



Research Article

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Chromium (III) complexes: Synthesis, spectral characterization and microbial studies

Sulekh Chandra*¹ and Poonam Pipil²

¹Department of Chemistry, Zakir Husain Delhi College, University of Delhi, J.L. Nehru Marg, New Delhi, India

²Department of Chemistry Rajdhani College, University of Delhi, Raja Garden, Ring Road, New Delhi

ABSTRACT

Complexes of chromium(III) with macrocyclic ligand i.e. – 3, 4, 12, 13- tetraphenyl 2, 5, 11, 14 tetraaza tricyclo [13:3:1.1^{6,0}] Cosa – 1,2,4,6,8,10 (20) 11, 13, 14, 15 (19), 16 undecane. (BDPY) 3,5,13,15, tetramethyl – 2,6,12,16 tetraaza tricyclo [15.3.1.1^{7,11}] docosa – 1,2,5,7,9,11 (22), 12,15,:7 (21), 18-decane. (ADPY) 3,4,2,13 – tetramethyl – 2,5,11,14 – tetraaza – tricyclo [13.3.1.1^{6,10}] cosa – 1,2,4,6,8,10 (20), 11,13,15,(19), 16-decane. (DDPY) have been synthesized. All these complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, electronic and epr spectral studies. On the basis of elemental analysis the complexes were found to have composition CrLX₃ (X=Cl, NO₃⁻, NCS⁻), Molar conductance, measured in DMF solution indicates that the complexes are 1:1 electrolytes in nature, so these complexes may be formulated as [CrLX₂]X. Complexes show magnetic moment in the range of 3.80-3.84 B.M. corresponding to three unpaired electrons. EPR and electronic spectral studies reveal that the complexes possess six coordinated octahedral geometry. The ligand field parameters were calculated using various energy level diagrams. In vitro synthesized compounds and metal salts have also been tested against some species of plant pathogenic fungi and bacteria in order to assess their antimicrobial properties.

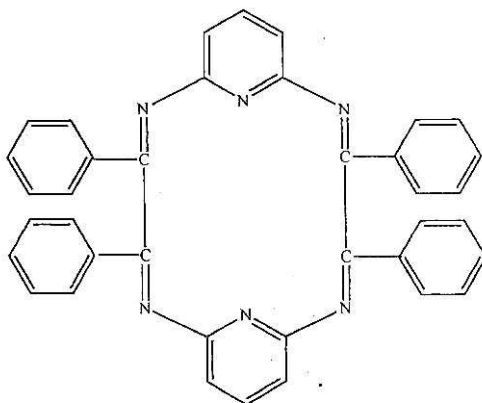
Keywords: Mass, IR, Magnetic moment, Electronic, EPR & Biological activity.

INTRODUCTION

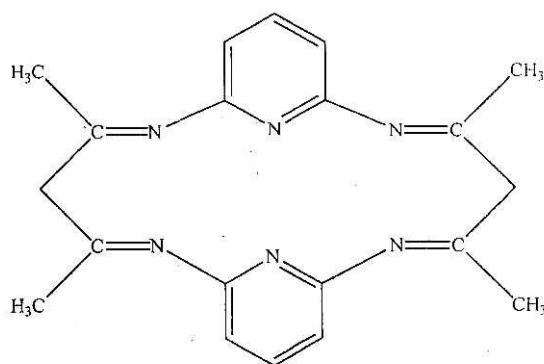
Macrocyclic species based on transition metal compounds and multidentate ligands are an interesting field in chemistry and has been the subject of extensive research due to their potential applications in building block macrocyclic-based chemistry [1,2] and environmental chemistry [3] and biomedical [4]. The chemistry of Schiff-base is an important field in coordination chemistry [5]. This is due to their ability to react with a range of metal ions forming stable complexes which have applications in different fields [6,7]. One interesting application in the field of coordination chemistry has been to investigate the use of Schiff-base ligands to develop phenoxo-bridged binuclear complexes with homometallic and/or heterometallic centres. Complexes based on Schiff base ligands play important roles in biomedical [8,9,10,11,12] mimic, and catalytic systems [13,14] and in supporting liquid crystalline phases [15]. A number of macrocyclic ligand complexes have been used as oxygen carriers to mimic complicated biological systems [7,14]. Furthermore, metal complexes of chromium, manganese, nickel, copper, zinc, and ruthenium with a wide variety of macrocyclic ligand are active oxidants for stoichiometric conversion and have been used as catalysis for carbonylation, hydrogenation, hydroformylation, and epoxidation reactions [16, 17].

A number of reviews are available on the physiology and biochemistry of chromium in mammals [18-22]. In view of above applications it is highly desirable to synthesis and characterize the Cr(III) complexes with macrocyclic ligand. In view of the above in the present paper we report the synthesis and characterization of macrocyclic ligand complexes of chromium (III) with 3, 4, 12, 13- tetraphenyl 2, 5, 11, 14 tetraaza tricyclo [13:3:1.1^{6,0}] Cosa – 1,2,4,6,8,10 (20) 11, 13, 14, 15 (19), 16 undecane. (BDPY) 3,5,13,15, tetramethyl – 2,6,12,16 tetraaza tricyclo

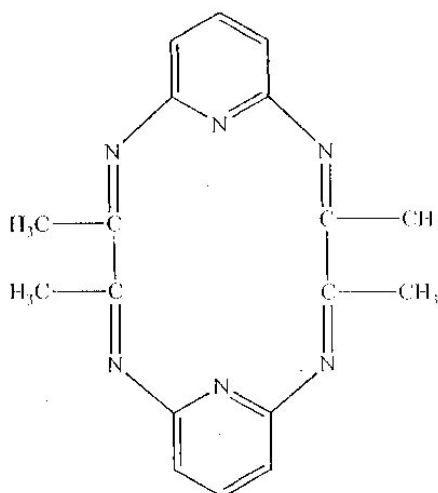
[15.3.1.1^{7,11}] docosa – 1,2,5,7,9,11 (22), 12,15,:7 (21), 18-decane. (ADPY) 3,4,2,13 – tetramethyl – 2,5,11,14 – tetraaza – tricyclo [13.3.1.1,^{6,10}] cosa – 1,2,4,6,8,10 (20), 11,13,15,(19), 16-decane. (DDPY)



(Fig - 1a) (BDPY)



(Fig - 1b) (ADPY)



(Fig - 1c) (DDPY)

Structure of ligands (Fig 1a-1c)

EXPERIMENTAL SECTION

Materials:-

All the chemicals used in the present work of high purity, AnalaR grade and purchased from Sigma-Aldrich. Metal salts were purchased from E.Merck and used as received. The solvent used were purchased from SRL/BDH or purified by the recommended methods.

Synthesis of complexes with 3, 4, 12, 13- tetraphenyl 2, 5, 11, 14 tetraaza tricyclo [13:3:1.1^{6,0}] Cosa – 1,2,4,6,8,10 (20) 11, 13, 14, 15 (19), 16 undecane. (BDPY)

The complexes were prepared by template synthesis. A hot ethanolic solution of benzil (0.01 mole) was added to an ethanolic solution of 2,6 diaminopyridine (0.01 mole) and the resulting solution was refluxed for half an hour at ~40°C. A solution of CrX₃.nH₂O (0.005 mole, n=0-6) (X=Cl⁻, NO₃⁻, NCS⁻ in ethanol and X= 1/2SO₄²⁻ in water) was then added to the above solution and refluxing was continued for a further four to six hours. On cooling the solution, a crystalline compound separated out. It was filtered, washed with ethanol, and dried under vacuum over P₄O₁₀. Cr(NCS)₃ was prepared by adding an ethanolic solution of CrCl₃ (0.05 moles) to the solution of KCNS (0.15 moles) in ethanol. After slight warming, this solution was filtered, and the residue discarded, while the filtrate was taken as Cr(SCN)₃ solution. (0.05 moles)

Synthesis of complexes with 3,5,13,15, tetramethyl – 2,6,12,16 tetraaza tricyclo [15.3.1.1^{7,11}] docosa – 1,2,5,7,9, 11 (22), 12,15,:7 (21), 18-decane. (ADPY)

An ethanolic solution of 2,6 diaminopyridine (0.01 mole) acetylacetone (0.01 mole), and CrX₃.nH₂O (0.005 mole) (X = Cl⁻, NO₃⁻, NCS⁻, n=0-6) /aqueous solution of Cr₂(SO₄)₃ were mixed together and the resulting solution was refluxed for about four hours. The solution was cooled below room temperature and left overnight. A crimson coloured complex formed. The complex was then filtered, washed with ethanol, and dried under vacuum over P₄O₁₀.

Synthesi of complexes with 3,4,2,13 – tetramethyl – 2,5,11,14 – tetraaza – tricyclo [13.3.1.1,^{6,10}] cosa – 1,2,4, 6, 8, 10 (20), 11,13,15,(19), 16-decane. (DDPY)

An ethanolic solution of diacetyl (0.01 mole) was added to an ethanolic solution of 2,6 diaminopyridine (0.01 mole) dropwise with constant stirring in a furnehood, and then a solution of CrX₃.nH₂O (0.005 mole, n=0-6) (X=Cl⁻, NO₃⁻, NCS⁻) in ethanol and (X=1/2SO₄²⁻) in water was added to this solution. The resulting solution was then refluxed for 5 hours when a dark green precipitate separated out. After cooling the solution overnight, it was filtered, and the precipitate washed with ethanol and dried in vacuum over P₄O₁₀.

Physical Measurement

The C, H and N were analysed in Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on a ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature, on CAHN-2000 magnetic susceptibility balance using CuSO₄.5H₂O as a calibrant. Infrared spectra of ligands and complexes were recorded as KBr pellets on a Perkin-Elmer 1310 spectrophotometer. The electronic spectra of complexes were recorded in DMSO, on a Shimadzu UV mini-1240 spectrophotometer. EPR spectra of complexes were recorded on JEOL, JES, FE3XG, EPR spectrometer. The spectra were recorded in solid as polycrystalline sample at room temperature on E₄-EPR spectrometer using the DPPH as the g-marker.

RESULTS AND DISCUSSION

On the basis of elemental analyses (**table 1**) the complexes were found to have CrLX₃ (X=Cl⁻, NO₃⁻, NCS⁻) composition. Molar conductance, measured in DMF solution (**table 1**) indicates that these complexes are 1:1 electrolytes in nature, therefore, may be formulated as [CrLX₂]X.

Table 1 Elemental analyses and Molar Conductance Data of Chromium(III) Complexes

Complex	Colour	Molar Conductance (Ω ⁻¹ cm ⁻¹ mol ⁻¹)	% Yield	Elemental Analysis Data Calculated (Found) %				M.Pt (°C)
				C	H	N	Cr.	
[Cr(BDPY)Cl ₂]Cl	Green	89	63	63.62 (63.13)	3.50 (3.60)	11.20 (11.53)	7.64 (7.13)	269
[Cr ₉ BDPY)(NO ₃) ₂)(NO ₃)	Green	83	60	56.44 (56.93)	3.00 (3.24)	15.20 (15.59)	5.96 (6.43)	272
[Cr(ADPY)(NO ₃) ₂)(NO ₃)	Dark Brown	93	66	41.25 (41.31)	3.20 (3.78)	21.68 (21.50)	8.68 (8.87)	273
[Cr(ADPY)[NCS ₂](NCS)	Bluish Green	88.7	63	48.80 (48.44)	3.60 (3.86)	21.45 (21.93)	9.35 (9.04)	268
[Cr(DDPY)Cl ₂]Cl	Green	82.4	68	45.98 (45.54)	4.18 (3.79)	17.68 (17.56)	10.20 (10.86)	267
[Cr(DDPY)(NO ₃) ₂)(NO ₃)	Dark Green	90.6	71	39.25 (39.06)	3.60 (3.25)	22.36 (22.59)	8.50 (9.32)	273
[Cr(DDPY)(ncs) ₂](NCS)	Olive Green	83.7	62	46.25 (46.52)	3.15 (3.32)	23.54 (23.06)	9.75 (9.51)	279

IR Spectra of ligands -

The IR spectra of the ligands show vibrations corresponding to azomethine groups. The bands at 1595, 1570, 1460 and 1405 cm⁻¹ regions can be assigned to ν(C=C) and ν(C=N) skeletal frequencies while bands appearing at 960,

800, and 407 cm^{-1} may be assigned to ring breathing mode, C-11 deformation and C-C deformations respectively. The strong frequencies of ca.1595 cm^{-1} are usually associated to $\nu(\text{C}=\text{N})$ coupled with phenyl ring vibrations. The band appearing at 1635 cm^{-1} may be assigned to symmetric and asymmetric $\nu(\text{C}=\text{N})$ vibrations respectively. The absence of bands in the range 3300-3200 cm^{-1} indicates that the amino group of 2,6 diaminopyridine and 1,3 diaminopropane have been condensed with the diketone. The presence of bands of ca. 1680-1670, ca 1550, ca.2920, ca.1350, ca.1265, ca.1190 and ca.680 cm^{-1} can be assigned to $\nu(\text{C}=\text{O})$, $\nu(\text{CO}) + \nu(\text{C}=\text{C})$, $\nu(\text{CH}_3) \delta_{\text{sym}}(\text{CH}_3)$, $\nu(\text{C}-\text{CH}_3)$, $\delta(\text{CH})+\text{c}(\text{C}-\text{CH}_3)$ and ring deformation modes.

IR Spectra of the complexes

Vibrations of free or coordinated C=O group or NH group at ca.1680-1700 or ca.1550 and ca.670 cm^{-1} are not observed in any of the compounds. The strong bands appearing as doublets around 1590-1620 cm^{-1} may be assigned to $\nu(\text{C}=\text{N})$ vibrations indicating the presence of coordinated azomethine groups. In the case of BDPY, phenyl ring absorptions appear in the 1600-1400 cm^{-1} region. Absorption bands in the region 900-700 cm^{-1} can be exclusively assigned to the imine and $-\text{CH}_2$ absorptions of the macrocycles. IR spectral band at $\sim 450 \text{ cm}^{-1}$ is characteristic of metal ligand vibrations. The lowering of the $\nu(\text{C}=\text{N})$ band (1620 cm^{-1}) indicates coordination through the nitrogen of $\nu(\text{C}=\text{N})$ group. The bands at 1620 cm^{-1} and ca. 840 cm^{-1} may be assigned to NH deformation coupled with Thus complexes ADPY, BDPY and DDPY, in presence of metal salts, from a quadridentate macrocycle which coordinates through azomethine nitrogens while the pyridine nitrogen does not take part in coordination due to the formation of unstable four membered rings. The IR spectra of the nitrate complexes of ADPY, BDPY and DDPY show bands corresponding to both coordinated and uncoordinated nitrate groups.

The appearance of new bands at 1438-1430 cm^{-1} (ν_1), 1370-1375 cm^{-1} (ν_3), 1210-1215 cm^{-1} (ν_5), 1010-1015 cm^{-1} (ν_2) and 850-840 cm^{-1} (ν_6) show consistency with the monodentate nature of the nitrate group. The broad absorption band at 1405 cm^{-1} can be assigned to ν_3 of the uncoordinated nitrate group in the complex of ligand with $\text{Cr}(\text{NO}_3)_3$. In thiocyanato complexes, strong bands are observed at ca. 2087 (ν_1) $\nu(\text{C}=\text{N})$, ca. 480 (ν_2) NCS banding and ca. 778 cm^{-1} (ν_3), $\nu(\text{C}=\text{S})$ of the NCS group, respectively which are consistent with a monodentate N-bonded thioyanato group. The sulphato complexes of BDPY and DDPY show the splitting of ν_3 and ν_4 into two bands each at ~ 1136 and 1058 cm^{-1} and 619 cm^{-1} and 605 cm^{-1} respectively corresponding to unidentate sulphate group Fig (2a-2c).

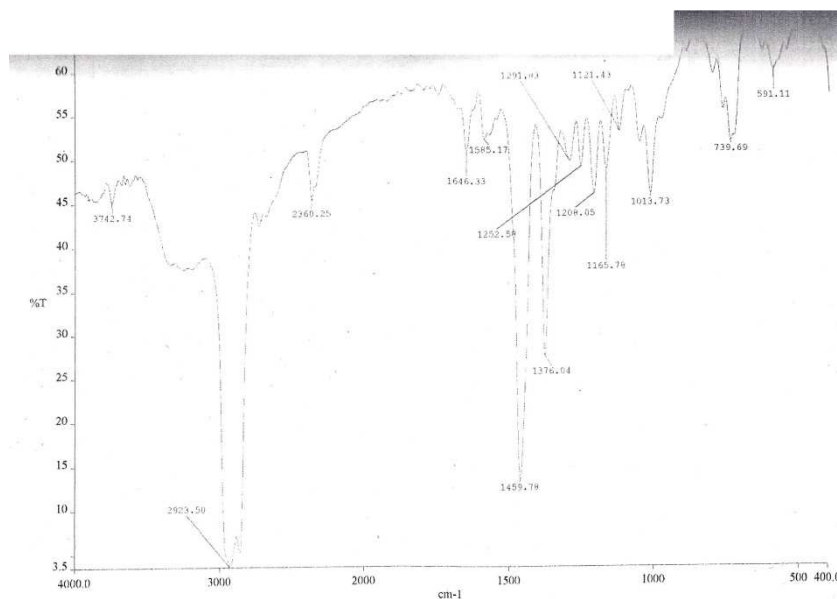
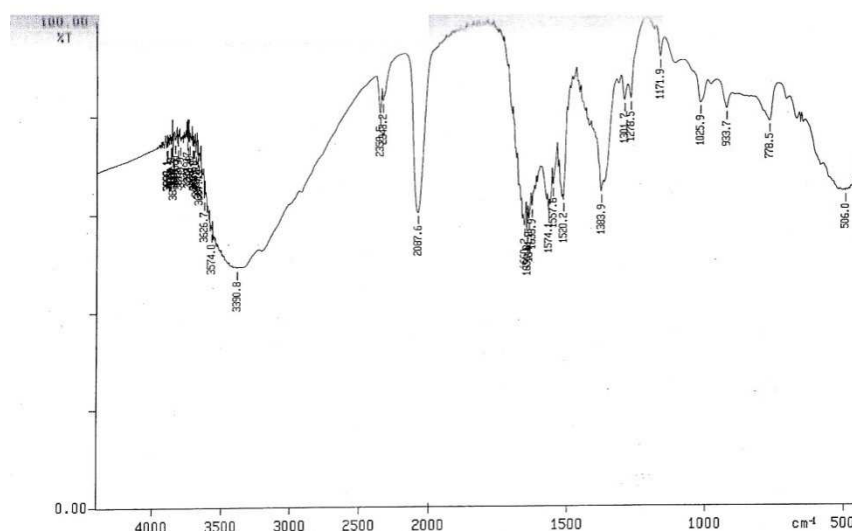
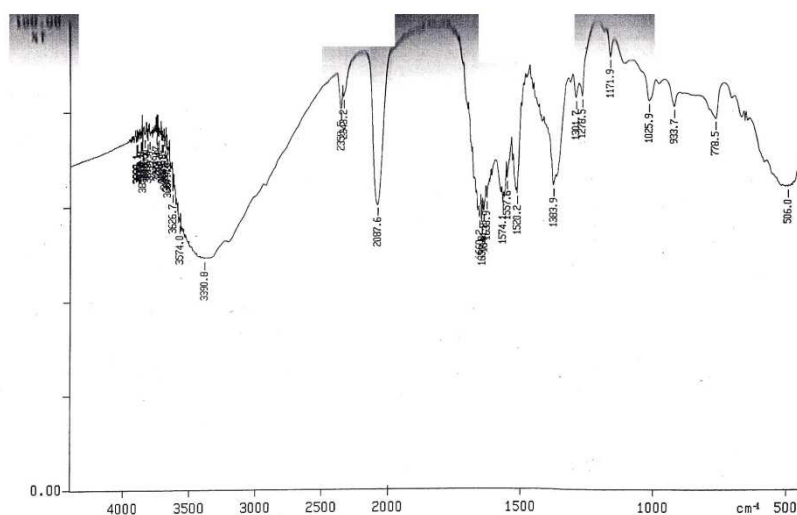


Fig - 2a IR Spectrum of $[\text{Cr}(\text{BDPY})(\text{NO}_3)_2](\text{NO}_3)$ Complex

Fig. 2b IR Spectrum of [Cr(ADPY)(SCN)₂](SCN) ComplexFig. 2c IR Spectrum of [Cr(ADPY)(SCN)₂](SCN) Complex

Electronic Spectra of the complexes

The electronic spectra of all the above complexes show bands in the region 18000, 22000, 25000 and 28000 cm^{-1} which are consistent with the octahedral geometry. Thus, an octahedral may be assigned to these complexes. Electronic spectra of the complexes were recorded in DMF. They display four bands at 17465-18800 (ν_1), 22100-22900 (ν_2), 24200-25680 (ν_3) and 27700 – 29400 cm^{-1} (ν_4). (table 2). Six coordinate complexes with O_h symmetry show three spin-allowed bands[23]. Which the highest energy band assignable to the ${}^4A_{1g} \rightarrow {}^4A_{2g}$ transition, occurs above 30000 cm^{-1} . The spectra of the complexes under study show four bands below 30000 cm^{-1} which cannot be interpreted in terms of idealized O_h symmetry. The spectra can however be explained by assuming the presence of lower symmetry elements in the complexes, Such six – coordinated chromium can have either effective C_{4v} or D_{4h} symmetry. In the present complexes the four transitions observed can be assigned ${}^4B_{1g} \rightarrow {}^4E_g^a(\nu_1)$, ${}^4B_{1g} \rightarrow {}^4B_{2g}(\nu_2)$, ${}^4B_{1g} \rightarrow {}^4E_g^b(\nu_3)$ and ${}^4B_{1g} \rightarrow {}^4A_{1g}^a(\nu_4)$ transitions arising from the lifting of the degeneracy of the orbital triplet (in octahedral symmetry) in the order of increasing energy and assuming the effective symmetry around the metal ion of D_{4h} . In O_h symmetry (ν_1) and (ν_2) are derived from the ${}^4T_{2g}$ level, whilst ν_3 and ν_4 from ${}^4T_{1g}(F)$. The C_{4v} symmetry has been ruled out because of the greater splitting of the first band.

Magnetic Moment of the complexes

The magnetic moment of these complexes, at room temperature (296 K), lie in the range of 3.71 – 3.84 B.M. as shown in (Table 2), which are close to spin only value of 3.86 B.M. thereby, suggesting an octahedral geometry around the chromium ion.

Table 2 Magnetic and Electronic Spectral Bands of Chromium(III) Complexes

Complex	$\mu_{\text{eff}}(\text{B.M.})$	$V_1(\text{cm}^{-1})$	$V_2(\text{cm}^{-1})$	$V_3(\text{cm}^{-1})$	$V_4(\text{cm}^{-1})$
[Cr(BDPY)Cl ₂]Cl	3.77	18278	22384	25218	28397
[Cr(BDPY)(NO ₃) ₂](NO ₃)	3.74	18310	22964	25380	27700
[Cr(ADPY)(NO ₃) ₂](NO ₃)	3.73	17884	22648	24630	27776
[Cr(ADPY)(NCS) ₂](NCS)	3.76	17678	22904	24635	27894
[Cr(DDPY)Cl ₂](NO ₃)	3.81	18204	22610	24856	28110
[Cr(DDPY)(NO ₃) ₂](NO ₃)	3.77	18104	22576	24458	27972
[Cr(DDPY)(NCS) ₂](NCS)	3.72	18406	22456	25310	27788

EPR Spectra of the complexes

The EPR spectra of the polycrystalline samples have been recorded (Fig. 3a – Fig. 3c) at room temperature. The 'g' values lie in the range 1.98-2.01 (table.3). The 'g' values are calculated using the expression.

$$g = 2.0023(1 - 4\lambda/10Dq)$$

Where λ is the spin-orbit coupling constant for the metal ion in the complex. Owen²⁴ noted that the reduction of spin orbit coupling from the free-ion value of 90cm⁻¹ for chromium (III) can be employed as a measure of metal-ligand covalency. It is possible to define a covalency parameter analogous to the nephelauxetic parameter which is the ratio of the spin-orbit coupling constant for the complex and the free Cr³⁺ ions.

Energy of the first spin allowed transition $^4A_{2g} \rightarrow ^4T_{2g}$ directly gives the value of 10Dq.

Spin Hamiltonian for Cr(III) complexes (S =3/2) may be written as

$$H = g \beta \cdot S \cdot H + D[S_z^2 - 5/4] + E[S_z^2 - S_y^2]$$

The 4F state of d³ ion in octahedral symmetry has the orbital singlet state lowest in energy with all excited states at much higher energies. Thus, the d³ ion has relatively long spin relaxation effects and gives narrow ESR absorption line, even at room temperature. In octahedral symmetry, ground state belongs to A_{2g} irreducible representation and is connected through the spin-orbit coupling to the excited T_{2g} state only, and so, the g and A terms are very nearly isotropic even in highly distorted crystal fields. In d³ ions the symmetry of the nearly field is primarily exhibited through spin-spin terms D and E.

Thus, on the basis of elemental analysis, molar conductance measurements, magnetic susceptibility measurements, ir, electronic. and esr spectral studies, the following structures may be proposed for the complexes. (Structure of complexes) (4a-4c)

Table 3 Ligand Field Parameters and ESR Spectral Data of Chromium(III) Complexes

Complex	Dq (cm-1)	B (cm-1)	C	β	Z	LFSE KJ/Mole	g
[Cr(BDPY)Cl ₂]Cl	2238.4	368.9	1475.6	0.40	0.29	267	1.98
[Cr(BDPY)(NO ₃) ₂](NO ₃)	2296.4	423.9	1695.6	0.46	0.08	274.3	1.98
[Cr(ADPY)(NO ₃) ₂](NO ₃)	2264.8	416.9	1667.6	0.45	0.10	270.6	1.91
[Cr(ADPY)(NCS) ₂](NCS)	2290.4	486.5	1946	0.52	0.07	273.6	1.96
[Cr(DDPY)Cl ₂]Cl	2261.0	399	1596	0.43	0.16	270.1	1.98
[Cr(DDPY)(NO ₃) ₂](NO ₃)	2257.6	441.9	1767	0.48	0.03	269.7	1.98
[Cr(DDPY)(NCS) ₂](NCS)	2245.6	363.1	1452.4	0.39	0.32	268.2	1.98

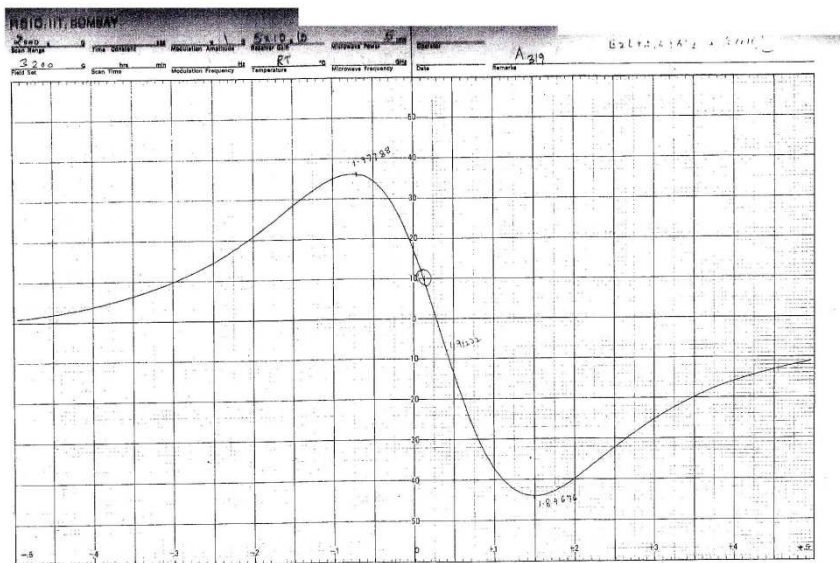


Fig. 3a ESR Spectrum of $[Cr(ADPY)(NO_3)_2](NO_3)$ Complex

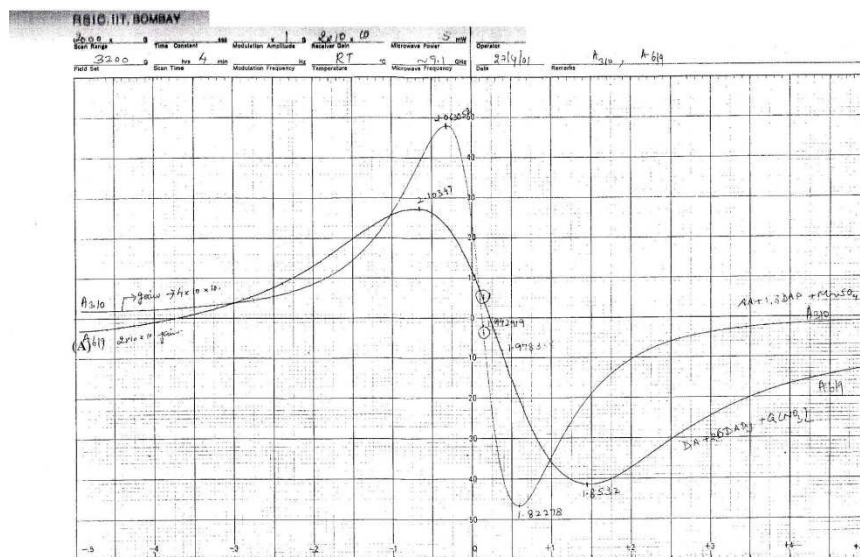


Fig. 3b (A) ESR Spectrum of $[Cr(DDPY)(NO_3)_2](NO_3)$ Complex

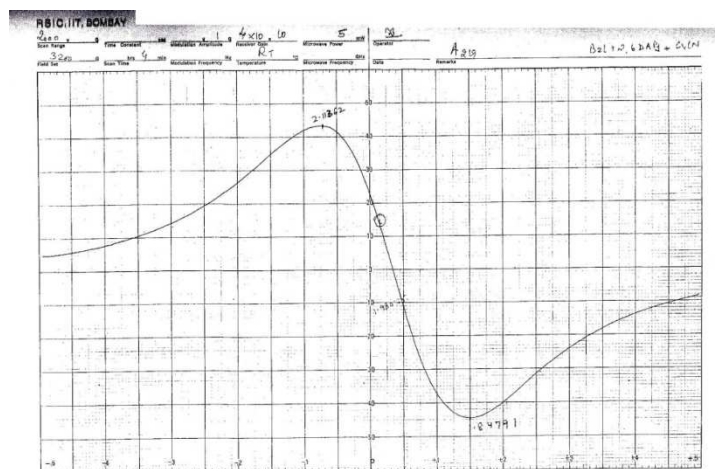


Fig. 3c ESR Spectrum of $[Cr(BDPY)(NO_3)_2](NO_3)$ Complex

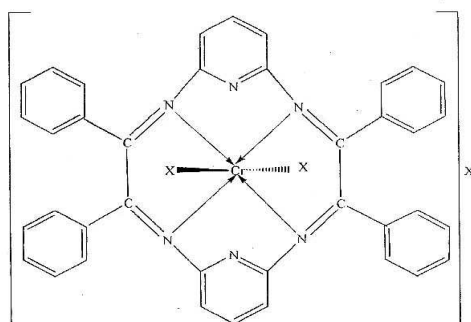
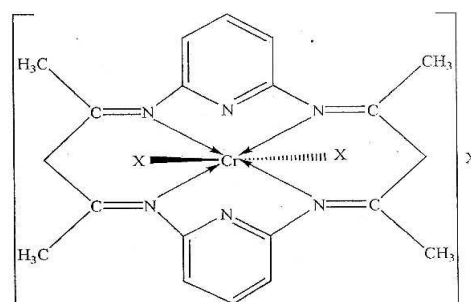
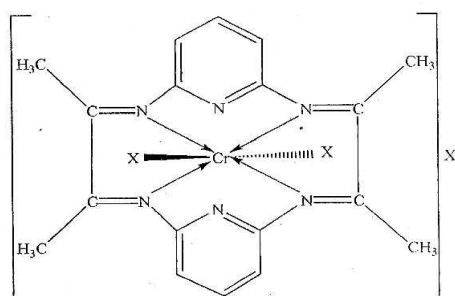
Fig. 4a [Cr(BDPY)X₂]XFig. 4b [Cr(ADPY)X₂]XFig. 4c [Cr(DDPY)X₂]X

Fig 4a-4C Structure of Complexes

Ligand Field Parameters

Various ligand field parameters have been evaluated and are listed in (table 3 and 4). The energy of the first spin-allowed transition ${}^4B_{1g} \rightarrow {}^4E_g^a$ directly gives the values of $10Dq$. B has been evaluated from the relation,

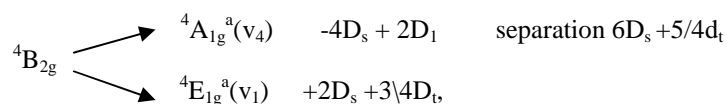
$$B = \frac{2v_1^2 - 3v_1v_2 + v_2^2}{15v_2 - 27v_1}$$

Where v_1 and v_2 are the energies of the transitions $4B_{1g} \rightarrow 4E_g^a$ and, $4B_{1g} \rightarrow 4B_{2g}$, respectively, the nephelauxetic parameter, β is readily obtained using the relation $\beta = B(\text{complex}) / B(\text{free ion})$, where $B(\text{free ion}) = 918 \text{ cm}^{-1}$. The results are presented in table 3. The value of β lies in the range of 0.31 – 0.52. These values indicate that the complexes have appreciable covalent character.

According to Jorgensen²⁵ for the 3d transition, B is well expressed by the relation $B(\text{cm}^{-1}) = 384 + 58q + 124(Z+1) - 540/(Z+1)$

From this relation the values of Z for the present complexes lie in the range 0.02 – 0.48 (table 3) which is considerably below the format +3 oxidation state of chromium. Some other ligand field parameters have also been calculated (table 3)

The transition v_2 is equal to $10Dq^{xy}$ and the separation between v_1 and v_2 is of first order (35/4) D_t and D_t is related to the in-plane and out-of-plane field strengths as $D_t=(4/7) [Dq^{xy}$ and Dq^z are in-plane (xy) and out-of-plane (z) Field strength, respectively. The radial parameter D_s has been calculated from the splitting of



The values of these parameters (table 4) are comparable to those observed for chromium complexes involving similar set of chromophore²⁶. However, it may be pointed out that these parameters are not standardised and thus require modifications. To overcome the shortcoming of various parameters of the classical Hamiltonian for tetragonal complexes, Lever et al²⁷⁻²⁸ had advanced the theory of a Normalised Spherical Harmonic (NSH) Hamiltonian. The NSH parameters DQ, DS, DT, DQ^{xy} , and DQ^z are fully capitalized to relate them to the corresponding crystal field parameters. Yet emphasize their distinction. The NSH classical parameters are related by,

$$DS = -7D_s$$

$$DT + [(7\sqrt{15})/2]D_t$$

$$DQ = (6\sqrt{21}DDq^{xy} - [7\sqrt{21}]DT$$

There are several advantages of NSH Hamiltonian theory : (a) the theory takes into account an off-diagonal contribution to D_t (b) DQ is a measure of the average ligand field experienced by the metal ion, unlike the classical Dq which is the measure of the in-plane field only and (c) the parameters of NSH theory are independent of the coordinate system used for the calculated and may be compared with the crystal field or angular overlap parameters DQ^{xy} (in plane field strength) and DQ^z (out-of-plane field strength) which are determined by the equations.

$$DQ = (1/6)[(4DQ^{xy} = 2DQ^z)$$

$$DT = (\sqrt{5} \sqrt{7})[DQ^{xy} - DQ]$$

However it may be pointed out that these parameters have artificial significance. For DQ itself is a measure of average ligand field strength. Further, the ratio (DT/DQ) has been shown to be a good measure of the degree of tetragonal distortion. The values of (DT/DQ) lie in the range 0.033-0.034. These values are much lower than the limiting value (0.4226) for a square planar complex and suggest a small distortion from idealized cubic symmetry in these complexes.

Table 4 NSH Hamiltonian Parameters of the Chromium (III) Complexes

Complex	Dt	Ds	DS	DT	DQ	DT/DQ
[Cr(BDPY)Cl ₂]Cl	2088.9	1251.3	8759.2	28315.9	846772.5	0.033
[Cr(BDPY)(NO ₃) ₂](NO ₃)	2092.6	1129.04	7903.3	28366.1	846788.0	0.033
[Cr(ADPY)(NO ₃) ₂](NO ₃)	2043.9	1222.8	8559.9	27705.96	826480.9	0.034
[Cr(ADPY)(NCS) ₂](NCS)	2020.3	1281.77	8972.4	27386.0	815513.3	0.034
[Cr(DDPY)Cl ₂]Cl	2080.4	1217.6	8523.1	28200.7	842455.7	0.033
[Cr(DDPY)(NO ₃) ₂](NO ₃)	2069.0	1213.6	8495.4	28046.2	837593.1	0.033
[Cr(DDPY)(NCS) ₂](NCS)	2103.5	1125.4	7878.1	28513.9	852925.9	0.033

Biological study

The ligand (L) **3, 4, 12, 13-tetraphenyl 2, 5, 11, 14 tetraaza tricycle [13:3:1.1^{6,0}]** Cosa – 1,2,4,6,8,10 (20) 11, 13, 14, 15 (19), 16 undecane. (BDPY), ligand free metal ions and its complexes were evaluated against different species of bacteria and fungi as per the procedure reported earlier [29-32]. In both, antibacterial and antifungal studies ligand free metal ions in solution show inhibition capacity slightly more than the ligand but much less than complexes against all the species under study.

Antibacterial screening

The compounds were screened against *Sarcinalutea* (gram-positive) and *Escherchiacoli* (gram-negative) bacteria, as growth inhibitor by disc diffusion technique [29-30]. The results of the antibacterial screening show the maximum inhibition by the (CrL(NO₃)]NO₃ complexes

Antifungal screening

Aspergillus-niger and *Aspergillus-glaucus* fungi were used as the test organism for all the newly synthesized compounds for the purpose of antifungal screening by agar plate technique [31-32]. All the complexes show nearly the same inhibition.

CONCLUSION

The present study revealed six coordinated octahedral geometry for the Cr(III) complexes. All the ligands act as a tetradentate manner coordinating through four nitrogens of the azonethine groups in an N N N N fashion moreover, the fungicidal data reveal that the complexes were superior to the free ligand in the inhibition of the tested fungi it is proposed that concentration plays a vital role in increasing the degree of inhibition, the activity increased with increasing concentration of the complexes.

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