type $Mo(CO)_3L_2X_2$ may be formed.[1–3] Excess pyridine, 2,2′-bipyridine, and 1,10-phenanthroline give complexes of the type $Mo(CO)_2L_2X_2$.[4] These reactions were carried out by dissolving the reactants in a suitable solvent. We were interested to learn whether the use of neat liquid donors would lead to more highly substituted products. Such was found to be the case with trimethyl phosphite which gave $Mo(CO)_2[(CH_3O)_3P]_3X_2$ During the course of this work, Bonati and Mighetti showed that molybdenum halocarbonyls react with excess isocyanides to give complexes with the formulation MoL_5X_2.[5] We have found that reaction of the halocarbonyls with pure $AsEt_3$ in excess gave a photosensitive product of the approximate composition $Mo(CO)_3(AsEt_3)Cl_2$. This is surprising because $AsPh_3$ gives $Mo(CO)_3(AsPh_3)_2Cl_2$.[2]

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