

Study of Tetragonally Compressed Complexes of Fe(II), Ni(II) and Cu(II)

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4'-Nitrobenzaldehyde-4-phenylsemicarbazone and 4'-nitrobenzaldehyde-4-phenylthiosemicarbazone have been used as primary ligands for complexation with Fe(II), Ni(II) and Cu(II). The complexes have been formulated as $[M(NBPS)_2X_2]$ and $[M(NBPTS)_2X_2]$ where, M = Fe(II), Ni(II) and Cu(II), NBPS = 4'-nitrobenzaldehyde-4-phenylsemicarbazone and NBPTS = 4'-nitrobenzaldehyde-4-phenylthiosemicarbazone and X = CH_3COO^- . The IR spectra of the metal-complexes in comparison to free ligands reveal that ligands act as monoanionic bidentate forming five membered chelate rings around the metal ion. The electronic spectra of the metal-complexes indicate tetragonally distorted octahedral geometry around the metal ion in complexes. The various crystal field parameters have been derived from the electronic spectra of the complexes. The greater value of $Dq_{(z)}$ in comparison to the $Dq_{(xy)}$ values as well as the negative values of D_1 clearly indicate tetragonal compression along Z-axis. The complexes have also been evaluated for their biological activities and it has been observed that biological activities of free ligands enhanced after complex formation.

Keywords: Tetragonally compressed octahedral, $Dq_{(z)}$, D_1 .

INTRODUCTION

The degeneracy of orbitals can be removed by the lowering of symmetry of molecules. This can be achieved by Jahn-Teller distortion theorem. This may be stated as – “In a non-linear molecule if degenerate orbitals are asymmetrically occupied a distortion occurs to remove the degeneracy.” or it may also be stated as “In an electronically degenerated state a non-linear molecule undergoes distortion to remove the degeneracy by lowering the symmetry and thus by lowering the energy” [1-3]. The distortion may also be caused by putting different ligands in XY-plane and along Z-axis as they are likely to produce crystal field of different strength in XY-plane and along Z-axis. The tetragonal distortion may either be Z-out distortion or Z-in distortion depending upon elongation along Z-axis or compression along Z-axis. The elongation along Z-axis is most preferred and has been widely studied in respect of Z-in distortion [4-8].

Semicarbazones and thiosemicarbazones have emerged as promising ligands in the coordination chemistry in the light of their excellent binding capability. The literature survey revealed a plethora of work in the field of semicarbazones and thiosemicarbazones and their transition metal complexes because of their fascinating structural properties and broad spectrum of their application in various field [9-15]. Due to

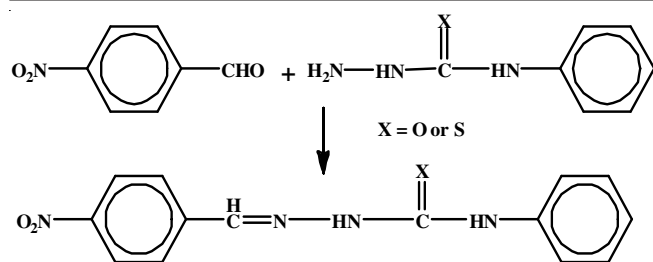
their pharmaceutical properties which are frequently higher for the metal complexes than the free ligands, they have extensively been studied during recent years.

The present paper deals with the synthesis, structural and biological evaluation of tetragonally compressed octahedral complexes of 4'-nitrobenzaldehyde-4-phenylsemicarbazone and 4'-nitrobenzaldehyde-4-phenylthiosemicarbazone with Fe(II), Ni(II) and Cu(II).

EXPERIMENTAL

All the chemicals used were of AnalR Grade. 4'-Nitrobenzaldehyde was procured from Fluka and 4-phenylsemicarbazide and 4-phenylthiosemicarbazide were purchased from Sigma Aldrich. $Fe(CH_3COO)_2$, $Ni(CH_3COO)_2$ and $Cu(CH_3COO)_2$ were purchased from E. Merck. All the chemicals were used without further purification. The ligand 4'-nitrobenzaldehyde-4-phenylsemicarbazone was prepared by refluxing the mixture of equimolar solution of nitrobenzaldehyde and 4-phenylsemicarbazide in ethanol in the presence of few drops of conc. H_2SO_4 for 1 h (Scheme-I). The solid obtained on cooling the solution was recrystallized in ethanol into yellowish white crystal with 85 % yield.

The other ligand *i.e.*, 4'-nitrobenzaldehyde-4-phenylthiosemicarbazone was prepared by the similar method of reflux like above wherein 4-phenylsemicarbazide was replaced by 4-phenylthiosemicarbazide. The crude solid was recrystallized



Scheme-I: Structure of 4'-nitrobenzaldehyde-4-phenyl semicarbazone (NBPS) and 4'-nitrobenzaldehyde-4-phenyl thiosemicarbazone (NBPTS)

in ethanol whereby light yellow crystal were obtained with 86 % yield.

Both ligands were used for complexation with Fe(II), Ni(II) and Cu(II) by the usual method of refluxing, the mixture of metal(II) acetate with ligands taken in 1:2 ratio in ethanol for 3-4 h. The precipitate was dried in desiccators on anhydrous calcium chloride. The yields were 74-80 %. Their melting point was recorded.

Physical and analytical measurements: C, H, N content of ligands and complexes was determined using Perkin-Elmer 2400 CHN Elemental Analyzer. Iron was estimated by volumetrically using N/10 $K_2Cr_2O_7$ solution. Copper was estimated iodometrically using standard sodium thiosulphate solution. Cobalt was estimated gravimetrically using α -nitroso β -naphthol. The molar conductivity of complexes was determined using CG-857 Schott-Grat Gambit Conductivity meter in DMF solution of 10^{-3} M molar concentration. The IR spectra of ligands as well as complexes were recorded on Perkin-Elmer FTIR-Spectrometer, Spectrum-two in range of 4000-400 cm^{-1} using KBr Pellets. The electronic spectra of complexes were recorded on Perkin-Elmer UV visible Spectrometer Lambda-25 using DMSO solution. The magnetic susceptibility of complexes was determined on Gouy balance at room temperature using mercury tetrathiocyanatocobaltate as calibrate.

RESULTS AND DISCUSSION

The percentage composition of ligands and complexes have been displayed in Table-1. On the basis of percentage

composition and molar conductivity values, the complexes have been formulated as $[ML_2X_2]$ where $M = Fe(II)$, $Ni(II)$ and $Cu(II)$, $L = NBPS$ or $NBPTS$ and $X = CH_3COO^-$. The conductivity values of complexes are too low which indicate their non-electrolytic nature [16-19].

IR spectra of ligands and complexes: The IR spectra of free ligand 4'-nitrobenzaldehyde-4-phenyl semicarbazone a sharp band appears at 3150 cm^{-1} which is assigned to $\nu(N-H)$ [20]. It is further supported by a medium band at 1555 cm^{-1} due to bending vibration of $\delta(N-H)$. The strong band appearing at 3035 cm^{-1} is due to $\nu(C-H)$ stretching of benzene ring [21,22]. The medium band appearing at 2845 cm^{-1} is due to $\nu(C-H)$ of azomethine group. The strong band appearing at 1665 cm^{-1} is fairly assigned to $\nu(C=O)$ stretching of semicarbazone [23]. In the IR spectra of complexes of NBPS this band undergoes negative shift and appears at 1640 cm^{-1} which is indicative of its coordination to the metal ions through oxygen [24,25]. The medium band appearing at 1630 cm^{-1} in the IR spectra of free ligand is attributed to $\nu(C=N)$ of azomethine group of the ligand [26]. In the IR spectra of complexes this band shifts to a lower frequency and appears at 1600 cm^{-1} . This shows the coordination of the ligand through azomethine nitrogen [27,28]. The medium and weak bands appearing at 1580, 1510 and 1455 cm^{-1} are the characteristic absorption frequency of benzene ring vibration. The sharp band appearing at 1535 and 1340 cm^{-1} may be assigned to $\nu_{asy}(NO_2)$ and $\nu_{sym}(NO_2)$ respectively. In the IR spectra of 4'-nitrobenzaldehyde-4-phenyl thiosemicarbazone the band near 1665 cm^{-1} doesn't appear which shows the absence of C=O group in this ligand. This ligand absorbs strongly at 1230 cm^{-1} due to $\nu(C=S)$ stretching, which undergoes negative shift in its complexes. It is indicative of coordination through sulphur of C=S group of this ligand to the metal ions [29]. In the spectra of all the complexes two new bands appear at 1335 and 1330 cm^{-1} . These bands are the characteristic absorption bands for monodentately coordinated CH_3COO^- ion to the metal ion in all the complexes. Thus on the basis of IR spectra of complexes in comparison to that of the free ligands, it may be asserted that the ligand NBPS acts as bidentate neutral ligand co-ordinating through carbonyl oxygen and azomethine nitrogen while the second ligand NBPTS also

TABLE-1
COMPOSITION (%) FOUND (CALCD.)

Compounds	Colour	Yield (%)	m.p. (°C)	M	C	H	N	S	$\lambda_m (\Omega^{-1} cm^2 mol^{-1})$
NBPS	Yellowish white	85	176	—	89.82 (59.20)	3.98 (4.20)	19.42 (19.7)	—	—
NBPTS	Light yellow	86	198	—	56.41 (56.00)	3.89 (4.00)	18.46 (18.60)	10.59 (10.70)	—
$[Fe(NBPS)_2(CH_3COO)_2]$	Brilliant green	74	240	7.22 (7.50)	51.98 (51.80)	3.81 (4.00)	14.97 (15.10)	—	15
$[Fe(NBPTS)_2(CH_3COO)_2]$	Dull green	80	242	6.98 (7.20)	49.91 (49.60)	3.72 (3.90)	14.29 (14.50)	8.12 (8.30)	16
$[Ni(NBPS)_2(CH_3COO)_2]$	Dull red	80	240	7.90 (8.00)	51.76 (51.50)	3.91 (4.00)	14.87 (15.00)	—	13
$[Ni(NBPTS)_2(CH_3COO)_2]$	Light red	78	246	7.43 (7.60)	49.68 (49.40)	3.72 (3.90)	14.28 (14.40)	8.12 (8.20)	15
$[Cu(NBPS)_2(CH_3COO)_2]$	Bright blue	74	248	8.34 (8.50)	51.46 (51.20)	3.88 (4.00)	14.79 (14.90)	—	15
$[Cu(NBPTS)_2(CH_3COO)_2]$	Blue	76	252	8.00 (8.20)	49.41 (49.10)	3.62 (3.80)	14.12 (14.30)	8.00 (8.10)	17

acts as bidentate neutral ligand coordinating through thiosulphur and azomethine nitrogen forming 5-membered chelate ring.

Magnetic moment and electronic spectra: The magnetic moment and electronic spectra of Fe(II) complexes have been given in Table-2.

TABLE-2

Complexes	ν_{1-1} (cm^{-1})	ν_{2-1} (cm^{-1})	ν_{3-1} (cm^{-1})	μ (BM)
[Fe(NBPS) ₂ (CH ₃ COO) ₂]	5600	9800	12800	5.08
[Fe(NBPTS) ₂ (CH ₃ COO) ₂]	5400	9200	12600	5.07

The magnetic moment of Fe(II) complexes are found to be 5.07 and 5.08 BM which correspond to high spin octahedral geometry to these complexes [30,31]. Fe(II) is a d^6 system for which the ground state term is 5D which splits into $^5T_{2g}$ and 5E_g and thus only one band is expected in Fe(II) complexes. But here the complexes display three bands which indicates that the complexes have undergone tetragonal distortion (D_{4h}). This causes further splitting of T_{2g} in $^5B_{2g}$ and 5E_g while, the excited state 5E_g splits into $^5B_{1g}$ and $^5A_{1g}$. Thus these three bands may be assigned to $^5B_{2g} \rightarrow ^5E_g = \nu_1$, $^5B_{2g} \rightarrow ^5B_{1g} = \nu_2$ and $^5B_{2g} \rightarrow ^5A_{1g} = \nu_3$ [32]. ν_2 is the major of 10 $D_{q_{xy}}$ while ν_1 and ν_3 involve also the other parameters like D_s and D_t . The values of different crystal field parameters are given in Table-3.

TABLE-3

Complexes	$D_{q_{xy}}$ (cm^{-1})	D_{q_z} (cm^{-1})	D_s (cm^{-1})	D_t (cm^{-1})
[Fe(NBPS) ₂ (CH ₃ COO) ₂]	980	1650	1229	-383
[Fe(NBPTS) ₂ (CH ₃ COO) ₂]	920	1490	1257	-326

In these complexes the greater value of D_{q_z} than $D_{q_{xy}}$ and negative value of D_t conspicuously indicate tetragonal compression along Z-axis in octahedral symmetry.

The magnetic moment and electronic spectra of Ni(II) complexes have been displayed in Table-4.

The magnetic moment of Ni(II) complexes are 3.35 and 3.40 BM at room temperature which are higher than μ_s for two unpaired electrons of Ni(II) octahedral complexes. This increase in magnetic moment may be attributed to strong spin orbit coupling under which $\mu_{\text{eff}} = \mu_{\text{S.O.}} (1-4\lambda/10Dq)$. As the spin orbit coupling constant λ for d^8 system is negative ($\lambda = -315$), μ_{eff} becomes greater than $\mu_{\text{S.O.}}$ [33,34].

The electronic spectra of these complexes display four bands which may be assigned to $^3B_{1g} \rightarrow ^3B_{2g} = \nu_1$, $^3B_{1g} \rightarrow ^3E_g^{(a)} = \nu_2$, $^3B_{1g} \rightarrow ^3A_{2g} = \nu_3$ and $^3B_{1g} \rightarrow ^3E_g^{(b)} = \nu_4$. Here ν_1 is the major of 10 Dq and other transitions involve D_s and D_t parameters also. The values of various crystal field parameters are given in Table-5.

The appearance of four bands is indicative of appreciable tetragonal deviation from octahedral symmetry while greater value of D_{q_z} in respect of $D_{q_{xy}}$ and negative value of D_t confirm the tetragonal compression along Z-axis [35-37].

TABLE-4

Complexes	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	μ (BM)
[Ni(NBPS) ₂ (CH ₃ COO) ₂]	11550	14550	16000	24170	3.35
[Ni(NBPTS) ₂ (CH ₃ COO) ₂]	11300	14560	16300	24100	3.40

TABLE-5

Complexes	$D_{q_{xy}}$ (cm^{-1})	D_{q_z} (cm^{-1})	D_s (cm^{-1})	D_t (cm^{-1})
[Ni(NBPS) ₂ (CH ₃ COO) ₂]	1155	1755	1290	-343
[Ni(NBPTS) ₂ (CH ₃ COO) ₂]	1130	1782	1222	-373

The magnetic moment and electronic spectral bands of Cu(II) complexes have been displayed in Table-6.

TABLE-6

Complexes	ν_{1-1} (cm^{-1})	ν_{2-1} (cm^{-1})	ν_{3-1} (cm^{-1})	μ (BM)
[Cu(NBPS) ₂ (CH ₃ COO) ₂]	7200	18600	21000	1.96
[Cu(NBPTS) ₂ (CH ₃ COO) ₂]	7000	18250	21100	1.98

The magnetic moment of Cu(II) complexes are 1.96 and 1.98 BM at room temperature which indicate that the complexes are magnetically dilute with octahedral or distorted octahedral geometry [38,39].

The electronic spectra of Cu(II) complexes display three bands which may be assigned to $^2A_{1g} \rightarrow ^2B_{1g} = \nu_1$, $^2A_{1g} \rightarrow ^2B_{2g} = \nu_2$ and $^2A_{1g} \rightarrow ^2E_g = \nu_3$. The various crystal field parameters derived from these spin allowed transition are given in Table-7.

TABLE-7

Complexes	$D_{q_{xy}}$ (cm^{-1})	D_{q_z} (cm^{-1})	D_s (cm^{-1})	D_t (cm^{-1})
[Cu(NBPS) ₂ (CH ₃ COO) ₂]	1140	2701	685	-892
[Cu(NBPTS) ₂ (CH ₃ COO) ₂]	1125	27045	592	-926

The appearance of three bands is clearly the consequence of tetragonal distortion in O_h symmetry while the greater value of D_{q_z} than $D_{q_{xy}}$ with negative value of D_t show without doubt that there is compression along Z-axis of O_h symmetry [40,41].

Biological evaluation: The ligands as well as their metal complexes were screened against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli* at concentration 50 and 100 ppm in DMSO and the results were compared with straptomycin as standard. The activity index of ligands as well as their metal complexes was derived by the expression:

$$\text{Activity index} = \frac{\text{Inhibition zone by test compound (diameter)}}{\text{Inhibition zone by control (diameter)}} \times 100$$

The results displayed in Table-8 clearly indicates that both ligands are biological active. It also indicates that the antibacterial activity gets enhanced after complexation. The activity increases with increasing concentration of ligands and complexes, however all the ligands and complexes show less antibacterial activity in comparison to the standard. The thio ligand and its metal complexes record greater activity than semi-carbazone ligand and their complexes, which may be due to the presence of sulphur in place of oxygen in thiosemi-carbazone. Copper complex with thiosemicarbazone shows

TABLE-8
ANTIBACTERIAL SCREENING DATA OF LIGANDS AND COMPLEXES
[DIAMETER OF INHIBITION ZONE (mm) AFTER 24 h INCUBATION]

Compounds	<i>Staphylococcus aureus</i>				<i>Escherichia coli</i>			
	Diameter of inhibition zone		Activity (%)		Diameter of inhibition zone		Activity (%)	
Concentration (ppm)	50	100	50	100	50	100	50	100
NBPS	25	35	55.5	58	28	39	54	61.0
NBPTS	27	38	60.0	63	30	42	58	66.0
[Fe(NBPS) ₂ (CH ₃ COO) ₂]	28	36	62.0	60	34	45	65	70.0
[Fe(NBPTS) ₂ (CH ₃ COO) ₂]	32	40	71.0	67	36	48	69	75.0
[Ni(NBPS) ₂ (CH ₃ COO) ₂]	28	37	62.0	62	35	46	67	72.0
[Ni(NBPTS) ₂ (CH ₃ COO) ₂]	34	41	75.5	68	37	50	71	78.0
[Cu(NBPS) ₂ (CH ₃ COO) ₂]	38	45	84.0	75	40	49	77	76.5
[Cu(NBPTS) ₂ (CH ₃ COO) ₂]	40	49	89.0	82	46	54	88	84.0
Streptomycin (standard)	45	60	100.0	100	52	64	100	100.0

the greatest activity than all other complexes which may be due to a toxic nature of copper metal. The increases in antibacterial activity of ligands after complexation may be attributed to the formation of chelates in complexes [12,22].

Conclusion

The study reveals that the ligands are weakly coordinated to the metal ions in XY plane than acetate ions along Z-axis due to the presence of strongly electron withdrawing-NO₂ group in planar ligands. This makes tetragonally distorted octahedral complexes with appreciable compression along Z-axis which is well supported by the higher values of D_{q(z)} than D_{q(xy)} and negative value of D_t in all the complexes. The antibacterial screening of complexes reveals that all the complexes have greater antibacterial activity than the free ligands confirming the concept of enhancement of antibacterial activities of a compound after complexation.

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