

Preparation and Characterization of Some Hexa Coordinated Cyanonitrosyl Complexes of Chromium with Some Potentially Mono-, Bi- And Tri-Dentate Ligands



Lata

Head

Deptt. of Chemistry,
Khandelwal College of
Management Science and
Technology,
Bareilly

Neeraj Kumar

Head/Incharge

Deptt. of Chemistry,
S.S.M.V. (P.G.) College,
Shikarpur, Buland Shahr

Saurabh Sharma

Head/Incharge

Deptt. of Chemistry,
Model Public Education College,
Chandausi, Sambhal

Shalini Gupta

Associate Professor

Deptt. of Chemistry,
Khandelwal College of
Management Science and
Technology, Bareilly

Abstract

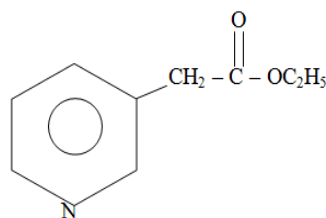
Some novel mixed-ligand cyanonitrosyl complexes of chromium(I) with formulation $[\text{Cr}(\text{NO})(\text{CN})_2(\text{L})_2(\text{H}_2\text{O})]$ (where L=Ethyl, 3-Pyridylacetate, 4-(2-methylaminoethyl)-pyridine, 4-picolylchloride hydrochloride picolinamide, pyridine-3-amidoxime) have been synthesized in the solid state by the interaction of potassium pentacyanonitrosylchromate(I) monohydrate, $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_2(\text{H}_2\text{O})]$ with the said heterocyclic bases, L. The complexes, which have been characterized by elemental analysis, magnetic measurement, 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 position, and NO is trans to water at axial position has been proposed for the complexes.

Keywords: Mixed-Ligand, cyanonitrosyl, bi- and Tri-Dentate Ligands.

Introduction

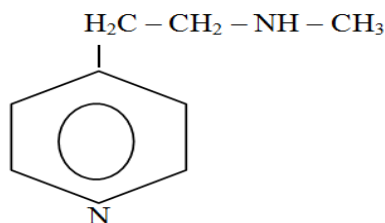
Synthesis and physico-chemical studies of some novel mixed-ligand cyanonitrosyl $\{\text{CrNO}\}^5$ complexes of chromium(I) with some potentially monodentate pyridine derivatives like 3-pyridine-propanol and potentially bidentate pyridine based organic compounds like nicotine acid n-hexylester and 3-pyridyl ethyl ketone have been discussed in the previous chapter. As a part of our programme to synthesize and characterize some more neutral mixed-ligand cyanonitrosyl complexes of monovalent chromium, attempts are being made under this investigation to synthesize such complexes with some new potentially mono-, bi- and tridentate ligands. 2-methyl-5-isopropylaniline, 4-tert-butylaniline, and 2,4,6-trimethoxyaniline and potentially bidentate aromatic amine line 3-cyanoaniline have been discussed in chapter-II. As a part of our programme to synthesize and characterize some neutral mixed-ligand cyanonitrosyl complexes of monovalent chromium, studies have been extended using some N, alkyl-, N-N-dialkyl- and N-benxyl-N-alkyl-aniline(s).

Although considerable importance has been shown to the study of the neutral mixed-ligand cyanonitrosyl complexes of chromium (I-IV), cyanonitrosyl complexes of chromium (I) with diethyl 3-pyridyl acetate, 4-(2-methylaminoethyl) pyridine, 4-picolylchloride hydrochloride, picolinamide and pyridine-3-amidoxime have not been described hitherto. We, therefore, report here the first synthesis of neutral cyanonitrosyl complexes of monovalent chromium with the aforesaid ligands and the present chapter described the result of this study.

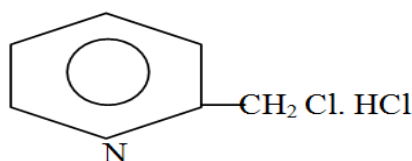


Ethyl-3-pyridylacetate

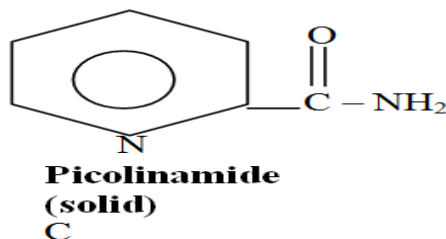
d = 1.086



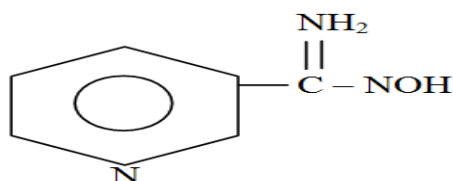
4-(2-Methylaminoethyl)pyridine
d = 0.981



4-Picolyl chloride hydrochloride
(solid)



Picolinamide
(solid)



Pyridine-3-amidoxime
(solid)

Experimental

Material Used

Ethyl-3-pyridyl acetate and 4-picolylchloride hydrochloride were obtained from Aldrich Chemical Co. U.S.A. 4-(2-Methylaminoethyl) Pyridine was a product of K&K Laboratories, Rare & Fine Chemicals New York, while picolinamide was supplied by Tokyo Chemicals Industry Co. Ltd., Japan, Pyridine-3-aminoxine was prepared by adopting the method reported elsewhere (15). Distilled water was used in all operations.

Analysis of the Constituent Elements

Carbon, hydrogen and nitrogen present in the investigated complexes were estimated micro-analytically.

Physical Method

Magnetic Measurements

Magnetic susceptibility measurements of the synthesized complexes were made by Gouy method at room temperature. Cobalt mercury tetrathiocyanate

Hg[Co(NCS)₄] was used as calibrant. Magnetic moments were calculated using the equation:

$$\mu_{\text{eff}} = 2.84 (\chi^{\text{Mcorr}} \cdot T)^{1/2}$$

Infrared Spectral Measurements

Infrared spectra of the uncoordinated ligands and of the complexes were recorded in nujol mulls on a Bechman IR-20 spectrophotometer at the RSIC, C.D.R.I. Luchnow. Spectra were recorded in the range 4000-600 cm⁻¹.

Electron Spin Resonance Spectra

Electron spin resonance spectra were recorded for 'g' values at room temperature using powdered sample on a Varian E-3 spectrometer at C.D.R.I. Luchnow. Spectra were recorded at the microwave frequency 9.53 GHz and 'g' values were calculated using the equation:

$$g = \frac{714.44 \times \nu(\text{GHz})}{H(\text{G})}$$

Thermogravimetric Analysis

The t.g. curves were recorded on a G-70 Thermoanalyser SKETARAM, Lyon, France, in air at a heating rate 10°C min⁻¹, and upto 800°C

Preparation of Parent Compounds

The starting compound, potassium pentacyanonitrosylchromate(I) monohydrate, K₃[Cr(NO)(CN)₅].H₂O was prepared according to the procedure of Griffith and Wilkinson (16). The purity of the compound was checked by elemental analysis and comparison of the infrared spectral data with those recorded in the literature (16).

Preparation of The Complexes With Potentially Monodentate Ligand

Preparation of [Cr(NO)(CN)₂(4-PIC)₂(H₂O)]

To a filtered aqueous solution of the parent compound, K₃[Cr(NO)(CN)₅].H₂O (0.01 M, 50ml), an aqueous acetic acid solution (10ml, 1:1) of the 4-picolyl-chloride hydrochloride was added with shaking. The resulting green solution was heated over a hot plate for 15 minutes at 80°C. CO₂ was bubbled through the solution for a few hours, to chase the liberated HCN. During this time a yellow coloured solid was precipitated. The precipitate was filtered, washed several times with distilled water and finally with ethanol and dried in a vacuum desiccators over silica gel at room temperature to a constant weight. The analytical data are given in Table 2.

Preparation of The Complexes With Some Potentially Bidentate Ligand

Preparation of [Cr(NO)(CN)₂(EPYA)₂(H₂O)]

To a filtered aqueous solution of the potassium pentacyanonitrosylchromate (I) monohydrate (0.01 M), an aqueous acetic acid (1:1) solution of ethyl-3-pyridylacetate (0.02M) was added with shaking, when a Brownish yellow coloured solid was precipitated on warming for 20 minutes. The resulting mixture was freed from liberated HCN by passing a current of CO₂ through the mixture for approximately 2-3 hours. The precipitate was suction filtered, washed several times with distilled water and finally with ethanol and dried over silica gel in a vacuum desiccators at room temperature. The analytical data are given in Table 2.

Preparation of [Cr(NO)(CN)₂(4-MAEP)₂(H₂O)]

An identical procedure as above was employed in synthesis of this compound just replacing ethyl 3-pyridylacetate by 4-(2-methylaminoethyl) pyridine. The complex was analyzed and the results are given in Table 2.

Preparation of [Cr(NO)(CN)₂(PICAM)₂(H₂O)]

For the preparation of this complex, almost similar procedure as above was applied taking picolinamide instead of 4-(2-methylaminoethyl) pyridine. The obtained analytical data are given in Table 2.

Preparation of [Cr(NO)(CN)₂(PYAM)₂(H₂O)]

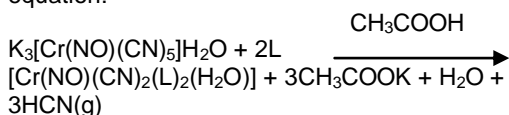
An identical procedure was adopted in synthesis of this compound taking pyridine-3-amidoxime in place of picolinamide. The complex was analyzed and analytical data are given in Table 2.

Properties of The Complexes

All the complexes are colored solids (Table 3) and stable in air. All the compounds after decomposition with KOH following by acidifying with acetic acid give a pink colour with few drops of Griess Reagent (17). They are thermally stable and do not melt or decompose below 285°C. All these complexes are insoluble in common solvents as well as in water and, therefore, their molar conductivity values and molecular weights could not be measured.

RESULTS AND DISCUSSION:

The mixed-ligand cyanonitrosyl complexes [Cr(NO)(CN)₂(L)₂(H₂O)] (see Table 1 for legend names) were synthesized according to the following equation:



Where L = EPYA, 4-MAEP, 4-PIC, PICAM or PYAM

The partial replacement of the cyano groups in the hexa-coordinated complex, K₃[Cr(NO)(CN)₅]H₂O by two molecules of ligand arises from the trans effect of NO group. Studies of Raynor and co-worker (18) on the stepwise equation of the pentacyanonitrosylchromate(I) [Cr(NO)(CN)₅]³⁻ to attain [Cr(NO)(CN)₂(H₂O)₃] favour the above reaction scheme.

Compounds were characterized on the basis of the following results:

Magnetic and E.S.R. Studies

The magnetic and electron spin resonance data of complexes are given in Table 5. The magnetic moments 1.70 to 1.75 B.M. at room temperature and 'g' values, 1.976 – 1.982 of powdered compounds, which are comparable to the observation made by Manoharan and Gray (19) and L.S. Meriwether et.al. (20) are consistent with low-spin d⁵ - configuration of chromium (I).

Thermogravimetric Analysis

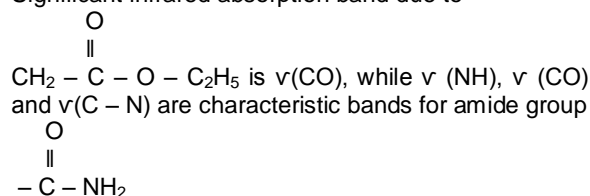
The dehydration temperature obtained by thermogravimetric analysis for all the compounds are presented in Table 4. The weight loss observed at the dehydration temperature for each compound corresponds to the elimination of one molecule of water (21). This result supports the presence of one

molecule of water in each compound (vide infrared discussion for co-ordinated water in these complexes).

Infrared Spectra Studies

The important infrared spectral bands of the complexes are presented in Table 6. The appearance of a very strong band in the region 1700 to 1710 cm⁻¹ and a strong band in the region 2150 to 2160 cm⁻¹ are assigned to ν(NO)⁺ and ν(C≡N) modes respectively, which are in accordance with assignment made for other reported complexes (22,23).

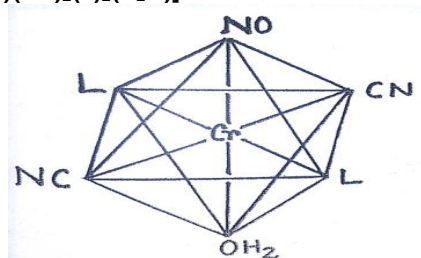
All the ligands (except 4-PIC) used in the present study – EPYA 4 – MAEP and PICAM possess two potential donor sites: (i) Pyridine ring nitrogen (ii) carbonyl oxygen of ester group in EPYA or amino nitrogen in 4 – MAEP or the amide oxygen in picolinamide. PYAM possesses three potential donor sites: (i) Pyridine ring nitrogen (ii) The oxime group nitrogen; and (iii) The amino group nitrogen, while 4 – PIC contains only pyridine ring as the donor site. Significant infrared absorption band due to



In amides and other carbonyl donors (24), a significant negative shift of the carbonyl frequency takes place because of the co-ordination through the carbonyl oxygen. The ν(CO) occurring at approximately 1675 cm⁻¹ in ethyl – 3 – pyridylacetate remains unperturbed in the infrared spectrum of its complex, thus excluding the possibility oxygen (ester) – to chromium bonding. The ν(NH), ν(CO) and ν(C – N) of the free picolinamide remain unchanged in its complex. These features clearly indicate that the amide oxygen is inert towards co-ordination in the complex. The ν(NH) in uncoordinated 4 – (2 – methyl – aminoethyl) pyridine remains unchanged in its complex, thus suggesting the inertness of amino nitrogen in the said amine.

Pyridine – 3 – amidoxime exhibits two sharp bands at 3350 and 3465 cm⁻¹ which may be assigned to ν(NH) asymmetric and ν(NH) symmetric, respectively. A broad band in the 3175 – 2970 cm⁻¹ may be due to associated ν(OH) and ν(NH)₂. Another broad band in the 2850 – 2735 cm⁻¹ may be due to (OH) free involved in hydrogen bonding. The band at 1630 cm⁻¹ has been assigned to ν(C=N) and the one appearing at 955 cm⁻¹ to ν(N – O). The ν(NH), ν(CO) and ν(C – N), frequencies of the uncoordinated pyridine-3-aminoxime remain almost unperturbed in the complex No.5. However, evidence of co-ordination of the pyridine ring nitrogen in all the ligands under study is manifested by a significant positive shift of pyridine ring breathing mode occurring at approximately 1000 cm⁻¹ in the free ligands (25-27).

Figure 1: Proposed Octahedral Structure of $[Cr(NO)(CN)_2(L)_2(H_2O)]$



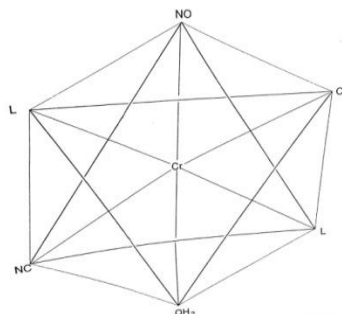
Where L=EPYA, 4-MAEP, 4-PIC, PICAM OR PYAM.

All the complexes exhibit a broad band in $3580-3400\text{ cm}^{-1}$ region, indicating presence of water, probably co-ordinated (although bands attributed to coordinated water are not easily discernible from its spectra due to ligand interference) (28-30).

The analytical data and all the evidences presented here suggest the formulation of these complexes as $[Cr(NO)(CN)_2(L)_2(H_2O)]$. This it is reasonable to propose an octahedral geometry for these compounds, where CN is trans to CN and L is

trans to L at equatorial position, whereas NO is trans to water in the axial position. The nitrosyl group trans to water would labilize the water and help to account for the low-temperature at which these complexes dehydrate.

Figure 1: Proposed Octahedral Structure of $[Cr(NO)(CN)_2(L)_2(H_2O)]$



Where L=EPYA, 4 - MAEP, 4 - PIC, PICAM OR PYAM

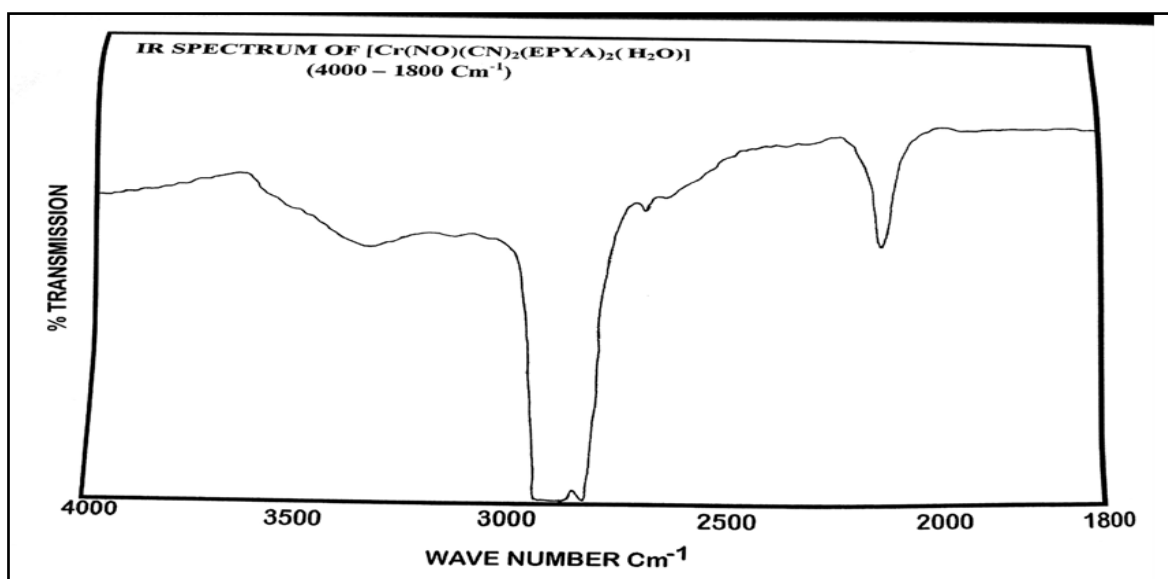
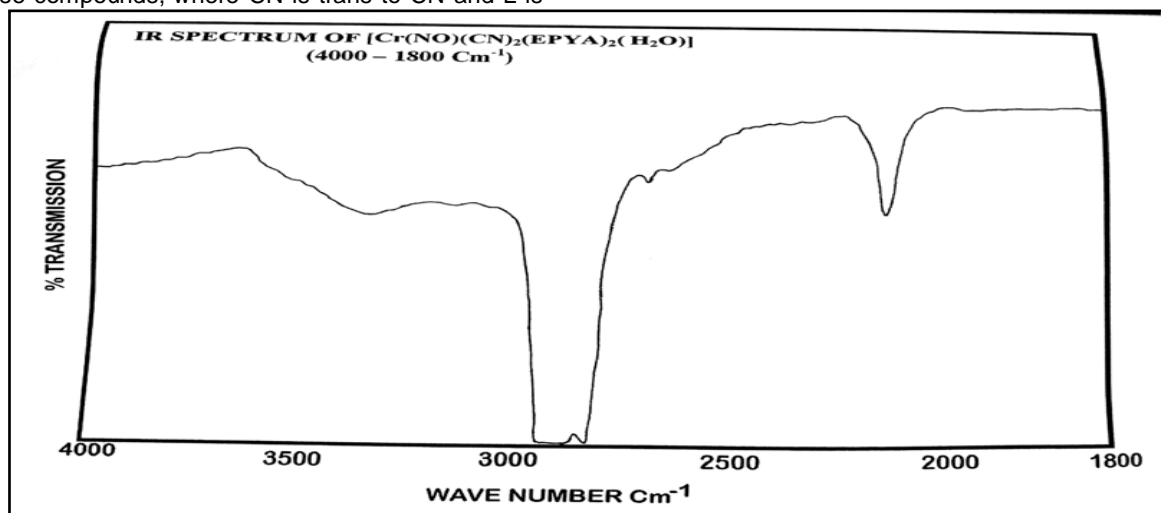
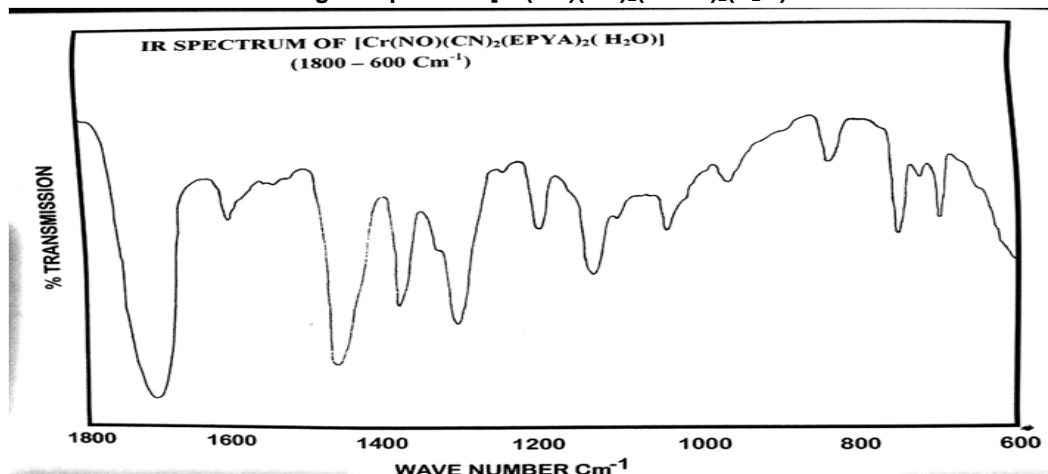
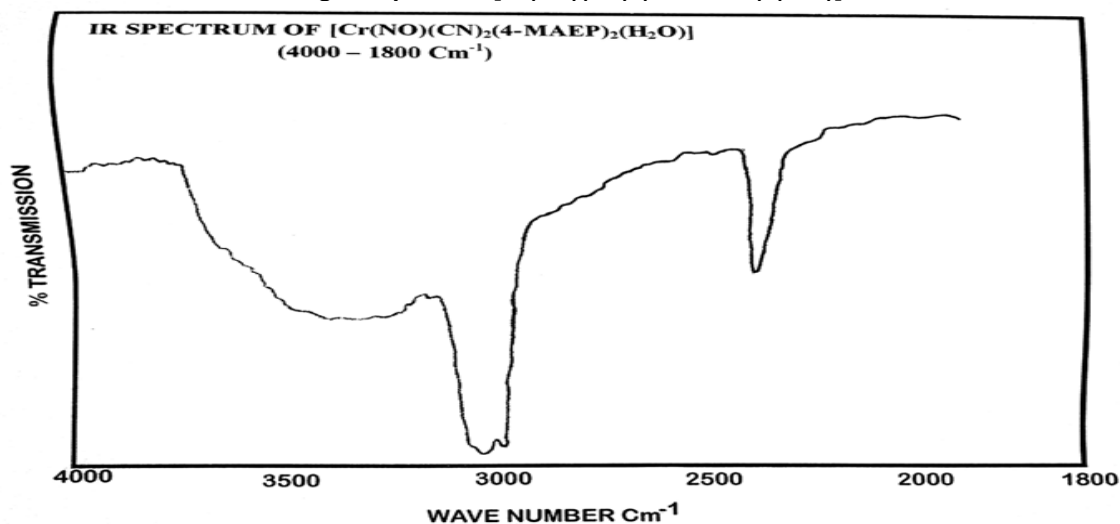


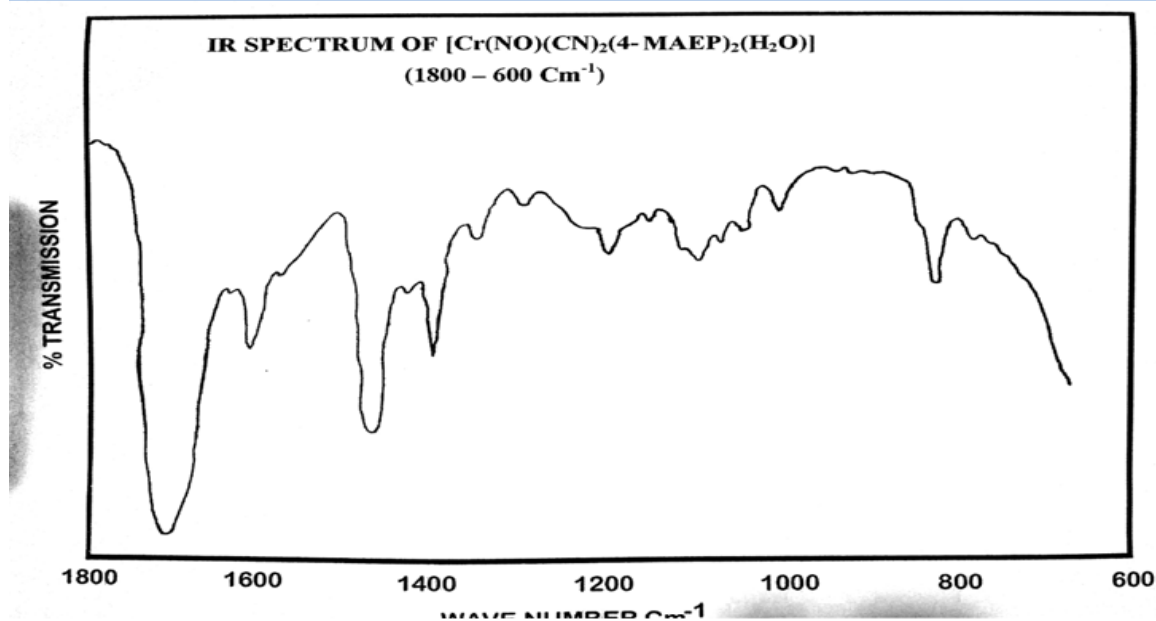
Fig. IR Spectrum $[\text{Cr}(\text{NO})(\text{CN})_2(\text{EPYA})_2(\text{H}_2\text{O})]$ Table 1
Nomenclature and Electron Configuration of The Synthesized Complexes

S.No	Compound	IUPAC Name	Electronic Configuration
1	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{EPYA})_2(\text{H}_2\text{O})]$	Aquadicyanobis (ethyl 3 - pyridylacetate) - nitrosylchromium(I)	$\{\text{CrNO}\}^5$
2	$[\text{Cr}(\text{NO})(\text{CN})_2(4\text{-MAEP})_2(\text{H}_2\text{O})]$	Aquadicyanobis (4-(2-methylaminoethyl-pyridine) - nitrosylchromium(I)	$\{\text{CrNO}\}^5$
3	$[\text{Cr}(\text{NO})(\text{CN})_2(4\text{-PIC})_2(\text{H}_2\text{O})]$	Aquadicyanobis (4-picolyl chloride) - nitrosylchromium(I)	$\{\text{CrNO}\}^5$
4	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PICAM})_2(\text{H}_2\text{O})]$	Aquadicyanobis (picolinamide) - nitrosylchromium(I)	$\{\text{CrNO}\}^5$
5	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PYAM})_2(\text{H}_2\text{O})]$	Aquadicyanobis (pyridine-3-amidoxime) - nitrosylchromium(I)	$\{\text{CrNO}\}^5$

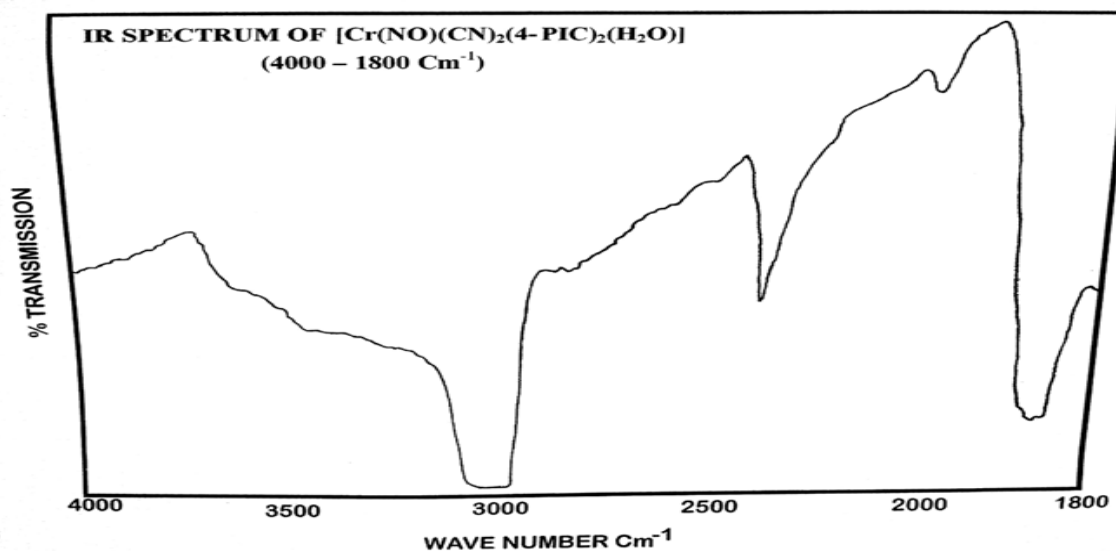
EPYA = ethyl 3 - pyridylacetate; 4 - MAEP = 4-(2-methylaminoethyl) - pyridine; 4 - PIC = 4-picolyl chloride; PICAM = picolinamide
PYAM = pyridine-3-amidoxime

Fig. IR Spectrum $[\text{Cr}(\text{NO})(\text{CN})_2(4\text{-MAEP})_2(\text{H}_2\text{O})]$ Table 2
Analytical Data of the Synthesized Complexes

S.No.	Compound	% Cr Found (Calc.)	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)
1	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{EPYA})_2(\text{H}_2\text{O})]$	10.86 (10.78)	49.56 (49.79)	5.11 (4.91)	14.68 (14.52)
2	$[\text{Cr}(\text{NO})(\text{CN})_2(4\text{-MAEP})_2(\text{H}_2\text{O})]$	12.11 (12.20)	50.78 (50.94)	6.26 (6.13)	23.38 (23.11)
3	$[\text{Cr}(\text{NO})(\text{CN})_2(4\text{-PIC})_2(\text{H}_2\text{O})]$	12.50 (12.77)	41.38 (41.27)	3.51 (3.43)	17.30 (17.19)
4	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PICAM})_2(\text{H}_2\text{O})]$	13.27 (13.13)	42.60 (42.41)	3.39 (3.53)	24.50 (24.74)
5	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PYAM})_2(\text{H}_2\text{O})]$	12.212 (12.20)	39.28 (39.43)	3.89 (3.75)	29.38 (29.57)

Fig. IR Spectrum $[\text{Cr}(\text{NO})(\text{CN})_2(4 - \text{MAEP})_2(\text{H}_2\text{O})]$ Table 3
Colour, Decomposition Temperature And % Yield

S.No.	Compound	Colour	Decomposition Temp. °C	% Yield
1	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{EPYA})_2(\text{H}_2\text{O})]$	Brownish Yellow	>295	50
2	$[\text{Cr}(\text{NO})(\text{CN})_2(4 - \text{MAEP})_2(\text{H}_2\text{O})]$	Yellow	>299	47
3	$[\text{Cr}(\text{NO})(\text{CN})_2(4 - \text{PIC})_2(\text{H}_2\text{O})]$	Yellow	>310	49
4	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PICAM})_2(\text{H}_2\text{O})]$	Yellowish brown	>285	51
5	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PYAM})_2(\text{H}_2\text{O})]$	Brownish Yellow	>290	53

Fig. IR Spectrum $[\text{Cr}(\text{NO})(\text{CN})_2(4 - \text{PIC})_2(\text{H}_2\text{O})]$ Table 4
Dehydration Temperature of The Complexes

S.No.	Compound	Decomposition Temp. °C
1	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{EPYA})_2(\text{H}_2\text{O})]$	110
2	$[\text{Cr}(\text{NO})(\text{CN})_2(4 - \text{MAEP})_2(\text{H}_2\text{O})]$	115
3	$[\text{Cr}(\text{NO})(\text{CN})_2(4 - \text{PIC})_2(\text{H}_2\text{O})]$	113
4	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PICAM})_2(\text{H}_2\text{O})]$	117
5	$[\text{Cr}(\text{NO})(\text{CN})_2(\text{PYAM})_2(\text{H}_2\text{O})]$	119

Fig. IR Spectrum [Cr(NO)(CN)₂(4 - PIC)₂(H₂O)]

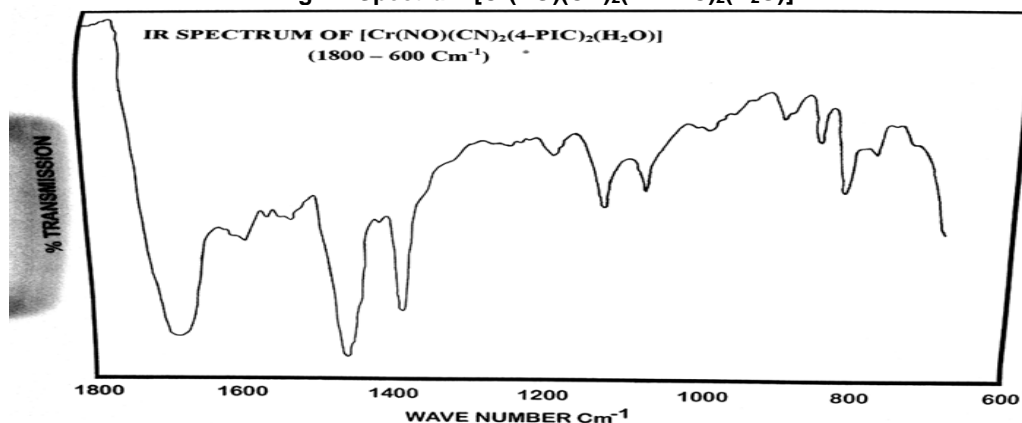


Table 5
Magnetic and E.S.R. Data of The Complexes

S.No.	Compound	μ_{eff} (B.M.)	'g'
1	[Cr(NO)(CN) ₂ (EPYA) ₂ (H ₂ O)]	1.72	1.978
2	[Cr(NO)(CN) ₂ (4 - MAEP) ₂ (H ₂ O)]	1.70	1.976
3	[Cr(NO)(CN) ₂ (4 - PIC) ₂ (H ₂ O)]	1.75	1.980
4	[Cr(NO)(CN) ₂ (PICAM) ₂ (H ₂ O)]	1.74	1.981
5	[Cr(NO)(CN) ₂ (PYAM) ₂ (H ₂ O)]	1.71	1.980

Fig. IR Spectrum[Cr(NO)(CN)₂(PICAM)₂(H₂O)]

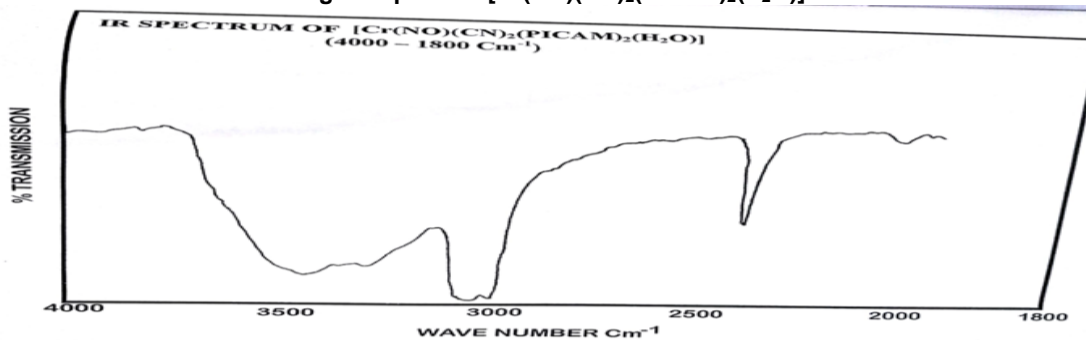


Table 6
Important I.R. Bands and Their Assignments

S.No.	Compound	$\nu(\text{NO})^+$	$\nu(\text{C}=\text{N})$	Pyridine ring breathing mode (cm ⁻¹)
1	[Cr(NO)(CN) ₂ (EPYA) ₂ (H ₂ O)]	1700(vs)	2160(s)	1030
2	[Cr(NO)(CN) ₂ (4 - MAEP) ₂ (H ₂ O)]	1705(vs)	2155(s)	1020
3	[Cr(NO)(CN) ₂ (4 - PIC) ₂ (H ₂ O)]	1700(vs)	2150(s)	1025
4	[Cr(NO)(CN) ₂ (PICAM) ₂ (H ₂ O)]	1710(vs)	2160(s)	1035
5	[Cr(NO)(CN) ₂ (PYAM) ₂ (H ₂ O)]	1700(vs)	2150(s)	1020

Fig. IR spectrum[Cr(NO)(CN)₂(PICAM)₂(H₂O)]

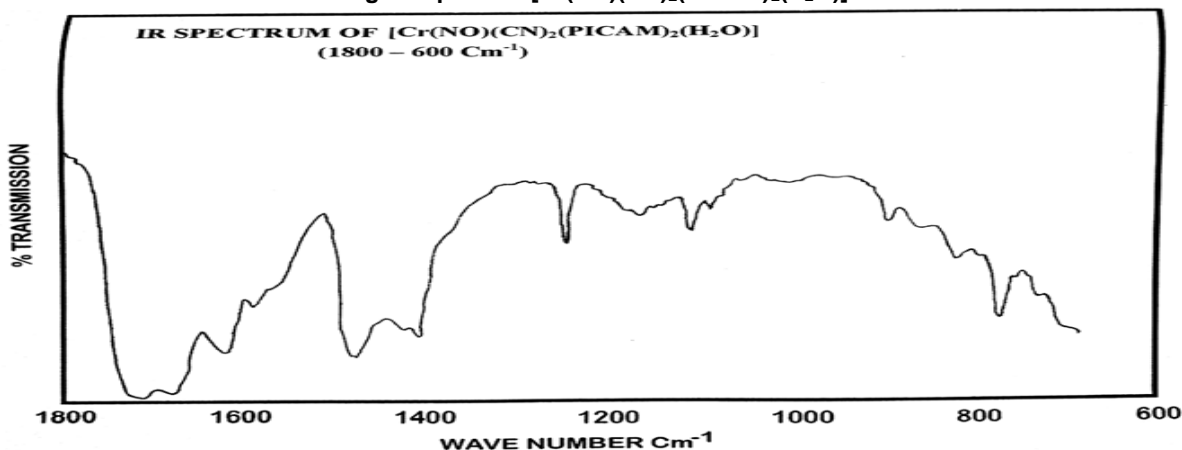
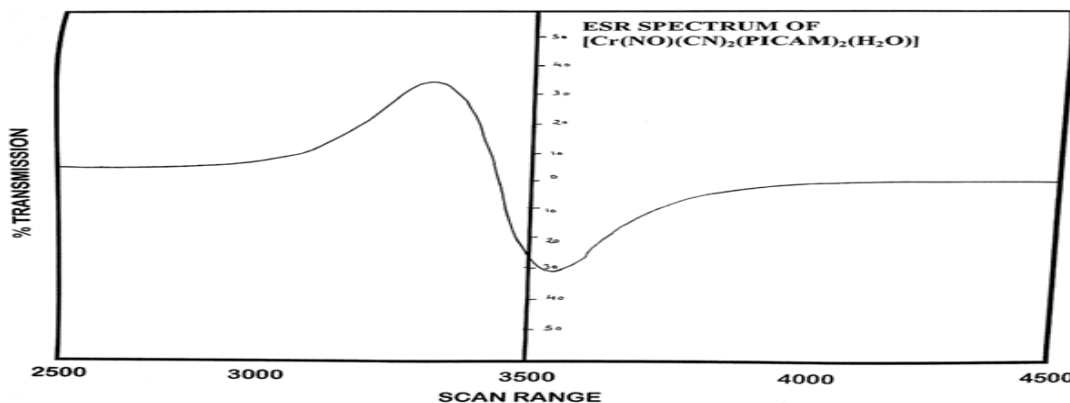


Fig. of ESR Spectrum $[\text{Cr}(\text{NO})(\text{CN})_2(\text{PICAM})_2(\text{H}_2\text{O})]$ 

References

- J.L. Sheats, R.S. Czernuszewicz, G.C. Dismukes, A.L. Rheingold, V. Petrouleas, J. Stubbe, N.H. Armonstrong, R.H. Bear & S.J. Lippard, *J. Am. Chem. Soc.* 109, 1435 (1987).
- M. Koikawa & H. Okawa, *J. Chem. Soc. Dalton Trans.* 641 (1988).
- K. Weighardt, *Angew Chem. Int. Ed. Engl.* 28, 1153 (1989).
- J.A. Kriby, A.S. Robertson, J.P. Smith, A.C. Thompson, S.R. Cooper & M.P. Klein, *J. Am. Chem. Soc.* 103, 5529 (1981).
- J.C. Depaula & G.W. Brudving, *J. Am. Chem. Soc.* 109, 2643 (1985).
- M. N. Bhattacharjee and M.K. Chaudhri *Polyhedron* 3, 599 (1984).
- M. N. Bhattacharjee, M.K. Chaudhri & R.N. Dutta *Pur Kayastha, Inorg. Chem.* 24, 447 (1985).
- M. N. Bhattacharjee, M.K. Chaudhri, H.S. Das Gupta & A. Kathipiri *Polyhedron* 4, 621 (1985).
- M. N. Bhattacharjee, M.K. Chaudhri & R.N. Dutta *Pur Kayastha, Inorg. Chem.* 28, 3747 (1989).
- D.P. Poe, *Inorg. Chem.* 27, 1280 (1988).
- M. N. Bhattacharjee & S.K. Ghosh *Inorg. Chem.* 21, 4020 (1982).
- W.U. Malik, S.K. Shrivastava, D.C. Gupta, R.C. Maurya, R. Shukla, N. Anadam, *Trans. Met. Chem.* 12, 203 (1987).
- W.U. Malik, R.C. Maurya, R. Shukla, D.C. Gupta, N. Anadam, *Synth. React. Inorg. Met. Org. Chem.* 16(19) 1243 (1986).
- W.B. Wright and G.S.D. King, *Acta Cryst.* 6, 305 (1953).
- E. Bernasek, *J. Org. Chem.* 22, 1263 (1957).
- W.P. Griffith and G. Wilkinson, *J. Chem. Soc.* 872 (1959).
- P. Griess, *Chem. Ber.* 12, 427 (1979).
- J. Burgees, B.A. Goodman and J.B. Raynor, *J. Chem. Soc. (A)* 501 (1968).
- P.T. Manoharan and H.B. Gray, *Inorg. Chem.* 5, 823 (1966).
- L.S. Meriwether, S.D. Robinson & G. Wilkinson, *J. Chem. Soc.* 1488 (1966).
- S. Sproules, P. Banerjee, T. Weyhermuller & K. Wieghardt, *Inorg. Chem.* 50, 7106 (2011).
- C. Milsmann, E. Bothe, E. Bill, T. Weyhermuller & K. Wieghardt *Inorg. Chem.* 48, 6211 (2009).
- N. Paul S. Samanta & S. Goswami, *Inorg. Chem.* 49, 2649 (2010).
- R. Eisenberg & H.B. Gray, *Inorg. Chem.* 50, 9741 (2011).
- Z. Li, S. Li, Y. Li & W. Sun, *Inorg. Chem.* 49, 1337 (2010).
- E. Shikhova, E.O. Danilov; S. Kinayyigi et al., *Inorg. Chem.* 46, 3038 (2007).
- W.T. Lowther & B.W. Matthews, *Chem. Rev.* 102, 4581 (2002).
- R.N. Patel, N. Singh, K.K. Shukla, U.K. Chauhan, J. Gutierrez Nicolas & A. Castineira, *Inorg. Chem. Acta* 357, 2469 (2004).
- C. Sissi, F. Mancin, M. Gatos, M. Palumbo, P. Tecilla & U. Tonellato, *Inorg. Chem.* 44, 2310 (2005).
- R. Ren. P. Yang, W. Zheng & Z. Hua, *Inorg. Chem.* 39, 5454 (2000).