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Synthesis, Spectroscopic and Biological Activity of Cu(II), Ni(II) and Co(II) Transition Metals Complexes with the Ligand 2-Amino-4-(P- Dihydroxy Phenyl) Thiazoline

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ABSTRACT

A series of new copper(II), cobalt(II) and nickel(II) complexes of the ligand 2-amino-4-(p-dihydroxy phenyl) thiazoline were prepared and characterized. Complexes were formed by the treatment of metal salts with ligand 2-amino-4-(p-dihydroxy phenyl) thiazoline in 1:2 molar ratio in ethanolic medium and yield was about 76-79%. From the analytical and spectral data the stoichiometry of these complexes have been found to be of the type ML_2X_2 (where M = Cu (II), Co (II) and Ni (II)). Evidences indicate that these complexes exhibit octahedral and square planar geometry. The fungicidal activities of ligands and metal complexes were screened by growth method against various fungi i.e. *Dreschlere setramera*, *Fusarium oxysporum*, *Macrophomera phaseoli* at different concentrations. It is found that the activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand.

1. Introduction

Thiazoline complexes play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The chemistry and wide range of application of thiazoline compounds have been reported in literature. These compounds have shown wide range of applications, they can be used as industrial, anti-fungal, anti-bacterial, anticancer, anti-tubercular activities and chelating agents. Thiazoles and their thiazoline analogues are well known to coordinate to transition metal fragments and a large number of such compounds have been isolated that can potentially ligate transition metals. Complexes of transition metals ions containing ligands with N, S and N, S, O donors are known to exhibit interesting stereo chemical, electrochemical and electronic properties. Such compounds can also be used as local anesthetic, anti-radiation drugs, anti-viral and anti-protozoan agents and also in the rubber industry as vulcanization accelerators. The synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes were studied by many workers [1, 2]. Schiff's base derived complexes of derivatives of DHA, their spectra and synthesis under microwave irradiation were also studied by many workers [3, 4]. Attempts have been made to study their structure with the help of elemental analysis, magnetic measurements, spectral studies and conductance measurements. The present paper deals with the preparation and characterization of Cu(II), Co(II) and Ni(II) complexes with 2-amino-4-(p-methoxy phenyl) thiazoline ligand. Metal complexes play an important role in biological activity. In many cases metal complexes are more potent than free ligands. These newly synthesized complexes were also screened for their antifungal activity against fungi viz. *Drechslera-tetramera, Fusarium-oxysporum* and *Macrophomera-phoseoli* at different concentrations [5]. Similar experiments on fungicidal and antimicrobial activities of Cu (II), Co (II) and Ni (II) Complexes with O, N, and S donor, their EPR and electronic spectral studies were also conducted by many workers [6-11].

2. Experimental Methods

All the chemicals and reagents used were of analytical grade; otherwise they were purified before use. Organic solvent used was absolute alcohol. IR spectra of the ligand and complexes are recorded in nujolmull. The fungicidal activity of ligands as well as complexes was determined by using the Growth method. The electronic spectra were recorded in MgO at room temperature on VSU-22 spectrophotometer. The measurements were carried out Guru Nanak Dev University, Amritsar. Metal and sulphur contents of these complexes were estimated using the standard procedures reported in literature [12, 13].

Table 1 Elemental analysis data

Complexes	%Calc./ Obs.					
	C	H	S	N	O	M
$C_{21}H_{16}N_2O_2S$	73.25	4.65	9.30	8.13	4.65	-
	73.17	4.61	9.26	8.11	4.59	-
$[Cu(C_{21}H_{16}N_2O_2S)_2Cl_2]$	58.99	3.73	7.49	6.53	7.47	7.46
	58.87	3.69	7.47	6.50	7.44	7.42
$[Ni(C_{21}H_{16}N_2O_2S)_2Cl_2]$	58.98	3.74	7.48	6.55	7.48	7.43
	58.82	3.68	7.44	6.53	7.44	7.42
$[Co(C_{21}H_{16}N_2O_2S)_2Cl_2]$	59.29	3.76	7.52	6.58	7.52	6.94
	59.22	3.68	7.44	6.56	7.44	6.92
$[Cu(C_{21}H_{16}N_2O_2S)_2(CH_3COO)_2]$	61.23	4.21	7.09	6.21	14.18	7.04
	61.22	4.18	7.04	6.16	14.14	7.02
$[Ni(C_{21}H_{16}N_2O_2S)_2(CH_3COO)_2]$	61.50	4.25	7.14	6.26	14.25	6.56
	61.52	4.23	7.11	6.19	14.19	6.53
$[Co(C_{21}H_{16}N_2O_2S)_2(CH_3COO)_2]$	61.53	4.23	7.13	6.24	14.26	6.57
	61.52	4.22	7.11	6.16	14.19	6.52

Table 2 Characteristic IR bands of ligands and complexes

Complexes	IR Bands (cm^{-1})					
	νN-H	νC-S	νC-H	νC=C	νC=N	νM-S
$C_{21}H_{16}N_2O_2S$	3472-3289	853-702	3103-3070	1646-1609	1643-1629	--
$[Cu(C_{21}H_{16}N_2O_2S)_2Cl_2]$	3398-3279	781-638	3105-3088	1641-1596	1639-1629	319-292
$[Ni(C_{21}H_{16}N_2O_2S)_2Cl_2]$	3379-3271	784-633	3097-3053	1636-1606	1635-1630	321-311
$[Co(C_{21}H_{16}N_2O_2S)_2Cl_2]$	3393-3283	789-630	3101-3089	1639-1601	1640-1632	325-310
$[Cu(C_{21}H_{16}N_2O_2S)_2(CH_3COO)_2]$	3400-3284	791-631	3100-3094	1644-1600	1642-1628	323-311
$[Ni(C_{21}H_{16}N_2O_2S)_2(CH_3COO)_2]$	3398-3279	792-630	3109-3095	1643-1613	1648-1627	328-316
$[Co(C_{21}H_{16}N_2O_2S)_2(CH_3COO)_2]$	3402-3285	783-630	3102-3091	1642-1610	1637-1625	331-322

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The estimation of carbon, hydrogen, sulphur and nitrogen were carried out at BHU, Varanasi and CDRI, Lucknow and results are given in Table 1. Magnetic measurements were carried out at IIT Roorkee at room temperature using Co [$Hg(CNS)_4$] as a calibrant. The ligand 2-amino-4-(p-dihydroxy phenyl) thiazoline was prepared using the procedure reported in the literature [14].

A shift in the νC-S and νN-H band frequencies is observed in all the complexes. This shows that the lone pair of electron presents on the sulphur atom of thiazoline ring and nitrogen atom of free amino group is taking part in co-ordination (Table 2).

Table 3 Electronic reflectance spectral data and their assignments of Ni(II) complex

Complexes	ν_1	ν_2	ν_3	Dq	B	ν_2/ν_1	ν_3(Calc.)
$[Ni(C_{22}H_{18}N_2OS)_2Cl_2]$	8526	14525	24459	1285.8	661.3	1.70	28970
$[Ni(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	8514	14520	24426	1283.0	662.4	1.70	28996

$\nu_1 = {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $\nu_2 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $\nu_3 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$.

Electronic reflectance spectral data and their assignments of Co(II) complex

Complexes	ν_1	ν_2	ν_3	Dq	B	ν_2/ν_1	ν_2(Calc.)
$[Co(C_{22}H_{18}N_2OS)_2Cl_2]$	8820	14249	20090	1198.6	667	1.61	27228
$[Co(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	8801	14251	20049	1197.3	667	1.62	27200

$\nu_1 = {}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $\nu_2 = {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $\nu_3 = {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$

Electronic reflectance spectral data and their assignments of Cu(II) complex

Complexes	ν_1	ν_2	ν_3	Dq	B	ν_2/ν_1	ν_2(Calc.)
$[Cu(C_{22}H_{18}N_2OS)_2Cl_2]$	15335	19128	--	--	--	--	--
$[Cu(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	15330	19131	--	--	--	--	--

$\nu_1 = {}^2B_{1g} \rightarrow {}^2A_{1g}$ and $\nu_2 = {}^2B_{1g} \rightarrow {}^2E_g$

CZ-record UV-Viz. spectrometer provided with an automatic recorder was used to record the electronic spectra of the complexes in ethanol at room temperature (Table 3).

2.1 Preparation of Metal Complexes

The respective metal (II) salts dissolved in water (4 mL) was added with constant stirring to a solution of 2-amino-4-(p-dihydroxy phenyl) thiazoline in 1:2 molar ratio in ethanolic medium on water bath for one hour. The pH of the solution was slowly raised to obtain the appropriate pH for the formation of the complex by the drop wise addition of 0.1 N sodium hydroxide solutions. The solution was concentrated to half of its volume then it was kept for some time. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum over fused $CaCl_2$. Similarly all the complexes were prepared. Similarly some complexes of thiazoline were also synthesized by many workers [15-17].

3. Results and Discussion

Adducts of all the complexes were prepared by refluxing the respective metal salts with ligands in 1:2 molar ratio in ethanolic medium. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum. In the present complexes the various vibrational modes due to ν(M-S) stretching frequency were observed in the region 328-311, 331-310 and 323-292 cm^{-1} which may be assigned to ν(Ni-S), ν(Co-S) and ν(Cu-S) stretching vibrations respectively. A band appeared in the region 335-285 cm^{-1} in all the cases were assigned to metal sulphur stretching vibrations. Number of workers observed similar result in case of some complexes formed by S-donor ligands.

The band observed at 853-702 cm^{-1} in the free ligand assigned to asymmetric ν(C-S) is shifted to lower frequency after complexation. But the symmetric ν (C-S) frequency completely disappears or intensity of this band is reduced after complexation. These facts confirm that the ring sulphur is taking part in complex formation. IR Studies: The ν (C=N) band frequencies observed at 1643-1629 cm^{-1} in the free ligand remain unaffected on complexation. The unchanged position of the band indicates that the ring nitrogen does not take any part in the coordination. The ν(N-H) asymmetric and symmetric stretching frequencies appearing in the region 3472 and 3289 cm^{-1} respectively, also decreases in the complex. This shows that the lone pair of electron available on nitrogen atom took part in coordination. From the above observation it is clear that the nitrogen of the $-NH_2$ group and ring sulphur take part in coordination.

3.1 Electronic Reflectance Spectral Studies

The electronic spectral studies of ligand complexes of Co(II), Ni(II) and Cu(II) were carried out in nujolmull. In the electronic spectra of Ni (II) complexes three bands at 8514-8526, 14520-14525 and 24426-24459 cm^{-1} were observed which may be assigned for ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) which are characteristic of octahedral Ni(II) ion. The spectral parameters of Ni(II) complex are as follows: Dq = 1283 -1285.8 cm^{-1} and B = 661.3-662.4 cm^{-1} The magnetic moment values are found in the range 2.90-3.20 BM. The $\nu_2:\nu_1$ ratio is 1.70, which is in the usual range reported for an octahedral Ni(II) complexes. This is in support of high spin octahedral complex. The value is however is raised only to a small extent suggesting that the splitting is weak and that the environment is quite close to an octahedral one [22].

Three bands were observed at 8801-8820, 14249-14251 and 20049-20090 cm^{-1} which may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively for octahedral complexes. The spectral parameters of Co(II) complex are as follows: Dq = 1197.3 - 1198.6 cm^{-1} and B = 667 cm^{-1} The observed value of magnetic moment is found in the range 2.97-3.55 BM which is expected for octahedral Co(II) complex.

Two bands were observed in the electronic spectra of Cu(II) complexes in the region 15330-15335 and 19128-19131 cm^{-1} which may be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ respectively in a planar field. The square-planar geometry of Cu(II) ion in the complex is confirmed by the measured magnetic moments values, 1.62- 1.71 BM.

The fungicidal activities of the ligand as well as of metal complexes were screened against different fungi at different concentrations 100, 50 and 20 ppm in Czapek's dox agar medium. It has been observed that the fugitoxicity of the metal complexes are lesser than the free ligand. This might be due to the fact that the group which is responsible for toxicity is not free in complexes due to co-ordination however it is free in ligand. The ligand as well as the metal complexes is most toxic at higher concentration i.e. the fungicidal activity decreases with the decrease of concentration.

4. Conclusion

The elemental analysis, magnetic susceptibility, electronic, IR and ESR spectral observations suggest the octahedral geometry for the Co(II), Ni(II) and Cu(II) complexes and exhibit coordination number six. On observing the fungicidal activities of ligand and complexes at different concentrations, it is found that complexes are less toxic than free ligand and the toxicity increases with concentration.

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