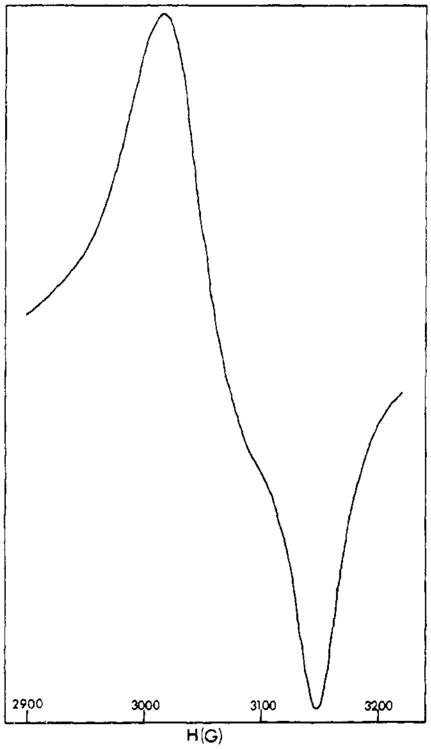

**Figure 2.** Epr spectrum of (carnosine)copper; R, T, and X bands.

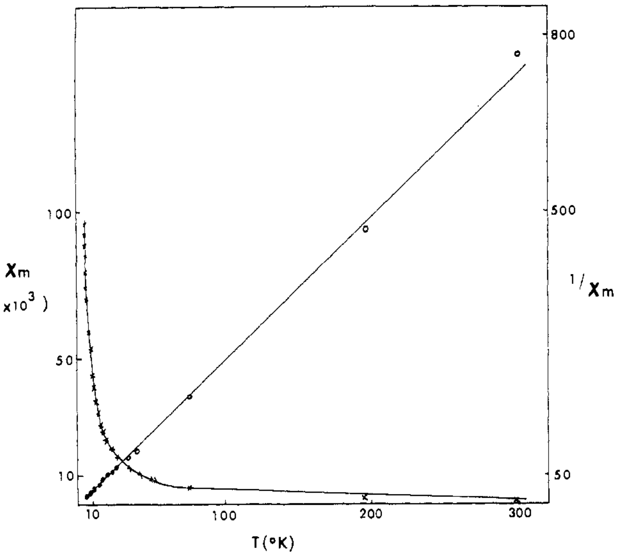

**Figure 3.** Magnetic susceptibility dependence on $T$ of (carnosine)copper.

it is 3-3.5 Å. The copper-carnosine compound that we report here has a Cu-Cu separation of about 4 Å.

The room-temperature and 77°K epr spectra are consistent with a $C_{4v}$ symmetry for each Cu(II) ion in the dimer. The electronic spectrum is also consistent with an axial symmetry approximately $D_{4h}$ or $C_{4v}$. There is no evidence of spin interactions from these spectra nor from the frozen solution epr spectrum. $H_{\min}$, usually in the 1500-G region of the epr spectra of spin-coupled copper compounds, was also absent for the copper-carnosine system.

The magnetic susceptibility is most revealing. This compound follows the Curie law from room temperature to 4°K. This is indicative of no spin interactions between the Cu(II) ions in the dimer. Furthermore, the usual Weiss constant $\Theta$ is 0 in this case which can be interpreted as a lack of spin interactions among Cu(II) ions in different dimers.

Apparently, the Cu-Cu separation in the dimer is too large for intradimer spin coupling through space since the dipolar coupling increases as an inverse function of distance. Also, the possible spin delocalization through the bridging ligands is not effective in this case because there are two successive carbon atoms with sp$^3$ hybridization which will stop any $\pi$ type spin delocalization (see Figure 1). The $\sigma$-bond type coupling is expected to be negligible in this case where there are six intervening atoms between the two Cu(II) ions. Finally, the organic skeleton and water molecules surrounding the Cu(II) ions are bulky enough to dictate large separations among the metal ions in different dimers, therefore, stopping any intermolecular interactions.

This is, then, the first well-documented example of a completely magnetically dilute Cu(II) dimer free from intra- and interionic spin coupling, rather different from the now well-known cases of spin-coupled (dimethylglyoxime)copper and (diethyldithiocarbamato)copper dimers.

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**Registry No.** (Carnosine)copper dimer, 51095-95-5.

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# Resonance Raman Effect and Far-Infrared Spectra of Rhodium-Doped Silver Bromide Crystals

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Considerable interest has been shown in the study of impurity-induced vibrational spectra, particularly in alkali halides, silicon, and some group III-V compounds. Similar studies on silver halides have not been extensive owing to difficulties in instrument sensitivities, sample handling, and the solubilities of impurities in the host lattice. With improved instrumentation for the far-infrared spectrum and taking advantage of a resonance Raman effect, we have been able to observe the far-infrared and laser Raman spectra in rhodium-doped silver bromide crystals.

Large boules of high-purity silver bromide doped with 200 ppm of rhodium tribromide were grown by the standard Bridgman method. These impurity-doped silver bromide samples were light sensitive and corrosive and were handled with care under red light. The Rh ion concentration was determined by atomic absorption spectroscopy. The far-infrared absorption spectrum has been measured in the 10-500-cm$^{-1}$ spectral region using a Fourier transform spectrometer, Polytec Model 30, at a resolution of ~0.5 cm$^{-1}$. The Raman spectra were recorded with a Spex Ramalog spectrometer that has photon-counting capabilities and is equipped with an argon and a krypton laser from Coherent-Radiation Laboratories. All spectra presented here were measured at 20°K by using a Cryogenic Technology closed-cycle refrigerator, Model Spectrim II, and quartz optics. The optical spectra of single-crystal specimens were obtained at 77°K from thin (~0.02 in.) AgBr sheets using a standard Cary Model 14 spectrophotometer. $Cs_3RhBr_6$ was prepared by dissolving $K_3RhBr_6$ in a 1:1 HBr solution and adding an aqueous solution of CsBr to form the precipitate.

Figure 1 shows the far-infrared spectrum of rhodium-doped AgBr at 20°K. The sample thickness was approximately 3 mm. The spectrum consists of three closely spaced absorption lines at 246.4, 248.8, and 253.8 $cm^{-1}$. These lines occur on the shoulder of the intense phonon bands of the host crystal[1] which are centered at about 100 $cm^{-1}$. The absorption peak at 246.4 $cm^{-1}$ appears to be split into two components, with maxima at 245.5 and 246 $cm^{-1}$. The room-temperature spectrum (not shown) consists of a strong band at 245 $cm^{-1}$ with a very weak shoulder at 253 $cm^{-1}$. The Raman spectrum of the same crystal at 20°K is shown in Figure 2. It consists of three distinct peaks: a strong one at 183 $cm^{-1}$, a medium-intensity line at 171 $cm^{-1}$, and a weaker line at 136 $cm^{-1}$. At room temperature, the bands are much weaker in intensity, the line at 136 $cm^{-1}$ disappearing altogether, possibly obscured by the high background of the exciting laser line. All these impurity lines are much stronger than the second-order Raman spectrum of AgBr[2] (first-order spectra being forbidden in pure crystals with $O_h$ symmetry at each lattice site).

The vibrational spectra presented in this note may be interpreted in terms of the following model. The rhodium ion in the trivalent state[3] enters the AgBr lattice substitutionally and is covalently bonded to its six nearest-neighbor bromide ions to form an octahedral complex $RhBr_6^{3-}$. The existence of this molecular complex in silver bromide photographic emulsion has been demonstrated by analytical methods.[4] The isolated ion $RhBr_6^{3-}$ has octahedral symmetry and is expected to exhibit six fundamental vibrational modes.[5] Two of these are infrared active: the deformation mode $\nu_3$ and the bent-stretch mode $\nu_4$. They are both of $F_{1u}$ symmetry. Three of the modes are Raman active: the total symmetric stretching mode $\nu_1$ (symmetry $A_{1g}$), the asymmetric stretching mode $\nu_2$ ($E_g$), and the deformation mode $\nu_5$ ($F_{2g}$). The remaining bending mode $\nu_6$ ($F_{2u}$) is neither infrared nor Raman active. These vibrations may be modified when the ion is imbedded in a crystal lattice owing to site group splittings, correlation field effects between adjacent dopant molecular ions, interactions between the vibrations of the host and dopant, and distortion of the dopant molecule by associated silver ion vacancies. There are many examples of similar studies of impurity-doped alkali halides (*e.g.*, $CrO_4^{2-}$ in KX in ref 6), where the vibrational characteristics of the system are discussed in terms of the vibrational characteristics of the dopant molecule modified by being imbedded in a host lattice.

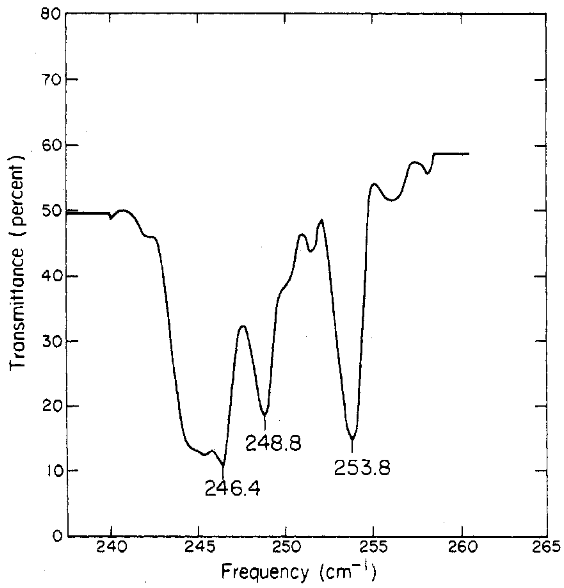

**Figure 1.** Far-infrared spectrum of a single crystal of AgBr doped with 200 ppm of $RhBr_3$. Spectrum is taken at 20° K.

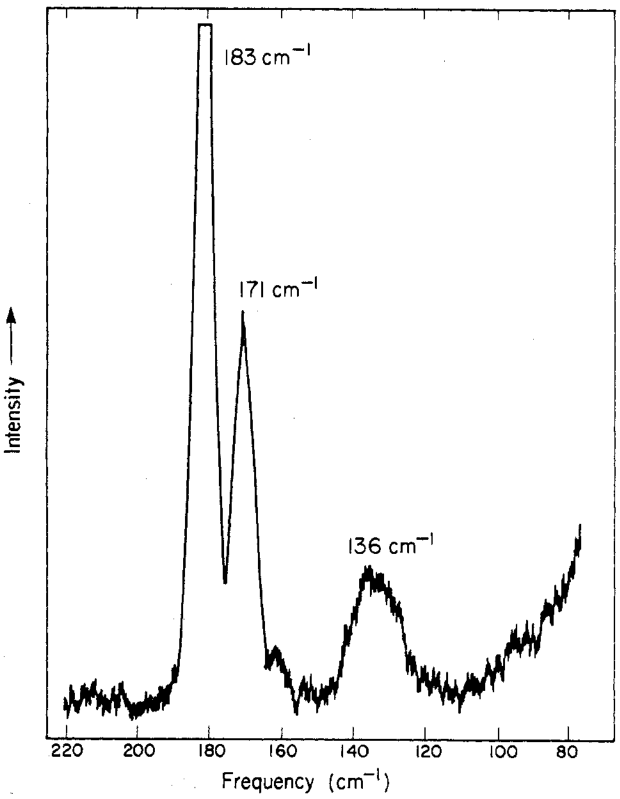

**Figure 2.** Raman spectrum of a single crystal of AgBr doped with 200 ppm of $RhBr_3$. Spectrum is taken at 20°K with a 5682-Å krypton line as the exciting source.

Studies of the vibrational spectra of hexabromo complexes of various transition metal ions have been published.[7,8] From these studies one can assign the observed Raman lines to $\nu_1$ (183 $cm^{-1}$), $\nu_2$ (171 $cm^{-1}$), and the $\nu_5$ (136 $cm^{-1}$) fundamentals. The observed far-infrared absorption lines can be ascribed to $\nu_3$, the triple degeneracy being partially

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lifted at room temperature and more completely lifted at low temperatures. Every $Rh^{3+}$ ion brings two extra positive charges into the lattice and causes the Frenkel equilibrium to shift in favor of increased concentration of silver ion vacancies. At the low temperatures used in these experiments, the vacancies are expected to be coulombically bound to the $RhBr_6^{3-}$ ion, but they can dissociate partially or completely as the temperature is raised. Examples of this vacancy association process are found in the esr studies of vanadium in silver chloride,[9,10] ferric ions in AgCl and AgBr,[11,12] and chromium in AgCl.[13] The two vacancies associated with $RhBr_6^{3-}$ at 20°K lower the symmetry of the impurity center and result in the lifting of the triplet degeneracy. The room-temperature data where only two lines are observed have been attributed to the partial dissociation of the vacancies from the center. As mentioned earlier, other interactions can also contribute to this splitting. It is conceivable that the coupling between the $\nu_3$ mode of $RhBr_6^{3-}$ and the nearby intense lattice vibration of the host AgBr contributes significantly to the splittings. Except for the effects of the vacancies mentioned above, $RhBr_6^{3-}$ in the AgBr lattice has the same symmetry as the isolated molecule, and no site-group splitting is expected. At the low dopant concentrations employed in this study (200 pm) the correlation field interactions cannot be very important and have not been detected by epr experiments.[3]

Calculations show that the bromide isotope effect can be responsible for the splitting of the 246.4-$cm^{-1}$ line. The other ir-active mode $\nu_4$, expected to have a frequency of around 100 $cm^{-1}$, has not been observed because of the intense lattice absorption of the host crystal in this spectral region. Reflectivity studies are currently under way to search for this band.

To substantiate these assignments further, the frequencies are compared in Table I with those measured for $Cs_3RhBr_6$.

The assignment of 136 $cm^{-1}$ as $\nu_5$ is somewhat tenuous, since the $\nu_5$ of $PtBr_6^{2-}$ is at 97 $cm^{-1}$,[14] and that of $ReBr_6^{2-}$, at 112 $cm^{-1}$.[15] The relative broadness of the band suggests it may be an impurity-induced multiphonon band of AgBr.

The optical spectrum of single crystals of rhodium-doped AgBr at 77°K is similar to one taken at ambient temperatures.[3] The broad absorption peaked at 550 nm has been attributed to the spin-allowed ($^1A_1 \rightarrow {}^1T_1, {}^1T_2$) transition. It is noted that this electronic transition of the scattering molecule occurs at the wavelength of the exciting light (5682 Å); hence, one expects to observe the resonance Raman effect (RRE). The high intensity of the fundamental observed in the Raman spectrum with 5682-Å irradiation is believed to be a manifestation of the RRE. A comparison of the preresonance Raman effect with the RRE is not possible because of the broadness of the electronic absorption band and because of the available laser exciting lines. However, the relative peak intensities of the Raman-scattered lines with the exciting laser lines have been studied. It is observed that as the exciting line moves away from the absorption maximum at 550 nm, the ratio of the intensity of $\nu_1$ to $\nu_2$ decreases. This is in agreement with the contention[16,17] that in RRE the totally symmetric vibration ($\nu_1$ in this case) is preferentially enhanced. No overtone progression has been observed, although a number of authors[10,11] have reported their appearance in conjunction with the observation of RRE. Further work is in progress to look for these overtones, although the appearance of such progressions is not a necessary condition for the observation of RRE.

**Table I.** Vibrational Frequencies ($cm^{-1}$) and Assignments

| AgBr/Rh (20°K) | AgBr/Rh (300°K) | $Cs_3RhBr_6$ (300°K) | Assignment |
|---|---|---|---|
| 246.4 | 245 | 253 | $\nu_3$ ($F_{1u}$) |
| 248.8 | | | |
| 253.8 | 251 | | |
| | | 130 | $\nu_4$($F_{1u}$) |
| 183 | 183 | 185 | $\nu_1$ ($A_{1g}$) |
| 171 | 171 | 164 | $\nu_2$ ($E_g$) |
| 136 | | | $\nu_5$ ($F_{2g}$) |

**Registry No.** AgBr, 7785-23-1; Rh(III), 16065-89-7; $Cs_3RhBr_6$, 50986-67-9.

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Contribution from Ames Laboratory–USAEC and the Department of Chemistry, Iowa State University, Ames, Iowa 50010

## Synthetic and Nuclear Quadrupole Resonance Study of Chlorodiiodinium Hexachloroantimonate(V), $I_2Cl^+SbCl_6^-$

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The $I_2Cl^+$ ion was evidently first postulated to account for the properties of appropriate solutions of $HIO_3$, $I_2$, and ICl in sulfuric acid.[1] Later work in this laboratory established that the reported[2] phase $2ICl{\cdot}AlCl_3$ not only had the indicated stoichiometry but also was correctly formulated as $I_2Cl^+AlCl_4^-$, the assignment being based on its halogen nqr and aluminum nmr spectra relative to those of $ICl_2^+$-$AlCl_4^-$, $I_3^+AlCl_4^-$, and $I_5^+AlCl_4^-$.[3] The work reported herein was undertaken to examine the possible formation of similar cations in the system $I_2$-ICl-$SbCl_5$. The only solid phase stable at room temperature is, however, $2ICl{\cdot}SbCl_5$. This compound does exhibit an unusually strong nqr spectrum for all isotopes possible ($^{35}Cl$, $^{37}Cl$, $^{121}Sb$, $^{123}Sb$, $^{127}I$) which allows appreciable information to be deduced regarding not only its formulation as $I_2Cl^+SbCl_6^-$ but also interactions in the solid structure. A different synthesis and Raman data for the same compound have recently also been reported by Shamir and Lustig.[4]

### Experimental Section

Commercial $SbCl_5$ (Research Inorganic/Organic Chemical

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