suggestive was the ^{11}B nmr spectrum of the carbon disulfide extract, which showed peaks no broader than normal for polyboranes. With δ measured in ppm upfield from trimethyl borate, the record showed a doublet at 4.8 (J = 139 cps), a doublet at 18.6 (J = 128 cps), a singlet at 41.3 (strongest peak, broad enough to suggest an unresolved multiplet), and a doublet at 61.7 (J = 167 cps). Efforts toward elucidation of the molecular identity of this component seem justified.

A similar action upon B_5H_9 by H_2S was attempted, but no reaction occurred. With CH_3SH or CH_3SSCH_3 in simple reaction tubes at 80–100°, B_5H_9 produced only resinous material and the known trimer $(CH_3SBH_2)_3$, recognized by its ^{11}B nmr spectrum.[8] This spectrum showed no trace of $B(SCH_3)_3$, which would have appeared as a relatively broad singlet at 42.6 ppm downfield of $B(OCH_3)_3$.[9]

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(8) E. L. Muetterties, N. E. Miller, K. J. Packer, and H. C. Miller, *Inorg. Chem.*, **3**, 870 (1964).

(9) As recorded for a sample kindly furnished to us by Dr. R. J. Brotherton of the U. S. Borax Research Laboratories.

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Polarized Raman Scattering by Tetraethylammonium Pentachloroindate(III) Single Crystals. Vibrational Assignments for the Square-Pyramidal $InCl_5^{2-}$ Ion

BY STEPHEN R. LEONE,[1a] BASIL SWANSON,[1b] AND D. F. SHRIVER[1c]

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There are two principal reasons for an interest in the molecular vibrations of $InCl_5^{2-}$. First, vibrational frequencies of MX_5 species are important because of the bearing they have on the problem of stereochemical nonrigidity, which is a common phenomenon for five-coordinate compounds.[2,3] Second, $InCl_5^{2-}$ is unusual in that it displays a square-pyramidal geometry in its tetraethylammonium salt.[4] With the exception of an analogous $TlCl_5^{2-}$ salt,[5] this geometry is unknown for other simple complexes of d^{10} ions. However, square-pyramidal intermediates or transition states generally are thought to be involved in the process by which apical and equatorial ligand interchange occurs for trigonal-bipyramidal molecules.[2,3]

Unlike the situation for tetrahedral MX_4 and octahedral MX_6 molecules, where assignment of the optically active modes is generally straightforward, the assignments for MX_5 species present significant difficulties. For example there are ambiguities in the description of the vibrations for such a simple molecule as PF_5.[3] Fortunately, single-crystal laser Raman spectroscopy affords a method of making otherwise difficult assignments, providing the compound crystallizes with high site symmetry and favorable orientation. This method is applied to $[(C_2H_5)_4N]_2[InCl_5]$ in the present paper.

Results and Discussion

The $[(C_2H_5)_4N]_2[InCl_5]$ salt crystallizes in a tetragonal space group P4/n (C_{4h}^3) with two formula units per unit cell related by a center of symmetry.[4] The site symmetry of $InCl_5^{2-}$ is C_4. For the hypothetical isolated $InCl_5^{2-}$ of C_{4v} symmetry the total vibrational representation is $\Gamma_v = 3\,A_1 + 2\,B_1 + 1\,B_2 + 3\,E$; of these 2 A_1, 1 B_1, and 1 E represent stretching modes and the remainder are deformations.

As a consequence of the center of symmetry, mutual exclusion of infrared and Raman modes is expected for the crystal, with only the motions which are in phase between the two $InCl_5^-$ ions having Raman activity. The pertinent correlations between isolated square-pyramidal $InCl_5^{2-}$ (C_{4v}) and the unit cell (C_{4h}^3) are $A_1 \rightarrow A_u, A_g$; $B_1 \rightarrow B_u, B_g$; $B_2 \rightarrow B_u, B_g$; $E \rightarrow E_u, E_g$. Thus, B_1 and B_2 modes of the isolated molecule take on identical selection rules in the solid, while the A_1 and E modes of the isolated complex maintain their totally symmetric and doubly degenerate character, respectively, in the crystal. The irreducible representations of the polarizability tensor elements are: for A_g: $\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$; for B_g: $\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$; for E_g: α_{yz}, α_{zx}. From this it is evident that scattering by A_g modes will preserve the orientation of the incident electric vector, while B_g modes will uniquely scatter incident x-polarized radiation in the y direction and E_g will uniquely scatter incident x or y polarized radiation in the z direction. Therefore, three alignments of the crystal and incident electric vector are necessary and sufficient to characterize the internal modes of $InCl_5^{2-}$. The spectra resulting from three such orientations are displayed in Figures 1–3. Complete extinction of peaks is not observed in all cases where it is expected, because the crystals possess some internal and surface imperfections as well as prismatic edges. (Errors introduced by the latter characteristic are probably the

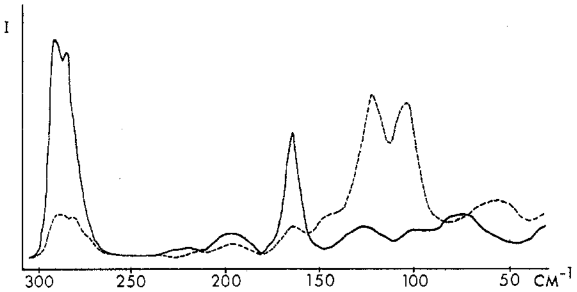

Figure 1.—Raman spectra of single-crystal $[(C_2H_5)_4N]_2$-$[InCl_5]$. Orientations: $z(x,x)y$ (——) and $z(x,z)y$ (-----). Intensities of the 289- and 294-cm^{-1} bands are reduced by one-third. Following the notation of T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.*, **142**, 570 (1966), the first coordinate specifies the direction of the incident laser beam, the second specifies the electric vector of the incident light, the third specifies the electric vector for the scattered light, and the fourth specifies the direction of the scattered light. All axes refer to the coordinates of the crystal.

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(2) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(3) R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).

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(5) D. F. Shriver and I. Wharf, *ibid.*, **8**, 2167 (1969).

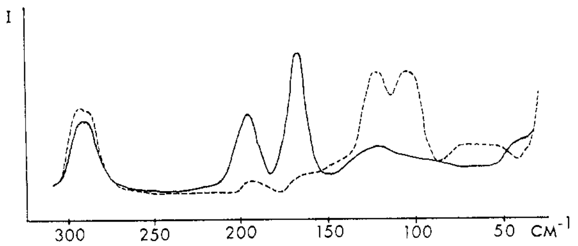

Figure 2.—Raman spectra of single-crystal $[(C_2H_5)_4N]_2[InCl_5]$. Orientations: $z(y,x)y$ (——) and $z(y,z)y$ (-----); this notation is explained in the caption to Figure 1.

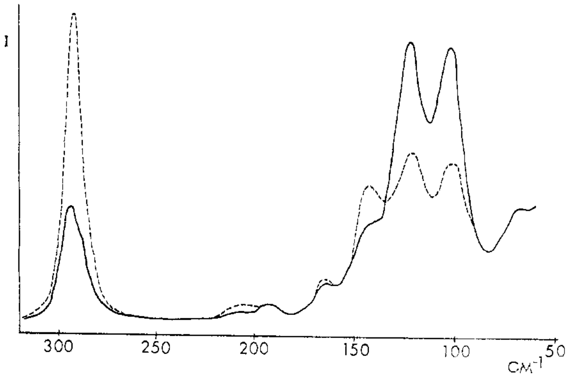

Figure 3.—Raman spectra of single-crystal $[(C_2H_5)_4N]_2[InCl_5]$. Orientations: $x(z,x)y$ (——) and $x(z,z)y$ (-----); this notation is in the caption to Figure 1.

most important since the poorest extinction is observed for the $x(z,x)y$ and $x(z,z)y$ spectra, Figure 3, where the light must enter and exit from wedge-shaped faces.) Nevertheless, the spectra allow clear assignments for all medium and strong lines.

Infrared data obtained from a polycrystalline sample are compared in Table I with the single-crystal Raman data. The E mode observed at 106 cm^{-1} in the Raman spectrum is not observed in the infrared spectrum, and the 124-cm^{-1} E mode is a very weak shoulder in the infrared spectrum. Four other peaks are observed in the infrared spectrum, three of which (142, 285, and 293 cm^{-1}) are assigned to A_u modes because of their agreement with the A_g modes observed in the single-crystal Raman spectra. The remaining peak in the infrared spectrum at 273 cm^{-1} is assigned to an E_u mode. An E_g counterpart is barely evident in some of the Raman spectra (see the $z(x,z)y$ spectrum in Figure 1).

TABLE I

THE NORMAL MODES OF $InCl_5^{2-}$

Freq,[a] cm⁻¹		Expected		
Raman	Ir	activity	Assignment[b]	
294 vs	293 sh	Raman, ir	A	ν_1
289 s	285 s	Raman, ir	A	ν_2
	273 s	Raman, ir	E	ν_7
(211?) vw		Raman	(B?)	ν_4
193 w		Raman	B	ν_5
165 m		Raman	B	ν_6
143 vw	142 s	Raman, ir	A	ν_3
124 m	121 sh, vw	Raman, ir	E	ν_8
106 m		Raman, ir	E	ν_9

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] As shown by the good agreement between infrared and Raman frequencies, factor group coupling is small; however, in a strict sense all infrared modes should be designated *ungerade* and all Raman modes *gerade.*

Eight of the nine fundamental vibrations have been assigned with only one B mode missing. One possible position for this mode is 211 cm^{-1}, where a weak shoulder is observed on the 193-cm^{-1} B_g line. This shoulder is most evident in spectra obtained on polycrystalline samples and it is too weak in single-crystal spectra to verify its assignment by polarization measurements. It is also possible that the third B_g mode is buried under more intense features and is undetected. A less likely possibility is that the mode in question may be attributed to one of the several weak and apparently spurious peaks which were occasionally seen; the most prominent of these was a line around 240 cm^{-1}.

In the foregoing discussion we have assumed that observed frequencies in the 300–100-cm^{-1} region arise from internal modes of $InCl_5^{2-}$. This interpretation is substantiated by previous work where only tin–chlorine fundamentals were observed in the 100–300-cm^{-1} region for tetraalkylammonium salts of $SnCl_6^{2-}$.[6] The agreement of observed infrared and Raman frequencies indicates that interionic correlation coupling is very small for $InCl_5^{2-}$ in this crystal. On the other hand, consistent disparities were observed between infrared and Raman frequencies of $TlCl_5^{2-}$ in $[(C_2H_5)_4N]_2[TlCl_5]$.[5] This indicates that upon going to a slightly larger complex with weaker M–Cl bonds the correlation coupling is increased.

Previously, tentative assignments for $InCl_5^{2-}$ were based on analogy with the BrF_5 spectrum.[5] However, the present work demonstrates several differences between $InCl_5^{2-}$ and BrF_5. In particular, the three highest stretching frrquencies of $InCl_5^{2-}$ are of A, A, and E symmetry, respectively, while in BrF_5 the order is A_1, E, and A_1. The very broad shoulder in the infrared spectrum at 150 cm^{-1} is now thought to be nonexistent (this region is complicated by a grating and speed change on the IR 11). It is certain from the Raman spectrum that the two lowest modes at 124 and 106 cm^{-1} must have E symmetry. The strong infrared band at 142 cm^{-1} is logically assigned A symmetry and the polarized Raman spectrum (Figure 3) confirms this assignment. Thus, the symmetric out-of-plane deformation ν_3 (A symmetry) lies higher in frequency than the axial In–Cl deformation ν_8 or ν_9 (E symmetry)—see S_3 in Figure 4. This is in marked contrast with BrF_5 where the order is reversed.[7] However, there is a very good correspondence between the relative Raman intensities of BrF_5 and those of polycrystalline $[(C_2H_5)_4N]_2[InCl_5]$, providing modes of the same symmetry type are compared.

The high frequency of ν_3 implies a surprising resistance to out-of-plane motion (S_3) relative to apical In–Cl deformation (S_8) and to in-plane deformation

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(6) I. Wharf and D. F. Shriver, *Inorg. Chem.*, **8**, 914 (1969).

(7) R. S. McDowell and L. B. Asprey, *J. Chem. Phys.*, **37**, 165 (1962).

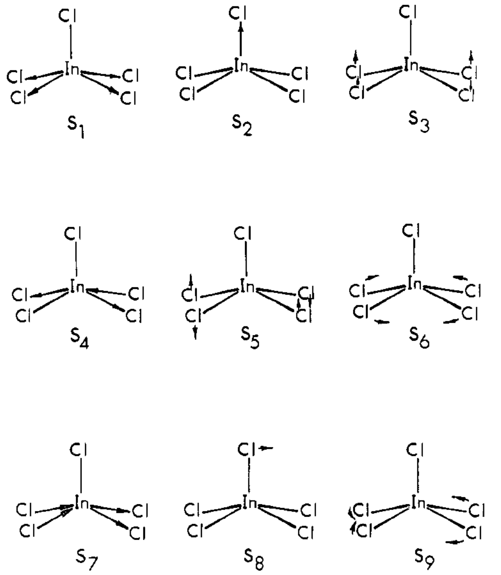

Figure 4.—Approximate symmetry coordinates for $InCl_5^{2-}$ (C_4 symmetry designations). S_1 through S_3 have A symmetry, S_4 through S_6 have B symmetry, and S_7 through S_9 have E symmetry.

(S_9). A similar, but less definite, indication of this effect may be seen from the proposed position of the B modes. Assuming these do fall in the 290–165-cm^{-1} region, either of the two lowest B modes may be attributed to antisymmetric out-of-plane deformation (S_5 of Figure 4), which is the dominant coordinate in the conversion of a square pyramid to a trigonal bipyramid. This places the frequency primarily associated with S_5 fourth or fifth from the lowest for $InCl_5^{2-}$ while it is second from the lowest for BrF_5. The resistance of $InCl_5^{2-}$ to out-of-plane distortion may be due to interionic steric repulsion because we have previously shown that the geometry of $InCl_5^{2-}$ is sensitive to the nature of the cation with which it is associated in the crystal.[5]

Experimental Section

Flat truncated bipyramidal crystals of $[(C_2H_5)_4N]_2[InCl_5]$ approximately 3–4 mm across were grown by slow evaporation of a methylene chloride solution saturated with $[(C_2H_5)_4N]_2[InCl_5]$ and containing an excess of $[(C_2H_5)_4N]Cl$. The C_4 crystallographic axis is perpendicular to the square flat faces as shown by lack of extinction when rotated under a polarizing microscope and by X-ray precession photographs. As usual, the fourfold axis is designated by z. The x and y axes were found to be perpendicular to the edges of the square faces.

Raman spectra were obtained on an instrument which has been described previously.[6] The 5145-Å line of a Coherent Radiation Model 52 Ar ion laser was employed for excitation. The incident beam was attenuated to avoid destruction of the crystal. Alignment of the single crystals was accomplished with the aid of cathetomer. Far-infrared spectra were obtained for Nujol mulls between polyethylene plates using a Beckman IR 11 instrument.

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The Circular Dichroism Spectra of Cobalt(III) Complexes Containing a Stereoselective Quadridentate Ligand

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Recent studies concerned with the relationship between the absolute configurations of metal complexes and the circular dichroism spectra shown by their d–d electronic transitions have largely relied on the use of stereoselective multidentate ligands. The most widely studied of these are the quadridentate systems which appear to provide a direct relationship with the bis-bidentate octahedral complexes and are capable of considerable variation with respect to both the ligand and the occupancy of the two remaining octahedral coordination sites.[2-4] In most of these quadridentate systems, however, work has concentrated on the symmetrical *cis-α* geometry where, at least in principle, there appears to be little ambiguity as to the particular stereoselective preference which the ligand will impart upon complexation. The factors involved in deciding the stereoselective preference are more complicated for the unsymmetrical *cis-β* geometry, and it is the purpose of this note to consider these with respect to the *cis-β* complexes formed by the ligand (shown in Figure 1) (+)-bis-N,N′-2-picolyl-2,3-diaminobutane (bnpic) derived from (+)-2,3-butanediamine.

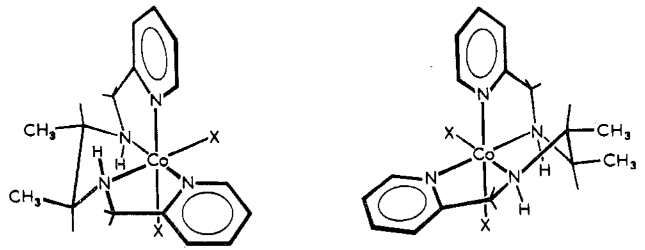

Figure 1.—Two isomers of the *cis-β*-Co(bnpic)X_2^+ complexes derived from (+)-2,3-butanediamine. The figure on the left shows the complex with optically active nitrogen atoms and the one on the right has the nitrogen atoms *meso*. Both absolute configurations of the complexes are those where the methyl groups are equatorially disposed.

The *cis*-octahedral complexes formed by the bnpic ligand have three sources of asymmetry: (1) the configurational asymmetry due to the overall molecular framework, (2) the asymmetry due to the asymmetric carbon atoms on the 2,3-diaminobutane linkage, and (3) the configurations of the two inner nitrogen atoms

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[3] J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.* **6**, 700 (1967).

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