Synthesis and Characterization of a Chromium(III) Complex of a Pentadentate Ligand

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Template synthesis is one of the most popular methods of synthesising metal complexes of macrocyclic ligands having nitrogen donors and has been extensively used in the case of divalent metal ions [1–3]. The use of trivalent metal ions in template synthesis is not well documented although we reported two Schiff base complexes of Cr(III) using the metal template synthetic route [4]. Since the coordination of an amine to a d^3 metal ion like Cr(III) is expected to render the ligand less nucleophilic, Schiff base type condensation between a coordinated amine and a carbonyl group of a ketone or aldehyde will be difficult. On the other hand, if a ketone like acetylacetone or an aldehyde like salicylaldehyde is coordinated to a tripositive metal ion initially, then the carbon may readily lend itself to nucleophilic addition by a free amine. Therefore we have examined the possibility of a metal template synthesis involving Cr(III) salicyladehydato complex and a triamine with a view to preparing a complex of pentadentate ligand.

The ligand of interest *viz.* bis(salicylidine-γ-iminopropyl)amine (Sal-DPT) is known to coordinate to several metal ions such as Ni(II) and Co(II) [5–7]. Successful template synthesis and characterization of a Cr(III)–Sal–DPT complex making use of a salicylaldehydato derivative of Cr(III) is reported here.

Experimental

Elemental Analysis

Carbon and hydrogen were analysed by courtesy of the School of Chemistry, University of Leeds, U.K.*. Nitrogen content was evaluated using the micro-Kjeldahl technique and chromium was analysed as chromate after oxidising an aqueous solution of the complex. Chloride was estimated by the flask combustion method [8].

Spectral Measurements

The electronic spectrum of an ethanolic solution of the complex was obtained using a Pye-Unicam SP 1800 spectrophotometer. IR spectra of the complex were obtained with a Perkin-Elmer 337 model grating spectrophotometer and the KBr mull sampling technique.

Preparation of Chloro Bis(salicylidine-γ-iminopropyl)-aminechromium(III), (Sal-DPT)CrCl

Anhydrous sodium carbonate (0.03 mol) was added to a mixture of $CrCl_3 \cdot 6H_2O$ (0.01 mol) and salicylaldehyde (0.03 mol) in boiling ethanol (100 ml). The solution was refluxed until the evolution of CO_2 ceased and a brown crude product was obtained. The (salicylaldehydato)chromium(III) (0.05 mol) derivative so prepared, was dissolved in ethanol (100 ml) and treated with 3,3′-iminobispropylamine (0.049 mol). The mixture was refluxed for 5 h. The volume of the solution was then reduced to *ca.* 25 ml. A solid product was obtained on cooling the solution. It was recrystallised from dilute perchloric acid (0.2 M). *Anal.* Calc. for $Cr(C_{20}H_{23}N_3O_2)Cl$: C, 56.5; H, 5.4; N, 9.89; Cl, 8.35. Found: C, 55.8; H, 5.55; N, 9.35; Cl, 7.93%.

Results and Discussion

The success of the metal template synthesis adopted in this study is evident from the elemental analysis data as well as the infrared spectrum shown in Fig. 1. The IR spectrum of the chromium(III) product shows the characteristic features of both the salicylaldehyde ring and dipropylenetriamine. Bands were observed at 1620, 1560, 1380 and 1060 cm^{-1} in the infrared spectrum of the Cr–Sal DPT

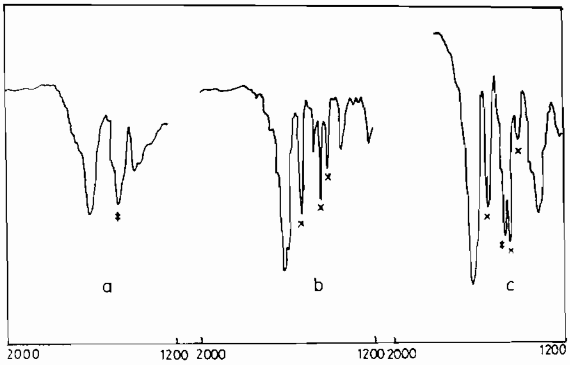

Fig. 1. The infrared spectra of (a) 3,3′ iminobis(propylamine), (b) tris-salicylaldehydatochromium(III) and (c) Cr(Sal-DPT)Cl.

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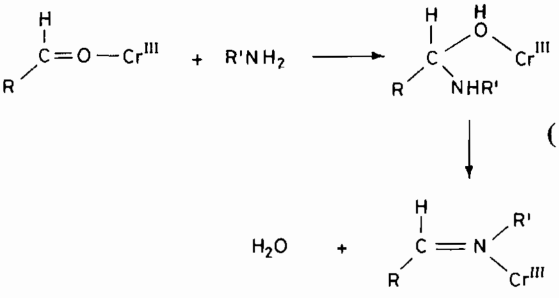
derivative, which may be assigned to $\nu(C=N)$, aromatic ring breathing, $\nu_s(C-O)$ and $\nu(C-N)$, respectively. Characteristic of methylene units in the molecule, a doublet peak was observed in the region of 820–850 cm^{-1}, which may be assigned to the rocking vibrations, $\rho_r(CH_2)$.

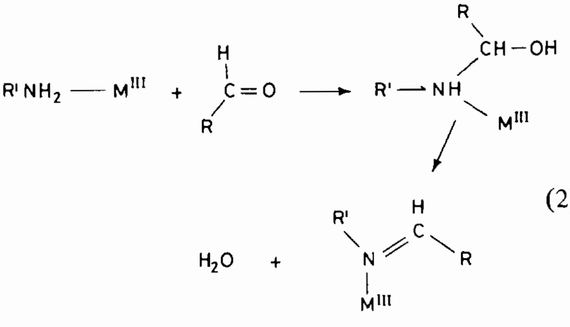
Additional support for the formulation of the Cr(Sal–DPT)Cl type derivative is obtained from the electronic spectrum. The observed absorption maxima at 560 nm (32 M^{-1} cm^{-1}) and 388 nm (84 M^{-1} cm^{-1}) can be compared with 1,2,3-Cr(dien)$(H_2O)_2Cl^{2+}$ (535 nm and 394 nm) [9]. The spectra of 1,2,6-Cr(dien)$(H_2O)_2Cl^{2+}$ is not known to the best of our knowledge. Although 1,2,6-Cr(dien)Cl_3, in which dien spans the axial positions of the octahedron, is distinguished from the 1,2,3-Cr(dien)Cl_3 complex on the basis of the electronic spectrum [9], direct comparison in assigning geometrical isomers of our complex is difficult. However, the observed electronic spectrum of the complex prepared in this study is in keeping with the assigned formulation *viz.* Cr(Sal–DPT)Cl. The success of the synthetic route (eqn. (1)) is expected to partly arise from the influence of a tri-positive metal ion like Cr(III) on the carbonyl carbon of a salicylaldehyde derivative.



(1)

(A)

The synthetic route (eqn. (2)) is unrealistic in the case of an ion like Cr(III) with high ligand field stabilisation energy and because of the need to maintain acidic conditions in dealing with Cr(III) amines.



(2)

(A)

Thus whereas both synthetic routes (1) and (2) may seem applicable for divalent ions, in the case of Cr(III) route (1) has a distinct advantage.

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