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Note

The thermal olation reaction of *cis*- $[Co(en)_2(OH)(H_2O)]S_2O_6$

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Hydroxoaquo complexes of cobalt(III) containing ammonia and/or amino acid ions as the other groups in the inner coordination sphere, when heated, undergo thermal olation reactions. Studies involving the kinetics, thermochemistry, mechanism, etc., of these reactions for several complexes in the solid-state have been reported[1-3]. The purpose of this communication is to add to these studies our investigation of the olation reaction of *cis*-aquobis(ethylenediamine)hydroxocobalt(III) dithionate, which has not been reported thus far.

EXPERIMENTAL PART

Preparation

cis-$[Co(en)_2(OH)(H_2O)]S_2O_6$ was prepared by the method described in literature[4].

Apparatus

Differential thermal analysis (DTA) curves at normal and high pressures were obtained on a DuPont high pressure DSC cell and the TG studies on a DuPont 950 thermal analyzer—both of them being plug in modules for the DuPont 900 differential thermal analyzer. Infrared absorption spectra were obtained on a Perkin-Elmer Model 457 grating infrared spectrophotometer. The reflectance studies were carried out using the heated sample holder previously described[5] and a Beckman Model DK-2A spectroreflectometer. MgO was used as the standard. Heats of olation were measured by the use of Perkin-Elmer differential scanning calorimeter DSC-1B.

RESULTS AND DISCUSSION

The DTA and TG curves of *cis*-$[Co(en)_2(OH)(H_2O)]S_2O_6$ are shown in Fig. 1. The endothermic peak at ~185°C appears due to the olation reaction. The removal of a mole of water per mole of complex associated with this process is shown

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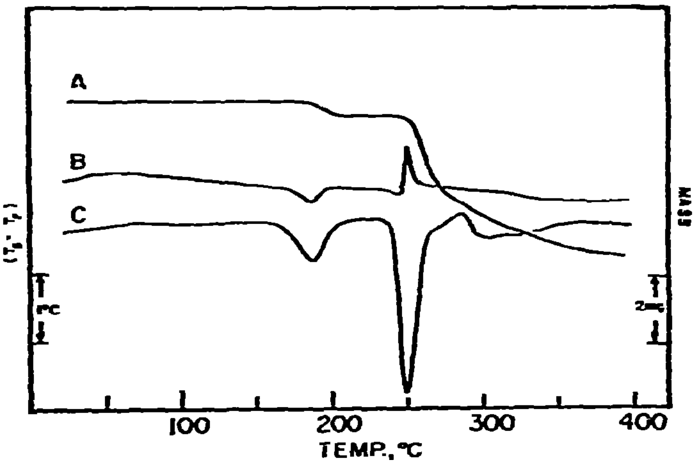


Fig. 1. DTA and TG curves of *cis*-[Co(en)$_2$(OH)(H$_2$O)]-S$_2$O$_6$. (A) TG curve at 1 atm.; (B) DTA curve at ~ 65 atm.; (C) DTA curve at 1 atm.

TABLE 1

INFRARED DATA FOR *cis*-[Co(en)$_2$(OH)(H$_2$O)]S$_2$O$_6$ DURING THE OLATION REACTION

Compound	*Frequencies (cm^{-1})*[a]
cis-[Co(en)$_2$(OH)(OH$_2$)]S$_2$O$_6$	1570 (m), 1382 (vs), 1242 (vs), 1212 (s), 1125 (m), 1057 (m), 998 (vs), 770 (w), 572 (vs), 520 (s).
cis-[Co(en)$_2$(OH)(OH$_2$)]S$_2$O$_6$ Heated to 150°C	1545 (m), 1380 (vs), 1238 (vs), 1211 (s), 1144 (m), 1115 (m), 1057 (m), 1022 (w), 990 (s), 755 (w), 575 (s), 560 (s, sh), 515 (s).

[a] The abbreviations vs, s, m, w and sh stand for very strong, strong, medium, weak and shoulder, respectively.

as a mass-loss on the TG curve at about this same temperature. At high pressures, an exothermic peak due to the second part of the olation reaction, i.e., –OH bridge formation, was expected since the endothermic effect due to the removal of water would be reduced. However, using the same amount of sample at 1 and 65 atm, it was observed that the DTA curve at the higher pressure showed only a reduction in the area of the endothermic peak. The exothermic peak at 250°C on the curve at high pressure could be due to decomposition/oxidation of ethylenediamine. This indicates that any exothermicity associated with the Co–OH–Co bridge formation is much less than the endothermicity of the Co–OH$_2$ bond breaking process.

The changes in the infrared spectrum of *cis*-[Co(en)$_2$(OH)(OH$_2$)]S$_2$O$_6$ on olation are shown in Table 1. The absorption at 506 cm^{-1}, in the case of *cis*-[Co(en)$_2$ (OH(H$_2$O)]S$_2$O$_6$ which has been heated at 150°C, seems to be due to the skeletal

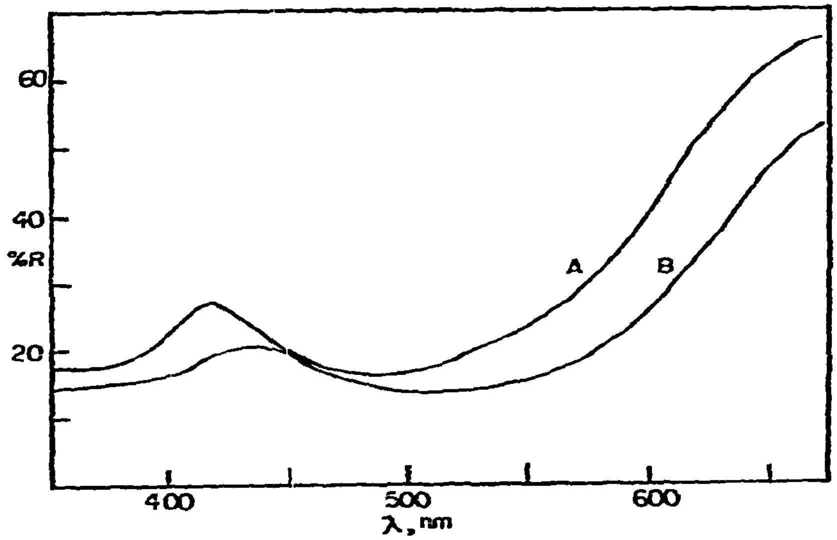


Fig 2. Reflectance curves of *cis*-[en)$_2$(OH)(OH$_2$)]S_2O_6; (A) at 22 °C; and (B) at 170 °C.

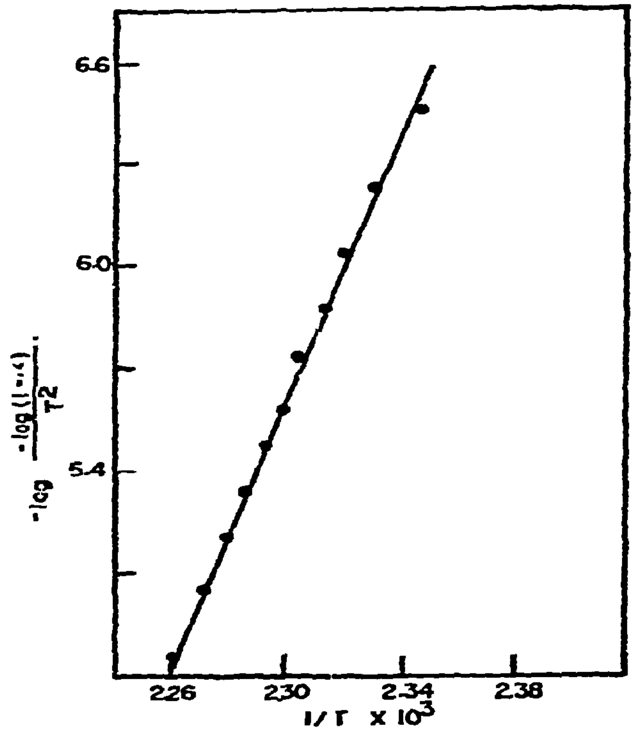
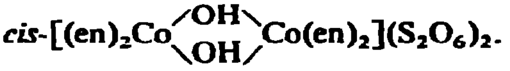


Fig. 3. Coats and Redfern kinetics plot for *cis*-[Co(en)$_2$(OH)(H$_2$O)]S_2O_6.

vibration of $-\mathrm{Co}-(\mathrm{OH})_2-\mathrm{Co}-$ that is present in the olation product of this compound,  $\mathit{cis}\text{-}[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\diagup\mathrm{OH}\diagdown\\ \diagdown\mathrm{OH}\diagup\end{smallmatrix}\mathrm{Co}(\mathrm{en})_2](\mathrm{S_2O_6})_2$. Also, a peak of medium intensity at 1125 cm^{-1} is split into two well-resolved peaks of the same intensity appearing at 1144 and 1115 cm^{-1}. This splitting may be due to the olation reaction and the consequent possible distortion of the crystal lattice.

The reflectance curves, as illustrated in Fig. 2, show that the peak at a maximum of 416 nm for $\mathit{cis}\text{-}[\mathrm{Co}(\mathrm{en}_2)(\mathrm{OH})(\mathrm{OH}_2)]\mathrm{S_2O_6}$ at 22°C shifts to higher wavelengths as the material is heated and at 170°C, appears at 431 nm with reduced intensity. This indicates that some change or modification of the structure occurs due to the olation reaction.

The kinetics of the olation reaction was calculated using the method of Coats and Redfern[6]. A straight line curve representing the reaction from $\alpha = 0.1$ to $\alpha = 0.9$ was obtained, as shown in Fig. 3. It follows from the equation used that the order of the reaction, n, is equal to 1. An activation energy, E, of 49 kcal mol^{-1} was calculated for the reaction.

The heat of the olation reaction, ΔH, was determined using the standard DSC technique. A value of 10.0 ± 0.2 kcal mol^{-1} was obtained.

ACKNOWLEDGMENT

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