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The Solid-State Spectra of Several Rhodizonates[1)]

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Synopsis. The charge-transfer transitions between the anions were observed in the absorption spectra of alkali-metal rhodizonates in the solid state. Ammonium ions enhanced the electronic transition of this kind, whereas the solid-state spectrum of the barium salt was similar to the solution spectrum of the rhodizonate ion.

More than a decade ago, West *et al.* pointed out that the oxocarbons with a general formula of $C_nO_n^{2-}$ may be considered as a new class of aromatic compounds.[2)] The assignment of the vibrational spectra confirmed the presence of aromaticity in the dianion of rhodizonic acid ($C_6O_6^{2-}$).[3)] The electronic spectra of the rhodizonates have often been observed in aqueous solutions.[4)] Though the absorption spectra for the crystals are lacking, some salts are strikingly characterized by deep coloration in the solid state. In order to clarify the electronic structure of these rhodizonates, we attempted to obtain the absorption spectra of the salts in the solid state.

Experimental

The lithium, sodium, potassium, and ammonium rhodizonates were prepared from inositol and the corresponding acetates by the method developed by Preisler and Berger.[5)] The rubidium, cesium, and strontium salts were prepared by the metathesis reaction of the lithium salt. Commercial barium salt was used without further treatment. The absorption spectra of the solid rhodizonates were obtained by applying the Kubelka-Munk function to the diffuse reflection spectra of the samples dispersed in sodium chloride. The gross spectral shapes were in good accordance with those derived from the transmission spectra of the Nujol mulls.

Results and Discussion

Figure 1 shows the absorption spectra of three typical rhodizonates in the solid state. The solution spectrum of rubidium rhodizonate is therein compared to them. As may easily be seen, the solid-state spectrum of the brown barium salt has a close resemblance to that of the aqueous solution. In both absorption spectra, there is a distinct and isolated band in the visible region. The absorption maximum of this principal band is located at 20800 cm^{-1} in the solution spectrum and is followed by an accompanying shoulder near 22700 cm^{-1}. It has been suggested that such a doublet structure is due to the Jahn-Teller distortion in the excited state.[2)] On the basis of the similarity to the solution spectrum, the first absorption band of the barium salt is attributable to the intramolecular transition of the rhodizonate ion except for the perceptible absorption tail on the low-energy side. The corresponding peak and shoulder are present at 19800 and 22500 cm^{-1} respectively in the spectrum of the solid barium salt. The absorption spectrum of the red-brown strontium salt is of the same type as that of the barium salt.

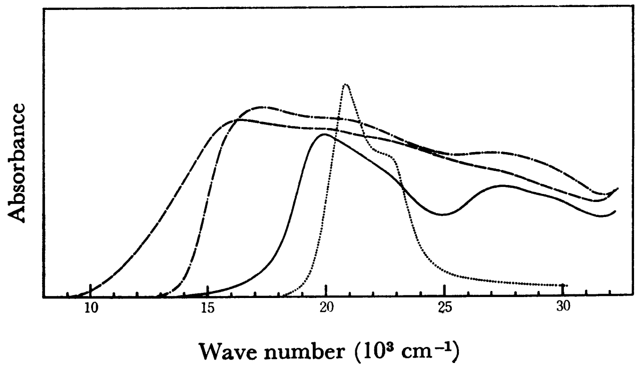

Fig. 1. The absorption spectra of the solid barium (——), rubidium (-·-·-), and ammonium (——) rhodizonates, and the aqueous solution of rubidium rhodizonate (····).

On the contrary, the solid rubidium rhodizonate appears almost black; indeed, it exhibits quite a different spectrum, one in which the principal band is considerably diffused around 20000 cm^{-1}. Here, it must be noted that the principal band is noticeably preceded by an intense new absorption band probably centered at about 17000 cm^{-1}. This additional band was found neither in the spectrum of the solid barium salt nor in the solution spectrum. The low-energy portion of the spectrum was found by diffuse reflection spectroscopy to diminish gradually when the sample was ground with sodium chloride. That is, the intensity ratio of the principal band to the additional one increases by this treatment. From this viewpoint, the interionic character of the latter band is strongly supported for this salt. Such a peculiar feature is substantially common to all alkali-metal salts except for the lithium salt, though the colors of the salts vary from the dark green of sodium salt to the dark violet of potassium and cesium salts.

Another clue to this effect is given by the crystal structure of rubidium rhodizonate as determined by X-ray diffraction.[2)] This salt forms a layer-type structure with the planar anions arranged in stacks. A more interesting finding was that the carbon atoms of anions in the adjacent layers approach each other quite closely. The separation distance is 3.30 Å, which is closer than the van der Waals distance. Such a crystal structure is a replica of the crystalline TCNQ (Tetracyanoquinodimethane) anion-radical salt, where the TCNQ anions are stacked face-to-face in the same columns.[6)]

If one remembers that the charge-transfer occurs between the TCNQ anions in the crystal and induces the absorption band in the near infrared region,[7)] the same effect can be expected in the rubidium rhodizonate crystal. In other words, it may be reasoned by analogy with the columnar structure and the related electronic spectrum of the solid TCNQ salt that the additional absorption band found in the solid-state spectrum of rubidium rhodizonate can be assigned with little difficulty to the charge-transfer transition between the adjacent rhodizonate anions. It must have been this kind of absorption band that MacIntyre and Werkema predicted for the solid potassium squarate ($K_2C_4O_4$).[8] They concluded that the formation of the charge-transfer self-complex can be nicely represented by a crystal structure similar to that of the TCNQ salt.

The black ammonium rhodizonate crystal has similar spectral features, with the additional charge-transfer band further broadened to the lower-energy side. This fact is suggestive of the closer stacking of the rhodizonate anions in the solid. As in the ammonium croconate crystal ($(NH_4)_2C_5O_5$),[9] each ammonium ion is supposedly bonded to two oxygen atoms in the molecular plane below the nitrogen atom, and to two more oxygen atoms in the plane above, so as to enhance the charge-transfer interaction between anions. The charge-transfer band of the dark green lithium salt is similarly broadened.

On the other hand, the proposed structure of the barium salt is a chain polymer,[10] in which each rhodizonate ion is chelated to two different barium ions, giving a square planar arrangement of oxygen atoms about the barium ion. Since such a structure does not always coincide with the most favorable arrangement for the interaction between the anions in the different chains, the long absorption tail of the barium salt may be a result of the weakened interionic charge-transfer interaction. In all cases, the principal band is preserved around 20000 cm^{-1}.

So far, the appearance of the charge-transfer band between the same kind of ions in the crystal has been considered as one of the most distinguished characteristics of the organic ion-radical salt. In conclusion, it should be emphasized that such diamagnetic compounds as alkali-metal rhodizonates also exhibit pronounced charge-transfer bands between anions in the solid state.

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