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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL MIXED LIGEND CYANONITROSYUS {CrNO} [5] COMPLEXES OF CHROMIUM WITH SOME N-ALKYL, N,N-DIALKYL AND N-BENZYL-N-ALKYL NILINE(S)

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ABSTRACT

It was therefore though worthwhile to synthesize and characterize some neutral mixed lignad cyanbo nitrosyl (Cr NO)5 complexes of chromium and Fe(NO)6 with some monodentate aromatic amines like 4-amino cumenes; 2-methyl-5-isopopyl amine, 4-tertiary butyl aniline and 2,4,6-trimethoxy aniline and bidentte aromatic amine like 3-cyano aniline. The complexes this synthesized would require an attention of reactivities, which can be dealt using different physico-chemicals techniques. Thus a correlation can be made on the changes notice with the help of existing theories in band.

Key words: Novel Mixed Ligend, N-Benzyl-N-Alkyl Niline And Cyanonitrosyus.

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INTRODUCTION

Synthesis and characteriziation of some mixed-ligend cyanonitrosyl complexes of chromium(I) with some potentially monodentate aromatic amines like 4-aminocumene, 2-methyl-5-isopropylaniline, 4-tert-butylaniline, and 2,4,6-trimethoxyaniline and potentially bidenate aromatic amine line 3-cyanoaniline . As a part of our programme to systhesise and characterize come neutral mixed-ligend cyanonitrosyl complexes of monovalent chromium, studies have been extended using some N, alkyl-, N-N-dialkyl- and N-benxyl-N-alkyl-aniline(s). In recent years, a great deal of interest has been shown to the study of neutral mixed-ligend cyanonitrosyl complexes of chromium having $\{CrNO\}^5$ electron configuration (1-14). No attempt have been made so far to isolate ayanomitrosyl complexes of monovalent chromium with N-alkyl_, N,N-dialkyl_ and N-benzyl-N-alkyl-aniline(s). We, therefore, report here the first systhesis of some neutral mixed-ligend cyanonitrosyl $\{CrNO\}^5$ complexes of chromium with some N-alkyl-anilines like N-methyl aniline, N-ethyl-o-tuluidine and N-ethyl-p-toluidine, N-N dialkylaniline like N,N-diethyl-m-toluidine and N-benzyl-N-alkyl aniline such as N-Benzyl-N-ethyl aniline.

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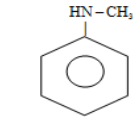
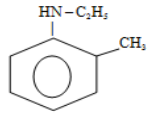


N-methylaniline
d = 0.987



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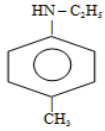

N-ethyl-p-toluidine
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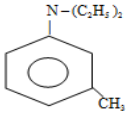
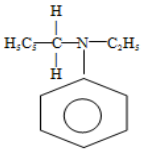


N,N-diethyl-m-toluidine
d = 0.920



N-nenzyl-N-ethylaniline
d = 1.03

Experimental

- **Material Used:**

N-ethyl-o-toluidne, N-ethyl-p-toluidine, N,N-diethyl-m-toluidine, and N-benzyl-N-ethylaniline was a product of

Aldrich Chemical Co., U.S.A. Hydroxylammonium chloride and chromic acid were supplied by SD's Lab-Chem. Industry, Bambay. Patassiuk cyanine was procured from May and Baker Limited, Dagenham England. Distilled water used in all the operation.

Analysis of the constituent elements

Carbon, hydrogen and nitrogen were estimated micro-analytically.

Physical methed

Magnetic measurements

Room temperature magnetic susceptibility measurements of the investigated complexes were made by Gouy method. Cobalt mercury tetrathiocyanate was sued as calibrant.

Infrared Spectral measurements

Infrared spectra (4000-600 cm^{-1}) were recorded in nujol mulls on a Bechman-I.R. 20 spectrophotometer at the C.F.R.I. Lucknow.

Electron Spin Resonance spectra

Synthesized complexes were scanned for electron spin resonance spectra at room temperature using powdered sample on a Varian E-3 spectrometer at Indian Institute of Science, Bangalor.

Thermo gravimetric 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 Starting Compounds: Potassium pentacy anonitrosylchromate (I) Monohydrate prepared by the method reported by Wilkinson and co-workers (15).

Preparation of the Complexes with N-Alkylanilines

Preparation of $[Cr(NO)(CN)_2(N\text{-}MA)_2(H_2O)]$: To a filtered aqueous solution of the potassium salt of pentacyanonitrosyl-chromate(I) monohydrate (0.1M, 50 ml.), an aqueous acetic acid solution (10 ml, 1:1) of the N-methylaniline (0.2M) was added with shaking. A coloured solid precipitated on heating the mixture for 20 minutes on a hot plate at 80°C. The resulting mixture was freed from the liberated HCN by passing a current of CO_2 through the mixture for a few hours. The precipitate was suction filtered washed several times with 10% dilute acetic acid and finally with water and dried in vacuo over silica gel at room temperature to a constant weight. The analytical data are given in Table 1.2.

Preparation of $[Cr(NO)(CN)_2(N\text{-}E\text{-}o\text{-}T)_2(H_2O)]$: To prepare this complex, an identical procedure was supplied only replacing N-methylaniline by N-ethyl-o-toluidine. The analytical data are given in Table 1.2.

Preparation of $[Cr\ (NO)\ (CN)_2(N\text{-}E\text{-}p\text{-}T)_2(H_2O)]$

This complex was prepared by applying the above procedure. Here, N-ethyl-p-toluidine was taken instead of N-ethyl-o-toluidine. The analytical data are given in Table 1.2.

Preparation of the Complexes with N,N-Dialkylanilines

Preparation of $[Cr(NO)(CN)_2(N,N\text{-}DE\text{-}m\text{-}T)_2(H_2O)]$: To a filtered H_2O solution of $K_3[Cr(NO)(CN)_5]H_2O$ 1:1 H_2O-AcOH solution of the N,N-diethyl-m-toluidine was added with shaking and a coloured solid precipitated on warming the mixture for 15 minutes. The liberated HCN by removed by passing a current of CO_2 through the mixture for a few hours. The resulting precipitate was filtered, washed several times with 10% dilute AcOH and dried at room temperature. The analytical data are given in Table 1.2.

Preparation of the Complexes With N-Benzyl-N-Alkylanilines

Preparation of $[Cr(NO)(CN)_2(N\text{-}B\text{-}N\text{-}EA)_2(H_2O)]$

An identical procedure given above was used in the preparation of this complex taking parent compound and B-benzyl-N-ethylaniline. The analytical data are given in Table 1.2.

Preparation of the Complexes

All the complexes are colored solids (Table 1.3 for colours). They are stable in air. Solubility of these complexes in different solvents are given in Table 1.4. The complexes are thermally stable and do not melt or decompose upto 300°C (Table 1.3). They decompose in dilute acids and alkalis only on heating. All the compounds after decomposition in KOH followed by acidifying with acetic acid give a pink colour with 1-2 drops of Griess Reagent (16). This reaction indicates the presence of NO group in the complexes.

RESULTS AND DISCUSSION

The mixed-ligend complexes $[Cr(NO)(CN)_2(L)_2(H_2O)]$(Table 1.1 for legend names) were synthesized according to the following equation:

$$Kr[Cr(NO)(CN)_5]H_2O + 2L \xrightarrow[H_2O]{CH_3COOH} [Cr(NO)(CN)_2(L)_2(H_2O)] + 3CH_3COOK + H_2O + 3HCN \quad (1)$$

Where L = N-MA, N-E-o-T, N-E-p-T, N,N-DE-m-T or N-B-N-EA

The partial replacement of the cyano groups in the parent complex, by two molecules of legend, L, is facilitated by trans-effect of the NO group, Raynor and co-worker (17) studies the stepwise equation of $[Cr(NO)(CN)^5]^{3-}$ and obtained the tris(aqua) species, $[Cr(NO)(CN)_2(H_2O)_3]$, which is consistent with eq. (1).

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 1.5. The magnetic moments 1.70 to 1.75 B.M. at room temperature and 'g' values, 1.984 to 1.987 of powdered compounds, which are comparable to the observation made by Manoharan and Gray (18) and Meriwether (19) et.al. are consistent with low-spin $\{CrNO\}^5$ electron configuration of chromium (I).

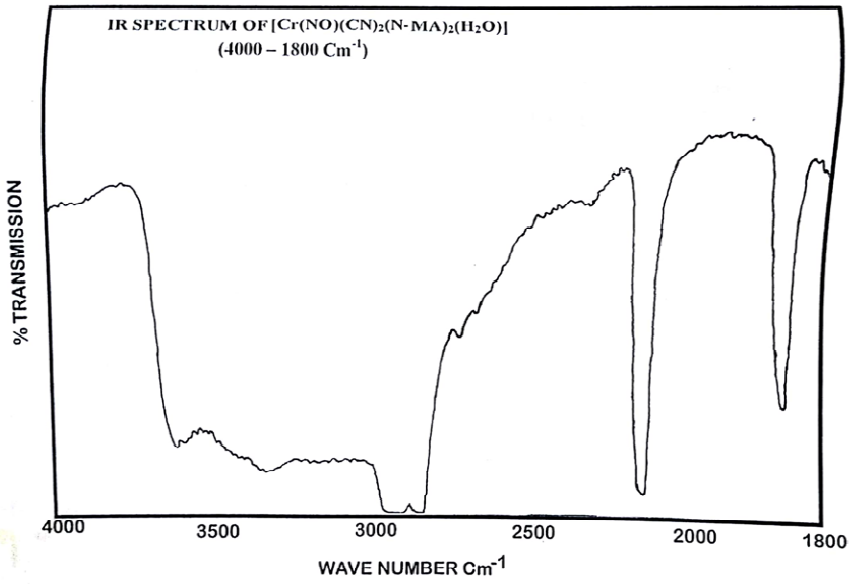


Table 1.1. Iupac name and electron configuration of the synthesized complexes

S.NO.	Compound	IUPAC Name	Electronic Configuration
1	$[Cr(NO)(CN)_2(N-MA)_2(H_2O)]$	Aquadicyanobis (N-methylaniline) – nitrosylchromium(I)	$\{CrNO\}^5$
2	$[Cr(NO)(CN)_2(N-E-O-T)_2(H_2O)]$	Aquadicyanobis (N-ethyl-o-toluidine) – nitrosylchromium(I)	$\{CrNO\}^5$
3	$[Cr(NO)(CN)_2(N-E-P-T)_2(H_2O)]$	Aquadicyanobis (N-ethyl-p-toluidine) – nitrosylchromium(I)	$\{CrNO\}^5$
4	$[Cr(NO)(CN)_2(N,N-DE-m-T)_2(H_2O)]$	Aquadicyanobis (N,N-diethyl-m-toluidine) – nitrosylchromium(I)	$\{CrNO\}^5$
5	$[Cr(NO)(CN)_2(N-B-N-EA)_2(H_2O)]$	Aquadicyanobis (N-nenzyl-N-ethylaniline) – nitrosylchromium(I)	$\{CrNO\}^5$

N – MA = N – methylaniline; N-E-o-T = N-ethyl-o-toluidine; N-E-p-T = N-ethyl-p-toluidine; N,N-DE-m-T = N,N – diethyl-m-toluidine; N-B-N-EA = N-benzyl-N-ethylaniline

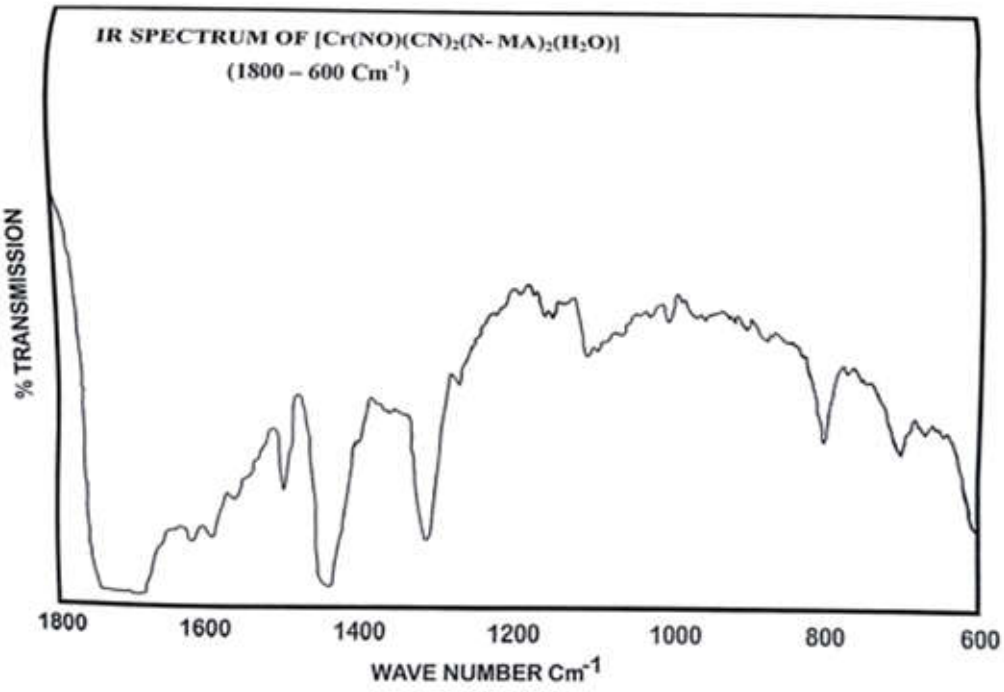


Table 1.2. Analytical data and electron configuration of the synthesized complexes

S.NO.	Compound	% Cr Found (Calc.)	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)
1	$[Cr(NO)(CN)_2(N-MA)_2(H_2O)]$	14.35 (14.20)	52.20 (52.46)	5.57 (5.46)	19.02 (19.12)
2	$[Cr(NO)(CN)_2(N-E-O-T)_2(H_2O)]$	12.18 (12.32)	56.91 (56.87)	6.41 (6.63)	16.38 (16.58)
3	$[Cr(NO)(CN)_2(N-E-P-T)_2(H_2O)]$	12.39 (12.32)	56.61 (56.87	6.72 (6.63)	16.69 (16.58)
4	$[Cr(NO)(CN)_2(N,N-DE-m-T)_2(H_2O)]$	10.68 (10.87)	60.12 (60.25)	7.70 (7.53)	14.50 (14.64)
5	$[Cr(NO)(CN)_2(N-B-N-EA)_2(H_2O)]$	9.21 (9.05)	66.62 (66.89)	6.10 (6.27)	12.28 (12.19)

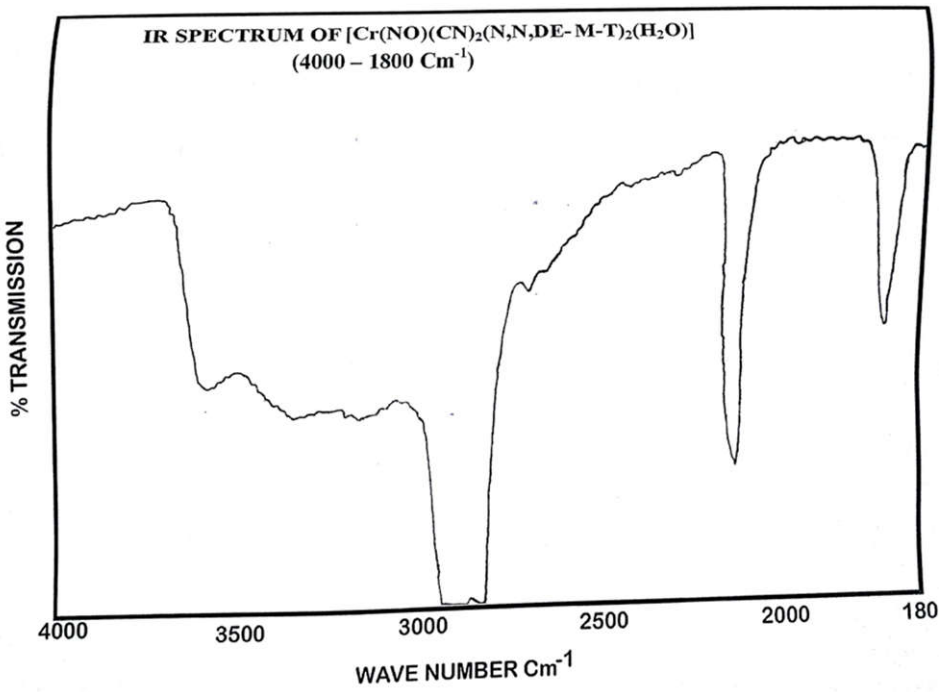


Table 1.3. Colour, decomposition temperature and % yield of the complexes

S.NO.	Compound	Colour	Decomposition Temp. ^{o}C	% Yield
1	$[Cr(NO)(CN)_2(N-MA)_2(H_2O)]$	Yellowish brown	>300	48
2	$[Cr(NO)(CN)_2(N-E-O-T)_2(H_2O)]$	Yellowish brown	>300	50
3	$[Cr(NO)(CN)_2(N-E-P-T)_2(H_2O)]$	Yellowish brown	>300	50
4	$[Cr(NO)(CN)_2(N,N-DE-m-T)_2(H_2O)]$	Yellow	>300	52
5	$[Cr(NO)(CN)_2(N-B-N-EA)_2(H_2O)]$	Yellowish brown	>300	52

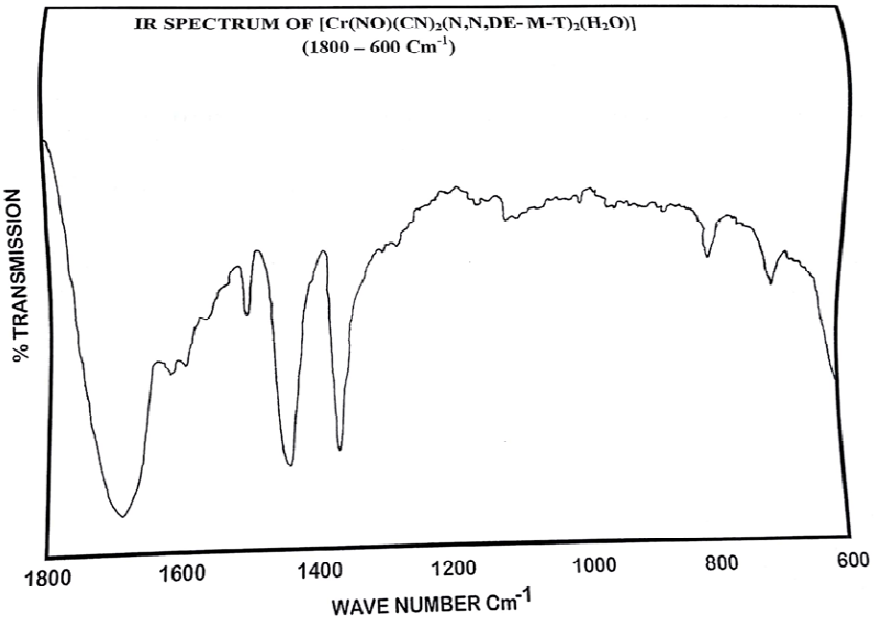


Table 1.4. Solubilities of the complexes in different solvents

S.NO.	Compound	DMF	DMSO	EtOH	MeOH	Nitrobenzene
1	$[Cr(NO)(CN)_2(N-MA)_2(H_2O)]$	70%	60%	50%	40%	Insoluble
2	$[Cr(NO)(CN)_2(N-E-O-T)_2(H_2O)]$	70%	60%	50%	40%	Insoluble
3	$[Cr(NO)(CN)_2(N-E-P-T)_2(H_2O)]$	75%	60%	50%	40%	Insoluble
4	$[Cr(NO)(CN)_2(N,N-DE-m-T)_2(H_2O)]$	65%	60%	50%	50%	Insoluble
5	$[Cr(NO)(CN)_2(N-B-N-EA)_2(H_2O)]$	70%	60%	50%	50%	Insoluble

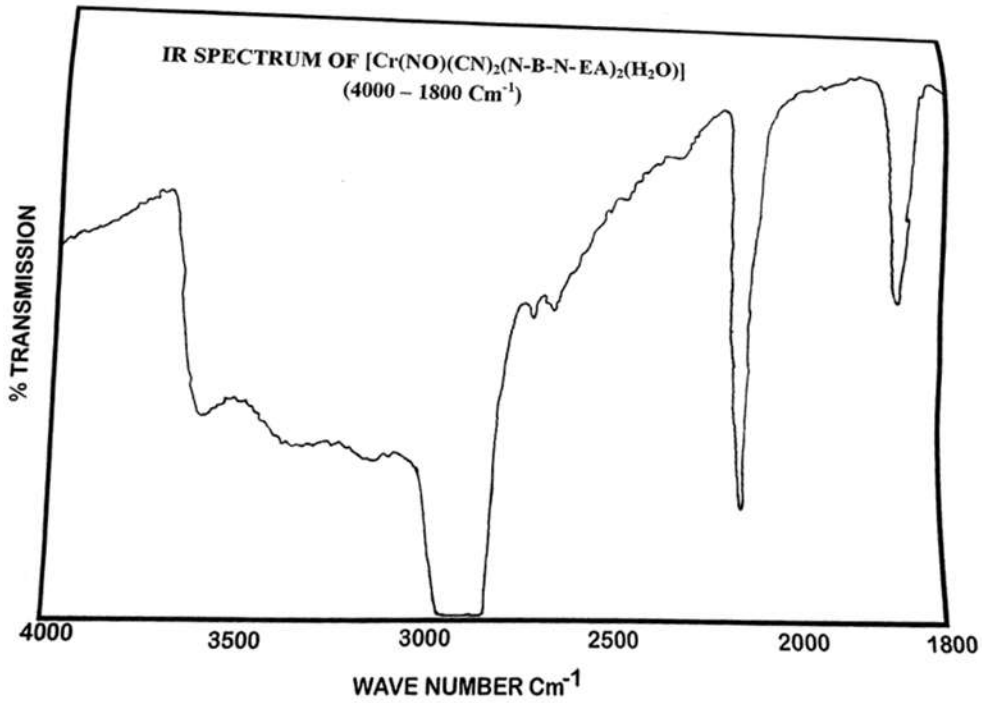


Table 1.5. Magnetic and e.s.r. data of the complexes

S.NO.	Compound	μ_{eff} (B.M.)	'g'
1	$[Cr(NO)(CN)_2(N-MA)_2(H_2O)]$	1.71	1.985
2	$[Cr(NO)(CN)_2(N-E-O-T)_2(H_2O)]$	1.72	1.987
3	$[Cr(NO)(CN)_2(N-E-P-T)_2(H_2O)]$	1.70	1.984
4	$[Cr(NO)(CN)_2(N,N-DE-m-T)_2(H_2O)]$	1.75	1.985
5	$[Cr(NO)(CN)_2(N-B-N-EA)_2(H_2O)]$	1.74	1.984

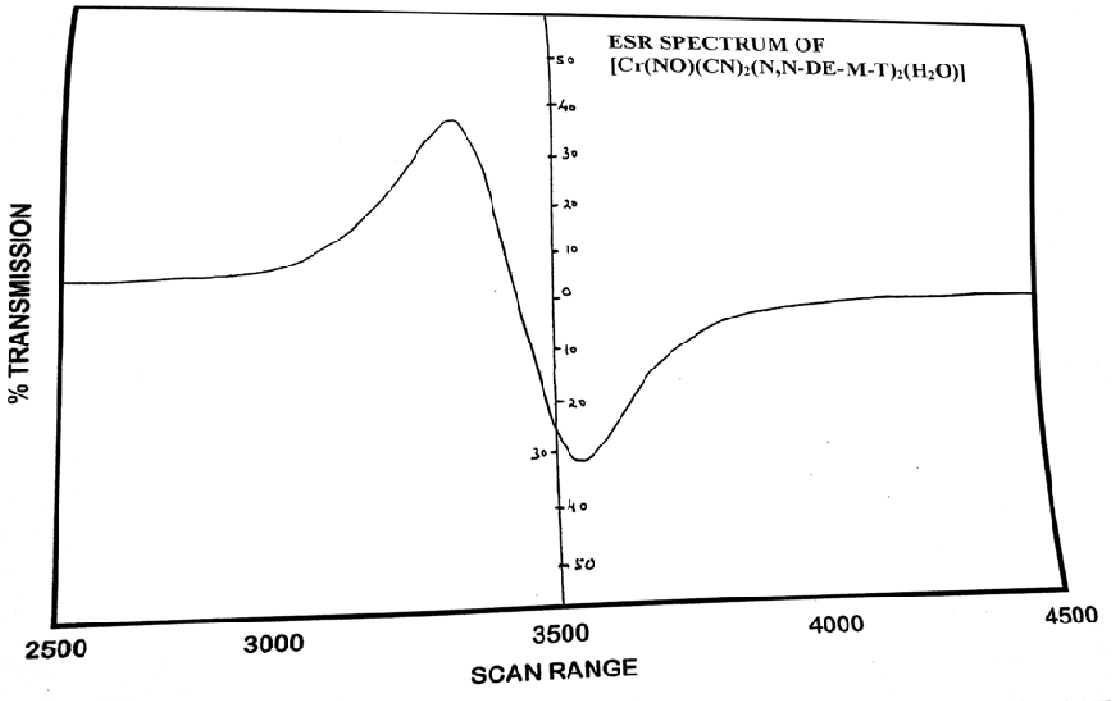


Table 1.6 Important i.r. bonds and their assignments

S.NO.	Compound	$V(NO)^+$	V(C=N)	V(C-N)	V(OH)
1	$[Cr(NO)(CN)_2(N-MA)_2(H_2O)]$	1710	2145	1350	3560 3375
2	$[Cr(NO)(CN)_2(N-E-O-T)_2(H_2O)]$	1705	2140	1345	3570 3380
3	$[Cr(NO)(CN)_2(N-E-P-T)_2(H_2O)]$	1705	2150	1348	3580 3400
4	$[Cr(NO)(CN)_2(N,N-DE-m-T)_2(H_2O)]$	1700	2145	1380	3575 3400
5	$[Cr(NO)(CN)_2(N-B-N-EA)_2(H_2O)]$	1705	2150	1385	3580 3380

Infrared Spectra Studies

The important infrared spectral bands of the complexes are presented in Table 1.6. The appearance of a very strong band in the region 1700 to 1710 cm^{-1} and a strong band in the region 2140 to 2150 cm^{-1} are assigned to ν(NO)+ and ν(C≡N), respectively, which are in agreement with the results reported elsewhere (20). The broad bands in the 3560 to 3580 cm^{-1} are 3375 to 3400 cm^{-1} region are due to ν(OH) of co-ordinated water (21) in all the complexes. A comparison of the infrared spectral bands of the free N-alkuylanilines and their complexes shows that the ν(C-N) observed around 1320 cm-1 in N-MA, N-E-o-T and N-E-p-T is shifted to 1350, 1345 and 1348 cm-1 in their respective complexes. In the similar fashion the ν(C-N) observed at approximately 1350 cm-1 in N,N-DE-m-T and N-B-N-EA, is shifted to 1380 and 1385 cm-1 in their respective complexes. The lowering in ν(NH) is also observed in the complexes 1,2 and 3 in comparison to their free ligends. These observations indicate the bonding of nitrogen in aniline derivatives to chromium in all these complexes (22-24).

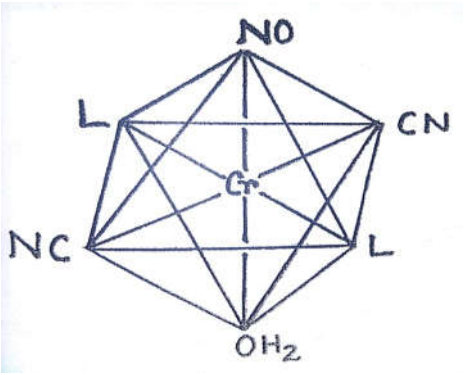


Figure 1.1: Proposed octahedral structure of $[Cr(NO)(CN)_2(L)_2(H_2O)]$

Where L=N-MA, N-E-o-T, N-E-p-T, N,N-DE-m-T or N-B-N-EA

The analytical data and physic-chemical studies presented above suggest that the complexes may be formulated as $[Cr(NO)(CN)_2(L)_2(H_2O)]$. Since these complexes show one CN stretching band and one NO stretching bank, it is reasonable to proposed an octahedral structure (25-30) with CN trans to CN, L trans to L and NO trans to water molecule, for all the complexes.

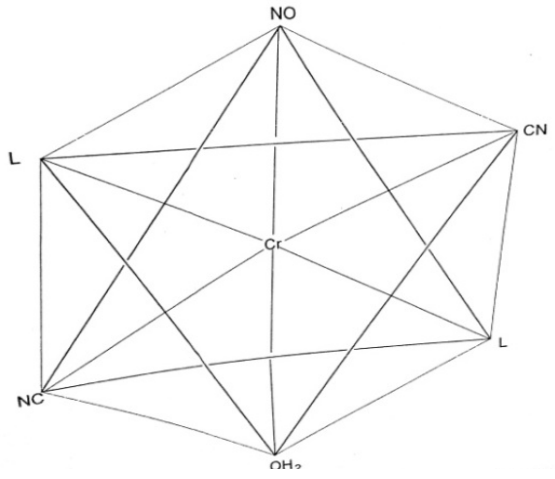


Figure 1.1. Proposed octahedral structure of $[Cr(NO)(CN)_2(L)_2(H_2O)]$

Where L=N-MA, N-E-o-T, N-E-p-T, N,N-DE-m-T or N-B-N-EA

Five novel mixed-ligend hexa-coordinated cyanonitrosyl complexes of monovalent chromium of the general formula $[Cr(NO)(CN)_2(L)_2(H_2O)]$ (where L=N-methylaniline, N-ethyl-o-toluidine, N-ethyl-p-toluidine, N,N-diethyl-m-toluidine or N-benzyl-N-ethylaniline) have been prepared by the interaction of potassium pentacyanonitrosylchromate (I) monohydrate with the said ligands. The complexes, which have been characterized by elemental analysis, magnetic measurement, conductance studies, molecular weight determination, electron spin resonance and infrared spectral studies, contain chromium (I) in a low-spin $\{CrNO\}^5$ electron configuration. A suitable octahedral structure, where CN is trans to CN and L is trans to L, and NO is trans to water is proposed for all the complexes. It is observed that:

All the complexes are air stable colored solids.
They are soluble in DMF, DMSO, ethanol and methanol but insoluble in nitrobenzene and ethyl acetate.
All the complexes contain $\{CrNO\}^5$ electron configuration.
All the compounds are thermally stable up to 300°C.
They all give pink color with Griess Reagent.

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