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NEW COMPOUNDS

Synthesis and Characterization of Some Mixed-Ligand Cyanonitrosyl–$\{CrNO\}^5$ Complexes of Chromium with Some Potentially Mono-, Bi-, and Tridentate Ligands

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Some novel mixed-ligand cyanonitrosyl complexes of chromium(I) having the $\{CrNO\}^5$ electron configuration with the formulation $[Cr(NO)(CN)_2(L)_2(H_2O)]$ (where L = 2- or 4-vinylpyridine, 2-, 3-, or 4-pyridinaldoxime, or pyridin-2-amidoxime) have been synthesized in the solid state by the interaction of potassium pentacyanonitrosylchromate(I) monohydrate, $K_3[Cr(NO)(CN)_5]\cdot H_2O$, with the heterocyclic bases L. The complexes, which have been characterized by elemental analyses, magnetic measurements, electron spin resonance, and infrared spectral studies, contain chromium(I) in a low-spin d^5 configuration. An octahedral structure, where CN is trans to CN and L is trans to L in equatorial positions and NO is trans to water at axial position, has been proposed for the complexes.

Introduction

A survey of the literature of neutral mixed-ligand nitrosyl complexes of monovalent chromium reveals few reports on such complexes (*2–10*). In recent years, a great deal of interest has been shown to the study of neutral mixed-ligand cyanonitrosyl complexes of chromium(I) (*5–10*). No attempt have been made so far to isolate cyanonitrosyl complexes of chromium(I) with vinylpyridines (VPY), pyridinaldoximes (PYA), and pyridin-2-amidoxime (PYAM). It was, therefore, considered worthwhile to prepare and characterize neutral cyanonitrosyl complexes of chromium(I) with 2- and 4-vinylpyridines, 2-, 3-, and 4-pyridinaldoximes, and pyridin-2-amidoxime and the present paper deals with the results of this study.

Experimental Section

Materials. Vinylpyridines and pyridinaldomixes were obtained from Aldrich Chemical Co., and used as such. Pyridin-2-amidoxime was prepared by adopting the literature method (*11*). Hydroxyammonium chloride and chromic acid were supplied by SD'S Lab-chem Industry, Bombay. Potassium cyanide was procured from May and Baker Ltd, Dagenham, England. Distilled water was used in all the operations. The potassium salt of pentacyanonitrosylchromate(I) monohydrate, $K_3[CrNO(CN)_5]\cdot H_2O$, prepared by the method of Griffith and Wilkinson (*12*), was used as the parent compound for the preparation of all the complexes.

Synthesis of the Complexes. An 1:1 H_2O–OHAc solution of the appropriate base was added with shaking to a filtered aqueous solution of $K_3[CrNO(CN)_5]\cdot H_2O$ and a colored solid precipitated after the mixture was warmed for 20–30 min. The resulting mixture was freed from liberated HCN by passage of a current of CO_2 for a few hours. The precipitate was filtered, washed several times with H_2O, EtOH, and Et_2O, and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data were found satisfactory. (The analytical data were submitted for review.)

Analyses. Chromium was determined as Cr_2O_3 by a method reported elsewhere (*7*, *8*). Carbon, hydrogen, and nitrogen were determined microanalytically.

Physical Methods. Infrared spectra (4000–600 cm^{-1}) were recorded in Nujol on a Beckman IR-20 spectrophotometer. The magnetic susceptibilities were measured at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as calibrant. Effective magnetic moments were calculated after making diamagnetic corrections using Pascal's constants (*13*). Electron spin resonance spectra were recorded at room temperature on a Varian E-3 spectrometer using powdered samples at the microwave frequency 9.53 GHz.

Results

The mixed-ligand complexes $[Cr(NO)(CN)_2(L)_2(H_2O)]$ were prepared according to the equation

$$K_3[Cr(NO)(CN)_5]\cdot H_2O + 2L \xrightarrow[H_2O]{CH_3COOH} [Cr(NO)(CN)_2(L)_2(H_2O)] + 3CH_3COOK + 3HCN(g) + H_2O$$

(L = 2-VPY, 4-VPY, 2-PYA, 3-PYA, 4-PYA, or PYAM)

The resulting compounds are exceptionally stable in air. All of the compounds had decomposition temperature above 250 °C. All the compounds after decomposition with KOH followed by acidifying with acetic acid give a pink color with a few drops of Griess reagent (*14*). All the compounds are insoluble in common solvents as well as in water and, therefore, their molar conductivity values and molecular weights could not be mea-

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Table I. Color, Yield, and Some IR (cm^{-1}) Bands

compound[a]	color	yield, %	in-plane ring defrmn mode
$[Cr(NO)(CN)_2(2\text{-}VPY)_2(H_2O)]$	yellow	50	1010[b]
$[Cr(NO)(CN)_2(4\text{-}VPY)_2(H_2O)]$	yellow	52	1025[b]
$[Cr(NO)(CN)_2(2\text{-}PYA)_2(H_2O)]$	yellow	50	650
$[Cr(NO)(CN)_2(3\text{-}PYA)_2(H_2O)]$	yellow	55	660
$[Cr(NO)(CN)_2(4\text{-}PYA)_2(H_2O)]$	yellow	58	662
$[Cr(NO)(CN)_2(PYAM)_2(H_2O)]$	brownish yellow	52	645

[a] VPY = vinylpyridine; PYA = pyridinaldoxime; PYAM = pyridin-2-amidoxime. [b] Pyridine ring breathing vibration.

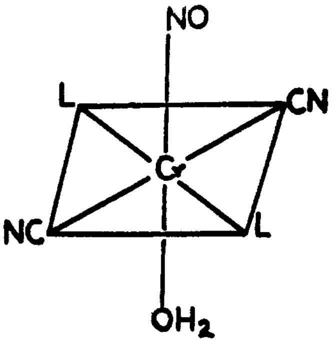

Figure 1. Proposed structure for $[CrNO(CN)_2(L)_2(H_2O)]$.

sured. The compounds were characterized on the basis of the following results.

(*I*) ***Infrared Spectra*.** Some infrared spectral bands for the complexes are given in Table I. The appearance of a very strong band in 1705–1720-cm^{-1} region and a strong band in the 2150–2190-cm^{-1} region are assigned to $\nu(NO)^+$ and $\nu(CN)$ modes, respectively, which are in accordance with the assignment made for the other reported compounds (*8*, *12*).

(*II*) ***Thermogravimetric Analysis*.** The weight loss observed by TGA at 120 ± 5 °C corresponds to the elimination of one molecule of water (*7*, *15*) and further supports the presence of one molecule of the coordinated water in the complexes.

(*III*) ***Magnetic Studies and ESR Spectra*.** The magnetic moments, 1.70–1.74 μ_B, at room temperature and g values, 1.982–1.986, of powdered samples, which are comparable to the observations made by Manoharan and Gray (*16*) and Meriwether et al. (*17*), consistent with a low-spin d^5 configuration of chromium(I).

The satisfactory analytical data and all the above results suggest the formulation of these complexes as $[Cr(NO)(CN)_2(L)_2(H_2O)]$ (Figure 1). Thus it is reasonable to propose an octahedral geometry (*4*, *7*) for these compounds.

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Registry No. $[Cr(NO)(CN)_2(2\text{-}VPY)_2(H_2O)]$, 112817-22-8; $[Cr(NO)(CN)_2(4\text{-}VPY)_2(H_2O)]$, 112817-23-9; $[Cr(NO)(CN)_2(2\text{-}PYA)_2(H_2O)]$, 112839-67-5; $[Cr(NO)(CN)_2(3\text{-}PYA)_2(H_2O)]$, 112839-68-6; $[Cr(NO)(CN)_2(4\text{-}PYA)_2(H_2O)]$, 112839-69-7; $[Cr(NO)(CN)_2(PYAM)_2(H_2O)]$, 112817-24-0; $K_3[Cr(NO)(CN)_5]$, 14100-08-4.

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Syntheses of 1-Phenyl-2-(4-pyrimidinyl)ethanone and Related Ethanones

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Eleven 1-phenyl-2-(4-pyrimidinyl)ethanones were synthesized by the condensation of 4-methylpyrimidine and the requisite methyl benzoate ester with sodium hydride as the condensing agent. Substituents in the 3- and 4-position of the phenyl ring were chloro, dimethylamino, methoxy, methyl, and trifluoromethyl.

In connection with our interest in enolizable ketones (*1*) we recently had need of some 1-phenyl-2-(4-pyrimidinyl)ethanones which carried substituents in the 3- or 4-position of the phenyl moiety, the substituents being chloro, dimethylamino, methoxy, methyl, and trifluoromethyl. The parent compound as well as the 3-chloro, 4-chloro, 3-methoxy, and 4-methoxy compounds have been prepared by Fauran et al. (*2*). The method of Rauch

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