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Solid-state Isomerisation of the Potassium Salts of *Cis*- and *Trans*-Diaquabis(oxalato)chromate(III)

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The possibility of the solid-state isomerisation of the potassium salts of *cis*- and *trans*-diaquabis(oxalato)chromate(III) has been mentioned in an earlier publication.[1] In the present report, the isomerisation is demonstrated and a novel method for the preparation of the *trans*-isomer is reported.

Experimental

The *cis*- and *trans*-salts were prepared and analysed as described elsewhere.[1] When a 0.5*M* solution of the *cis*-salt was allowed to stand at room temperature for a few days, crystals of the *trans*-isomer separated. The crystals were filtered and dried and their identity, indicated by their appearance, was confirmed by comparing the absorbance of a 10^{-2} *M* solution with the published data for the *trans*-salt. As expected, the absorbance of the solution increased with time. The crystals assayed $(C_2O_4)^{2-}$, 48%; water lost at 383K, 15%. (theor., $(C_2O_4)^{2-}$, 49.1%; water of crystallisation 15.1%;) using the usual analytical methods. This novel method of preparation is a further confirmation of the establishment of an equilibrium between the cis- and *trans*-anions in solution.[2] The observed separation of crystals of the *trans*-isomer from a 0.5*M* solution of the *cis*-isomer is ascribed to the lower solubility of the former. The visible spectra were measured using a Perkin-Elmer Coleman 55 spectrophotometer and the infrared spectra were obtained for KBr discs on a Pye Unicam SP1200 spectrophotometer.

Results and Discussion

The infrared spectrum of the *trans*-isomer was similar to the published spectrum,[3] but some of the bands were slightly shifted. A very broad structured band was observed instead of the bands reported at 3430 and 3360 cm^{-1}. The infrared spectrum of the *cis*-compound was generally similar to that of the *trans*-isomer but some bands were broader and slightly shifted compared to the bands of the latter compound. Two bands at 965 and 1012 cm^{-1} were reported for the *trans*-isomer and were ascribed to co-ordinated water.[4] However, only the latter band was observed in the spectrum of the *cis*-isomer and was found at 1020 cm^{-1}. The absence of a band at 965–980 cm^{-1} may be taken to distinguish the *cis*- from the *trans*-isomer.

On dissolving the product obtained by heating the *trans*-salt to 473K, the solution did not exhibit the characteristic increase in absorbance with time. The absorbance of a 10^{-2} *M* solution of the product obtained by heating the *trans*-salt to 383K for 2–4 hours was appreciably higher than that of the original compound. The increase in absorbance with time was less sharp compared to that of a solution of the original *trans*-compound. The infrared spectra of the products obtained on heating did not exhibit a band at 980 cm^{-1}, resembling the spectrum of the *cis*-isomer. It can be concluded that heating the *trans*-compound led to some isomerisation. No explanation is available for the absorption band at 2480–2490 cm^{-1} observed in the spectra of the products obtained on heating the *trans*-salt.

The molar extinction coefficients of a solution of the product of heating the *cis*-isomer at 463 K for 2 hours were 12 and 21% lower than that of a solution of the unheated salt at 420 and 570 nm respec-

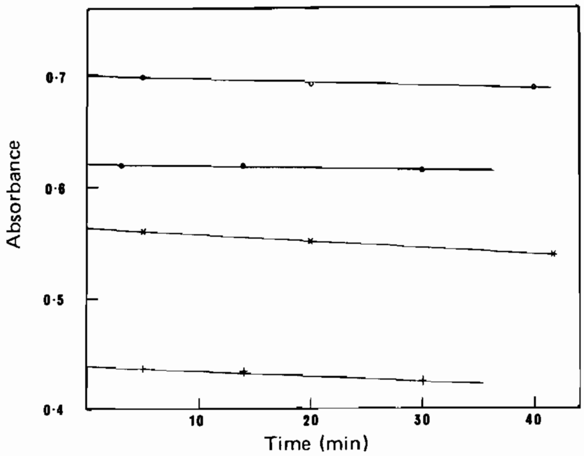

Fig. 1. The variation of the absorbance of 10^{-2} *M* solutions in 1 cm cell with time: ○ unheated *cis* at 420 nm; ● heated *cis* at 420 nm; × unheated *cis* at 570 nm; + heated *cis* at 570 nm.

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tively. There was a noticeable decrease in the solubility of the salt after heating. When the *cis*-compound was heated at 383K for 2 hours, the absorbance of a 10^{-2} *M* solution of the product was appreciably lower compared with a 10^{-2} *M* solution of the original *cis*-isomer (Fig. 1). The slow change in absorbance with time, shown in Fig. 1, indicates the slow approach to a *cis*- $\rightleftharpoons$ *trans*-equilibrium in solution.

It can be concluded that heating of the *cis*-compound led to some isomerisation.

The solid salts start losing coordinated water when heated to 383K, suggesting that the resulting penta-coordinate intermediate may be involved in the isomerisation reactions.

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