The Single-crystal Absorption Spectra of the Basic Rhodo Chromic Perchlorate

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In several spectroscopic studies [1-5] concerned with the binuclear complexes of chromium(III), it has been found that the basic rhodo chromic complex, $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5]^{4+}$, shows some unfamiliar sharp absorption bands in the near-ultraviolet region. Previously, one of the present authors (Y. K.) has reported[6] that these sharp bands are strongly polarized. Recently, the crystal structure of the basic rhodo chromic chloride has been determined.[7,8] In the present communication, the polarized absorption spectra of the basic rhodo chromic complex salt related to the orientation of the dimeric unit will be reported.

The basic rhodo chromic complexes are situated on the centers of symmetry in the orthorhombic (space group *Pbca*) system of the chloride crystal, and the chromium atoms are located at $x=\pm 0.62$, $y=\pm 1.11$, and $z=\pm 1.27$ (Å) if we take the point of origin as the symmetry center.[7] Unfortunately, the crystals, although they exhibit a dichroism (blue—through the light polarized parallel to the *a* axis, greenish blue—parallel to the *c* axis), are unsuitable for study by means of the microspectroscopic technique because of their shapes. However, a similar dichroism can be observed more distinctly on the thin plates of the perchlorate crystals, which *are* suitable for the microspectroscopic study. As the color of the chloride crystals has been related to the orientation of the complex, it seems reasonable to say that the absorption parallel to the four-fold rotation axis of the complex contributes greatly to the polarized absorption spectrum along the extinction direction of the perchlorate crystal, which shows greenish blue with the polarized light having the parallel electronic vector.

For the measurement of the absorption spectrum of the single crystal of microsize, an apparatus was constructed using a Hitachi EPS-3T spectrophotometer and a Nippon Kogaku POH polarizing microscope, together with two Olympus MO90 reflecting-type objectives (×90). The polarized absorption spectra of the basic rhodo chromic perchlorate are shown in Fig. 1.

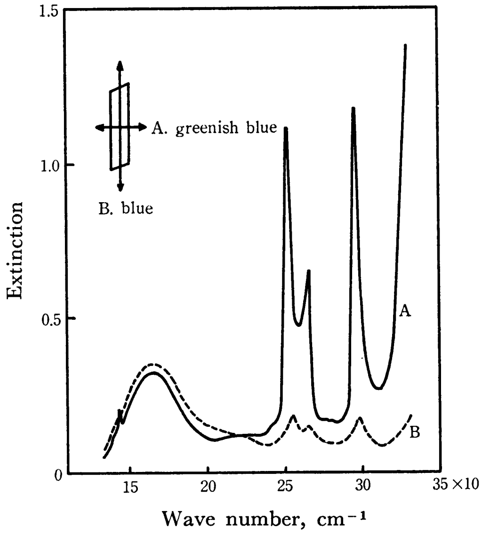

Fig. 1. Polarized absorption spectra of the basic rhodo chromic perchlorate.

It was found that: (i) the characteristic sharp absorption bands at 14320 cm^{-1} and in the near-ultraviolet region are all polarized along the four-fold rotation axis of the complex; (ii) the broad band in the 16600 cm^{-1} region seems to be slightly reduced in intensity along the four-fold rotation axis; (iii) the position of the absorption maxima of two broad bands, *i. e.*, 16600 cm^{-1} and 22000 cm^{-1}, seem to correspond to that of the so-called "first band" of the octahedrally-coordinated $Cr(III)O_6$ and $Cr(III)N_6$ types of complexes, respectively; (iv) the so-called "second band" of the *d–d* transition is obscure; and (v) as the total of the integrated intensities of the sharp bands in the near ultraviolet region is almost comparable to that of the band at 16600 cm^{-1}, the intensities of these bands are not so large as the ordinary charge-transfer absorption band shows. The characterization of the absorption bands of the basic rhodo chromic complex is very complicated. However, the assignment of the bands should be consistent with the results of the polarized spectroscopy. Further measurements at low temperatures are now in progress.

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