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Synthesis, Characterization and Fungitoxicity of Bidentate High-spin Six Coordinate 3d Metal Complexes with N-(5-phenyl-1,3,4-thiadiazol-2-yl) Aceta/Benzamidines

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Thiadiazole derivatives have been reported to be biologically versatile compounds, having antiviral [1] antibacterial [2] antipyretic [3] herbicidal [4] fungicidal [5] hypoglycemic [6] and analgesic [7] activities. The toxicological importance of $-\mathrm{N}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{S}-$ moiety have been well-established in many fungicides, presence of a thiadiazole ring may be expected to impart fungicidal activity [8–10]. Various amidines are also known to exhibit useful fungicidal, bactericidal and trypanoicidal properties [11, 12]. Several metal chelates are also known to possess bactericidal [13], fungicidal [14] and antiviral [15] activities. In several cases the metal chelates have been found to be more fungitoxic than the chelating agent themselves [14]. This prompted us to prepare and characterise the complexes reported in this paper.

Experimental

Synthesis

All chemicals used were of AR grade or equivalent quality. N-(5-phenyl-1,3,4-thiadiazol-2-yl) acetamidine and N-(5-phenyl-1,3,4-thiadiazol-2-yl) benzamidine (hereafter abbreviated as aceta and benza respectively) were prepared by the method employed by Giri *et al.* [16]. The complexes were all prepared by the following method.

A solution of the metal salt in ethanol was added with stirring to a sodium salt of amidine in ethanol. The whole mixture was refluxed for 3–4 hours. This was cooled, filtered off, washed with water followed by ethanol and dried in a vacuum desiccator. The analytical results are given in Table I.

Physical measurements

The complexes were analysed for their metal content after destroying the organic residue with a mixture of concentrated hydrochloric and nitric acids. Standard methods were used for the purpose [17].

The water content of the complexes was determined by heating them in the range of 150–300 °C and determining the loss in weight.

Conductivity titration and molar conductance were measured with the help of Toshniwal's conductivity bridge (type CL 01/01), using a dipping type cell at the room temperature (303 K).

For Magnetic susceptibility measurements Gouy method was employed. Cobalt mercury tetrathiocyanate was used as the standard. Diamagnetic corrections were also made by using Pascal's constants.

The electronic spectra of the complexes and the chelating agent were recorded on a Unicam SP 8000 UV Spectrophotometer in Nujol mull.

Infrared spectra (400–4000 cm^{-1}) of ligands and complexes were recorded on a Perkin-Elmer model Spectrophotometer in KBr.

TABLE I. Analytical Data and General Behaviour of the Complexes.

Complexes[a]	M.P. °C	Metal		Nitrogen %		Sulphur %		μ_{eff} B.M.
		Obs.	Cal.	Obs.	Cal.	Obs.	Cal	
Mn[(aceta)$_2$(H$_2$O)$_2$]	>250	11.10	11.29	22.90	22.81	13.00	13.04	5.94
Mn[(benza)$_2$(H$_2$O)$_2$]	>250	8.72	8.44	17.50	17.20	10.00	9.83	5.92
Fe[(aceta)$_2$(H$_2$O)$_2$]	>250	11.12	11.38	22.69	22.76	13.22	13.02	5.00
Fe[(benza)$_2$(H$_2$O)$_2$]	240	8.85	8.58	17.05	17.17	9.98	9.81	4.97
Co[(aceta)$_2$(H$_2$O)$_2$]	238	11.96	11.80	22.71	22.62	12.78	12.92	4.70
Co[(benza)$_2$(H$_2$O)$_2$]	>250	9.00	9.07	17.76	17.99	9.72	9.77	4.71
Ni[(aceta)$_2$(H$_2$O)$_2$]	240	11.75	11.80	22.65	22.62	13.00	12.92	3.10
Ni[(benza)$_2$(H$_2$O)$_2$]	212	8.98	9.07	18.25	17.99	9.82	9.77	3.06
Cu[(aceta)$_2$(H$_2$O)$_2$]	176	13.00	12.80	22.37	22.40	12.75	12.80	1.92
Cu[(benza)$_2$(H$_2$O)$_2$]	202	9.76	9.55	17.10	16.99	9.68	9.71	1.90

[a] Satsifactory carbon and hydrogen analyses have been obtained for all the complexes.

TABLE II Fungicidal Screening Data

Compound serial as in Table I	Average Percentage inhibition after 96 hours					
	Organism-Rhizopus nigracans concentration used			Organism-Curvularia lunata concentration used		
	10 ppm	100 ppm	1000 ppm	10 ppm	100 ppm	1000 ppm
1	29 6	44 0	55 2	30 0	46 2	54 0
	30 0	40 2	55 7	29 5	47 5	55 0
2	32 0	45 0	59 6	31 0	47 6	55 2
	31 9	42 6	58 8	31 0	49 5	57 2
3	38 2	52 0	77 6	33 6	55 0	69 0
	35 7	50 4	69 5	32 6	52 8	68 0
4	42 2	57 0	95 2	42 0	59 2	88 0
	41 2	57 0	89 6	40 0	59 0	79 8
5	51 5	70 4	101 6	50 0	67 4	100 0
	50 6	68 7	98 2	49 0	72 0	100 7
aceta	26 4	39 7	46 4	26 6	38 5	47 0
benza	27 2	35 0	46 2	27 2	39 4	50 0

^{1}H NMR spectra were recorded on a Varian-60D Spectrometer

Fungitoxicity was evaluated against *Rhizopus nigracans* and *Curvularia lunata* by the agar-plate method [18], at three concentrations, *viz* 10 ppm, 100 ppm and 1000 ppm The number of replications in each case was three The percentage inhibition by various compounds are recorded in Table II

$$\text{Percentage Inhibition} = \frac{(C - T) \times 100}{C}$$

where, C = Diameter of the fungus colony in the control plate after 96 hours and T = diameter of the fungus colony in treated plates after 96 hours

Results and Discussion

The stoichiometries of the complexes are confirmed by the elemental analyses reported in Table I The molar conductivities range between 2–9 cm^2 Ω^{-1} mol^{-}1, which clearly indicates that all the complexes behave as nonelectrolytes in ethanol This confirms coordination of amidines anion From the established stoichiometries and the nature of the donor atoms of the ligands, one would foresee somewhat distorted hexacoordinate structures for these complexes Evidence for such is found in the magnetic susceptibility and electronic spectral data

The corrected magnetic moments for the Mn(II) complex is 5.94 BM, quite typical of 6-coordinate complexes The electronic spectrum of the Mn(II) complex exhibits two d–d bands, one at 25100 cm^{-1} and other at 16000 cm^{-1} and a charge transfer band at 35000 cm^{-1} The two d–d bands in this complex may be assigned as $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), ^4Eg (G) and $^6A_{1g} \rightarrow {}^4T_{2g}$ (G), $^4T_{1g}$ (G) On this basis a distorted hexacoordinate geometry may be proposed for Mn(II) complex

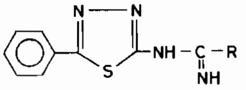
The magnetic moment of the Fe(II) complex was found to be 5 00 BM and is consistent with octahedral stereochemistry around Fe(II) ion The electronic spectrum of the Fe(II) complex shows a weak absorption band at 10,000 cm^{-1} due to the $^5T_{2g} \rightarrow {}^5Eg$ transition and is characteristic of the octahedral symmetry around Fe(II) ion

The magnetic moment for the Co(II) is 4 70 BM, quite typical of hexacoordinate complex For Co(II) a loss of degeneracy of the $^4T_{1g}$ (O_h) ground term as a result of symmetry lower than O_h is expected to yield magnetic moments lower than those for truely octahedral species due to a partial quenching of the orbital contribution [18, 20] The electronic spectrum of Co(II) complex has two very broad band with centres at 9,500 and 19,000 cm^{-1} with the transitions, $^4T_{1g}$(F) $\rightarrow$ $^4T_{2g}$ (ν_1) and $4T_{1g}$(F) $\rightarrow$ $^4T_{1g}$(P) (ν_3) respectively These spectral data are very much like those reported for Co(II) complexes and are consistent with the assignment of distorted 6-coordinate geometry From the values of ν_1 and ν_3, values of Dq, B$'$ and ν_2 work out as 950, 784 and 17,113 cm^{-1} respectively The ν_2/ν_1 ratio 2 0 lies well within the limit reported for 6-coordinate structure of the Co(II) complex [21]

The magnetic moment of Ni(II) complex (3 1 BM) is typical of hexacoordinate Ni(II) complex The singly degenerate $^3A_{2g}$ (O_h) ground state for the nickel species, however would not be greatly affected by distortion Three spin-allowed d–d transitions are observed in the electronic spectra However, if the complex is distorted, a lifting of the degeneracy of the triply degenerate states in the lower symmetry fields should result in some broadening or splitting of the spectral bands [20, 22] For the Ni(II) complex, reported here, only two major absorption bands that can be attributed to spin-allowed d–d transitions are observed, one very broad band with centre at 11 050 ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$) ($\nu_1$) and the other band consisting of two components in the region 17,000–18,000 ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$) ($\nu_2$) cm^{-1} The onset of charge transfer peaks apparently masks the expected third or highest energy band The ratio $\nu_2/\nu_1 \approx 1\ 58$ is accepted for most of the 6-coordinated Ni(II) complexes Using these frequencies the values of Dq, B′ and β have been calculated, which are 1005 cm^{-1}, 728 cm^{-1} and 0 67 respectively These values are well within the ranges of O_h symmetry around the Ni(II) ion

Only one absorption band due to $^2E_g \rightarrow {}^2T_{2g}$ transition is expected for octahedral Cu(II) complexes [22, 23] Since ^2E_g state is highly susceptible to Jahn-Teller distortion, the Cu(II) complexes possessed distorted octahedral geometry

The infrared spectrum of the N-(5-phenyl-1,3,4-thiadiazol-2-yl) aceta/benzamidines revealed two absorption bands, one at 1660 cm^{-1} due to exocyclic –N=C group and the other at 1600 cm^{-1} due to ν N=C of the thiadiazole nucleus. An absorption band appearing at 3400 cm^{-1}, can be attributed to ν N–H group Moreover, the amidines exhibited the IR bands in the regions which were clearly attributable to the substituted benzene nuclei The reported amidines have two potential donor sites, nitrogen and sulphur as shown below



R= CH$_3$, C$_2$H$_5$

In the acetamidine and benzamidine the ν (C–S) bands are assigned at 718 and 730 cm^{-1} respectively These bands show a positive shift of approximately 20 cm^{-1} on complex formation This rules out the possibility of coordination through the sulphur of $-\overset{|}{\underset{|}{C}}-S-$ group The positions of the absorption bands due to cyclic and exocyclic –N=C modes, remain practically unchanged This too rules out the possibility of coordination through the nitrogen of cyclic and exocyclic –N=C groups A negative shift of 25–30 cm^{-1} in –N–N band or thiadiazole ring and disappearance of ν N–H band in the IR spectra of complexes as compared to the free ligands indicate bonding through the nitrogen of the –N–N group of the thiadiazole ring and the nitrogen of ν N–H group of the exocyclic ring This gave a six-membered chelate ring A highly unstable four-membered chelate ring will be formed if nitrogen of –NH group, directly attached to the thiadiazole ring is involved in coordination In addition to these absorption bands, the complexes exhibited bands in the region 650–880 cm^{-1} assignable to the coordinated water, which is absent in the free ligand

The ^{1}H NMR spectrum of amidines in MDSO-d$_6$ + CDCl$_3$ shows the following features a broad signal at $\delta = 7.90$ (NH), a sharp singlet at $\delta = 2\ 2$ (CH$_3$), a major peak at $\delta = 7\ 6$ (C$_6$H$_5$) and a pseudosinglet at $\delta = 8\ 0$ (NH) Metal complexation of N-(5-phenyl-1,3,4-thiadiazol-2-yl) aceta/benzamidines has been studied looking at NH, CH$_3$, C$_6$H$_5$ and NH resonances The proton spectra of the complexes show downfield shift of the –NH resonance relative to the free ligand This result indicates binding through the amide nitrogen

Fungicidal screening data (Table II) clearly indicate that the complexes are more fungitoxic than the free ligand Moreover it is also observed that the fungitoxicity of the complexes increases as the radius of the metal ion decreases

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