

Synthetic, Magnetic and Spectral Studies of some Mixed-ligand Cyanonitrosyl {CrNO}⁵ Complexes of Chromium with Potentially Bi-, Tri- and Tetradentate Organic Compounds

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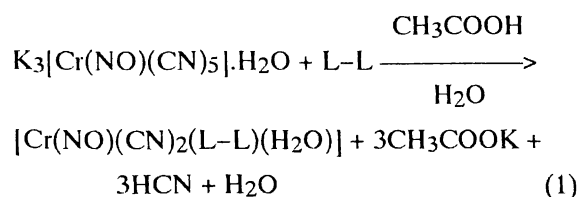
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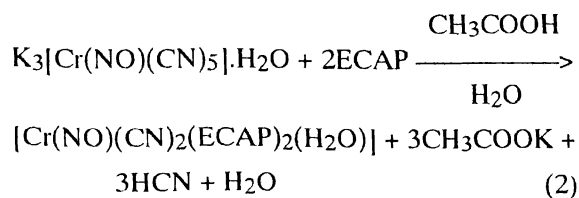
In recent years there has been a continuous interest in the synthesis and characterisation of some mixed-ligand nitrosyl {CrNO}⁵ complexes of chromium¹ involving hetero-donor organic compounds. However, the mixed-ligand derivatives of potassium pentacyanonitrosylchromate(I) with potentially bidentate aniline derivatives, viz. *o*-phenylenediamine (*o*-PDA), *m*-PDA, *p*-PDA and benzidine (BDN), potentially tetradentate derivative, viz. 4,4'-sulphonyldianiline (SDA) and potentially tridentate pyridine derivative, viz. 2-ethoxycarbonylaminopyridine (ECAP), have not been reported in the literature. Hence to observe the ligational behaviour of these aniline and pyridine derivative(s) with chromium, we report here the first synthesis of some neutral mixed-ligand cyanonitrosyl {CrNO}⁵ complexes of chromium(I) with the said organic donors.

Results and Discussion

The mixed-ligand complexes, [Cr(NO)(CN)₂(L-L)(H₂O)] and [Cr(NO)(CN)₂(ECAP)₂(H₂O)] were synthesised according to the equations,



where L-L = *o* PDA, *m* PDA, *p* PDA, BZN or SDA.



Resulting compounds under this investigation are non-hygroscopic, air-stable and coloured solids. They are thermally stable upto 300^o and give positive Griess reagent test².

The important infrared spectral bands of the complexes are presented in Table 1. The strong bands at 1 700–1 710 and 2 140–2 160 cm⁻¹ assigned to ν_{NO} and ν_{C-N} respectively, are in agreement with the results reported elsewhere⁴. The broad bands at 3 570 – 3 580 and 3 375 – 3.400 cm⁻¹ are due to ν_{OH} of coordinated water in all the complexes.

The ligands, *o*-PDA, *m*-PDA, *p*-PDA and BDN possess two amino groups as two potential donor sites while SDA contains four potential donor sites. (i) and (ii) amino group nitrogen, (iii) and (iv) sulphone group oxygen. The appearance of ν_{S=O} in the complex, 5 around the same frequency as that of the free ligand SDA indicates the inertness of sulphone group oxygen in bonding. The ν_{N-H} bands which occur at around 3 450 and 3 320 cm⁻¹ in all the aniline derivatives, undergo a low energy shift after complexation. Besides, a negative shift in the sp² ν_{C-N} mode and the appearance of a single sp² ν_{C-N} band at 1 245–1 260 cm⁻¹ in the spectra of complexes 1–5 (Table 1) suggest that both nitrogens of *o*-, *m*- *p*-PDA, BDN and SDA are involved in coordination¹.

The ligand ECAP possesses three potential donor sites : (i) the pyridine ring nitrogen, (ii) the amino nitrogen atom and (iii) the carbonyl oxygen of the side chain group. In RNH-C(=O)-OC₂H₅, the carbonyl absorption responsible for amide-I band is likely to be lowered after complexation through carbonyl oxygen. The amide-I band in ECAP appearing at 1 700 cm⁻¹

remains almost unchanged in its complex. This indicates that carbonyl group is inert towards coordination in this ligand. Further, the NH absorption in the free ligand occurs at about 3 200 and 3 120 cm^{-1} , which also remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom of the sidechain group. However, the pyridine ring breathing mode appearing at 998 cm^{-1} undergoes significant positive shift and appears at 1 020 cm^{-1} in its complex, indicating the coordination of pyridine ring nitrogen to chromium⁵.

was added dropwise at 0° to 2-aminopyridine (0.01 mol) in excess pyridine with constant stirring. After 2 h the mixture was poured into water to yield cream coloured 2-ethoxycarbonylaminopyridine (70%), m.p. 103°.

Potassium pentacyanonitrosylchromate (I) was prepared by the reported method⁷.

Synthesis of the complexes : An 1 : 1 aqueous acetic acid solution (8 ml) of the corresponding aniline derivative (0.01 mol) or 2-ethoxycarbonylaminopyridine (0.02 mol) was added with shaking to a

TABLE I—ANALYTICAL AND IMPORTANT IR SPECTRAL (cm^{-1}) DATA OF THE COMPLEXES

Sl. no.	Compd. / (Colour)	Analysis % : Found / (Calcd.)				ν_{NO}	$\nu_{\text{C-N}}$	$\nu_{\text{C-N}}$	ν_{NH}
		Cr	C	H	N				
1.	[Cr(NO)(CN) ₂ (<i>o</i> -PDA)(H ₂ O)] (Brownish yellow)	20.35 (20.00)	36.70 (36.92)	3.63 (3.84)	26.68 (26.92)	1 700	2 155	1 260	3 320 3 250
2.	[Cr(NO)(CN) ₂ (<i>m</i> -PDA)(H ₂ O)] (Brownish yellow)	20.46 (20.00)	36.69 (36.92)	3.54 (3.84)	26.72 (26.92)	1 705	2 150	1 245	3 360 3 250
3.	[Cr(NO)(CN) ₂ (<i>p</i> -PDA)(H ₂ O)] (Brownish yellow)	19.80 (20.00)	36.59 (36.92)	4.12 (3.84)	26.73 (26.92)	1 710	2 160	1 250	3 360 3 280
4.	[Cr(NO)(CN) ₂ (BDN)(H ₂ O)] (Brown)	15.32 (15.47)	42.29 (50.00)	4.37 (4.16)	20.52 (20.83)	1 700	2 145	1 255	3 350 3 270
5.	[Cr(NO)(CN) ₂ (SDA)(H ₂ O)] (Yellow)	13.32 (13.00)	42.32 (42.00)	3.25 (3.50)	17.82 (17.60)	1 710	2 160	1 250	3 350 3 280
6.	[Cr(NO)(CN) ₂ (ECAP) ₂ (H ₂ O)] (Greenish yellow)	10.58 (10.74)	44.30 (44.62)	4.72 (4.54)	20.53 (20.24)	1 705	2 140	—	1 020 ^a

^a Pyridine ring breathing mode.

The observed magnetic moment (1.70–1.76 B.M.) and *g* values (1.981–1.986) are consistent with a low-spin {CrNO}⁵ electronic configuration of chromium(I)⁶.

Due to the very poor solubility of the complexes in most of the commonly available organic solvents as well as in water, the conductance measurement of the compounds could not be carried out. The analytical data and the above results suggest the formulation of these complexes as [Cr(NO)(CN)₂(L-L)(H₂O)], (where L-L = *o*-PDA, *p*-PDA, *m*-PDA, BDN or SDA) and [Cr(NO)(CN)₂(ECAP)₂(H₂O)]. An octahedral structure has been suggested for the complexes.

Experimental

PDA and BZN (E. Merck) were used as such. SDA was obtained as a gift sample. ECAP was prepared as follows. Ethyl chloroformate (0.01 mol)

filtered aqueous solution of the parent compound, K₃[Cr(NO)(CN)₅].H₂O (0.01 mol, 35 ml). A coloured solid was obtained on heating and stirring the mixture for ~ 0.5 h at 80°. The resulting mixture was freed from the liberated HCN by passing CO₂ for a few hours. The resulting solid was washed several times with dilute acetic acid and finally with water and dried under reduced pressure.

Carbon, hydrogen and nitrogen present in the synthesised complexes were estimated microanalytically. Chromium was estimated as Cr₂O₃ by the standard method. Physical methods used in the present study were the same as reported earlier communication³.

Acknowledgement

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NOTE

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