

Synthesis and physico-chemical studies of some mixed-ligand isothiocyanatonitrosyl $\{\text{CrNO}\}^5$ complexes of chromium(I) with biologically active organic compounds

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A new series of hexa-coordinate mixed-ligand isothiocyanatonitrosyl $\{\text{CrNO}\}^5$ complexes of chromium(I) of the type $[\text{Cr}(\text{NO})(\text{NCS})_2(\text{L})_2(\text{H}_2\text{O})]$ (where L = chloropheniramine maleate, pheniramine maleate, mepyramine maleate, isonicotinic acid hydrazide, picolinic acid hydrazide or nicotinic acid hydrazide) have been synthesized in the solid state by the interaction of pentaithiocyanatonitrosylchromate(I) anion, $[\text{Cr}(\text{NO})(\text{NCS})_5]^{3-}$ with the appropriate biologically active organic compounds. The products, which have been characterized by elemental analyses, molar conductances, magnetic measurements, ESR, electronic and infrared spectral studies, contain chromium(I) in a low-spin $\{\text{CrNO}\}^5$ electron configuration. An octahedral structure has been suggested for the complexes.

A literature survey of isothiocyanatonitrosyl $\{\text{CrNO}\}^5$ complexes of monovalent chromium reveals only rare reports¹⁻³. Since very little work has been done on mixed-ligand isothiocyanatonitrosyl complexes of chromium(I), it was thought worthwhile to synthesize and characterize such complexes using biologically active organic compounds^{4,5} like chloropheniramine maleate (CHPHM, I), pheniramine maleate (PHM, II), mepyramine maleate (MEPM, III), isonicotinic acid hydrazide (INAH, IV), picolinic acid hydrazide (PAH, V) and nicotinic acid hydrazide (NAH, VI). The purpose of selecting these organic compounds is to find out the coordination sites in these bio-active compounds. As the biological activity of bio-active compounds is reported^{6,7} to be considerably affected on coordination, it is also anticipated to obtain mixed-ligand complexes of potential biological importance.

Experimental

Picolinic acid hydrazide (Tokyo Chemical Co., Japan), nicotinic acid hydrazide (Fluka AG, Swit-

zerland), chloropheniramine maleate, pheniramine maleate, mepyramine maleate (obtained as gift samples from different Indian drugs manufacturing companies), hydroxylammoniumchloride (BDH, Bombay), potassium chromate (Sarabhai M Chemicals, Baroda), and ammonium thiocyanate (Ranbaxy, New Delhi) were used as supplied. Distilled water was used in all the operations.

Preparation of the parent compound

The parent compound, pentaithiocyanatonitrosylchromate(I) anion, $[\text{Cr}(\text{NO})(\text{NCS})_5]^{3-}$, was prepared by following the procedure of Bhattacharya *et al.*¹ as given below.

A solution of 0.5 g (2.5 mmol) of K_2CrO_4 and 1.9 g NH_4SCN (25 mmol) in 25 ml water was combined with 2.7 g $\text{NH}_2\text{OH}\cdot\text{HCl}$ (37.5 mmol) with stirring. The resulting solution was heated at 80°C for about 40 min when a clear greenish violet solution was obtained.

Synthesis of the complexes

To a greenish violet solution of the parent anion, $[\text{Cr}(\text{NO})(\text{NCS})_5]^{3-}$, obtained as above, an aqueous acetic acid solution (10 cm^3 , 1:1) of isonicotinic acid hydrazide/nicotinic acid hydrazide/picolinic acid hydrazide (0.7 g)/chloropheniramine maleate/pheniramine maleate/mepyramine maleate (2.0 g) was added with shaking. A coloured solid precipitated on refluxing the resulting mixture for 1-2 h over a hot plate at 80°C and keeping the resulting mixture for ice cooling in a refrigerator. The resulting precipitate was filtered by suction, washed several times with dilute acetic acid, finally with water and dried *in vacuo* at room temperature to a constant weight. The analytical data are given in Table 1. Chromium was determined as Cr_2O_3 by the method reported elsewhere⁸. C, H and N were determined micro-analytically.

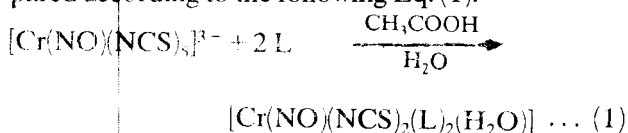
The IR spectra ($4000\text{--}600\text{ cm}^{-1}$) were recorded in nujol mulls on a Perkin Elmer-457 grating infrared spectrometer. The magnetic susceptibility measurements were made at room temperature on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. Pascal's constants were used for diamagnetic corrections. The ESR spectra were recorded at room temperature on a Varian E-3 spectrometer using the powdered sample at 9.53 GHz.

Table 1—Characterization data of chromium complexes

Compound (yield %), colour	Decomp. temp.	Found (Calcd), %					μ_{eff} (BM)	'g'
		Cr	C	H	N	S		
[Cr(NO)(NCS) ₂ (CHPHM) ₂ (H ₂ O)] (40) Dark brown	38	5.01 (5.21)	55.78 (50.55)	4.43 (4.81)	9.54 (9.82)	6.73 (6.41)	1.76	1.976
[Cr(NO)(NCS) ₂ (PHM) ₂ (H ₂ O)] (45) Dark brown	42	5.30 (5.60)	54.73 (54.31)	5.21 (5.38)	10.30 (10.56)	6.42 (6.89)	1.74	1.978
[Cr(NO)(NCS) ₂ (MEPH) ₂ (H ₂ O)] (40) Brown	45	5.36 (5.10)	51.39 (51.86)	5.73 (5.50)	12.49 (12.37)	6.01 (6.28)	1.71	1.980
[Cr(NO)(NCS) ₂ (INAH) ₂ (H ₂ O)] (55) Grey	215	10.32 (10.61)	34.03 (34.28)	3.43 (3.26)	25.32 (25.71)	13.51 (13.66)	1.76	1.982
[Cr(NO)(NCS) ₂ (PAH) ₂ (H ₂ O)] (50) Bluish black	190	10.75 (10.61)	34.07 (34.28)	3.58 (3.26)	25.28 (25.71)	13.92 (13.66)	1.70	1.978
[Cr(NO)(NCS) ₂ (NAH) ₂ (H ₂ O)] (60) Bluish black	210	10.83 (10.61)	34.68 (34.28)	3.53 (3.26)	25.40 (25.71)	13.79 (13.66)	1.72	1.982

Results and discussion

The mixed-ligand complexes [Cr(NO)(NCS)₂(L)₂(H₂O)] (see Table 1) were prepared according to the following Eq. (1).



All the compounds are coloured air stable solids. They decompose in dilute acids and alkalis only on heating and give a positive Griess test⁹. Their molar conductances measured in 10⁻³ M DMF are in the range 5.8–6.9 ohm⁻¹cm²mol⁻¹ and hence they are non-electrolytes.

In the IR spectra, the tentative assignments have been discussed. The appearance of a very strong band in the region 1695–1710 cm⁻¹ is assigned to $\nu(\text{NO})^+$, in agreement with the published data⁶. The thiocyanato group, may coordinate to the chromium through either the nitrogen or the sulphur atom or both. Chromium, being in the first transition series, has been placed as a class 'A' metal where the bonding of the SCN⁻ group to the chromium is generally reported to be of the Cr-NCS type. On coordination, $\nu(\text{CN})$ of the thiocyanato group is generally lowered in N-bonded complexes (near and below 2050 cm⁻¹) than in S-bonded complexes (near 2100 cm⁻¹). A comparison of the observed $\nu(\text{CN})$ at 2025–2035 cm⁻¹ in the complexes of this investigation with those of the reported thiocyanato complexes, suggests N-bonded thiocyanato groups in these complexes.

The drugs, CHPHM and PHM possess two donor sites: (i) the pyridine ring nitrogen and (ii)

the amino nitrogen. MEPM contains three potential donor sites: (i) the pyridine ring nitrogen, (ii) and (iii) side chain tertiary nitrogens. The characteristic sp^3 $\nu(\text{C}-\text{N})$ (ref. 10) appearing ~1180 cm⁻¹ in free CHPHM, PHM and MEPM and sp^2 $\nu(\text{C}-\text{N})$ (ref. 10) at 1320 cm⁻¹ in free MEPM remain unperturbed in their respective complexes indicating the inertness of side chain nitrogen towards coordination to chromium. However, the presence of ring $\nu(\text{C}=\text{N})$ and the pyridine ring breathing mode in the range 1590–1610 and 1020–1030 cm⁻¹, respectively, indicate the coordination of pyridine ring nitrogen in all these drugs^{11,12}. The ligands INAH, NAH and PAH possess three donor sites: (i) the pyridine ring nitrogen (ii) the amide group oxygen and (iii) the hydrazine nitrogen. These ligands show amide-I band (νCO mode) ~1670 cm⁻¹ and symmetric and asymmetric $\nu(\text{NH})$ modes at 3300–3350 and 3200–3250 cm⁻¹, respectively. These remain unaffected after complexation, thus indicating that neither amide oxygen nor hydrazine nitrogen participates in coordination with chromium. The pyridine ring $\nu(\text{C}=\text{N})$ appearing at ~1580 cm⁻¹ and pyridine ring breathing mode at ~995 cm⁻¹ in the ligands IV–VI, undergo a significant shift to higher wavenumber at 1600–1610 and 1020–1035 cm⁻¹, respectively, in its complexes. This is considered to be diagnostic of the coordinated pyridine nitrogen^{12,13}.

The observed magnetic moments and ESR data of the synthesized complexes are given in Table 1. These values are consistent with the low spin {CrNO}⁵ complexes of chromium(I)^{13,14}.

The electronic spectra of two representative compounds (2 and 6) were recorded in DMF.

They show three characteristic absorption peaks at 330-360, 410-430 and 650-665 nm. The electronic transitions responsible for these characteristic UV-Vis peaks in the complexes are likely to be as $1b_2 \rightarrow 4a_1$, $1b_2 \rightarrow 1b_1$ and $1b_2 \rightarrow 3e$, respectively considering the MO picture applicable to hexacoordinated mononitrosyl complexes of C_{4v} symmetry¹⁵. These observations are comparable to results reported elsewhere¹⁶.

The satisfactory analytical and spectral data suggest that the complexes may be formulated as $[\text{Cr}(\text{NO})(\text{NCS})_2(\text{L})_2(\text{H}_2\text{O})]$. As these complexes exhibit one NCS stretching and one NO stretching band, it is reasonable to propose an octahedral structure for these complexes where NCS is *trans* to NCS and L is *trans* to L at equatorial positions and NO is *trans* to water in axial positions.

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