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Magnetic and Spectroscopic Studies of the $Mo_2X_9^{3-}$ Ion

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Thermal preparations of $Cs_3Mo_2X_9$ (X = Cl or Br) are reported. The products are isomorphous with their Cr analogs. The unique position of the enneahalodimolybdates is discussed and, as expected, properties intermediate between those of the Cr and W compounds are observed. Thermal stability decreases according to Cr–Cr > Mo–Mo > W–W. Temperature-independent paramagnetism occurs with $Cs_3Mo_2Cl_9$, while $Cs_3Mo_2Br_9$ possesses weak, temperature-dependent paramagnetism The polarized crystal spectrum of $Cs_3Mo_2Cl_9$ does not clarify the interpretation of the spectra.

Our continuing interest[1-3] in the chemistry of enneahalodimetalates has led to the thermal preparations of $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ and an investigation of their magnetic and spectroscopic properties. These compounds occupy a unique position since $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ represent extremes in metal–metal interaction. While the former possesses essentially no interaction between the widely separated metal atoms, the metal atoms in the tungsten compound are displaced toward one another as a result of extensive interaction which is sufficient to be termed a metal–metal bond. The enneahalodimolybdates offered the interesting possibility of an intermediate interaction between the metal atoms which would result in intermediate properties. This possibility has now been confirmed.

Although both of these compounds have been previously prepared by other methods,[4,5] most of the details and properties were unavailable to us until we had entirely completed our own investigation. We then found a number of differences in analytical and magnetic data. In addition, we were able to obtain the polarized crystal spectrum of $Cs_3Mo_2Cl_9$ in the region where the assignments are most controversial.

Experimental Section

Materials.—Anhydrous $MoCl_3$ was prepared according to the method of Mallock,[6] which yielded a slightly contaminated product. The contaminants were easily removed by sublimation at 175° in a stream of anhydrous HCl. At completion $MoCl_3$ remained in the reaction vessel. Molybdenum tribromide was obtained quantitatively through the union of the elements at 375°.[7] The corresponding cesium halides were reagent grade and used without further treatment.

Preparation of $Cs_3Mo_2Cl_9$.—This compound was prepared by treating 0.320 g of CsCl with 0.284 g of $MoCl_3$, calculated to be in slight excess of the exact stoichiometric ratio of 3:2. The excess was needed to suppress the production of $CsMoCl_6$, some of which was always present. The reaction was carried out in a sealed Vycor tube for 24–48 hr at 800°. During this time dark hexagonal rods sublimed away from the melt. The tube was cooled and gently opened by fusing a thin rod of Pyrex around the Vycor tube which cracked the Vycor tube on cooling. This opening technique protected the products from mechanical shock as well as small fragments of glass. The zones were easily separated and $Cs_3Mo_2Cl_9$ was obtained as a mixture of red-brown hexagonal rods and plates. The red-brown hexagonal rods were strongly dichroic passing from light red-brown to nearly opaque, dark red-brown. The thin red-brown hexagonal plates were not dichroic and did not extinguish under crossed polarizers. The compound was stable to air, insoluble in water, and showed no reaction to pyridine even after refluxing for 72 hr. *Anal.* Calcd for $Cs_3Mo_2Cl_9$: Cl, 35.07; Mo, 21.09. Found: Cl, 34.87; Mo, 20.97. The melt region contained a light red polycrystalline material which was Cs_3MoCl_6. *Anal.* Calcd for Cs_3MoCl_6: Cl, 30.05. Found: Cl, 30.05.

$Cs_3Mo_2Br_9$.—The reaction of 1.07 g of $MoBr_3$ and 1.02 g of CsBr at 770° for 8 days in a sealed Vycor tube produced several products. At the coolest end (*ca.* 400°) there were some inhomogeneous, highly colored products, whereas, the region of the melt contained a steel gray amorphous solid and some deep red crystals. The amorphous solid was shown to be Cs_3MoBr_6. *Anal.* Calcd for Cs_3MoBr_6: Br, 49.15; Mo, 12.90. Found: Br, 49.05; Mo, 12.81. This undesirable product is apparently the result of prolonged or excessive heating. The deep red crystals were thickly packed and the aggregates were brushlike in appearance. After mechanical separation 1.6 g of the gray and deep red materials was combined with an additional 0.05 g of $MoBr_3$ and resublimed at 770°. The result was a preponderance of deep red hexagonal rods, which were stable to air and stable but insoluble in water. Their very dark red coloration prevented observations with a polarizing microscope. The crystals crumbled to a brick red powder on grinding. *Anal.* Calcd for $Cs_3Mo_2Br_9$: Br, 54.91; Mo, 14.62. Found: Br, 54.90; Mo, 14.41.

Attempt to Prepare $K_3Mo_2Cl_9$.—Several attempts were made to prepare $K_3Mo_2Cl_9$ without success. The reactions were conducted in Vycor tubes at temperatures ranging from 650 to 950° using stoichiometric amounts of KCl and $MoCl_3$. Repeated sublimations of K_3MoCl_6 with excess $MoCl_3$ yielded only mixtures of inseparable products and K_3MoCl_6.

Crystallography.—Single crystals of $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ were studied using the precession technique. Molybdenum Kα radiation passed through a zirconium filter was used to study $Cs_3Mo_2Cl_9$. Nickel-filtered Cu Kα radiation was used to examine the bromide complex. The crystals were mounted both parallel and perpendicular to the needle axis. The Laue symmetry was shown to be 6/mmm. Upper level precession photographs showed the only condition for extinction was $l \neq 2n$ for $hh\bar{2h}l$ reflections. Consequently, the space group for both complexes is D_{6h}^4-P6$_3$/mmc. The lattice constants are: for $Cs_3Mo_2Cl_9$, $a = 7.36$ and $c = 17.55$ Å; for $Cs_3Mo_2Br_9$, $a = 7.65$ and $c = 18.34$ Å. The former are in good agreement with those reported by Smith,[4] but no data for the bromide were presented. The calculated densities for these compounds are 3.68 g/cm^3

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[1] R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

[2] R. Saillant and R. A. D. Wentworth, *ibid.*, **7**, 1606 (1968).

[3] J. L. Hayden and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **90**, 5291 (1968).

[4] P. W. Smith, Ph.D. Thesis, University College, London, 1962. A copy is now available on a loan basis from the Center for Research Libraries, Chicago, Ill. 60637.

[5] A. J. Edwards, R. D. Peacock, and A. Said, *J. Chem. Soc.*, 4643 (1962).

[6] A. K. Mallock, *Inorg. Nucl. Chem. Letters*, **3**, 441 (1967).

[7] P. J. H. Carnell, R. E. McCarley, and R. D. Hogue, *Inorg. Syn.*, **10**, 49 (1967).

for $Cs_3Mo_2Cl_9$ and 4.66 g/cm^3 for $Cs_3Mo_2Br_9$ on the basis of two molecules per unit cell. Both compounds were observed to have densities greater than methylene iodide ($\rho = 3.33$ g/cm^3).

Measurements.—All magnetic susceptibility determinations were made with hand-picked crystals using a Faraday apparatus. The single-crystal spectrum was obtained as previously described.[8] The spectrum of $Cs_3Mo_2Br_9$ was observed using a Nujol mull of the finely ground compound supported on filter paper in a Cary 14 spectrophotometer.

Results and Discussion

Samples of both enneahalodimolybdates were prepared through the reaction of the anhydrous molybdenum trihalide and the appropriate cesium salt at elevated temperatures. This method of preparation contrasts with those reported by Smith[4] and Edwards, *et al.*[5] Smith was able to obtain $Cs_3Mo_2Cl_9$ by the addition of CsCl to a concentrated Mo(III) solution in a concentrated hydrochloric acid medium. Edwards reported the reduction of MoX_6^{2-} with liquid ammonia and the subsequent isolation of $Mo_2X_9^{3-}$. He also reported $Rb_3Mo_2Br_9$ to be gray-brown which contrasts to our observation that $Mo_2Br_9^{3-}$ is brick red in powder form. Smith reported the correct color.

Our synthetic procedure is completely analogous to those employed in the preparation of various salts of $Cr_2X_9^{3-}$, which were not amenable to synthesis in aqueous media. In contrast, salts of $W_2Cl_9^{3-}$ have been prepared exclusively from aqueous solutions. When $Cs_3W_2Cl_9$ is heated *in vacuo*, decomposition occurs with the formation of several products. One of these is crystalline and appears to be $Cs_3W_2Cl_8$.[9] The thermal decomposition of $K_3W_2Cl_9$, however, yields a mixture of noncrystalline products. The molybdenum salts appear to have thermal and hydrolytic stabilities which are intermediate between those of $W_2X_9^{3-}$ and $Cr_2X_9^{3-}$. Their relative inertness to aqueous media facilitates their synthesis by wet methods, while their insensitivity to elevated temperatures does not preclude their synthesis by thermal methods. We have noticed that prolonged heating of $Cs_3Mo_2Br_9$ at about 850–900° yields a grayish product which resists attempts to produce $Cs_3Mo_2Br_9$ reversibly. Furthermore, in the course of our study we attempted repeatedly to prepare $K_3Mo_2Cl_9$ through the interaction of both KCl and $MoCl_3$ and $MoCl_3$ with K_3MoCl_6 without success. The crystal lattice of $K_3Mo_2Cl_9$ appears to be unstable at elevated temperatures. Conversely, $K_3Cr_2Cl_9$ was easily prepared and is thermally stable. Thus, it appears that the order of decreasing thermal stability of $M'_3M_2X_9$ is Cr > Mo > W, with the stability of any member increased by employing heavier alkali metal ions.

Magnetism.—Since the varying magnetic properties of the enneahalodimetalates are believed to have their origin, at least to some extent, in the magnitudes of the metal–metal interactions, the separation of the molybdenum atoms in $Mo_2X_9^{3-}$ is of importance. A three-dimensional X-ray study of these compounds is, at present, sufficiently complete to give the desired distances as about 2.67 and 2.78 Å for $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$, respectively. Since a smooth decrease in the metal–metal separation occurs, such that Cr–Cr > Mo–Mo > W–W, one would expect trends in both magnetic and spectroscopic properties to occur.

In agreement with the intermediate metal atom separations, the magnetic moments at room temperature of $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ are 0.6 and 0.8 BM, respectively. Smith[4] reported that the magnetic moments for these compounds are 0.6–0.7 and 1.26 BM, respectively. We have also found that the susceptibility of $Cs_3Mo_2Cl_9$ is completely temperature independent between 80 and 300°K, but the susceptibility of $Cs_3Mo_2Br_9$ decreases rapidly with decreasing temperature, as shown in Figure 1. Typical results in cgs units and absolute temperatures are 250×10^{-6} at 300°, 110×10^{-6} at 195°, and about 10×10^{-6} between 80 and 100°. These results are not unexpected in view of our recent study[2] of the magnetic properties of $Cs_3Cr_2Cl_9$ and $Cs_3W_2Cl_9$. The former is magnetically normal, behaving as if the adjacent chromium atoms were only slightly coupled. In the latter, the paramagnetism is extremely small and completely independent of temperature. Similar results were obtained with the corresponding bromides.[2,3] With the chromium compounds the width of the lowest spin multiplet (or the energy required to decouple the electrons) is about 0.1 kcal/mol, while with the tungsten analogs the width must be considerably greater than kT. Using the equation of Earnshaw and Lewis,[10] the width of this multiplet in $Cs_3Mo_2Br_9$ has been estimated to be about 9 kcal/mol. As shown in Figure 1, it was not possible to match the observed experimental behavior exactly. However, the results are only approximate for several reasons. First, experimental inaccuracies are rather large because of the very weak paramagnetism. Second, since magnetic dilution in salts of $Cr_2Cl_9^{3-}$ is only obtained using large alkylammonium cations,[2] some effect due to the lack of magnetic dilution can probably be expected with the molybdenum analogs. Third, the Heisenberg formalism, from which the equation of Earnshaw and Lewis arises, cannot be expected to give an adequate estimate of spin-dependent energies in strongly coupled systems. The extent to which the spin state energies in these compounds deviates from the predicted proportionality to $S'(S' + 1)$ is impossible to evaluate at present. Nevertheless, our estimate undoubtedly represents a lower limit for the electron decoupling energy. Furthermore, this decoupling energy must be a very sensitive function of either the magnitude of the separation of the metal atoms or the nature of the bridging halogen atom since substitution of chlorine for bromine and the concomitant decrease in the metal atom separation of only 0.1 Å were sufficient to remove completely all temperature-dependent paramagnetism.[11] Evidently,

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[8] R. A. D. Wentworth, *Inorg. Chem.*, **5**, 496 (1966).

[9] R. Saillant and R. A. D. Wentworth, unpublished results.

[10] A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

[11] Using the equation of Earnshaw and Lewis, the minimum multiplet width for both $Mo_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ can be estimated as 25 kcal/mol. This value simply represents the minimum energy required to lose completely the temperature-dependent paramagnetism.

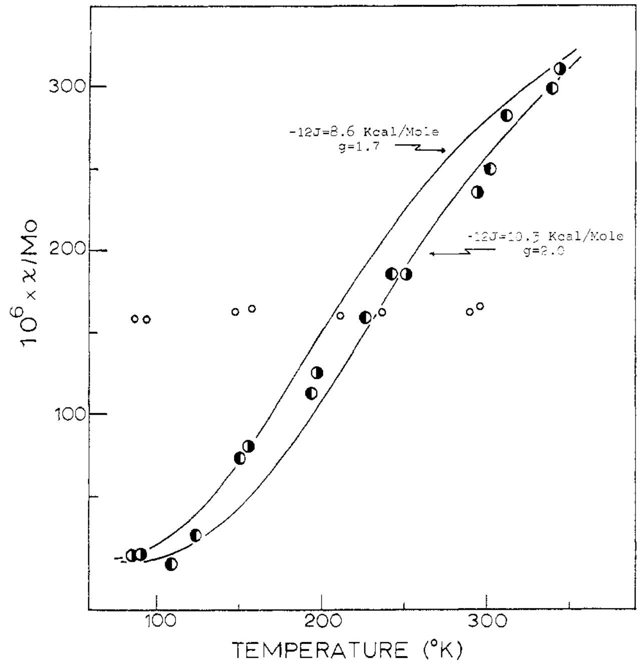

Figure 1.—Variation of the susceptibilities per Mo atom of $Cs_3Mo_2X_9$ (X = Cl or Br) with temperature: ○, $Cs_3Mo_2Cl_9$; ◐ and ◑, two separate preparations of $Cs_3Mo_2Br_9$. Diamagnetic corrections in cgsu were: Cs, -35×10^{-6}; Cl, -23×10^{-6}; Br, -35×10^{-6}. The solid lines represent the calculated temperature dependence of the susceptibility and include a temperature-independent susceptibility of 10×10^{-6} cgsu.

the temperature-independent paramagnetism is also sensitive to these factors as well, since we find a value of about 160×10^{-6} cgsu for $Cs_3Mo_2Cl_9$ but a near-zero value for $Cs_3Mo_2Br_9$. No simple theoretical explanation for this phenomenon is readily found but the difference may be due, at least in part, to inaccuracies in the diamagnetic corrections.

TABLE I

SPECTROSCOPIC PROPERTIES OF $Mo_2X_9^{3-}$ AND MoX_6^{3-} (X = Cl or Br)[a]

Compound	Ref	$Cm^{-1} \times 10^{-3}$
$Cs_3Mo_2Cl_9$	*b*	11.95 (13), 13.35 (78), 15.15 (100)
	c	12.4 sh (5), 12.95 (10), 15.32 (12), 16.60 (4), 19.7 sh (120)
$Cs_3Mo_2Br_9$	*d*	12.75, 13.5 sh, 14.5 sh, 15.9 sh, 17.0 sh, 17.7, 22.0
$MoCl_6^{3-}$	*e, f*	9.5 (4), 14.5 (6), 18.3 (33), 23.2

[a] Extinction coefficients appear in parentheses. [b] Perpendicular polarization. [c] Parallel polarization. [d] Nujol mull spectrum. [e] Solution spectra from C. Furlani and O. Piovesano, *Mol. Phys.*, **9**, 341 (1965). [f] Last band taken from the reflectance spectrum.

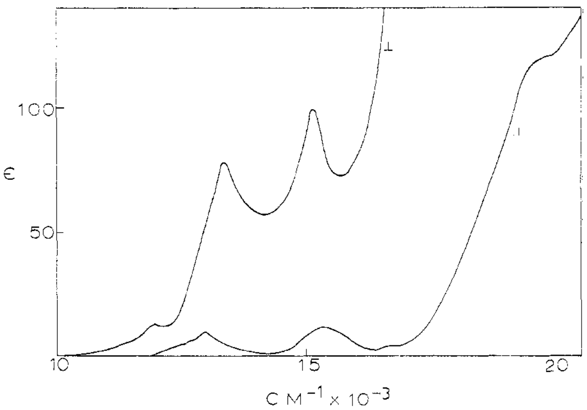

Figure 2.—Crystal spectra of $Cs_3Mo_2Cl_9$ with incident light on a 110 face of the hexagonal crystal and polarized parallel and perpendicular to the threefold axis of the anion. The molar extinction coefficients were computed from the crystal thickness and the calculated crystal density.

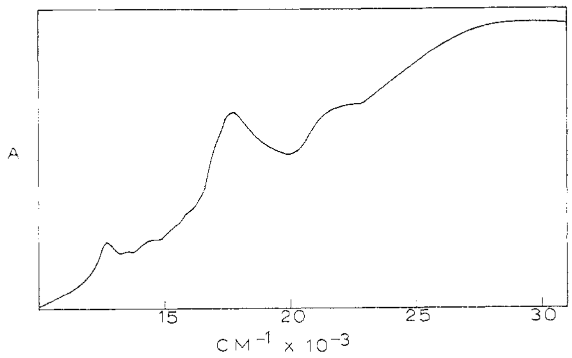

Figure 3.—Absorption spectrum of $Cs_3Mo_2Br_9$ supported in a Nujol mull.

Spectroscopic Properties.—The polarized crystal spectra of $Cs_3Mo_2Cl_9$ are given in Table I and Figure 2. In addition, the mull spectrum of $Cs_3Mo_2Br_9$ can be found in Figure 3. The spectra of both contain similar features and agree reasonably with those given by Smith,[4] who also reported two strong bands for $Cs_3Mo_2Cl_9$ at 18,900 and 23,700 cm^{-1}. The former probably corresponds to the shoulder at about 19,700 cm^{-1} in the parallel polarization. At lower wave numbers, two bands appear in perpendicular polarization at 13,350 and 15,150 cm^{-1}. In the opposite polarization, their intensities have diminished considerably while the band maxima have shifted to slightly lower and higher energies, respectively. These strong polarizations probably indicate that the excited states have E′ symmetry in D_{3h}, the point group of the molecule, or E symmetry in C_{3v}, the local symmetry about each molybdenum atom. The first assignment would apply if the spectrum is to be interpreted as a strongly coupled dimeric unit, while the second would be useful for an interpretation which assigned the spectrum as transitions occurring predominantly within each isolated chromophore. However, Smith[4] points out that, while the higher energy bands at 18,900 and 23,700 cm^{-1} could reasonably be assigned according to the second method as $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$, it is not possible to reconcile the assignment of the lower energy bands as the typical spin-forbidden transitions that occur in $MoCl_6^{3-}$. He further suggests that the lower symmetry might be responsible. This suggestion is probably untenable owing to the high extinction coefficients which are observed for these bands. In fact, the intensity and position of the bands at 13,350 and 15,150

cm^{-1} are similar to a pair of bands at 13,200 and 15,900 cm^{-1} in the spectrum[1] of $W_2Cl_9^{3-}$. In the spectrum of the latter, however, there is also an intense band at 21,900 cm^{-1} which has no counterpart in the spectrum of $Mo_2Cl_9^{3-}$. Equivalent similarities and differences also occur in the spectra of $Mo_2Br_9^{3-}$ and $W_2Br_9^{3-}$.[3] Thus, the spectra of the enneahalodimolybdates possess certain features which resemble those of the corresponding MoX_6^{3-} and others which resemble those found in $W_2X_9^{3-}$. The only clear fact that emerges from this comparison is the enigmatic nature of these spectra.

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Infrared and Raman Spectra of the Se_4^{2+} Ion

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Infrared and Raman spectra have been recorded for a number of compounds that have been shown to contain the Se_4^{2+} ion. Characteristic vibrational frequencies for Se_4^{2+} were observed at 188 and 327 cm^{-1} in the Raman spectrum and at ~306 cm^{-1} in the infrared spectrum. These have been assigned, respectively, to the B_{2g}, A_{1g}, and E_u fundamentals of a square-planar (D_{4h}) arrangement of selenium atoms. A normal-coordinate analysis based on a Urey–Bradley force field yields a value of 2.2 mdyn/Å for the Se–Se stretching force constant. A relatively novel technique for recording the infrared spectra of highly reactive solids is described.

Introduction

Selenium dissolves in sulfuric and fluorosulfuric acids in the presence of oxidizing agents to form intensely green or yellow solutions. Investigation of the yellow solutions by conductometric, cryoscopic, spectrophotometric, and magnetic methods has shown that the selenium is present as the polyatomic cation Se_4^{2+}.[1] A number of salts of Se_4^{2+} have been prepared and characterized: $Se_4(SO_3F)_2$ (I), $Se_4(HS_2O_7)_2$ (II), $Se_4(S_4O_{13})$ (III), and $Se_4(Sb_2F_{11})_2$ (IV).[2] Crystals of II have been examined by X-ray diffraction and have been found to be monoclinic, space group $P2_1/c$ (C_{2h}^5), containing two units of $Se_4(HS_2O_7)_2$ per unit cell. The Se_4^{2+} ion has been found to have a square-planar (D_{4h}) structure with an Se–Se separation of about 2.3 Å.[3] In this paper we report on the infrared and Raman spectra of compounds I–IV.

Experimental Section

Preparation of Materials.—Compounds I–IV were prepared as described in ref 2. They are bright orange to yellow solids and are extremely hygroscopic; they were prepared and handled in a dry nitrogen atmosphere. It was not possible to obtain solutions of I–IV in the usual spectroscopic solvents. For example, I and II are insoluble in CCl_4, C_6H_5F, BCl_3, and liquid SO_2. When mixed with CH_3NO_2, CH_3CN, $(CH_3)_2SO$, and CS_2, they are immediately reduced to selenium. All of the compounds are very soluble in the parent acids. Solutions of I–IV in fluorosulfuric acid or in dilute oleum were employed for Raman spectra.

Potassium hydrogen disulfate (KHS_2O_7) was made by dissolving "Analar" grade K_2SO_4 in hot 30% oleum (sulfuric acid containing 30% w/w of sulfur trioxide). Large columnar crystals appeared on cooling the solution. The crystals were washed with 10% oleum and subsequently with liquid SO_2 at −11° to remove any adhering acid. The dry material melted at 170–173° (mp 168°[4]); analyses for sulfur and for the sulfuric acid equivalent upon hydrolysis were within 0.7% of the values expected for KHS_2O_7.

Potassium fluorosulfate was prepared by carefully neutralizing ice-cold aqueous KOH with HSO_3F. The salt which separates out was recrystallized from hot (95°) water.

Raman Spectra.—Raman spectra were taken with a Spex Industries Model 1400 spectrometer employing a 50-mW Spectra Physics Model 125 He–Ne laser source at 6328 Å, a double monochromator, and a photomultiplier detector followed by an electrometer amplifier and recorder. A convenient and particularly effective method of mounting samples was devised. Liquid, powdered, or crystalline samples were contained in 1.2-mm i.d. (melting point) capillary tubes mounted horizontally with their axes perpendicular to the collimated laser beam. The beam was focused near the center of the tube and the light scattered at 90° to the incident radiation and to the axis of the tube was focused on the slits of the monochromator. For liquid samples this arrangement gave Raman signals of better than 10 times the intensity obtained when using Supersil cuvettes of square cross section as sample containers. Also, by using capillary tubes, the size of sample and any absorption of the exciting radiation are kept to a minimum. Depolarization ratio measurements taken on CCl_4 lines compared favorably with depolarization data recorded with CCl_4 in the optically superior cuvettes. The readout of the monochromator was calibrated against emission lines of neon.

Infrared Spectra.—Compounds I–IV readily attack Nujol, polyethylene, and cesium iodide; hence the usual methods for taking infrared spectra could not be applied. A rather novel sampling technique was developed in which the compounds were supported as finely divided solids on a cold cesium iodide plate. This allowed coverage of the full CsI range (~180–4000 cm^{-1})

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(1) J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

(2) J. Barr, D. B. Crump, R. J. Gillespie, R. Kapoor, and P. K. Ummat, *ibid.*, **46**, 3607 (1968).

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(4) A. C. Schultz-Sellack, *Ber.*, **4**, 109 (1871).