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The Polarized Crystal Spectra of *trans*(O)-$[Co(OCOCH_3)_2(en)_2]^+$ and *trans*(O)-$[Co(OCOCH_3)_2(py)_2en]^+$

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Synopsis. The polarized crystal spectra of *trans*-(O)-$[Co(OCOCH_3)_2(en)_2]Cl$ have exhibited a dichroism which can be understood by means of a vibronic D_{4h} model. On the other hand, the spectra of a new complex, *trans*(O)-$[Co(OCOCH_3)_2(py)_2en]ClO_4$, have shown a different dichroism from that in the bis(ethylenediamine) complex.

Polarized crystal spectra are useful for the assignment of the absorption bands of complexes. The spectra of various complexes of cobalt(III),[1] chromium(III),[1,2] platinum(II),[3] *etc.* have been investigated, but interest has been particularly centered on the spectra of *trans*-dihalobis(ethylenediamine)-type cobalt(III) complexes[4–6] because of the marked splitting of the first absorption band ($^1T_{1g}$ band).

In the present work we succeeded in obtaining *trans*-bis(acetato)bis(pyridine)ethylenediaminecobalt(III) perchlorate, *trans*(O)-$[Co(OCOCH_3)_2(py)_2en]ClO_4$, whose absorption spectrum in solution exhibits a marked splitting of the $^1T_{1g}$ band. The corresponding bis(ethylenediamine) complex, *trans*(O)-$[Co(OCOCH_3)_2(en)_2]^+$, has already been reported.[7,8] Thus, in this paper the polarized crystal spectra of the two *trans*(O) complexes will be reported. The spectra were measured with a microspectrophotometer which had been constructed by the present authors.

Experimental

Measurements. The microspectrophotometer was constructed according to the literature.[9] The assembly consists of a Hitachi 323 recording spectrophotometer and a specially designed sample compartment containing a microscope. As light sources, a tungsten filament lamp and a deuterium discharge lamp were used for the visible and near-ultraviolet regions respectively. As the microscope, an Olympus POM polarising microscope was used, together with an Olympus MO 90 reflecting objective (90 X) or a Zeiss-Jena reflecting objective (40 X). The light was polarized by a quartz Rochon prism. The photomultiplier tube was a Hamamatsu TV Co., Ltd., head-on type R376.

With this apparatus the crystal spectra were measured over the frequency range from 15000 to 30000 cm^{-1} at room temperature with incident light polarized parallel (‖) and perpendicular (⊥) to a suitable axis. The axis was chosen under a polarizing microscope as a direction exhibiting a remarkable dichroism. Since no attempt was made to determine the thickness of the crystal, the molar extinction was not evaluated. The reliability of this apparatus was checked with the spectra of *trans*-$[CoCl_2(en)_2]Cl \cdot HCl \cdot 2H_2O$.[4,5]

Preparation of the Complex. The known complex, *trans*(O)-$[Co(OCOCH_3)_2(en)_2]^+$, was prepared as the chloride according to the method in the literature.[8] A new complex, *trans*(O)-$[Co(OCOCH_3)_2(py)_2en]ClO_4$, was prepared according to the following procedure; to an aqueous solution of *cis*-$K[Co(CO_3)_2(py)_2] \cdot 3H_2O$[10] (21.5 g, 0.05 mol) in water (100 ml), we added ethylenediamine monohydrate (3.0 g, 0.05 mol) and 3 M acetic acid (100 ml), after which the mixture was stirred at room temperature for a few days, whereby the solution became red-violet. A portion of the resulting solution was charged on a column of an ion-exchange resin (Dowex 50 WX8, Na-form), and the complexes were eluted with a 0.3 M $NaClO_4$ aqueous solution, whereupon the desired complex was eluted first, followed by *cis*-$[CoCO_3(py)_2en]^+$ and $[CoCO_3(en)_2]^+$. By repeated chromatographic separations the desired fraction was collected. After the fraction had been concentrated to a small volume, the concentrate was kept in a refrigerator to crystallize the desired complex. The recrystallization was performed from water. Yield, *ca.* 0.5 g.

Found: C, 38.80; H, 4.85; N, 11.19%. Calcd for $[Co(OCOCH_3)_2(py)_2(en)]ClO_4 = CoC_{16}H_{24}O_4N_4 \cdot ClO_4$: C, 38.84; H, 4.89; N, 11.32%.

Results and Discussion

The crystal spectra of *trans*-$[CoCl_2(en)_2]Cl \cdot HCl \cdot 2H_2O$ measured with our apparatus exhibited a peak at 1600 cm^{-1} with the ‖ polarization and two peaks at 16200 and 22700 cm^{-1} with the ⊥ polarization, which agreed with the values reported in the literature: 16000 (‖), 16200 (⊥) and 22700 cm^{-1} (⊥)[4] and 15900 (‖), 16100 (⊥) and 23100 cm^{-1} (⊥).[5] These spectral data proved the usefulness of our apparatus.

Trans*(O)-$[Co(OCOCH_3)_2(en)_2]Cl$.* The polarized crystal spectra are shown in Fig. 1, together with the solution spectrum. The dichroism was clearly observed in the $^1T_{1g}$ band; the $\tilde{\nu}_{Ia}$ maximum is observed at 18500 cm^{-1} with both ‖ and ⊥ polarization, and the $\tilde{\nu}_{Ib}$ maximum at 23000 cm^{-1} with the ⊥ polarization.

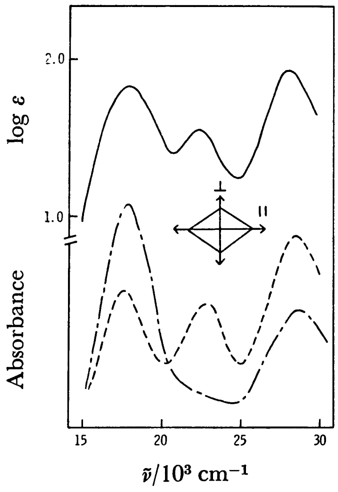

Fig. 1. Absorption spectra of *trans*(O)-$[Co(OCOCH_3)_2(en)_2]Cl$ (—— solution, ---- ⊥, —-— ‖).

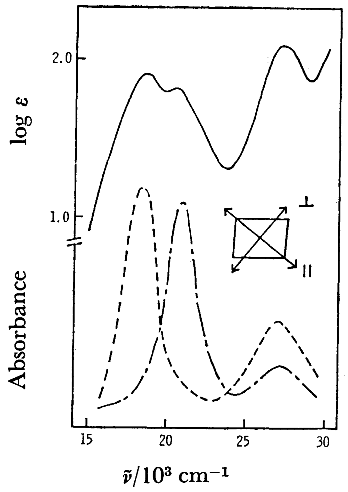

Fig. 2. Absorption spectra of *trans*(O)-$[Co(OCOCH_3)_2(py)_2en]ClO_4$ (—— solution, ---- ⊥, –·–·– ∥).

Those features are quite similar to those of the *trans*-dichloro complex. Although no crystal structure is known, the observed dichroism can be interpreted in terms of a vibronic D_{4h} model;[6] the $\tilde{\nu}_{Ia}$ is assigned to $^1E_g^a \leftarrow {}^1A_{1g}$, and the $\tilde{\nu}_{Ib}$, to $^1A_{2g} \leftarrow {}^1A_{1g}$. Concerning the second absorption band ($^1T_{2g}$ band), the maxima and intensities are different between the ∥ and ⊥ spectra. The maximum at 27600 cm^{-1} with the larger intensity may be assigned to $(^1B_{2g} + {}^1E_g^b) \leftarrow {}^1A_{1g}$, and the other maximum at 28100 cm^{-1} with the smaller intensity, to $^1E_g^b \leftarrow {}^1A_{1g}$.

trans(O)-$[Co(OCOCH_3)_2(py)_2en]ClO_4$. The solution and crystal spectra are shown in Fig. 2. This complex was identified as the *trans*(O) isomer on the basis of the splitting of the T_{1g} band. A preliminary X-ray investigation of this complex in this laboratory established that the crystal is monoclinic, with the space group C2/c, and that the O–Co–O axis makes an angle of *ca.* 45° with the crystal c axis and is on the ac plane. Thus, the ∥ polarization implies the incident light polarized along the O–Co–O axis.

In the crystal spectra, a marked dichroism is observed in the $^1T_{1g}$ band. With the ⊥ polarization, one peak is observed at 18400 and with the ∥ polarization, another peak at 21000 cm^{-1}. Those features of the dichroism differ from those of the *trans*(O)-bis(ethylenediamine) complex; hence, the vibronic D_{4h} model[6] is not applicable to the interpretation of this dichroism. Instead, a nonvibronic D_4 model may be applicable; the ⊥ band at 18400 cm^{-1} is assignable to $^1E \leftarrow {}^1A_1$, and the ∥ band at 2100 cm^{-1}, to $^1A_2 \leftarrow {}^1A_1$. As for the $^1T_{2g}$ band, the maxima and intensities are different between the ∥ and ⊥ spectra. However, the D_4 selection rule involves a forbidden $^1B_2 \leftarrow {}^1A_1$ transition.

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