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Synthesis and Characterisation of Some New Cyanonitrosyl Chromium(I) Complexes with Phenetidines and Anisidines

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Summary

A new series of cyano-substituted nitrosylchromium(I) complexes having octahedral stereochemistry around the metal ion, and of general formula, $[CrNO(CN)_2(L)_2(H_2O)]$ (L = *o*-, *m*- and *p*-phenetidines or *o*-, *m*-, and *p*-anisidines) have been isolated in the solid state by interaction of potassium pentacyanonitrosylchromate(I) monohydrate with the appropriately substituted aniline. The complexes, which have been characterised by elemental analysis, conductance, molecular weight determination, magnetic measurements, e.s.r. and i.r. spectral studies, contain chromium(I) in a low-spin d^5-configuration.

Introduction

A literature survey of neutral mixed-ligand nitrosyl complexes of monovalent chromium reveals few reports on such complexes(1–11). Although considerable importance is attached to the study of neutral mixed-ligand cyanonitrosyl complexes of chromium(I)(4–8, 11), cyanonitrosyl complexes of chromium(I) with aromatic amines have not been described hitherto. We, therefore, report here the first synthesis of neutral cyanonitrosyl complexes of chromium(I) with phenetidines and anisidines and the present paper deals with the results of this study.

Experimental

Materials

Anisidines (Koch-Light, UK), phenetidines (Fluka AG, Chemicals), NH_3OHCl (S.D. Fine Chem. Pvt. Ltd., India) and KCN (M & B, India) were used as supplied. Degassed H_2O was used in all the operations. $K_3[CrNO(CN)_5] \cdot H_2O$ was prepared by the method of Wilkinson *et al.*(12) and was used as the starting compound for all the complexes.

Analyses

Chromium was determined(4) as Cr_2O_3 after decomposing the complexes by heating with alkali followed by dissolving in HNO_3 and precipitating by NH_3. Carbon, hydrogen and nitrogen were determined microanalytically.

Physical methods

Conductances were measured in analytical grade MeOH using a dip-type cell and a Philips conductivity bridge. The molecular weights of the compounds were determined by Rast's method. The magnetic susceptibility was measured by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. E.s.r. spectra of the complexes were recorded at room temperature on a Varian E-3 spectrometer using the powdered sample at the microwave frequency 9.53 GHz. I.r. spectra of the complexes were recorded in Nujol mull using a Beckman IR-20 spectrometer.

Preparation of the complexes

To a filtered H_2O solution of $K_3[CrNO(CN)_5] \cdot H_2O$, a 1 : 1 H_2O-AcOH solution of the corresponding ligand was added with shaking, and a coloured solid precipitated on warming the mixture for 30 min. The liberated HCN was removed by passing a current of CO_2 through the mixture for a few h, and the resulting precipitate was filtered, washed several times with dilute AcOH, finally with H_2O and dried to a constant weight *in vacuo* at room temperature. The analytical data are given in Table 1.

Results and Discussion

The mixed ligand complexes, $[CrNO(CN)_2(L)_2(H_2O)]$ were prepared according to Equation 1:

$$K_3[CrNO(CN)_5] + 2\,L \quad \xrightarrow[\;]{} \text{(AcOH} \downarrow H_2O) \qquad (1)$$

$$[CrNO(CN)_2(L)_2(H_2O)] + 3\,AcOK + 3\,HCN + H_2O$$

The partial replacement of the cyano groups in the hexacoordinated complex, $K_3[CrNO(CN)_5] \cdot H_2O$ by two molecules of ligand arises from the *trans*-effect of the NO group. Studies by Raynor and coworkers(13) on the stepwise aquation of the pentacyanonitrosylchromate(I), $[CrNO(CN)_5]^{3-}$, thereby attaining the third aquated species of composition, $[CrNO(CN)_2(H_2O)_3]$ favour the above reaction scheme.

These compounds are brown to reddish brownish solids, stable in air, and soluble in alcohol, ether and acetone. The molar conductances of these complexes (10^{-3} M MeOH solution) indicate their non-electrolytic character(4) (Table 1).

The i.r. spectral bands and their tentative assignments for the complexes and organic ligands are presented in Tables 1 and 2. Very strong bands in the 1710–1730 cm^{-1} region and a strong band at 2150–2190 cm^{-1} are assigned to $\nu(NO)^+$ and $\nu(CN)$ respectively, and are in accordance with assignments made for the reported complexes(6, 7). The broad bands in the 3550–3580 cm^{-1} and 3350–3400 cm^{-1} regions are due to $\nu(OH)$ of coordinated water(14). Broad bands in the 3250–3260 cm^{-1} and 3150–3160 cm^{-1} region in all the complexes may be assigned to $\nu(NH)$ of coordinated amines(15, 16). The absorption bands in the 1600–1610 cm^{-1} and 830–850 cm^{-1} region are assigned to the coordinated H_2O molecules. The weight loss observed by t.g.a. between 90–110 °C corresponds to the elimination of one molecule of water(17) and supports further the presence of one molecule of coordinated water in the complexes.

The magnetic moments and g values of all the compounds are given in Table 1. The magnetic moments of 1.72–1.73

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Table 1. Analytical data, physical properties, and i.r., spectral bands and assignments.

Compound[a)]	Found (Calcd.) %				M.W. Found (Calcd.)	Λ_M (Ω^{-1}cm^2 mol^{-1})	g	μ_{eff} (B.M.)	Yield (%)	Dec. Temp. (°C)	ν(CN)	ν(NO)$^+$
	Cr	C	H	N								
[CrNO(CN)$_2$(*o*-PTD)$_2$(H$_2$O)]	12.3 (12.2)	50.4 (50.7)	5.5 (5.6)	16.6 (16.4)	448 (426)	15.7	1.988	1.73	65	>260	2170s	1710vs
[CrNO(CN)$_2$(*m*-PTD)$_2$(H$_2$O)]	12.0 (12.2)	50.6 (50.7)	5.7 (5.6)	16.3 (16.4)	451 (426)	14.3	1.987	1.72	64	>260	2175s	1730vs
[CrNO(CN)$_2$(*p*-PTD)$_2$(H$_2$O)]	12.4 (12.2)	50.4 (50.7)	5.8 (5.7)	16.6 (16.4)	439 (426)	16.2	1.988	1.74	62	>260	2190s	1730vs
[CrNO(CN)$_2$(*o*-ASD)$_2$(H$_2$O)]	13.6 (13.0)	48.6 (48.2)	5.3 (5.0)	17.2 (17.6)	419 (398)	17.2	1.986	1.72	66	>260	2170s	1710vs
[CrNO(CN)$_2$(*m*-ASD)$_2$(H$_2$O)]	13.4 (13.0)	48.5 (48.2)	5.4 (5.0)	17.2 (17.6)	423 (398)	14.9	1.986	1.73	65	>260	2150s	1710vs
[CrNO(CN)$_2$(*p*-ASD)$_2$(H$_2$O)]	13.2 (13.0)	48.6 (48.2)	5.5 (5.0)	17.4 (17.6)	422 (398)	16.5	1.987	1.73	63	>260	2160s	1710vs

[a)] PTD = phenetidine; ASD = anisidine.

Table 2. I.r. spectral bands (cm^{-1}) of the organic ligands.

Ligand	Bands
o-PtD	3550br, 3380br, 3250br, 3150br, 1610m, 1560w, 1500w, 1460s, 1380m, 1300w, 1260m, 1220w, 1100m, 1050w, 1030w, 830w, 750m.
m-PTD	3580br, 3400br, 3250br, 3150br, 1600m, 1550w, 1500w, 1460m, 1385m, 1190w, 1160w, 1120w, 1050w, 970w, 850w, 770w, 725w, 690w.
p-PTD	3575br, 3380br, 3250br, 3160br, 1610w, 1530m, 1480m, 1400m, 1320w, 1265m, 1190w, 1130w, 1060w, 940w, 840w, 770w, 740w.
o-ASD	3550br, 3380br, 3250br, 3150br, 1600w, 1590w, 1500m, 1460m, 1385m, 1350w, 1300w, 1260w, 1225w, 1120m, 1050m, 930m, 830w, 750m.
m-ASD	3550br, 3350br, 3250br, 3150br, 1600s, 1500w, 1460m, 1380m, 1320w, 1280m, 1200w, 1160m, 1100w, 1035m, 930m, 850m, 765m, 720w, 680w.
p-ASD	3550br, 3380br, 3260br, 3150br, 1600m, 1510m, 1460s, 1380m, 1305w, 1250s, 1180w, 1100w, 1030m, 830w, 740w.

[a)] PTD = phenitidine; ASD = anisidine.

B.M. at 303 K and g values of 1.986–1.988 of powdered samples are consistent with a low-spin d^5-configuration for chromium(I)(4, 18, 19).

Analytical data taken in conjunction with the above results suggest that the complexes may be formulated as [CrNO(CN)$_2$(L)$_2$(H$_2$O)]. Thus it is reasonable to propose an octahedral geometry for them(3, 13), where CN is *trans* to CN and the amine is *trans* to amine in the equatorial positions, whereas NO is *trans* to water in the axial position (Figure 1).

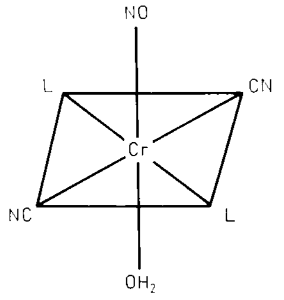

Figure 1. Octahedral Structure of [CrNO(CN)$_2$(L)$_2$(H$_2$O)].

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