

Synthesis, Spectral Characterization and Biological Evaluation of Chromium(III) Complexes of Schiff Base

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Abstract

Complexes of chromium(III) metal ion with schiff base *i.e.* 2,3,9,10 tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10 tetraene. (BPD) 2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12 tetraene. (ADP) 2,3,9,10 tetramethyl 1,4,8,11 tatraazatetredeca-1,3,8,10 tetraene (DDP) have been synthesized and 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 CrLX_3 ($\text{X} = \text{Cl}^-$, NO_3^- , NCS^-), Molar conductance, measured in DMF solution of these complexes indicates that the complexes are 1:1 electrolytes in nature, therefore the complexes may be formulated as $[\text{CrLX}_2]\text{X}$. These 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

1. Introduction

Azo Schiff base complexes contain both azo and azomethine groups. The azo group possesses excellent donor

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properties and is important in coordination chemistry [1]-[3] and some azo compounds have shown to possess good antibacterial activity [4] [5]. Schiff bases are well known to have antifungal, antitumor and herbicidal activities [6]-[14]. Many metal complexes of naturally occurring porphyrins, corrins and phthalocyanines have been investigated because of their potential as dyestuffs or pigments. A Schiff base complex is of great importance [15]-[18] in enhancing various industrial applications and in a number of biological processes such as photosynthesis and dioxygen transport [19]. A number of reviews are available on the physiology and biochemistry of chromium in mammals [20]-[24]. In view of above applications it is highly desirable to synthesize and characterize the Cr(III) complexes with Schiff base. In view of the above in the present paper we report the synthesis and characterization of Schiff base complexes of chromium (III) with 2,3,9,10 tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10 tetraene. (BPD) 2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12 tetraene. (ADP) 2,3,9,10 tetramethyl 1,4,8,11 tetraazatetradeca-1,3,8,10 tetraene (DDP) (Figures 1(a)-(c)).

2. Chemistry

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

2.1. Preparation of Ligands

2.1.1. Preparation of 2,3,9,10 Tetraphenyl-1,4,8,11-Tetraazacyclo Tetradeca-1,3,8,10 Tetraene. (BPD)

The ligand 2,3,9,10 tetraphenyl-1,4,8,11-tetraazacyclo tetradeca-1,3,8,10 tetraene. (BPD) was synthesized by refluxing an ethanolic solution of 1,3 diaminopropane (0.5 mole) with an ethanolic solution of benzyl, (0.5 mole) in presence of ~3 mL of conc. HCl for 3 - 4 hours. The resulting mixture was kept overnight, when an off-white coloured crystalline compound separated. This was then filtered, washed with ethanol, and dried over P_4O_{10} . The ligand is soluble in water and melted at 218°C .

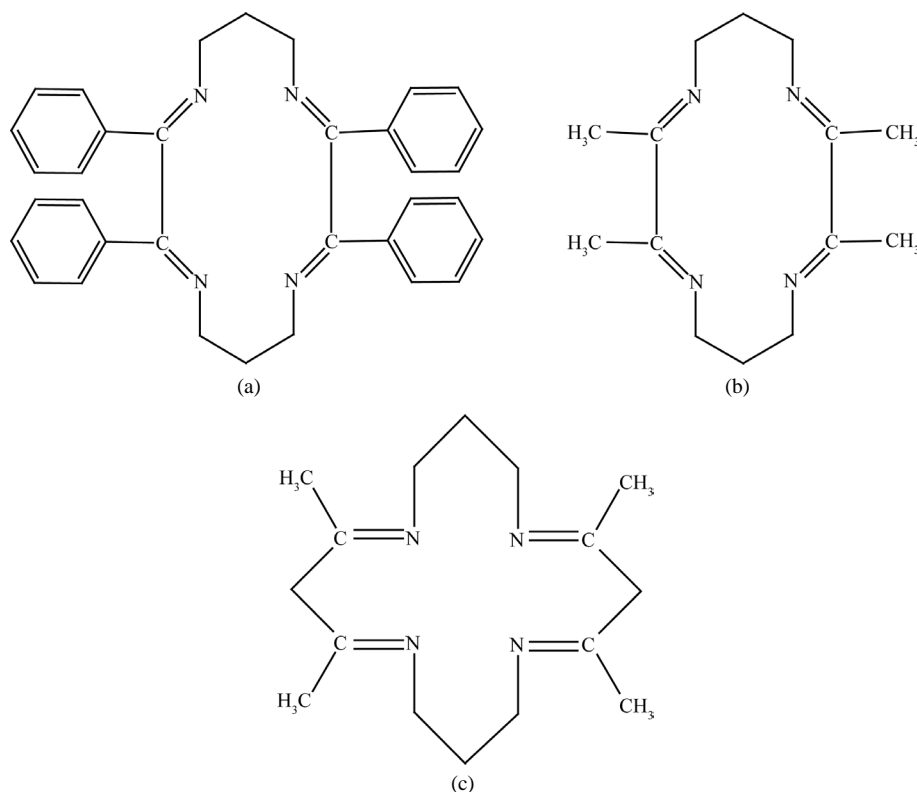


Figure 1. Structure of ligands. (a) BPD; (b) ADP; (c) DDP.

2.1.2. Preparation of 2,4,10,12-Tetramethyl-1,5,9,13-Tetraazacyclohexadeca-1,4,9,12 Tetraene. (ADP)

2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12 tetraene. (ADP) was prepared by adding an ethanolic solution of acetylacetone (0.5 mole) to an ethanolic solution of 1,3 diaminopropane (0.5 mole) in presence of ~3 mL conc. HCl and the resulting solution was refluxed for 4 hours and then kept overnight. A white crystalline compound separated on filtration which was washed with ethanol and then dried over P_4O_{10} . The compound was soluble in most organic solvents, and its melting point was recorded as 226°C .

2.1.3. Preparation of 2,3,9,10 Tetramethyl 1,4,8,11 Tatraazatetredeea-1,3,8,10 Tetraene (DDP)

2,3,9,10 tetramethyl 1,4,8,11 tatraazatetredeea-1,3,8,10 tetraene (DDP) ligand was synthesized by diacetyl (0.5 mole) to an ethanolic solution of 1,3 diaminopropane (0.5 mole) in presence of ~3 mL conc. HCl and the resulting solution was refluxed for 4 hours and then kept overnight. Light-yellow crystals separated on filtration, which were washed with ethanol and then dried over P_4O_{10} . The ligand is water soluble and melts at 221°C .

2.2. Preparation of Cr(III) Complexes with Ligands

The complexes with these ligands were synthesized by template method because the yield of the complexes was low when the ligands were treated with metal salt to form complexes.

A hot ethanolic solution of benzil/acetylacetone/diacetyl/ (0.01 mole) was added to an ethanolic solution of 1,3 diaminopropane (0.01 mole) and the resulting solution was refluxed for half an hour at $\sim 40^\circ\text{C}$. A solution of $\text{CrX}_3 \cdot n\text{H}_2\text{O}$ (0.005 mole) ($\text{X} = \text{Cl}^-$, NO_3^- , NCS^-) in ethanol and ($\text{X} = 1/2\text{SO}_4^{2-}$) 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 P_4O_{10} .

2.3. 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 E_4 -EPR spectrometer using the DPPH as the g-marker.

3. Results and Discussion

On the basis of elemental analyses (Table 1) the complexes were found to have CrLX_3 ($\text{X} = \text{Cl}^-$, NO_3^- , NCS^-) composition. Molar conductance, measured in DMF solution (Table 1) of these complexes indicates that these complexes are 1:1 electrolytes in nature, therefore, these complexes may be formulated as $[\text{CrLX}_2]\text{X}$.

3.1. 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 $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ 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 $3300 - 3200\text{ cm}^{-1}$ indicates that the amino group of 2,6 diaminopyridine and 1,3 diaminopropane have condensed with the diketone molecules. 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 respectively which indicates the presence of the diketone moiety in the ligands.

IR Spectra of the Complexes

Vibrations of free or coordinated $\text{C}=\text{O}$ group or NH group at ca. 1680 - 1700 or ca. 1550 and ca. 670 cm^{-1} are

Table 1. Elemental analyses and molar conductance data of chromium(III) complexes.

Complex	Colour	Molar Conductance $\text{cm}^{-1} \text{ mol}^{-1}$	C	Element Analysis, % Found/(calc.) H	N	Cr.	% Yield	M.P.C
$[\text{Cr}(\text{BDP})\text{Cl}_2]\text{Cl}$	Bluish Grey	80	62.31 (62.53)	5.25 (4.90)	8.32 (8.51)	7.45 (7.90)	72	262
$[\text{Cr}(\text{BDP})(\text{NO}_3)_2](\text{NO}_3)$	Bluish Grey	87	55.30 (55.80)	4.68 (4.37)	13.86 (13.29)	7.64 (7.05)	69	273
$[\text{Cr}(\text{BDP})(\text{NCS})_2](\text{NCS})$	Navy Blue Greenish	92	61.21 (61.67)	4.22 (4.44)	13.20 (13.49)	7.54 (7.16)	63	276
$[\text{Cr}(\text{ADP})\text{Cl}_2]\text{Cl}$	Blue Greyish	82	44.25 (44.39)	6.22 (6.47)	12.50 (12.84)	11.50 (11.91)	71	274
$[\text{Cr}(\text{ADP})(\text{NO}_3)_2](\text{NO}_3)$	Green Greyish	95	37.66 (37.55)	5.75 (5.47)	18.68 (19.00)	10.48 (10.08)	69	280
$[\text{Cr}(\text{ADP})(\text{NCS})_2](\text{NCS})$	Blue Greenish	91	45.36 (45.60)	5.78 (5.59)	19.66 (19.43)	10.60 (10.31)	70	264
$[\text{Cr}(\text{DDP})\text{Cl}_2]\text{Cl}_2\text{Cl}$	Grey Black	88	41.60 (41.53)	5.66 (5.93)	13.50 (13.72)	12.40 (12.74)	64	268
$[\text{Cr}(\text{DDP})(\text{NO}_3)_2](\text{NO}_3)$	Pinkish Brown	86	34.18 (34.76)	4.32 (4.96)	20.76 (20.10)	10.84 (10.66)	68	275
$[\text{Cr}(\text{DDP})(\text{NCS})_2](\text{NCS})$	Dark	90.6	42.72 (43.22)	5.85 (5.08)	20.96 (20.59)	10.82 (10.92)	70	266

not observed in any of the compounds. The strong bands appearing as doublets around $1590 - 1620 \text{ cm}^{-1}$ may be assigned to $\nu(\text{C}=\text{N})$ vibrations indicating the presence of coordinated azomethine groups. In these case ligands, phenyl ring absorptions appear in the $1600 - 1400 \text{ cm}^{-1}$ region. Absorption bands in the region $900 - 700 \text{ cm}^{-1}$ 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 NH out of plane bending.

The appearance of new bands at $1438 - 1430 \text{ cm}^{-1}$ (ν_1), $1370 - 1375 \text{ cm}^{-1}$ (ν_3), $1210 - 1215 \text{ cm}^{-1}$ (ν_5), $1010 - 1015 \text{ cm}^{-1}$ (ν_2) and $850 - 840 \text{ cm}^{-1}$ (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 thiocyanato group.

3.2. Electronic Spectra of the Complexes

The electronic spectra of all the above complexes show bands in the region $18,000$, $22,000$, $25,000$ and $28,000 \text{ cm}^{-1}$ 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 $17,465 - 18,800$ (ν_1), $22,100 - 22,900$ (ν_2), $24,200 - 25,680$ (ν_3) and $27,700 - 29,400 \text{ cm}^{-1}$ (ν_4). (Table 2). Six coordinate complexes with O_h symmetry show three spin-allowed bands [25]. Which the highest energy band assignable to the ${}^4\text{A}_{1g} \rightarrow {}^4\text{A}_{2g}$ transition, occurs above $30,000 \text{ cm}^{-1}$. The spectra of the complexes under study show four bands below $30,000 \text{ cm}^{-1}$ 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 ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_g^a$ (ν_1), ${}^4\text{B}_{1g} \rightarrow {}^4\text{B}_{2g}$ (ν_2), ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_g^b$ (ν_3) and ${}^4\text{B}_{1g} \rightarrow {}^4\text{A}_{1g}^a$ (ν_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.

3.3. 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.

3.4. EPR Spectra of the Complexes

The EPR spectra of the polycrystalline samples have been recorded (Figures 2(a)-(c)) 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. Owen [26] noted that the reduction of spin orbit coupling from the free-ion value of 90 cm^{-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 Cr^{3+} 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

Table 2. Magnetic and electronic spectral bands of chromium(III) complexes.

Complex	(B.M)	$V_1(\text{cm}^{-1})$	$V_2(\text{cm}^{-1})$	$V_3(\text{cm}^{-1})$	$V_4(\text{cm}^{-1})$
[Cr(BDP)Cl ₂]Cl	3.82	18,660	22,465	24,940	27,890
[Cr(BDP)(NO ₃) ₂](NO ₃)	3.84	18,436	22,685	25,068	27,970
[Cr(BDP)(NCS) ₂](NCS)	3.84	18,365	22,470	25,686	28,096
[Cr(ADP)Cl ₂]Cl	3.82	17,980	22,654	24,212	28,220
[Cr(ADP)(NO ₃) ₂](NO ₃)	3.76	18,024	22,568	24,510	29,411
[Cr(ADP)(NCS) ₂](NCS)	3.78	18,181	22,764	24,468	28,901
[Cr(DDP)Cl ₂]Cl	3.71	18,840	22,106	25,568	28,104
[Cr(DDP)(NO ₃) ₂](NO ₃)	3.76	17,993	22,440	24,960	28,397
[Cr(DDP)(NCS) ₂](NCS)	3.75	17,465	22,297	24,400	27,777

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(BDP)Cl ₂]Cl	2246.50	338.70	1354.80	0.37	0.48	268.00	0.98
[Cr(BDP)(NO ₃) ₂](NO ₃)	2268.50	382.70	1531.60	0.41	0.23	271.00	2.00
[Cr(BDP)(NCS) ₂](NCS)	2247.00	368.60	1474.40	0.40	0.29	268.00	1.99
[Cr(ADP)Cl ₂]Cl	2265.40	427.00	1708.00	0.46	0.07	270.60	1.99
[Cr(ADP)(NO ₃) ₂](NO ₃)	2256.80	413.50	1654.00	0.45	0.11	269.60	2.00
[Cr(ADP)(NCS) ₂](NCS)	2276.40	417.00	1668.00	0.45	0.10	271.90	1.98
[Cr(DDP)Cl ₂]Cl	2210.60	287.00	1148.00	0.31	0.11	264.00	1.99
[Cr(DDP)(NO ₃) ₂](NO ₃)	2244.00	403.71	1641.80	0.44	0.14	268.00	1.97
[Cr(DDP)(NCS) ₂](NCS)	2229.70	445.20	1780.10	0.48	0.02	266.00	1.98

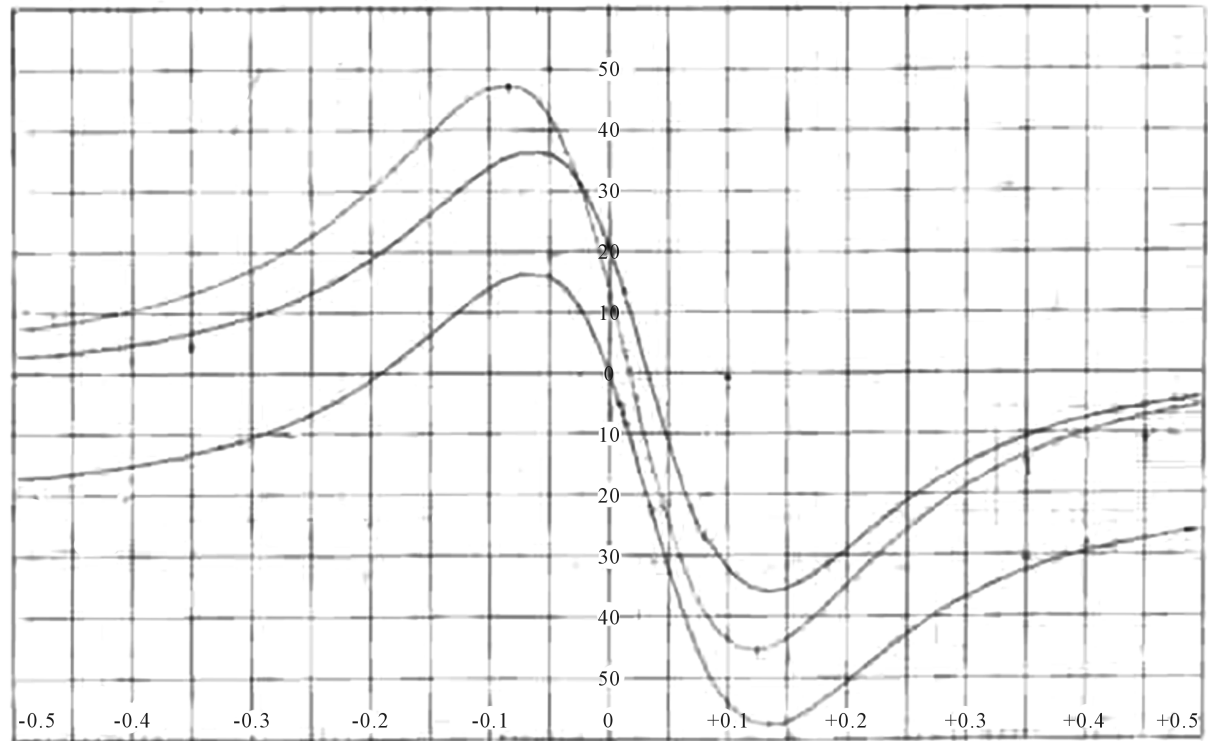
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Time Constant-
Scan Time-Hrs

Modulation Amplitude-1
Modulation Frequency-

Receive Gain- 4×10
Temperature-RT

Microwave power-5
Microwave Frequency--9.1



(a)

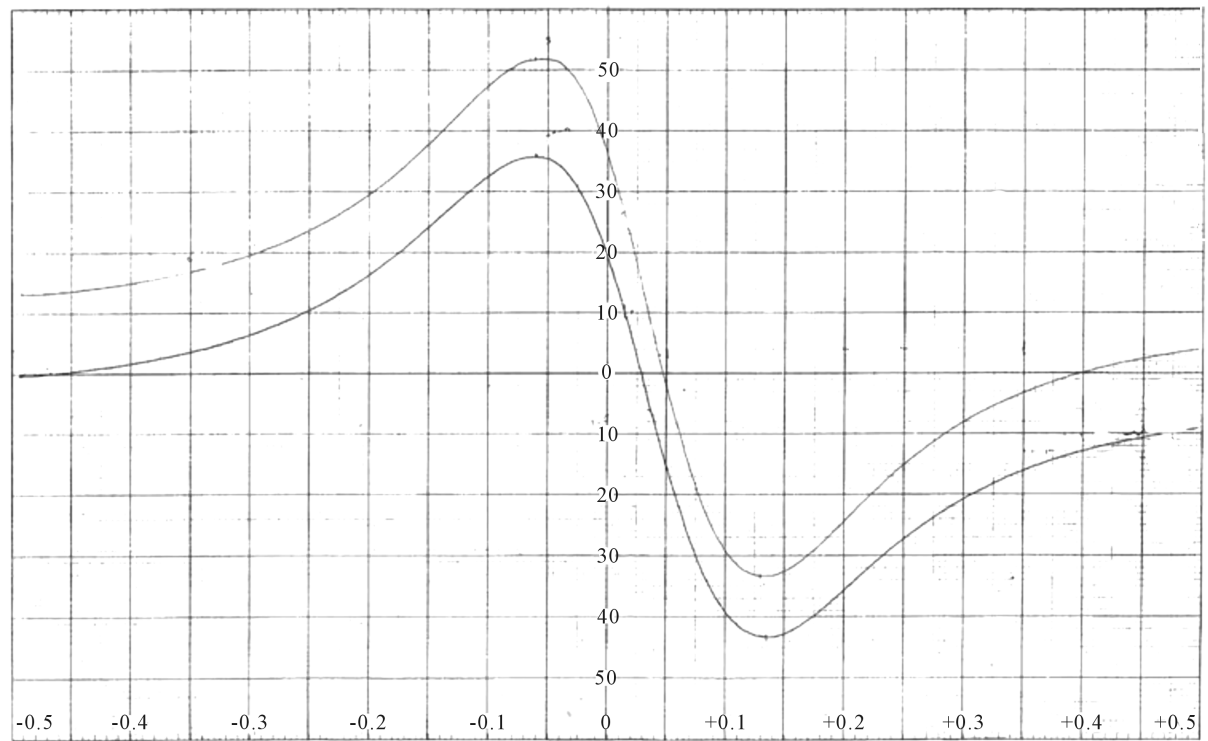
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Temperature-RT

Microwave power-5
Microwave Frequency--9.1



(b)

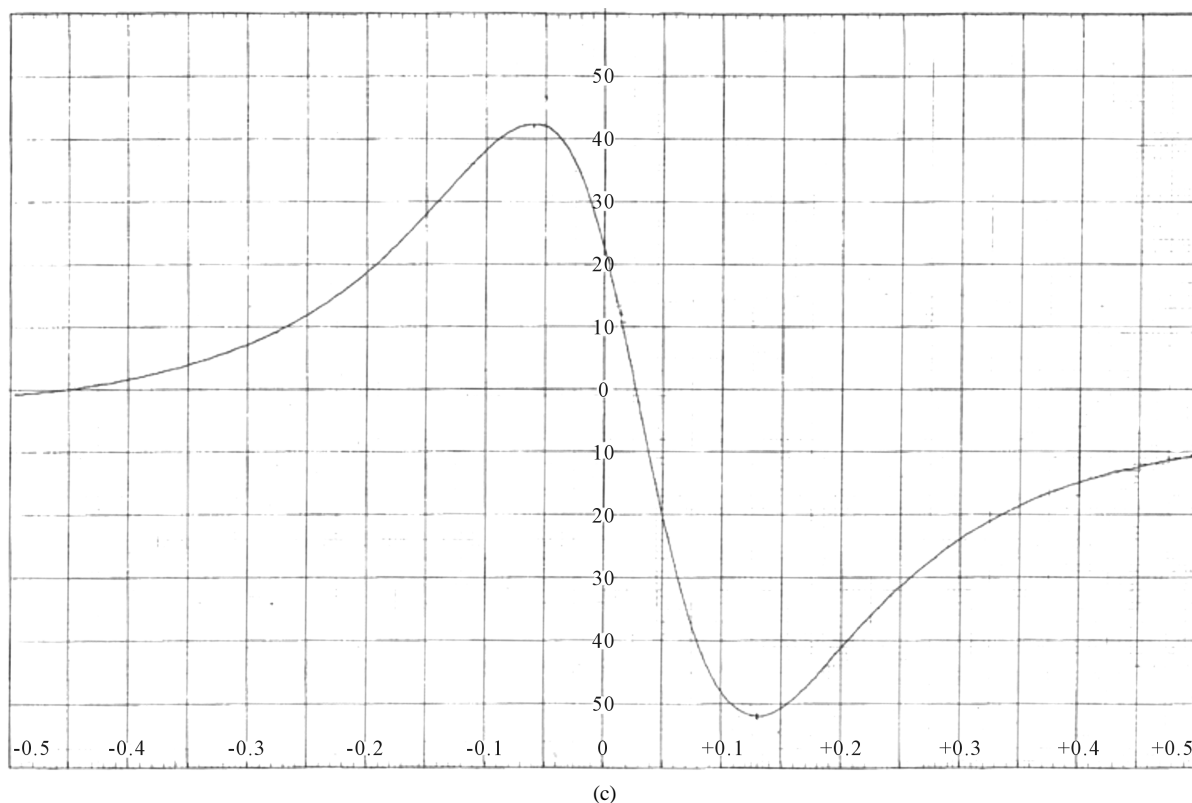
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Modulation Frequency-Receive Gain- $8 \times 10 \times 10$
Temperature-RTMicrowave power-5
Microwave Frequency--9.1

Figure 2. (a) ESR spectrum of $[\text{Cr}(\text{ADP})(\text{NO}_3)_2](\text{NO}_3)$ complex; (b) ESR spectrum of $[\text{Cr}(\text{DDP})\text{Cl}_2]\text{Cl}$ complex; (c) ESR spectrum of $[\text{Cr}(\text{DDP})(\text{SCN})_2](\text{SCN})$ complex.

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

The 4F state of d^3 ion in octahedral symmetry has the orbital singlet state lowest in energy with all excited states at much higher energies. Thus, the d^3 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 d^3 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) (**Figures 3(a)-(c)**).

Ligand Field Parameters

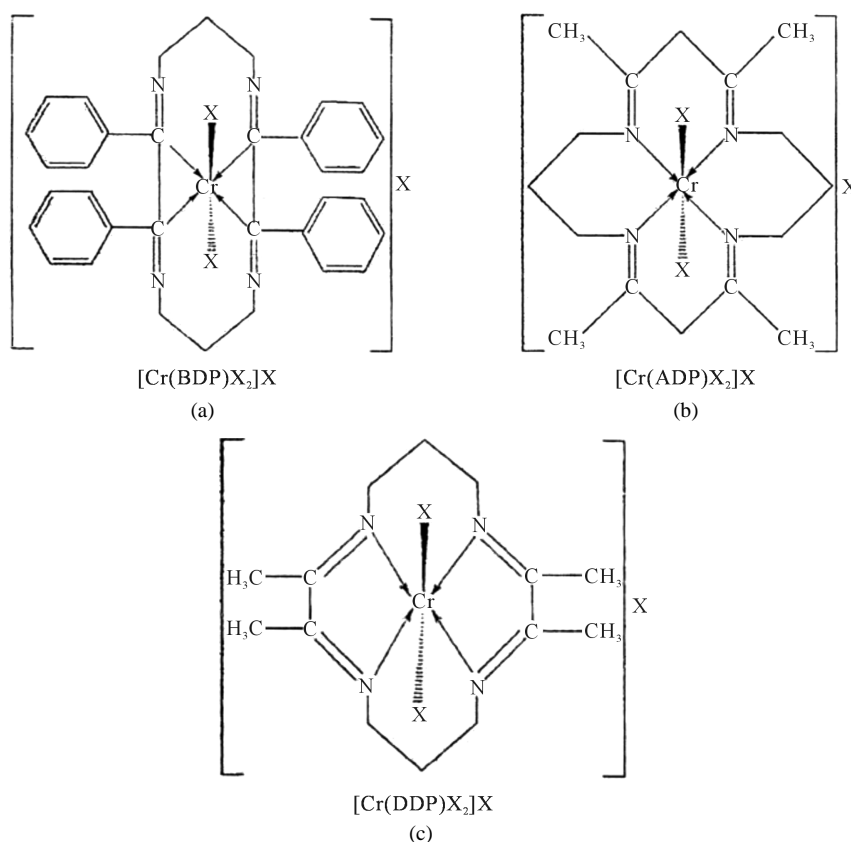
Various ligand field parameters have been evaluated and are listed in **Table 3** and **Table 4**. The energy of the first spin-allowed transition $^4B_{1g} \rightarrow ^4E_g^a$ directly gives the values of $10Dq$. B has been evaluated from the relation,

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

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.

Table 4. NSH hamiltonian parameters of the chromium(III) complexes.

Complex	Dt	Ds	DS	DT	DQ	DT/DQ
[Cr(BDP)Cl ₂]Cl	2132.60	1094.00	7658.30	28908.30	865552.80	0.033
[Cr(BDP)(NO ₃) ₂](NO ₃)	2106.90	1150.00	8050.00	28559.90	853771.90	0.033
[Cr(BDP)(NCS) ₂](NCS)	2098.80	1151.80	8062.80	28450.20	850844.10	0.033
[Cr(ADP)Cl ₂]Cl	2054.80	1193.70	8356.25	27853.70	831203.60	0.034
[Cr(ADP)(NO ₃) ₂](NO ₃)	2059.90	1277.50	8942.60	27922.80	833656.70	0.033
[Cr(ADP)(NCS) ₂](NCS)	2077.80	1353.70	10254.70	28165.50	840903.10	0.033
[Cr(DDP)Cl ₂]Cl	2153.10	1095.40	7668.10	29186.20	875454.30	0.033
[Cr(DDP)(NO ₃) ₂](NO ₃)	2056.30	1305.60	9139.20	27874.00	832443.20	0.033
[Cr(DDP)(NCS) ₂](NCS)	1996.00	1302.80	9119.80	27056.70	806619.00	0.034

**Figure 3.** Structure of complexes.

According to jorgensen [27] 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 ν_2 is equal to $10Dq^{xy}$ and the separation between ν_1 and ν_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

$${}^4B_{2g} \begin{cases} \nearrow {}^4A_{1g}^a(v_4) - 4D_s + 2D_t \text{ separation } 6D_s + 5/4d_t \\ \searrow {}^4E_{1g}^a(v_1) + 2D_s + 3/4D_t, \end{cases}$$

The values of these parameters (**Table 4**) are comparable to those observed for chromium complexes involving similar set of chromophore [28]. 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 al.* [29] [30] 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,

$$\begin{aligned} DS &= -7D_s \\ DT &+ \left[\left(7\sqrt{15} \right) / 2 \right] D_t \\ DQ &= \left(6\sqrt{21} \right) DQ^{xy} - \left[7\sqrt{21} \right] DT \end{aligned}$$

There are several advantages of NSH Hamiltonian theory: 1) the theory takes into account an off-diagonal contribution to D_t 2) DQ is a measure of the average ligand field experienced by the metal ion, unlike the classical D_q which is the measure of the in-plane field only and 3) 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.

$$\begin{aligned} DQ &= (1/6) \left[\left(4DQ^{xy} = 2DQ^z \right) \right] \\ DT &= \left(\sqrt{5}\sqrt{7} \right) \left[DQ^{xy} - DQ \right] \end{aligned}$$

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.

4. Biological Study

The ligand (L) 2,3,9,10 tetraphenyl-1,4,8,11-tetraazacyclo tetradeca-1,3,8,10 tetraene. (BPD), ligand free metal ions and its complexes were evaluated against different species of bacteria and fungi as per the procedure reported earlier [31]-[34]. 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.

4.1. Antibacterial Screening

The compounds were screened against *Sarcinalutea* (gram-positive) and *Escherchiacoli* (gram-negative) bacteria, as growth inhibitor by disc diffusion technique [31] [32]. The results of the antibacterial screening show the maximum inhibition by the (CrL(NO₃))NO₃ complexes.

4.2. 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 [33] [34]. All the complexes show nearly the same inhibition.

5. 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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