

sary to bring about the distortion. Thus, the most easily distorted molecule may turn out to form the strongest donor-acceptor bond.

To explain the thermodynamic data we note that for easily distorted Lewis acids, such as BCl_3 , ΔH_1 has a smaller positive value and ΔH_3 has a larger negative value than for a less easily distorted molecule such as BF_3 . The net effect is to make the donor-acceptor reaction enthalpy, ΔH_5 , more negative (exothermic) for the more easily distorted acid. Similarly, most spectroscopic studies and the present structural results indicate the more easily distorted acid forms

the stronger donor-acceptor bond. In summary, the model of partial reorganization, which is suggested by the structural results, affords a straightforward explanation of both spectral and thermodynamic data for a series of boron halides interacting with a common donor.

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Dianionic Rhenium Carbonyl Halides

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The dinegative rhenium carbonyl halide anions $\text{Re}(\text{CO})_3\text{X}_3^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{Re}_2(\text{CO})_6\text{X}_4^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) have been obtained as their tetraethylammonium salts from the reaction of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_6\text{L}_3]$ ($\text{L} = \text{H}, \text{C}_2\text{H}_5\text{O}, i\text{-C}_3\text{H}_7\text{O}$) with the hydrohalic acids. With the exception of the dimeric bromo complex, they can also be prepared by the action of halide ions on the appropriate halogenopentacarbonylrhenium. An isothiocyanato complex, $\text{Re}(\text{CO})_3(\text{NCS})_3^{2-}$, results from treating any of the dianions with SCN^- . Infrared spectra were determined, and the CO and ReX stretching frequencies were identified. The results are consistent with *cis* (C_{3v}) octahedral geometry for $\text{Re}(\text{CO})_3\text{X}_3^{2-}$ and with a doubly halogen-bridged dimeric arrangement for $\text{Re}_2(\text{CO})_6\text{X}_4^{2-}$. The ReX stretching frequencies of $\text{Re}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\text{Re}(\text{CO})_4\text{X}_2^-$ ($\text{X} = \text{Br}, \text{I}$), $\text{Re}_2(\text{CO})_8\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), and $\text{Re}_2(\text{CO})_7\text{X}_3^-$ ($\text{X} = \text{Cl}, \text{Br}$) are also reported and used to indicate probable structures.

Introduction

Rhenium forms a series of monomeric and also a series of dimeric carbonyl halide complexes. The monomer series is comprised of the pentacarbonyl halides,^{1,2} $\text{Re}(\text{CO})_5\text{X}$, the dihalogenotetracarbonyl anions,³ $\text{Re}(\text{CO})_4\text{XY}^-$ (X and $\text{Y} = \text{Cl}, \text{Br}, \text{or I}$), and the triiodotricarbonyl dianion,³ $\text{Re}(\text{CO})_3\text{I}_3^{2-}$. The dimer series consists of the dihalogenooctacarbonyldirhenates,⁴ $\text{Re}_2(\text{CO})_8\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), and the trihalogenoheptacarbonyldirhenate anions,³ $\text{Re}_2(\text{CO})_7\text{X}_2\text{Y}^-$ (X and $\text{Y} = \text{Cl}$ or Br). In the present paper we report two members of a new class of complex belonging to the dimer series, the tetrahalogenohexacarbonyldirhenate dianions, $\text{Re}_2(\text{CO})_6\text{X}_4^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) and also three new members of the known class of monomeric dianions, $\text{Re}(\text{CO})_3\text{X}_3^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$). These dinegative rhenium carbonyl halide anions were obtained as their tetraethylammonium salts from the reaction of tri- μ -hydrido- and tri- μ -alkoxy-hexacarbonyldirhenate(I),⁵ $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_6\text{L}_3]$ ($\text{L} = \text{H}, \text{C}_2\text{H}_5\text{O}, i\text{-C}_3\text{H}_7\text{O}$), with the hydrohalic acids. With the exception of the dimeric bromo complex, they have also been prepared

by the action of halide ions on the appropriate halogenopentacarbonylrhenium.

In order to characterize the $\text{Re}(\text{CO})_3\text{X}_3^{2-}$ and $\text{Re}_2(\text{CO})_6\text{X}_4^{2-}$ complexes it was necessary to study their far-infrared spectra in the metal-halogen stretching region and to compare the results with the spectra of the other rhenium carbonyl halides. The far-infrared spectra of the pentacarbonyl halides have been reported,⁶ but none of the other compounds appears to have been examined in this region. We therefore determined the infrared spectra in the metal-halogen stretching region of most of the known rhenium carbonyl halide complexes and interpreted the results in terms of probable structures.

Experimental Section

Far-infrared spectra were recorded on a Beckman IR 11 spectrophotometer over the range 400–80 cm^{-1} , for samples in CsI disks and Nujol mulls mounted between polyethylene plates. The instrument was calibrated by reference to part of the rotational spectrum of water vapor. The correction to the chart-read frequencies was within $\pm 1 \text{ cm}^{-1}$ over the whole range. The frequencies quoted should be accurate to $\pm 2 \text{ cm}^{-1}$. Infrared spectra in the range 4000–300 cm^{-1} were recorded on Perkin-Elmer 337 and 457 spectrophotometers, calibrated by reference to the spectrum of a polystyrene film. In the CO stretching region the frequencies quoted should be accurate to $\pm 2 \text{ cm}^{-1}$. Conductivities were measured at $25.0 \pm 0.1^\circ$ on a Serfass con-

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ductivity bridge, Model RCM 15B1, over a concentration range of 10^{-2} to 10^{-3} *N*. The conductivity cell, consisting of two 1-cm² platinized platinum electrodes separated by ~1 cm, was calibrated with 0.10 *M* KCl solution. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Alfred Bernhardt Laboratory, Mülheim, West Germany. Melting points were determined in evacuated tubes and are uncorrected. Bis(2-methoxyethyl) ether (diglyme) was dried over CaH₂ and then distilled from LiAlH₄ under N₂ at 62–63° (15 mm). Re(CO)₅Cl and Re(CO)₅Br were purchased from Pressure Chemical Co. and used as received.

Preparation of Complexes. 1. Bis(tetraethylammonium) Tetrachlorohexacarbonylrhenate(I).—A. [(C₂H₅)₄N][Re₂(CO)₆(*i*-C₃H₇O)₃] (0.465 g, 0.55 mmol) was dissolved in 10 ml of hot 2-propanol and 5 ml of a saturated solution of HCl in 2-propanol (~7.7 *N*) was added. A small amount of white solid slowly precipitated. After about 1 hr, 25 ml of anhydrous ether was added, producing more white solid. The product was collected, washed with ether, and dried at 56° (10⁻³ mm) to give 0.208 g (80% based on amount of (C₂H₅)₄N⁺ cation present) of a fine white powder, mp 291–293° dec. *Anal.* Calcd for [(C₂H₅)₄N]₂[Re₂(CO)₆Cl₄]: C, 28.02; H, 4.28; N, 2.97; O, 10.18; Cl, 15.04. Found: C, 28.61; H, 4.46; N, 3.04; O, 10.38; Cl, 15.15.

B. [(C₂H₅)₄N][Re₂(CO)₆H₃] (0.1085 g, 0.161 mmol) contained in an evacuated (10⁻⁴ mm) reaction vessel was treated with 5 ml of a degassed, saturated solution of HCl in 2-propanol. The orange rhenium carbonyl hydride dissolved completely with vigorous evolution of hydrogen and the formation of an orange solution. After 24 hr at room temperature, evolution of hydrogen had ceased and the solution had a faint yellow color; a small amount of white crystalline solid had formed. The measured amount of evolved H₂ gas was 2.8 mmol/mmol of [(C₂H₅)₄N][Re₂(CO)₆H₃] (theory, 3.0 mmol). (C₂H₅)₄NCl (0.0294 g, 0.178 mmol) was dissolved in a minimum amount of 2-propanol and added to the solution, which was then transferred to a small flask and evaporated to dryness (30°, 10⁻² mm) to give 0.14 g of white solid. Part of this material (0.085 g) was extracted with two 5-ml portions of absolute ethanol (*cf.* method 2A), and the undissolved white solid was washed with ether and dried at 82° (10⁻³ mm); yield, 0.038 g. *Anal.* Found: C, 28.23; H, 4.35; N, 3.04; O, 10.07; Cl, 14.88. The compound has the same infrared spectrum as the product obtained by method 1A.

C. Re(CO)₅Cl (0.375 g, 1.04 mmol) and (C₂H₅)₄NCl (0.172 g, 1.04 mmol) were suspended in 25 ml of freshly distilled diglyme. The reaction mixture was degassed and heated under N₂. At 50° the solid dissolved completely, giving a clear pale yellow solution. At 90° a white precipitate began to form. The solution was kept at 100–120° for 4 hr. The white solid was then collected and petroleum ether (bp 30–60°) was added to the filtrate to produce more white precipitate. The combined solids (0.33 g, 67%) were dried at 82° (10⁻³ mm). The product has the same infrared spectrum as the material obtained by methods 1A and 1B.

2. Bis(tetraethylammonium) Trichlorotricarbonylrhenate(I).—A. Anhydrous ether was added to the absolute ethanol extracts from the white solid obtained from the reaction of [(C₂H₅)₄N][Re₂(CO)₆H₃] and HCl in 2-propanol (method 1B). A white precipitate formed. The product was collected, washed with ether, and dried at 82° (10⁻³ mm); yield, 0.032 g; mp 308–310° dec. *Anal.* Calcd for [(C₂H₅)₄N]₂[Re(CO)₃Cl₃]: C, 35.81; H, 6.33; N, 4.40; O, 7.53; Cl, 16.69. Found: C, 34.48; H, 6.10; N, 4.23; O, 7.88; Cl, 16.84.

B. Re(CO)₅Cl (0.361 g, 1.0 mmol) and an excess of (C₂H₅)₄NCl (0.857 g, 5.2 mmol) were suspended in 175 ml of freshly distilled diglyme. The reaction mixture was degassed and then heated at 110° for 3 hr under N₂. As the temperature approached 60° the suspended solid dissolved completely, giving a clear faint yellow solution from which a white solid precipitated at 100–110°. The precipitate was collected by filtration at room temperature and washed with 10 ml of absolute ethanol. Almost all of the product dissolved on shaking with an additional 10 ml

of absolute ethanol. This solution was filtered and a white solid was precipitated by slowly adding ether to the filtrate. The product was collected and dried at 82° (10⁻³ mm); yield, 0.20 g (31%). *Anal.* Found: C, 35.65; H, 6.43; N, 4.45; O, 7.71; Cl, 16.65.

3. Bis(tetraethylammonium) Tetrabromohexacarbonylrhenate(I).—A. [(C₂H₅)₄N][Re₂(CO)₆(*i*-C₃H₇O)₃] (1.0 g, 1.2 mmol) was dissolved in a minimum amount of 2-propanol. Addition of 10 ml of a saturated solution of HBr in 2-propanol gave a white precipitate. The reaction mixture was left standing at room temperature for 15 hr. The solid was then collected, washed with ether, and dried (0.40 g). This product was extracted with two 10-ml portions of absolute ethanol. The remaining solid was washed with ether and dried at 82° (10⁻³ mm); yield, 0.24 g of pale cream powder; mp 259–260°. *Anal.* Calcd for [(C₂H₅)₄N]₂[Re₂(CO)₆Br₄]: C, 23.57; H, 3.60; N, 2.50; O, 8.56; Br, 28.52. Found: C, 23.60; H, 3.67; N, 2.54; O, 8.78, Br, 28.44.

B. Attempts to make [(C₂H₅)₄N]₂[Re₂(CO)₆Br₄] from Re(CO)₅Br and (C₂H₅)₄NBr resulted in the formation of [(C₂H₅)₄N]₂[Re(CO)₃Br₃] (*cf.* method 4B).

4. Bis(tetraethylammonium) Tribromotricarbonylrhenate(I).—A. (C₂H₅)₄NBr (0.75 g, 1.2 mmol) was dissolved in a minimum amount of 2-propanol and added to the filtrate from the reaction of [(C₂H₅)₄N][Re₂(CO)₆(*i*-C₃H₇O)₃] and HBr (method 3A). A cream-colored solid precipitated immediately. The solid was collected, washed with ether, and dried at 82° (10⁻³ mm); yield, 0.551 g; mp 281–282°. *Anal.* Calcd for [(C₂H₅)₄N]₂[Re(CO)₃Br₃]: C, 29.61; H, 5.23; N, 3.64; O, 6.23; Br, 31.11. Found: C, 29.65; H, 5.22; N, 3.59; O, 6.05; Br, 31.77.

B. Re(CO)₅Br (0.550 g, 1.35 mmol) and (C₂H₅)₄NBr (0.295 g, 1.35 mmol) were suspended in 150 ml of diglyme and heated at 120° for 3 hr under N₂. The suspended solid dissolved at ~60° giving a clear pale yellow solution. Gradually, as the temperature reached 100–110°, a precipitate formed. The solution was filtered hot to give a cream-colored solid which was washed with petroleum ether and dried at 82° (10⁻³ mm); yield, 0.255 g (50% based on amount of cation present). *Anal.* Found: C, 29.70; H, 5.32; N, 3.42; O, 6.88; Br, 30.70.

Addition of petroleum ether to the filtrate produced 0.237 g of [(C₂H₅)₄N][Re(CO)₃Br₃] as reported by Abel, *et al.*³

5. Bis(tetraethylammonium) Triiodotricarbonylrhenate(I).—A. [(C₂H₅)₄N][Re₂(CO)₆(*i*-C₃H₇O)₃] (0.120 g, 0.140 mmol) was dissolved in a minimum of hot 2-propanol and 3.0 ml of 2-propanol saturated with HI was added. A white precipitate formed immediately; the solid was collected, washed with ether, and air dried; yield, 0.040 g (63% based on amount of cation present). Addition of (C₂H₅)₄NI to the filtrate produced another 0.090 g of solid which was washed with absolute ethanol and air dried. Both solids gave the same infrared spectrum and were combined and dried at 82° (10⁻³ mm). *Anal.* Calcd for [(C₂H₅)₄N]₂[Re(CO)₃I₃]: C, 25.03; H, 4.42; N, 3.07; O, 5.27; I, 41.77. Found: C, 25.12; H, 4.26; N, 3.27; O, 5.29; I, 42.03.

B. The reaction of Re(CO)₅I and (C₂H₅)₄NI also afforded [(C₂H₅)₄N]₂[Re(CO)₃I₃] as reported by Abel, *et al.*³

6. Bis(tetraethylammonium) Triisothiocyanatotricarbonylrhenate(I).—[(C₂H₅)₄N]₂[Re(CO)₃Br₃] (0.305 g, 0.397 mmol) dissolved in acetonitrile (5 ml) was mixed with a solution of NaSCN (1.02 g, 1.25 mmol) in acetonitrile (20 ml) to give a pale yellow solution and a white precipitate of NaBr. The latter was filtered off, but further precipitation of NaBr continued in the filtrate, which was then refluxed under N₂ for 3 hr. After cooling to room temperature, the solution was filtered and the filtrate was concentrated to ~5 ml. Addition of anhydrous ether produced a copious gold-colored precipitate. This product dissolved in 30 ml of absolute ethanol to give a colorless solution and a small amount of gold-colored residue. The residue was filtered off and ether was added to the filtrate until a faint turbidity appeared. On standing, shiny pale pink crystals formed. The crystals were collected by filtration, washed with ether, and dried at 56° (10⁻³ mm); yield, 0.149 g (53%); mp 152–153°. *Anal.* Calcd for [(C₂H₅)₄N]₂[Re(CO)₃(NCS)₃]: C, 37.47; H,

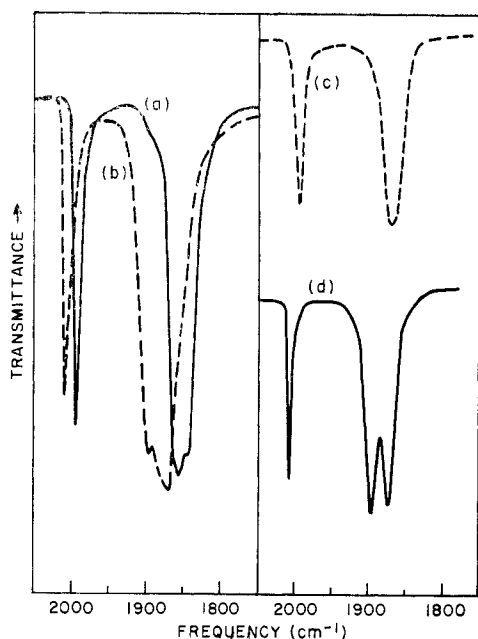


Figure 1.—Infrared spectra in the CO stretching region of (a) $[(C_2H_5)_4N]_2[Re(CO)_6Cl_3]$ (Fluorolube mull), (b) $[(C_2H_5)_4N]_2[Re_2(CO)_6Cl_4]$ (Fluorolube mull), (c) $[(C_2H_5)_4N]_2[Re(CO)_6I_3]$ in nitrobenzene solution, and (d) $[(C_2H_5)_4N]_2[Re(CO)_6Cl_3]$ or $[(C_2H_5)_4N]_2[Re_2(CO)_6Cl_4]$ in acetonitrile solution.

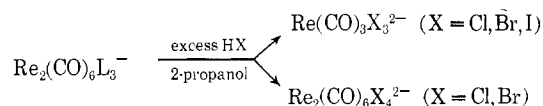
5.72; N, 9.93; O, 6.81; S, 13.64. Found: C, 37.73; H, 5.88; N, 10.25; O, 7.33; S, 13.65.

The reaction of the other dianionic rhenium carbonyl halides with NaSCN produced the same compound as identified by its infrared spectrum.

The following compounds were prepared by literature methods: $Re_2(CO)_6X_2$ ($X = Cl, Br, I$);⁴ $[(C_2H_5)_4N][Re(CO)_4X_2]$ ($X = Br, I$),³ and $[(C_2H_5)_4N][Re_2(CO)_7X_3]$ ($X = Cl, Br$).³

Results

Tri- μ -hydrido- and tri- μ -alkoxy-hexacarbonyldirhenate(I), $[(C_2H_5)_4N][Re_2(CO)_6L_3]$ ($L = H, C_2H_5O, i-C_3H_7O$), react with the hydrohalic acids in 2-propanol to give two types of rhenium carbonyl halide anion. These may be isolated as tetraethylammonium salts. The stoichiometry of one of the salts, $[(C_2H_5)_4N]_2[Re(CO)_3X_3]$, indicates that the anion is a dinegative six-coordinate monomer. The stoichiometry of the second salt is $[(C_2H_5)_4N][Re(CO)_3X_2]$. Since a five-coordinate Re(I) species is unlikely, the simplest formulation of this anion is as a dinegative dimer, $Re_2(CO)_6X_4^{2-}$. Both carbonyl halide ions can be prepared



with HCl and HBr, whereas with HI only $Re(CO)_3I_3^{2-}$ can be obtained. The latter has been prepared previously by Abel and coworkers³ from the reaction of iodide ion with iodopentacarbonylrhenium. We have also obtained the trichloro- and tribromotricarbonylrhenates from the respective rhenium pentacarbonyl halide and excess of tetraethylammonium halide. From the reaction of rhenium pentacarbonyl chloride with a stoichiometric amount of tetraethylammonium chloride the complex $[(C_2H_5)_4N]_2[Re_2(CO)_6Cl_4]$ was isolated. How-

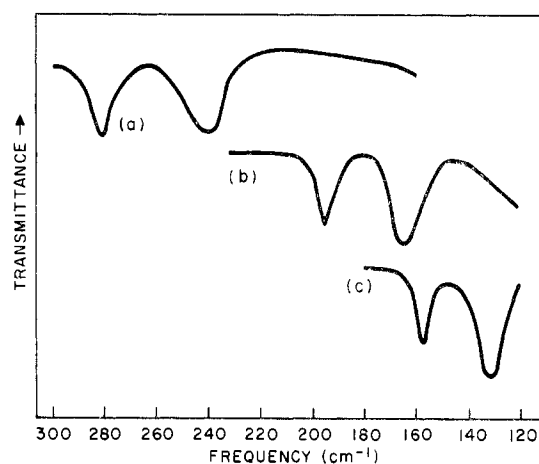


Figure 2.—Infrared spectra in the ReX stretching region of $[(C_2H_5)_4N]_2[Re(CO)_3X_3]$: (a) $X = Cl$; (b) $X = Br$; (c) $X = I$.

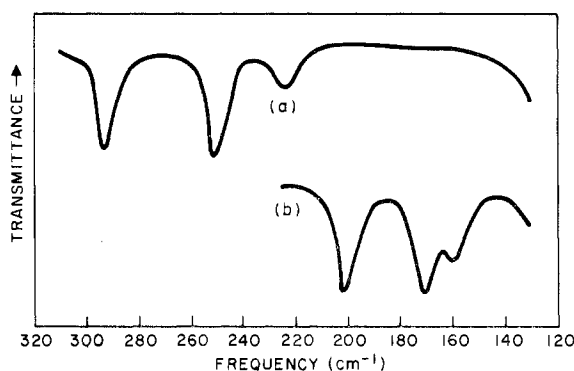
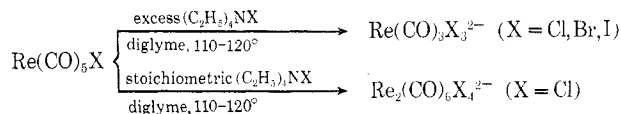
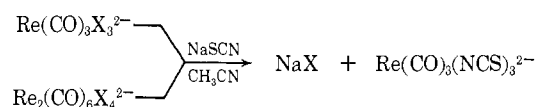


Figure 3.—Infrared spectra in the ReX stretching region of $[(C_2H_5)_4N]_2[Re_2(CO)_6X_4]$: (a) $X = Cl$; (b) $X = Br$.

ever, the corresponding bromide complex could not be obtained from the pentacarbonyl bromide and tetraethylammonium bromide.



Both types of rhenium carbonyl halide dianion react with sodium thiocyanate in acetonitrile solution to precipitate the respective sodium halide and form the triisothiocyanatotricarbonylrhenate(I) complex.



The infrared spectra of the dianionic complexes in the CO stretching region are illustrated in Figure 1 and the frequencies are summarized in Table I. Figures 2 and 3 show the infrared spectra of the dianionic complexes in the metal-halogen stretching region. The frequencies are listed in Table II. Also in Table II are the rhenium-halogen stretching frequencies of the other rhenium carbonyl halide complexes.

Conductivity measurements made in acetonitrile and nitrobenzene solution as a function of concentration^{7,8}

(7) P. Walden and E. J. Birr, *Z. Physik. Chem. (Leipzig)*, **144**, 269 (1929).

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TABLE I
 INFRARED-ACTIVE CO STRETCHING FREQUENCIES^a

Compound	$\nu(\text{CO}), \text{cm}^{-1}$	
	Solid (Fluorolube mull)	Solution
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{Cl}_3]$	2000 s, 1910 s, 1895 sh	CH_3CN : 2015 s, 1905 s, 1880 s $\text{C}_6\text{H}_5\text{NO}_2$: 2010 m, ^b 1999 m, 1895 s, ^b 1870 s
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{Br}_3]$	1999 s, 1865 s, 1848 s	CH_3CN : 2015 s, 1905 s, 1880 s $\text{C}_6\text{H}_5\text{NO}_2$: 2015 w, ^b 2002 s, 1905 sh, ^b 1868 s
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{I}_3]$	1998 s, 1930 s, 1905 s	CH_3CN : 2015 s, 1910 s, 1890 s $\text{C}_6\text{H}_5\text{NO}_2$: 2000 s, 1872 s
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3(\text{NCS})_3]$	2010 s, 1895 sh, 1870 s $\nu(\text{CN})$: 2115 sh, 2100 sh, 2090 s $\nu(\text{CS})$: 815 w	CH_3CN : 2015 s, 1900 s $\nu(\text{CN})$: 2130 s, 2110 s $\text{C}_6\text{H}_5\text{NO}_2$: 2010 s, 1892 s $\nu(\text{CN})$: 2120 sh, 2100 s
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{Cl}_4]$	2025 s, 1900 sh, 1875 s	CH_3CN : 2015 s, 1905 s, 1880 s $\text{C}_6\text{H}_5\text{NO}_2$: 2013 m, 1897 s, 1868 s
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{Br}_4]$	2020 s, 1880 s	CH_3CN : 2015 s, 1905 s, 1880 s $\text{C}_6\text{H}_5\text{NO}_2$: 2014 m, 1901 s, 1875 s

^a Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. ^b Decomposition product absorption.

 TABLE II
 INFRARED-ACTIVE RHENIUM-HALOGEN STRETCHING FREQUENCIES^a

Compound	$\nu(\text{ReX}), \text{cm}^{-1}$			$\nu(\text{ReBr})/\nu(\text{ReCl})$	$\nu(\text{ReI})/\nu(\text{ReBr})$
	Cl	Br	I		
$\text{Re}(\text{CO})_5\text{X}$	(294 m, 288 sh) ^b	(205, 202) ^b m	164 m	0.692	0.806
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}(\text{CO})_4\text{X}_2]$...	201 m	162 m	...	0.806
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$...	182 m	146 m	...	0.802
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$	282 mw	196 mw	157 mw	0.695	0.801
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$	241 m	165 m	132 m	0.685	0.800
$\text{Re}_2(\text{CO})_6\text{X}_2$	288 m	199 m	163 m	0.691	0.819
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$	240 mw	171 mw	142 w	0.712	0.830
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_7\text{X}_3]$	291 w	201 w	...	0.691	...
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_7\text{X}_3]$	272 m	190 m	...	0.698	...
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_7\text{X}_3]$	252 mw	171 m	...	0.678	...
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$	293 m	201 m	...	0.686	...
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$	251 m	170 m	...	0.677	...
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$	223 mw	158 mw	...	0.708	...

^a There are no significant differences between the Nujol mull and CsI disk spectra. Abbreviations: m, medium; w, weak; sh, shoulder. ^b Isotope splitting.

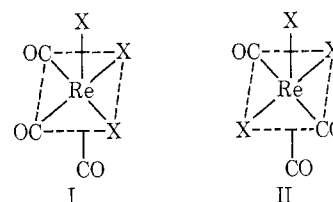
gave linear plots of Λ vs. \sqrt{C} over the range of measurement. The values of the intercept, Λ_0 , and the slope, A , are tabulated in Table III. Also given in Table III are the theoretical slopes calculated from the Onsager relation⁷ for 1:1 and 2:1 electrolytes with the measured Λ_0 .

 TABLE III
 CONDUCTIVITY DATA

Compound	$\Lambda_0, \text{ohm}^{-1} \text{cm}^2$	A	$-A(\text{theoret})$	
			1:1	2:1
Acetonitrile Solvent				
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{Cl}_3]$	166	400	352	692
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{Br}_3]$	162	312	350	685
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{I}_3]$	222	523	394	810
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3(\text{NCS})_3]$	181	599	364	724
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{Cl}_4]$	155	323	345	671
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{Br}_4]$	145	284	337	650
Nitrobenzene Solvent				
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{Cl}_3]$	35.0	216	66.8	142
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{Br}_3]$	31.5	122	68.1	134
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{I}_3]$	47.4	185	80.4	162
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3(\text{NCS})_3]$	31.0	142	67.7	133
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{Cl}_4]$	32.7	245	69.1	137
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{Br}_4]$	52.2	398	84.2	180

Discussion

$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$.—The trihalogenotricarbonylrhenate ion can have either structure I (*cis*, C_{3v}) or II (*trans*, C_{2v}). Structure I is predicted by



trans-effect arguments applied to formation of the complex from $\text{Re}(\text{CO})_5\text{X}$ and also by the *cis* arrangement of the CO groups⁵ in $\text{Re}_2(\text{CO})_6\text{L}_3^-$. It will give rise to two CO ($\nu(\text{CO}), A_1 + E$) and two metal-halogen ($\nu(\text{ReX}), A_1 + E$) infrared-active stretching modes. Structure II will have three $\nu(\text{CO})$ modes ($2 A_1 + B_1$) and three $\nu(\text{ReX})$ modes ($2 A_1 + B_2$) which are infrared active.

In nitrobenzene solution the $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$ complexes all behave as 2:1 electrolytes (Table III), although the slope for the chloro complex is somewhat high. The iodo and thiocyanato complexes in nitro-

benzene each have only two bands, both strong, in the CO stretching region at frequencies characteristic of terminal CO groups in an anionic complex (Table I). This is in agreement with structure I. Of the two bands, the lower energy one has the greater width and intensity, and we assign it as the E vibration.⁹ The bromo complex in nitrobenzene also has two strong bands in the CO stretching region, but in addition it has a weak band and a shoulder in this region. These additional features increase in intensity with time and are very close in frequency to two bands (1910, 2010 cm⁻¹) which slowly appear in the nitrobenzene solution spectrum of Re(CO)₃I₃²⁻ after ~1 hr standing in the spectrometer beam. Evidently, the bromo complex also has structure I and the extra $\nu(\text{CO})$ frequencies are due to a decomposition product. The chloro complex is like the bromo complex except that its decomposition in nitrobenzene is much more rapid and in the initial spectrum the bands due to the decomposition product are comparable in intensity with those due to Re(CO)₃Cl₃²⁻.

$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$ (X = Cl, Br, I) behaves as a 1:1 electrolyte in acetonitrile solution (Table III), and the solutions have three strong $\nu(\text{CO})$ frequencies (Table I). We attribute this to the solvolysis reaction



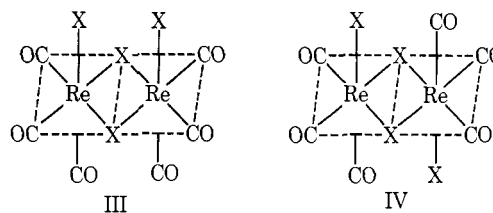
the products of which are singly charged anions. Re(CO)₃X₂CH₃CN⁻, derived from structure I, has C_s symmetry and will give rise to three $\nu(\text{CO})$ frequencies (2 A' + A''). Of the three bands observed, the pair at lower energy correspond to the A' and A'' components of the E vibration of the parent ion, and the remaining band is the A' vibration of the unique carbonyl group. Reaction of the thiocyanato complex, Re(CO)₃(NCS)₃²⁻, with acetonitrile does not appear to be appreciable. The infrared spectrum of the solution shows only two $\nu(\text{CO})$ frequencies and the conductivity results are much closer to a 2:1 than to a 1:1 electrolyte.

Solid-state infrared spectra of the $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}(\text{CO})_3\text{X}_3]$ complexes show the expected two bands in the CO stretching region with the lower energy E vibration split (15–25 cm⁻¹) by solid-state effects. In the metal-halogen stretching region (Table II and Figure 2) the required two bands are present; the lower energy one has the greater width and intensity and may be assigned as the degenerate E $\nu(\text{ReX})$ vibration. Identification of these bands as $\nu(\text{ReX})$ vibrations is based on their frequencies and the shift in passing along the sequence X = Cl, Br, I (Table II). Both of these are consistent with what is found in other rhenium carbonyl halides.

Acetonitrile and nitrobenzene solutions of Re(CO)₃(NCS)₃²⁻ have two CN stretching frequencies, $\nu(\text{CN})$ (Table I). In the solid state the E $\nu(\text{CN})$ vibration is split by 10 cm⁻¹. The solid-state spectrum also shows a weak band at 815 cm⁻¹ which is not present in the chloro, bromo, or iodo complexes. The position of this CS stretching frequency indicates that the thiocyanate

groups are N bonded.^{10,11} There is no absorption in the region (690–720 cm⁻¹) characteristic of S-bonded thiocyanate.

$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$.—This complex is expected to have a structure derived from the neutral dihalogenooctacarbonyldirhenium⁴ by replacement of two carbonyl groups by two halogen atoms. The same arguments used for Re(CO)₃X₃²⁻ predict that the CO groups on each rhenium atom will all be *cis* to each other so that the most likely structures are as represented by III and IV. Structure III has C_{2v} symmetry.



As discussed in the Appendix it should give rise to three infrared-active $\nu(\text{CO})$ and five infrared-active $\nu(\text{ReX})$ frequencies, of which two may be almost degenerate and one very weak. Structure IV has C_{2h} symmetry which allows three infrared-active $\nu(\text{CO})$ (A_u + 2 B_u) and three infrared-active $\nu(\text{ReX})$ (A_u + 2 B_u) frequencies. A five-coordinate monomer can have at most two $\nu(\text{ReX})$ frequencies.

Infrared spectra of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$ in the solid state have three bands which we assign as rhenium-halogen stretching vibrations on the basis of their frequencies and the shift on going from the chloro to the bromo complex (Table II, Figure 3). In view of the intensities and separation of these three bands, as compared to the $\nu(\text{ReX})$ bands of the other rhenium carbonyl halides (Table II), it appears very unlikely that any one of them has become infrared active because of solid-state interactions. The observation of three rhenium-halogen stretching frequencies therefore provides strong support for structure III or IV as against a five-coordinate monomeric species but does not allow a reliable distinction between III and IV.

Comparison with the $\nu(\text{ReX})$ absorptions of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_7\text{X}_3]$ suggests that the highest of the three $\nu(\text{ReX})$ frequencies of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Re}_2(\text{CO})_6\text{X}_4]$ is due to the terminal rhenium-halogen stretching vibration and that the two lower frequency bands result from the two bridge bond stretching modes (see discussion under $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Re}_2(\text{CO})_7\text{X}_3]$). In general, when a molecule contains both terminal and bridging halogen atoms, the bridging metal-halogen stretching vibrations can occur at either lower [e.g., M₂X₆²⁻ (M = Pd, Pt; X = Cl, Br, I)]¹² or higher [e.g., Mo₆X₈Y₆ (X = Cl, Br; Y = Cl, Br, I)]¹³ frequencies than the terminal metal-halogen stretching vibrations.

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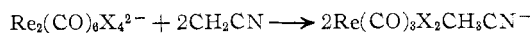
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(13) F. A. Cotton, R. M. Wing, and R. A. Zimmerman, *Inorg. Chem.*, **6**, 11 (1967).

Solid-state infrared spectra of $[(C_2H_5)_4N]_2[Re_2(CO)_6X_4]$ have two bands in the carbonyl stretching region at frequencies characteristic of terminal CO in an anionic complex. The lower energy band is much the broader and more intense of the two and is split in the chloro complex but appears unsplit in the bromo complex. We assign this band as the two (overlapped) in-plane $\nu(CO)$ vibrations of III or IV. The remaining band is then the out-of-plane $\nu(CO)$ vibration. Figure 1 illustrates the similarity between the spectra of $Re_2(CO)_6X_4^{2-}$ and $Re(CO)_3X_3^{2-}$ in the CO stretching region.

Nitrobenzene solutions of $[(C_2H_5)_4N][Re_2(CO)_6X_4]$ give three bands in the CO stretching region. However, the relative intensities of the bands and their frequencies slowly change over a 0.5-hr period. Furthermore, conductivity measurements give abnormally high slopes for the Λ vs. \sqrt{C} plots (Table III) indicating either decomposition to a more highly charged species or ion-pair formation. The infrared spectra in nitrobenzene solution may therefore not be characteristic of the dimeric dianion.

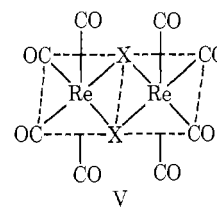
In acetonitrile solution, $[(C_2H_5)_4N]_2[Re_2(CO)_6X_4]$ behaves as a 1:1 electrolyte (Table III). The infrared spectrum of the solution in the CO stretching region is identical with that of $[(C_2H_5)_4N]_2[Re(CO)_3X_3]$ in this medium. This is attributed to a solvolysis reaction which results in the same product as the solvolysis of the monomeric dianion



$Re(CO)_5X$.—The spectra in the metal-halogen stretching region have been reported⁶ for the pentacarbonyl chloride and bromide. We have obtained the same results (Table II) except that a small (3 cm^{-1}) but reproducible splitting of the $\nu(ReBr)$ band was observed. As in the case of the $\nu(ReCl)$ band, the splitting of this nondegenerate (A_1) vibration is probably due to the presence of two isotopes, ^{79}Br and ^{81}Br (the relative abundance of ^{79}Br to ^{81}Br is 0.505:0.495). A calculation for a diatomic system in which the metal vibrates against ^{79}Br and ^{81}Br gives an isotopic splitting of 1–3 cm^{-1} as the mass of the metal is varied from 186 to ∞ . The pentacarbonyl iodide gives the expected single $\nu(ReI)$ frequency with no evidence of splitting.

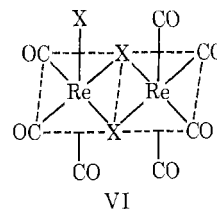
$[(C_2H_5)_4N][Re(CO)_4X_2]$.—The presence of four strong infrared bands in the CO stretching region of $Re(CO)_4X_2^-$ ($X = Br$ or I) is evidence for the *cis*-octahedral (C_{2v}) structure as opposed to the *trans*-octahedral (D_{4h}) structure.³ This *cis* geometry will also have two infrared-active $\nu(ReX)$ vibrations ($A_1 + B_1$) while the *trans* configuration will have only one such stretching mode (A_{2u}). Two well-defined $\nu(ReX)$ bands are found in the infrared spectrum of both the bromo and iodo complexes (Table II) consistent with the *cis* arrangement. The related neutral complexes $Fe(CO)_4X_2$ and $Os(CO)_4X_2$ have also been reported⁶ to have the *cis* configuration and two infrared-active $\nu(MX)$ frequencies.

$Re_2(CO)_8X_2$.—Structure V has been suggested for



these complexes ($X = Cl, Br, I$) and is supported by the infrared spectrum in the CO stretching region.⁴ A single-crystal X-ray diffraction study¹⁴ of the analogous manganese complex, $Mn_2(CO)_8Br_2$, has shown it to have this structure. The point group symmetry of V is D_{2h} and it should have two infrared-active rhenium-halogen stretching vibrations (B_{2u} and B_{3u}). In agreement with this we find just two bands (Table II) which can be assigned as $\nu(ReX)$ frequencies ($X = Cl, Br, I$).

$[(C_2H_5)_4N][Re_2(CO)_7X_3]$.—These complexes presumably have a structure derived from V by replacing one of the CO groups with a halogen atom. *trans*-Effect arguments applied to formation of the complex from $Re(CO)_5X$ suggest that the halogen atoms occupy positions *cis* to each other. The most likely structure is VI, which has C_s symmetry. Five $\nu(ReX)$ (see Appendix



and seven $\nu(CO)$ vibrations are infrared active in this structure. We find three bands (Table II) which can be assigned as $\nu(ReX)$ frequencies ($X = Cl$ or Br). The highest energy band of the three is much weaker than the other two, which have a relative intensity pattern similar to the two $\nu(ReX)$ bands in $Re_2(CO)_8X_2$ and the two lower energy $\nu(ReX)$ bands in $Re_2(CO)_6X_4^{2-}$. In the latter, where there are an equal number of terminal and bridging atoms, the highest frequency $\nu(ReX)$ is no longer weak compared to the two lower frequency bands. We therefore assign the highest energy band as a terminal $\nu(ReX)$ frequency and the two lower energy bands as bridging $\nu(ReX)$ frequencies in both $Re_2(CO)_7X_3^-$ and $Re_2(CO)_6X_4^{2-}$. Two additional bridging $\nu(ReX)$ vibrations expected for structure VI were not identified. The CO stretching region of $[(C_2H_5)_4N][Re_2(CO)_7X_3]$ was studied³ in chloroform solution. Low solubility prevented the measurement of satisfactory spectra, and only four clear maxima could be distinguished.

Shift in $\nu(ReX)$ for Varying X.—It is worth noting the approximate constancy of the ratios $\nu(ReBr)/\nu$

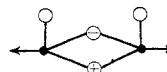
(ReCl) and $\nu(\text{ReI})/\nu(\text{ReBr})$ (Table II); these fall, respectively, in the ranges 0.68–0.71 and 0.80–0.83. For a diatomic M–X system in which only the reduced mass changes in passing along the sequence X = Cl, Br, I, the calculated ratios are $\nu(\text{ReBr})/\nu(\text{ReCl}) = 0.72$ and $\nu(\text{ReI})/\nu(\text{ReBr}) = 0.86$.

Appendix

Under its full point group symmetry (C_{2v}), structure III should give rise to five infrared-active $\nu(\text{CO})$ ($2 A_1 + 2 B_1 + B_2$) and five infrared-active $\nu(\text{ReX})$ ($2 A_1 + 2 B_1 + B_2$) bands. In the case of the CO vibrations, it is likely that interaction between the halves of the anion will be negligible. As a consequence, the two out-of-plane $\nu(\text{CO})$ vibrations (A_1^a and B_1^a) should be degenerate. Two of the in-plane $\nu(\text{CO})$ vibrations (A_1^b and B_1^b) should also be degenerate. We therefore expect that III will give rise to three infrared bands in the CO stretching region: ($A_1^a + B_1^a$), ($A_1^b + B_1^b$), and B_2 . The same conclusion is reached by the method of local symmetry in which the $\nu(\text{CO})$ frequencies are considered to arise from an $\text{Re}(\text{CO})_3\text{X}_3$ group having C_s symmetry.

By a similar argument, the two terminal $\nu(\text{ReX})$ vibrations (A_1^a and B_1^a) should be degenerate. The three remaining $\nu(\text{ReX})$ frequencies are vibrations of

the bridging halogen atoms. The A_1^b mode may be drawn as below.¹⁵ It does not involve a change in



dipole moment but must obtain intensity by coupling with the A_1^a vibration. If the coupling is appreciable, the degeneracy of the A_1^a and B_1^a vibrations will be lifted and the spectrum should show five bands in the ReX stretching region. If the coupling is weak the A_1^b vibration will not have much intensity and the A_1^a and B_1^a vibrations will remain nearly degenerate. In this case, only three $\nu(\text{ReX})$ frequencies might be observed.

Consideration of the full point group symmetry (C_s) for structure VI predicts five infrared-active $\nu(\text{ReX})$ frequencies ($3 A' + 2 A''$). None of these is expected to be degenerate, and examination of the symmetry modes indicates that they are all associated with a change in dipole moment.

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Laser Raman Spectra of a Single Crystal of Sodium Nitroprusside and the Vibrational Frequencies of the $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ Ion^{1a}

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The Raman spectra of an oriented single crystal of sodium nitroprusside excited by 6328-Å radiation from an He–Ne laser have been investigated in detail. The infrared absorption spectra of the polycrystalline sample have also been recorded at room temperature as well as at liquid N_2 temperature. The analysis of the data in the light of the crystal structure and earlier spectral data has enabled us to assign many of the vibrational frequencies of the $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ ion.

Introduction

There has been considerable interest, during the past few years, on the study of the vibrational spectra of the coordination complexes of transition metals. Among a large number of reports, mention may be made of the works on the infrared and Raman spectra of some metal cyanide complexes of the types $\text{M}(\text{CN})_2$, $\text{M}(\text{CN})_4$, $\text{M}(\text{CN})_6$, and $\text{M}(\text{CN})_8$.^{2–6} From the analysis of the

spectra several interesting conclusions on the nature of the metal–ligand bond and its correlation with the CN bond strengths were drawn. The assignments of the infrared-active vibrational frequencies reported in most of the above studies tend to be somewhat ambiguous because of insufficient data. One reason is that most of the transition metal cyanides are highly colored; consequently, their Raman spectra excited by the conventional Hg-arc sources are incomplete. However, with the availability of the laser sources (particularly, the He–Ne laser giving intense monochromatic radiation of λ 6328 Å), the Raman spectra of many colored substances can be recorded routinely. Also, the collimated and the polarized nature of the laser beam allows excitation of the Raman spectra of a properly oriented single crystal giving the different polarizability (derivative) components for a normal

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