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Intracrystalline Chemical Changes in Some Cr(III) Complexes Produced by LF-Excitate States

B. HÁJEK and F. BENDA

Department of Inorganic Chemistry, Prague Institute of Chemical Technology, Prague, Czechoslovakia

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The theoretical treatment of the reactivity of LF-excited states for Cr(III) coordination compounds (complexes possessing the O_h symmetry as well as mixed complexes) has so far been based on the study of their solutions. For such systems, some empirical rules have been postulated [1] and theoretical concepts based on the ligand field theory have been suggested [2] to account for the observed reactivity. In the present work the effects of the LF-excitation have been studied on crystals with the aim to seek how these processes could be employed for inducing solid state 'reactions' – in particular, substitutions in the coordination sphere without the participation of a solvent.

The underlying hypothesis was that the LF excitation, with its consequent effects on the geometry of the basic polyhedron, results primarily in a formation of active centres which in the crystal lattice represent a system of regularly distributed point defects. The change in the geometry within the basic polyhedron also stimulates consecutive substitution processes. The propagation of the defects through the crystal lattice need not be photochemical by nature. For such processes to occur, the substituent-to-be must lie close enough to the coordination sphere of the central ion. For this reason, coordination compounds were chosen such that the intended substituent constituted the anion to the complex cation under study.

First we studied the processes occurring on the irradiation of the crystalline $[Cr(en)_3]Cl_3$ and $[Cr(NH_3)_6]Cl_3$ complexes by investigating the region of the long-wavelength ligand field band (L_1) corresponding to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition. Solid state reactions of these substances in which, due to the optical excitation, the NH_3 or ethylenediamine ligand is replaced by the Cl^- anion, have so far only been examined qualitatively and the products identified indirectly [3, 4]. Therefore, in addition to the study of the course of the reaction itself, we paid attention also to the analysis of the resultant reaction mixture and identification of the products.

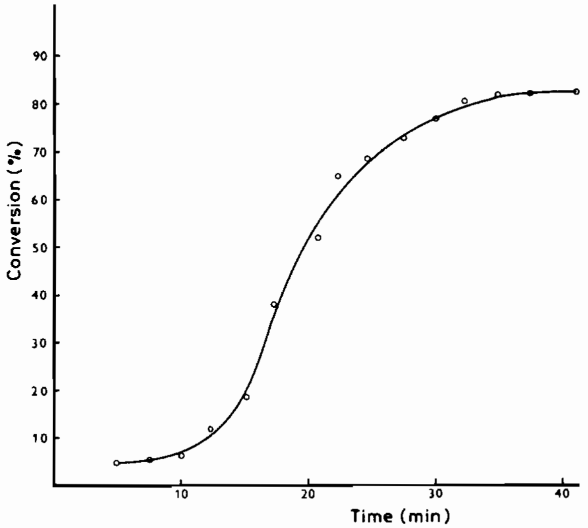

Fig. 1. Dependence of $[Cr(en)_3]Cl_3 \rightarrow cis[Cr(en)_2Cl_2]Cl$ conversion in the polycrystalline reaction mixture on time.

During continuous irradiation of $[Cr(en)_3]Cl_3$ a change took place in 5–30 min manifesting itself in the diffuse reflectance spectrum by an increase in the relative reflectance at 453 nm and a simultaneous decrease in the reflectance at 560 nm. The spectral patterns of the final reaction mixture correspond to *cis*-$[Cr(en)_2Cl_2]Cl$. The reaction mixture was subjected to separation treatment on a cation exchanger to give two fractions, whose electronic absorption spectra in conjunction with the results of the elemental analysis of their chloride complexes gave evidence that the starting complex was more than 80% converted to *cis*-$[Cr(en)_2Cl_2]Cl$ ($\lambda_1^{max} = 405$ nm, $\log \epsilon = 1.89$; $\lambda_2^{max} = 528$ nm, $\log \epsilon = 1.92$). A microscopic observation revealed that up to this degree of conversion no destruction of the crystals took place. On longer exposure, giving rise to *cis*-$[Cr(en)_2Cl_2]Cl$ in higher yields, the crystals in a Nujol mull transformed into a vitreous-syrupy matter on account of the liberation of ethylenediamine. *Cis*-$[Cr(en)_2Cl_2]Cl$ was isolated from the material by recrystallization from an aqueous solution. The course of the process was monitored by thin layer chromatography (TLC) and electrophoresis measurements; the results obtained are shown in Fig. 1. The slow concentration rise within the first quarter of the overall reaction period and the subsequent rapid increase in the second and third quarters are consistent with our concept of the primary creation of point defects and their consecutive propagation.

For $[Cr(NH_3)_6]Cl_3$, a shift of the maximum in the diffuse reflectance spectrum at 368 nm and

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formation of a broad band at 540 nm were observed within 2 min of irradiation. After 7 min the spectral patterns did not change any more. The band shift failed to assist in deciding between the expected products. The TLC treatment revealed the occurrence of two products, which according to their R_f values were probably $[Cr(NH_3)_5X]^{2+}$ and $[Cr(NH_3)_4XY]^+$. This assumption was also borne out by the electrophoresis measurements, the latter compound being subject to aquation during the treatment, with a simultaneous rise in the charge to 2+. The fractions from the separation on a cation exchanger were analyzed to identify $[Cr(NH_3)_5Cl]Cl_2$ and *cis*-$[Cr(NH_3)_4(H_2O)Cl]Cl_2$. Since it can be assumed that *cis*-$[Cr(NH_3)_4Cl_2]Cl$, if present, would be thermally aquated, the presence of *cis*-$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ in the reaction mixture can be looked upon as an evidence of the formation of *cis*-$[Cr(NH_3)_4Cl_2]Cl$, in addition to $[Cr(NH_3)_5Cl]Cl_2$, on the optical excitation of the starting substance.

An analogous study was performed also on $[Cr(en)_3]_2(CO_3)_3$. In 3 min of irradiation, the maximum at 445 nm in the reflectance spectrum shifted to longer wavelengths with a simultaneous increase in the relative reflectance. In 15 min the spectrum displayed a clear-cut maximum at 545 nm; no additional changes appeared on an extended exposition. The colour changed from yellow to dark red. When allowed to stand in air for several minutes, the product isolated from the Nujol mull transformed into a paste on account of the liberation of ethylenediamine; no changes were observed in the electronic absorption spectrum. The effect could be eliminated to an extent by conducting the irradiation at a reduced pressure (oil vacuum pump) to remove the ethylenediamine evolved. The product (both the crystals and the paste) was separated from the unreacted starting complex by recrystallization from 30% ethanol; $[Cr(en)_2CO_3]_2CO_3$ was identified by elemental analysis.

While failing to gain data for a determination of the quantum yields of the processes under study, we observed a significant interdependence between the crystal size of the starting substance and the 'rate' of the process: in standardized conditions the substitution was markedly faster for well-developed, untriturated large crystals (above 1 mm in size) as compared with powder samples prepared by trituration of the crystals. Although quantitative data are so far unavailable for a detailed discussion, this effect could be accounted for by our working hypothesis.

Experimental

Compounds

The substances $[Cr(en)_3]Cl_3$ and $[Cr(NH_3)_6]Cl_3$ were synthesized by standard methods [5, 6]. For obtaining $[Cr(en)_3]_2(CO_3)_3$, an aqueous solution of $[Cr(en)_3]Cl_3$ (4 *M*) was reacted with a stoichiometric quantity of freshly prepared Ag_2CO_3; AgCl was filtered off, and ethanol was added to the filtrate to give an approximately 30% solution. The product crystallized from this solution within 30 min.

Photochemical Study

Crystals of the starting complex were dispersed in Nujol (about 0.1 g of substance per 25 ml of Nujol), and the constantly stirred mixture was irradiated in a closed cylindrical glass reactor fitted with a jacket for water thermostatting. The apparatus was designed to allow for sampling, with a pipette, without discontinuing the exposition. The course of the processes was monitored discontinuously by measuring the changes in the reflectance at a chosen wavelength and by thin layer chromatography and electrophoresis measurements. The solid was reclaimed from the Nujol mull by removing the oil with benzene.

Apparatus

Irradiations were accomplished with a XBO Osram) 450W compact arc, high-pressure, xenon lamp. The collimation was obtained by means of two glass lenses with the aperture controlled by two diaphragms, so that a final, parallel beam of 2 cm diameter resulted. Monochromatization was by means of Corning glass blocking filters CS 3-73 and CS-4-97 (452 nm).

The diffuse reflectance spectra were obtained at ambient temperature on a Carl Zeiss Jena Model VSU-2P spectrophotometer.

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