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Short Communication

THE REVERSIBILITY OF THE OCTAHEDRAL → TETRAHEDRAL TRANSITION IN BIS(PYRIDINE)-COBALT(III) CHLORIDE $Co(py)_2Cl_2$

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The octahedral-tetrahedral structural transition of $Co(py)_2Cl_2$ was studied by high temperature reflectance spectroscopy and dynamic reflectance spectroscopy. The reversibility of the transition by standing at room temperature for 24 hrs was established.

The *octahedral → tetrahedral* structural transition of bis(pyridine)-cobalt(III) chloride, $Co(py)_2Cl_2$, has been the subject of a number of investigations [1—8]. Wendlandt and George [4] studied the transition using the techniques of high temperature reflectance spectroscopy (HTRS) and dynamic reflectance spectroscopy (DRS). The thermal transition was found to begin at about 100° and was completed at about 135°. The color change reported for the transition was from violet *(octahedral)* to a dark blue *(tetrahedral)* color; it was stated that the change was non-reversible on cooling to room temperature.

We wish to report here additional studies on this transition, namely, the effect of heating rate and also the fact that it is reversible on standing at room temperature for 24 hrs.

Experimental part

The violet form of $Co(py)_2Cl_2$ was prepared as previously described by the reaction of pyridine with cobalt(II) chloride in absolute ethanol [5]. Analysis of the compound gave: % Co, 20.98 theor., 20.5 found; % Cl, 24.60 theor., 24.3 found.

The DRS cell has previously been described [9]. The heating rate of the cell was controlled by the temperature programmer from a Deltatherm III DTA instrument; a static air atmosphere was employed. A multi-channel strip-chart recorder was used to record the DRS curve and also the sample temperature. The HTRS curves were recorded under isothermal conditions using a Beckman Model DK-2A spectroreflectometer. For the diffuse reflectance studies, freshly prepared magnesium oxide was employed as the reflectance standard.

Results and discussion

The HTRS curves of $Co(py)_2Cl_2$, at 20° and 120°, are given in Fig. 1. At 20°, reflectance minima were observed in the curve at 520 and 620 nm, with shoulders at 500 and 550 nm, respectively. The compound reflected rather strongly in the 350—450 nm region and at 580 nm. The blue *tetrahedral* form, at 120°, absorbed very strongly in the 500 to 700 nm region with shoulders at 425, 480, and 510 nm,

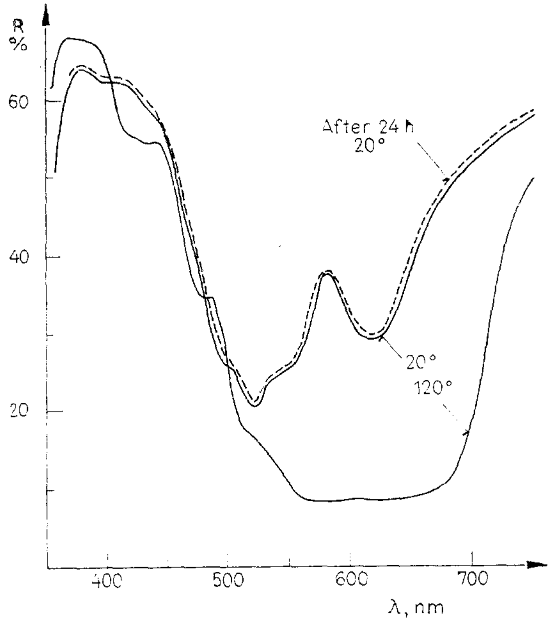

Fig. 1. HTRS curves of $Co(C_5H_5N)_2Cl_2$ at various temperatures

respectively. After standing 24 hrs at room temperature, the reflectance curve of the blue form was again recorded at 20°. As can be seen, the curve obtained was almost identical with that of the original violet compound having the *octahedral* structure. Thus, it is seen that the *tetrahedral → octahedral* transition takes place rather slowly on standing; it does not revert back to the *octahedral* form immediately upon cooling to room temperature.

The effect of heating rate on the *octahedral → tetrahedral* transition is shown by the DRS curves in Fig. 2. The heating rate varied from 1.25°/min to 10°/min, the latter value is considered to be rather high for DRS studies. Surprisingly, the procedural transition temperature was greatest (107°) for the 1.25°/min rate and lowest (95°) for the highest rate studied. However, on increasing the heating rate, the reaction temperature interval increased, from 95°—145° for the 10°/min rate to 107°—123° for the slowest heating rate. This is just the opposite to that observed in dissociation reactions involving volatile products.

A DTA curve was also recorded for the violet compound (not shown); a single endothermic peak beginning at a procedural temperature of 85° was observed. The ΔT_{min} for the peak was 108°. The heat of transition has been reported by Wendlandt and George [4] and by Beech *et al.* [6]. Heats of transition observed were 3,200 ± 100 cal. per mole for the former to 3,020 ± 70 cal. per mole for the latter.

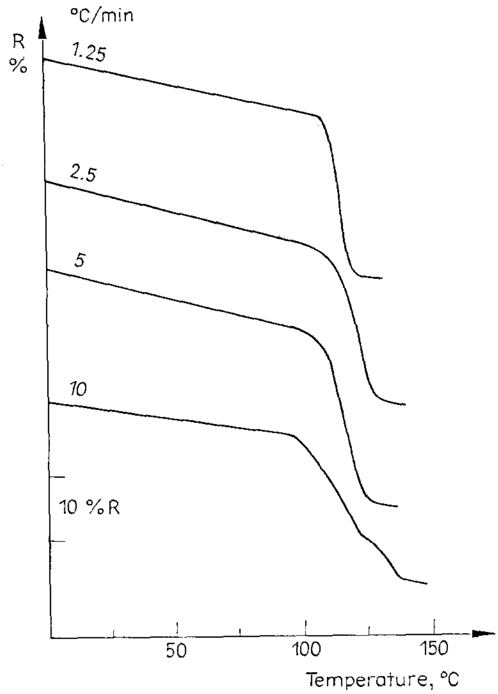

Fig. 2. DRS curves of $Co(C_5H_5N)_2Cl_2$ at various heating rates; curves recorded at 675 nm

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Résumé — On a pruvé par spectroscopie de reflexion de haute température et spectroscopie de reflexion dynamique la reversibilité de la transition structurale octaédrique-tetraédrique de $Co(py)_2Cl_2$ après 24 heures.

Zusammenfassung — Es wurde durch Hochtemperatur-Reflexions-Spektroskopie und dynamische Reflexions-Spektroskopie bewiesen, daß die strukturelle Umwandlung des oktaedrischen $Co(py)_2Cl_2$ in die tetraedrische Form nach 24 stündigem Stehen bei Zimmertemperatur reversibel ist.

Резюме. — Исследован переход восьмигранной — четырёхгранной конфигурации $Co[Py]_2Cl_2$ с помощью спектроскопии отражения при высокой температуре и спектроскопии динамического отражения. Обратимость перехода определяли выдерживанием при комнатной температуре в течение 24 часов.