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(12) It may be useful to distinguish between a "synthetic model" and a "synthetic analogue". The latter is a very close structural facsimile of the metal coordination in a metalloprotein with respect to ligand type, geometry, and physical properties while a model may mimic certain aspects only.

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Homonuclear Bonds in Sulfur–Selenium Mixed Crystals: A Raman Spectroscopic Study

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Both sulfur and selenium have at least one allotropic form in which they exist as S_8 and Se_8 (eight-membered) rings, respectively. Also, they are known to form "mixed crystals" as compounds of general formula Se_nS_{8-n}.[1] Single-crystal X-ray studies, done at this institute[2] and other laboratories,[3] indicate that these mixed crystals also consist of eight-membered rings. Further information about the structure of the moieties present in these mixed crystals could not be obtained by the X-ray studies as the crystals were found to be disordered systems. The disorder is believed to be due to orientational disorder and/or the presence of different Se_nS_{8-n} species at the crystallographically equivalent sites. One of the important but still unresolved questions in this subject is whether homonuclear bonds are present in these mixed crystals, particularly in the systems with low selenium or low sulfur content. Mass spectroscopic studies are also not able to answer the above question as the Se_nS_{8-n} compounds are thought to rearrange in the mass spectrometer.[4,5] Vibrational spectroscopy can give direct information about the conformation of molecules by the observation of characteristic frequencies for the different bonds and groups. Therefore, we have started a study of the vibrational spectra of these mixed crystals in order to gain structural information about the molecular units in the Se_nS_{8-n} mixed crystals. Here we report a Raman spectroscopic investigation of these systems undertaken to investigate the presence of Se–Se and S–S homonuclear bonds in these mixed crystals.

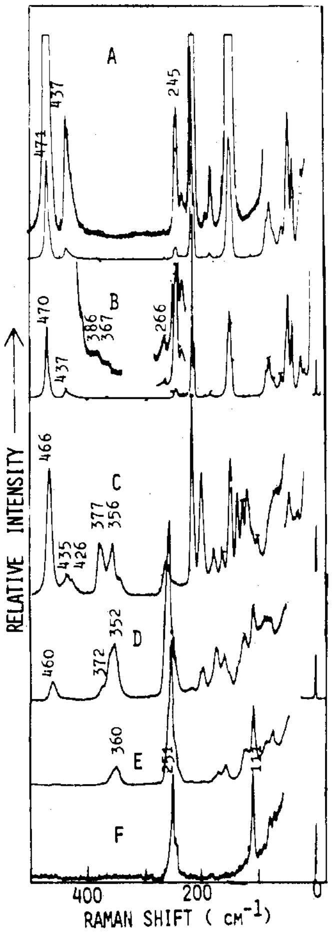

Figure 1. Raman spectra of polycrystalline samples at room temperature: (A) pure S_8 crystals (upper trace recorded at a gain 10 times that for the lower trace); (B) $Se_{0.05}S_{7.95}$ crystals (two upper traces recorded at gains 10 and 30 times, respectively, that for the lower trace); (C) $Se_{1.5}S_{6.5}$ mixed crystals; (D) $Se_{4.1}S_{3.9}$ mixed crystals; (E) $Se_{5.9}S_{2.1}$ mixed crystals; (F) pure Se_8 crystals. Exciting line is shown in spectra B–F.

Experimental Section

Materials. The polycrystalline samples were obtained by fractional crystallization of (a) commerical "SeS_2" obtained from Merck[2] and (b) the glassy products obtained from melts of equimolar amounts of sulfur and selenium.[3-5] The Se_nS_{8-n} mixed crystals were analyzed for their Se content by iodometric titrations. Many samples were double checked by gravimetric determination of their sulfur content as barium sulfate.

Spectra. Raman spectra of crystalline samples were obtained by using ~120 mW of 6328-Å radiation of a He–Ne laser (OIP, Gent). Cary 81 and Coderg PH1 monochromators were used. Both instruments are equipped with RCA C31034 photomultipliers, Servogor 5 strip-chart recorders, and necessary electronics. Spectra were recorded with a dc amplification system. Usual 90° scattering geometry was employed, but the incident laser radiation was focused as a line on the sample rather than as a point to avoid local heating of the colored samples. This was achieved with a combination of a cylinder lens and a convex lens in the incident beam. The polycrystalline samples were contained in a rectangular glass cell with flat walls which was placed at ~45° to both the incident radiation and the entrance slit. The frequency scale was calibrated by using the laser-emission lines and a Ne lamp.

Results and Discussion

Raman spectra of a few representative compositions of Se_nS_{8-n} mixed crystals, as polycrystalline samples, are shown in Figure 1. This figure also contains the spectra of pure S_8

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and Se_8 samples, for the purpose of comparison. These spectra were recorded at a resolution of ~ 2 cm^{-1}. The frequency values of the features marked in Figure 1 are accurate to ± 2 cm^{-1}. The strong band around 470 cm^{-1} in pure S_8 has been assigned to S–S stretching vibrations.[6-8] The bands at and below 244 cm^{-1} in S_8 are due to the deformation modes of S_8 rings. The Se–Se stretching vibration is assigned to the band at 251 cm^{-1} in pure Se_8.[9,10] All of the Se_8 deformation vibrations occur at and below 111 cm^{-1} (Figure 1). Many additional features are seen in the spectra of Se_nS_{8-n} mixed crystals.[11,12] The spectra can be classified into two groups: (i) the band(s) around 360 cm^{-1} and (ii) the bands below 220 cm^{-1} (Figure 1). The first group is easily assigned to S–Se stretching vibrations.[12,13] The second group arises from the skeleton deformations of Se_nS_{8-n} ring systems. Thus, it is clear from the above discussion that S–S, S–Se, and Se–Se stretching vibrations appear in the Raman spectra of sulfur–selenium eight-membered rings in the regions where their presence can be unambiguously established.[13] This brings us to the central point of this communication that the band corresponding to Se–Se stretching vibrations is seen in all of the Se_nS_{8-n} mixed-crystal spectra (Figure 1), indicating thereby the existence of Se–Se *homonuclear bonds* in these crystals. This is contrary to the published reports that the Se_nS_{8-n} mixed crystals should not contain Se–Se bonds.[4,14] The Se–Se stretching band is seen at a slightly higher frequency in the Se_nS_{8-n} compounds than in the pure Se_8 rings (Figure 1). Thus there is no possibility of this band being due to a skeleton-deformation mode. The fact that the Se–Se stretching band is seen at slightly higher frequency in the mixed crystals than in the pure Se_8 system also suggests that the band is primarily due to the stretching vibrations of neighboring Se atoms in rings containing both Se and S and does not arise only from Se_8 impurity, if any is present in the mixed-crystal samples. The conclusion that the Se–Se stretching band seen in the Raman spectra of "low Se content" sulfur–selenium mixed crystals (spectra B–D in Figure 1) cannot be due *only* to the Se_8 impurity is also supported by the fact that the Se–Se stretching band around 250 cm^{-1} and the Se_8 skeleton-deformation band around 110 cm^{-1} have nearly equal intensities in the Raman spectrum of Se_8 (spectrum F in Figure 1). But the intensity of the Se–Se stretching band in the Raman spectra of mixed crystals with low selenium content is many times greater than the intensity of any feature seen around 111 cm^{-1} in their spectra (Figure 1). This indicates that a major part of the intensity of the Se–Se stretching band in these mixed crystals *must* arise from Se_nS_{8-n} moieties *other than* Se_8 but having Se–Se bonds. Clearly the variation in the intensities of these two bands indicates that any argument based on the assignment of the two bands to only one chemical species, namely, Se_8 impurity, has to be completely discarded. We have studied Se_nS_{8-n} mixed crystals of more than 20 different compositions and recorded the spectra of each sample several times, on two different spectrometers. The samples with as low a selenium content as to give a nominal composition of $Se_{0.05}S_{7.95}$ also showed the "Se–Se stretching band" (Figure 1). These spectroscopic results indicate that selenium–sulfur moieties containing *homonuclear* Se–Se bonds are easily formed even in those mixed crystals in which there is nominally only one selenium atom per twenty rings. On the other hand, the S–S stretching band was not seen if the nominal content of sulfur dropped below that in Se_6S_2 (Figure 1). The near absence of the S–S stretching band in the spectrum of Se_6S_2 (spectrum E in Figure 1) cannot be accounted for only on the basis of the fact that the S–S stretching vibration is expected to be weaker than the Se–Se stretching vibration in the Raman spectrum. Our studies using an internal standard ($HgCl_2$) indicate that the Se–Se bonds are nearly 10 times stronger Raman scatterers than the S–S bonds in these mixed crystals if one uses the 6328-Å He–Ne line as the exciting radiation (the radiation used in the present work). This is consistent with the expected higher polarizability for the Se–Se bonds compared with that for the S–S bonds and can also be seen from the spectrum of $Se_{4.1}S_{3.9}$ (spectrum D in Figure 1) which should contain a nearly equal number of S–S and Se–Se homonuclear bonds. The above observations suggest that the formation of S–S homonuclear bonds is not favored in sulfur–selenium mixed crystals with low sulfur content.

It is known that the dissociation energies of the various bonds in the systems are in the order S–S > Se–S > Se–Se.[14] Also, sulfur and selenium molecules are known to break into radical fractions even at room temperature.[15] The existence of Se–Se bonds in the Se_nS_{8-n} ring systems with low selenium content can be explained by assuming that after one Se atom has been introduced into a sulfur molecule, the next Se atom radical can attack this moiety easily at a Se–S bond rather than at a S–S bond, leading to the formation of a Se–Se bond. On the other hand, in a selenium-rich system, an incoming S-atom radical will preferably break a Se–Se bond rather than a S–S or S–Se bond, which results in a lower probability for the formation of S–S homonuclear bonds in a system with low sulfur content.

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EPR Evidence for the Formation of the Mixed-Chelate (Diethyldithiocarbamato)(diethyldithiophosphato)copper(II) Complex in Solutions

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Diethyldithiocarbamate (dtc$^-$) and diethyldithiophosphate (dtp$^-$) anions are typical bidentate ligands which form four-membered chelate ring structures with various metal ions.[1] Cu(II) complexes of these ligands with a bis-chelate coor-

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