

Preparation of a New Oxotetracyano- (pyridine)chromate(IV) Anion

S. SARKAR, B. SHARMA*, R. C. MAURYA, S. C. CHAURASIA &
S. K. SRIVASTAVA

Department of Chemistry, T. D. College, Jaunpur 222002

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A new hexacoordinated Cr(VI) anion, $[\text{CrO}(\text{CN})_4\text{Py}]^{2-}$, isolated as potassium salt has been prepared and characterized on the basis of IR data.

Even though most of the IR absorption bands due to free ligands are modified in the complexes, a few important bands have been assigned and conclusion regarding the bonding has been derived on analysis of these bands.

$\nu(\text{C}=\text{S})$ in dithiourcas occurs around 780 cm^{-1} which is shifted in the complexes to $\sim 730\text{ cm}^{-1}$ indicating a decrease in bond order and providing an indirect evidence for bonding through the sulphur atom. Consequent upon bonding through sulphur, $\nu\text{C}-\text{N}$ which appears $\sim 1100\text{ cm}^{-1}$ in ligands is shifted to 1120 cm^{-1} . $\nu\text{N}-\text{H}$ of the free ligands which occurs $\sim 3200\text{ cm}^{-1}$ does not shift in the complexes indicating absence of coordination through nitrogen, except in cases of some chloro-complexes where the band broadens possibly due to hydrogen bonding of the anion with the N-H proton. In addition to it $\nu(\text{M}-\text{S})$ appears at $320-330\text{ cm}^{-1}$ providing a direct evidence of bonding through sulphur. Though it is possible to distinguish between octahedral, tetrahedral and planar complexes by the position of the metal thiourea stretching vibrations, metal-sulphur stretching vibrations did not permit the deduction of the stereochemistry, as the presence of metal-anion stretches complicate the vibrational analysis. This has been confirmed by earlier works^{6,7} on metal sulphur vibration frequencies of thiourea complexes. $\nu(\text{C}=\text{N})$ in the case of thiocyanato complexes is observed around $\sim 2150\text{ cm}^{-1}$, an increase of $70-80\text{ cm}^{-1}$ relative to free thiocyanate, indicating either a terminal sulphur bonding or the presence of a bridging thiocyanato group⁸.

The complexes may have two alternative stereochemistries, i.e. (a) tetrahedral or (b) octahedral, depending on the way the anion coordinates. If the thiocyanato group is terminal sulphur bonded and the halogens are not bridging the complexes may have a tetrahedral geometry on the basis of their composition. But in the far infrared spectra, the metal halogen stretching frequencies appear at $220-260\text{ cm}^{-1}$, providing a probable indication for the presence of bridging halogen atoms. Further most of the complexes are amorphous, have high melting points and are either insoluble or sparingly soluble in common organic solvents. This provides evidence for polymeric nature of the compounds. Hence, the possibility of an octahedral structure involving a halogen or pseudo-halogen bridge is not ruled out. This is in conformity with some earlier observations⁹ on thiourea complexes.

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COMPLEXES of chromium(IV) are rare¹⁻⁴. In this note we report the isolation and characterization of a new hexacoordinated chromium(IV) anion, $[\text{CrO}(\text{CN})_4\text{Py}]^{2-}$, as potassium salt.

Pyridinium chlorochromate(VI), $\text{PyH}[\text{CrO}_3\text{Cl}]$ (5 g) was dissolved in pyridine (5 ml) and to this was added ethanol (20 ml) and solution kept overnight to give a brown solution. To this, ethanolic solution of KCN (6.5 g) was added and heated at 150° for 10 min. On keeping the resulting deep red solution overnight, the complex separated as deep red oil which was purified by repeatedly dissolving it in little water and reprecipitating by adding ethanol till the wash liquor was cyanide free, finally adding absolute ethanol to get a brown powder which was dried over CaCl_2 under reduced pressure; yield 60% {Found: K, 22.70; Cr, 15.31; N, 19.85; H_2O (P_2O_5 drying), 5.20%. $\text{K}_2[\text{CrO}(\text{CN})_4\text{Py}] \cdot \text{H}_2\text{O}$ requires K, 22.52; Cr, 14.97; N, 20.16; H_2O , 5.18%}.

The salt is hygroscopic and is highly soluble in water, being insoluble in common organic solvents. The aqueous solution is red in colour which slowly decomposes with the expulsion of HCN. In KCN solution it is stable. Acid decomposes it immediately with disproportionation to Cr(III) and Cr(VI) while in alkaline medium it decomposes only on prolong keeping or warming. Its fresh aqueous solution gives insoluble coloured precipitates with many metal ions Cu^{2+} (greenish brown), Co^{2+} (orange brown), Ni^{2+} (bright brown), Mn^{2+} (orange), Ba^{2+} (flesh coloured from concentrated solution), Ag^+ (reddish brown).

The room temperature (24°) magnetic moment of the complex is 3.0 BM consistent with the d^2 -configuration of Cr(IV). The aqueous electronic spectrum in the presence of traces of free KCN shows bands at 20.41, 26.67, 38.00 and 38.99 kK. The first band appears as a shoulder. The bands at 38.00 and 38.99 kK are more intense. Its IR spectrum (nujol and KBr) shows important bands at 3550, 3440, 3130, 1620-25, 905, 625, 525, 450, 430 and 335 cm^{-1} .

The appearance of a sharp band of 2130 due νCN and at 905 cm^{-1} due to $\nu\text{Cr}=\text{O}$ suggests the coordination of pyridine *trans* to $\text{Cr}=\text{O}$ group. All the other bands observed are in conformity with earlier assignments of similar pyridine complexes^{5,8}.

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*Department of Chemistry, Gorakhpur University, Gorakhpur.

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Terdentate Ligands: Part II — Octahedral Ni(II), Co(II) & Cr(III) Complexes of Schiff Bases Derived from 2-(2'-Aminoethyl)pyridine

D. K. RASTOGI & P. C. PACHAURI

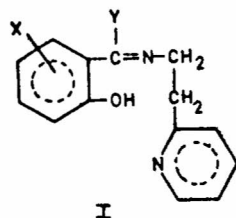
Department of Chemistry, Meerut College, Meerut 250001

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Preparation and characterization of a series of new Ni(II) and Co(II) complexes of the type $[ML_2]$, where L = tridentate Schiff base derived from 2-(2'-aminoethyl)pyridine and salicylaldehyde, substituted salicylaldehyde (X-Sal, X = 5-Cl, 5-NO₂, 5,6-Benzo) (X-Salaep), *o*-hydroxyacetophenone (Hapaep), *o*-hydroxypropiofenone (Hppaep) or *o*-hydroxybutyrofenone (Hbpaep) have been described. Chromium(III) complexes of the composition $[CrL_2]Cl$ are also reported. Analytical, conductance, magnetic, electronic and IR spectral data show that all the complexes have octahedral geometry.

EARLIER we have reported the preparations and characterization of several transition metal complexes of 2-(2'-aminoethyl)pyridine¹⁻³. Now we report here the preparation of Ni(II), Co(II) and Cr(III) complexes with tridentate Schiff bases (I) derived from 2-(2'-aminoethyl)pyridine and their characterization on the basis of analytical, conductivity, magnetic, electronic and IR spectral studies.

Complexes with X-Salaep — Salicylaldehyde and substituted salicylaldehyde (0.025 mole) and 2-(2'-aminoethyl)pyridine (0.025 mole) in ethanol were mixed and stirred on a magnetic stirrer for 15 min at 60-70°. After the addition of metal chloride (0.01 mole) in ethanol and an aqueous solution of sodium acetate (0.02 mole) the reaction mixture was stirred for 1 hr and then refluxed for 3-5 hr. The contents were kept in a silica dish for slow crys-



- X-Saldep; Y = H, X = H, 5-Cl, 5-NO₂ or 5, 6-Benzo
 Hapaep; X = H, Y = CH₃
 Hppaep; X = H, Y = C₂H₅
 Hbpaep; X = H, Y = C₃H₇

tallization and recrystallized from ethanol; yield 80-85%.

Complexes with Hapaep — A mixture of 2-(2'-aminoethyl)pyridine (0.025 mole) and *o*-hydroxyacetophenone (0.025 mole) in absolute ethanol was stirred and refluxed at 70° for about 3-4 hr. To this was added an ethanolic solution of metal chloride (0.01 mole) and the contents refluxed for about an hour. A solution of sodium ethoxide was added dropwise and the reaction mixture further refluxed for 8 hr with constant stirring. The contents were allowed to stand overnight when crystals of the crude complex were obtained which were recrystallized from ethanol; yield ~75%.

Complexes with Hppaep — They were prepared by a procedure similar to that used for Hapaep complexes using *o*-hydroxypropiofenone (0.025 mole) and reaction mixture was refluxed for 12 hr at about 70° and then concentrated *in vacuo*. It was refrigerated for two days when the crystals of the crude product were obtained. The compound was recrystallized twice from ethanol; yield 55-60%.

Complexes with Hbpaep — These were prepared as above employing *o*-hydroxybutyrofenone (0.025 mole) and the reaction mixture was refluxed at 70° for 18 hr. Concentration of reaction mixture and subsequent refrigeration did not produce crystals. The solution was evaporated *in vacuo* and on refrigeration for several days solid complexes were obtained. These were recrystallized from ethanol; yield 45-48%.

Analytical, magnetic moment, melting point and conductivity data of the complexes are listed in Table 1.

The magnetic moments observed for Ni(II) (2.96-3.42 BM), Co(II) (4.85-5.12 BM) and Cr(III) (3.70-3.82 BM) complexes are consistent with octahedral symmetry for these complexes. The increase in the magnetic moment from that of spin-only value in the case of Ni(II) complexes may be due to some "mixing in" of upper states via spin-orbit coupling⁴. Higher orbital contribution for octahedral Co(II) complexes of 2-(2'-aminoethyl)pyridine and other 2-substituted pyridine ligands has been observed by Rastogi¹ and Sutton *et al.*⁵. The value for Cr(III) complexes is slightly less⁶ than that expected for three unpaired spins in *O_h* environment.

Judging from the greater value of magnetic moment for X-Salaep (where X = H, 5-Cl, 5-NO₂ and 5,6-benzo) complexes of Ni(II) (3.31-3.42 BM), Co(II) (5.02-5.12 BM), Cr(III) (3.80-3.82 BM) as compared with the value of Hapaep [Ni(II), 3.01; Co(II) 4.95; Cr(III) 3.77 BM], Hppaep [Ni(II), 2.26; Co(II), 4.92; Cr(III), 3.75 BM] and Hbpaep [Ni(II), 2.96; Co(II), 4.85; Cr(III), 3.70 BM] complexes; it may be concluded that the geometry of the latter compounds is distorted from the regular octahedron.

Three bands have been observed in the electronic spectra of Ni(II) complexes in the region (10400-8980 cm⁻¹) [ν_1 , ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$], (16785-14000 cm⁻¹) [ν_2 , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$] and (27515-25050 cm⁻¹) [ν_3 , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$] indicating *O_h* geometry for these complexes. In the case of Co(II) complexes three bands observed in the region 8850-9850, 17000-19800 and 20850-21500 cm⁻¹ may be assigned to