

STUDIES OF Ni(II) & Cu(II) COMPLEXES WITH AMPICILLIN

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ABSTRACT

Ni(II) and Cu(II) complex with ampicillin have been synthesized and characterized. On the basis of elemental analysis and molar conductance, formulas $Ni(C_{16}H_{19}N_3O_4S)MoO_4 \cdot 4H_2O$ and $Cu(C_{16}H_{19}N_3O_4S)MoO_4 \cdot 4H_2O$ have been suggested for the complexes under study. The geometries of the complexes have been proposed on the basis of magnetic moment, electronic and infrared spectral data. Thermo-gravimetric analysis (TGA) has been carried out to determine the pattern of their decomposition. The crystal system, lattice parameters, unit cell volume and number of molecules in it have been determined by X-ray diffraction data (XRD). The aim of investigation is to study coordination behavior of Ni and Cu having molybdate anion (MoO_4), in the presence of ampicillin(6-[D(-)- α -Amino- α -Phenylacetamido]Penicillanic Acid).

INTRODUCTION

In continuation of the work being carried out in this laboratory on the metal molybdate with organic ligand, the present note describes two new complexes of nickel(II) and copper(II) with ampicillin ($C_{16}H_{19}N_3O_4S$) having molybdate. The complexes have been synthesized and characterized using analytical and spectral methods.

EXPERIMENTAL

The starting material $M MoO_4 \cdot 4H_2O$ [where $M = Ni(II) / Cu(II)$] was synthesized by reported methods^{1,2}. Complexes were isolated by shaking $MoO_4 \cdot nH_2O$ (0.01 mole) with a require amount of $C_{16}H_{19}N_3O_4S$ (0.03 mole) in water (~100 ml) The products were filtered, washed 3-4 times with ether and dried. The metals was estimated by usual methods of estimation³. Elemental analysis of prepared complexes were carried out at Lab India and ASCHO Lab Mumbai, X-ray diffraction analysis was carried out by Inter University Consortium (I.U.C.)Indore (M.P.), Infrared spectral analysis (FTIR) and

Thermo-gravimetric of synthesized complexes were performed at Centre for Advance Technology (CAT) Indore (M.P.), KBr pellets were used in FTIR spectral analyses. The weight loss measured by heating at the rate of $15^\circ C/min$ up to $950^\circ C$. Unico Gouy's balance using $Hg[Co(NCS)_4]$ as standard used for magnetic studies. The molar conductance of prepared complexes was measured in liquid phase using Conductivity Bridge.

RESULTS AND DISCUSSIONS

Table I shows Physical and analytical data of the prepared complexes. The nickel(II) and copper(II) complexes found green and brown in color respectively Molecular formula of the complexes has been worked out on the basis of the above data, to $M C_{16}H_{19}N_3O_4S MoO_4 \cdot 4H_2O$ [where $M = Ni(II) / Cu(II)$]. Synthesized complexes are insoluble in water and soluble in common organic solvents, indicating non-electrolyte nature of these complexes.

The magnetic moment of the Ni(II) complex is 3.42 B.M. Correspond to two

unpaired electrons. In the electronic spectra of the Ni(II) complex shows three distinct bands appears at 838 nm (ν_1), 516 nm (ν_2), 316.5 nm (ν_3) which may be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transition respectively. The ligand field parameter Dq (1193.6), B (614) and β (0.56) are in good agreement with those for an octahedral geometry for nickel(II) complexes.

The magnetic moment of the Cu(II) complex is 1.9 B.M. indicates the presence of one unpaired electron. The electronic spectra of the complex shows one broad band in the region 610 nm which may occur due to the overlapping of the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ band of ligand field transition, suggested a square planer geometry to the complex.

Interpretation of IR bands of the complex have been carried out comparing with the spectrum of IR of ampicillin and related compound have been well studied^{4,6}.

The bands present in the drug due to νNH_2 (3200 cm^{-1}) amide $C=O$ (1690 cm^{-1}) NH_2 (2860 cm^{-1}) and NH_3^+ (1495 cm^{-1}) remained almost lower side in the complex indicating involvement of these group in chelation a new amino group is produced due to degradation of β Lactum carbonyl group by metal ion. This group also take part in chelation in complex vibration due to this new group may be observed at 3100 cm^{-1} .

The band present at 1770 cm^{-1} in the drug was assigned to β Lactum carbonyl group and was found absent in complexes, because after degradation this group gets converted into $-COOH$ group (ampicillin \rightarrow ampicillonic acid) carboxylic group present in Ligand displays its vibration due to asym. and syn. stretching at 1612 cm^{-1} and 1410 cm^{-1} .

Although this group takes part in chelation by deprotonation but at the same time a

new carboxylic group is produced by degradation of β Lactum carbonyl group. Hence in complexes two new bands appearing at 1590 cm^{-1} and 1370 cm^{-1} were assigned to shifted asymmetric and symmetric stretch of original carboxylic group, new carboxyl group shown its vibration at normal frequencies (1620 cm^{-1}) and (1400 cm^{-1}).

In this complex presence of $-OH$ group is supported by a sharp and strong bond at 3380 cm^{-1} and also by the band present at 1115 cm^{-1} , which indicates Cu-OH bending, as shown in Table II and Fig.1 & 2.

The thermo-gravimetric data in shows the decomposition of complexes in two steps. First step weight loss 300-425 K which indicates the loss of loosely bound water of crystallization. The second step in the thermogram shows the loss of ligand molecules of the complex. Which occurs between 450-950 K. The metal oxide are formed in the both cases.

The X ray diffraction data of the these complexes shows in Table 2. It records 34 and 20 peaks for Ni(II) and Cu(II) respectively clearly indicating the crystalline nature of complexes. The X-ray pattern by trail and error method⁷⁻¹⁵. The unit cell parameters were calculated from indexed data. It is also clear from the data that Ni(II) complexes posses Tetragonal symmetry, whereas Cu(II) complexes posses cubic symmetry. The calculated and experimental values of density of the complexes are good agreement within the limits of experimental error, as shown in Table II - IV and Fig.3 & 4.

On the basis of above studies the structure in Fig 5 is suggested for the studied complexes.

Table I
Analytical and physical data of the complexes

Mol. formula	Observed/ calculated %							
	Colour	M. W.	Metal*	MoO ₄	C	H	N	S
Ni (C ₁₆ H ₁₉ N ₃ O ₄ S) MoO ₄ 4H ₂ O	Green	644.05	9.377 (9.115)	25.600 (25.454)	30.891 (29.811)	4.021 (4.192)	5.965 (6.521)	5.234 (4.968)
Cu (C ₁₆ H ₁₉ N ₃ O ₄ S) MoO ₄ 4H ₂ O	Brown	644.88	9.162 (9.79)	25.982 (25.265)	30.456 (29.589)	3.691 (3.698)	6.537 (6.472)	4.541 (4.931)

Metal* = Ni /Cu

Table II
Crystal parameters and density of the complexes

Complexes	Crystal lattice Edge (Å)			Cell volume	n	Density obs.	Crystal System
	a	b	c	Å ³		Density calc.	
Ni (C ₁₆ H ₁₉ N ₃ O ₄ S) MoO ₄ 4H ₂ O	17.3869	17.3869	11.9743	3619.9405	10	<u>3.169</u> 2.954	Tetragonal
Cu (C ₁₆ H ₁₉ N ₃ O ₄ S) MoO ₄ 4H ₂ O	12.3775	12.3775	12.3775	1896.2941	3	<u>1.699</u> 1.702	Cubic

Table III
X - ray powder diffraction data of Ni (C₁₆ H₁₉ N₃ O₄S) MoO₄·4H₂O Complex

Peak No.	d-Spacing	Relative Intensity I/I ₀ x100	Observed Sin ² θ	Calculated Sin ² θ	(hkl)
1	15.06279	63.1	0.00261	0.00261	(100)
2	9.36958	43.4	0.00675	0.00675	(101)
3	8.67498	32.6	0.00936	0.00936	(111)
4	6.85712	40.5	0.01317	0.01307	(210)
5	5.40059	15.4	0.02088	0.02078	(117)
6	5.08284	100	0.02373	0.02353	(300)
7	4.71288	25.1	0.02700	0.02700	(222)
8	3.64460	29.0	0.04589	0.04599	(401)
9	3.52466	82.4	0.04899	0.04859	(411)
10	3.26909	80.6	0.05029	0.05029	(213)
11	3.16703	22.2	0.05828	0.05838	(402)
12	3.06115	64.5	0.06176	0.06166	(004)
13	2.87351	48.7	0.07129	0.07139	(114)
14	2.81637	55.4	0.07913	0.07923	(214)
15	2.61255	100	0.08979	0.08969	(304)
16	2.54266	37.9	0.09424	0.09414	(600)
17	2.32606	27.7	0.10800	0.10800	(404)
18	2.28715	19.5	0.11655	0.11645	(215)
19	2.23171	25.6	0.11777	0.11767	(360)
20	2.20030	22.1	0.12691	0.12690	(305)
21	2.15045	25.1	0.12814	0.12813	(700)
22	1.90706	33.3	0.16183	0.16193	(216)

23	1.84575	16.9	0.16766	0.16736	(800)
24	1.76341	34.4	0.19692	0.19691	(554)
25	1.73371	46.2	0.19242	0.19241	(661)
26	1.71880	28.7	0.20262	0.20261	(007)
27	1.63430	27.2	0.22549	0.22549	(663)
28	1.57727	28.7	0.23402	0.23412	(555)
29	1.51351	20.5	0.24978	0.24968	(337)
30	1.44652	24.1	0.27991	0.27961	(556)
31	1.44053	14.9	0.28639	0.28629	(447)
32	1.40745	19.0	0.29155	0.29165	(665)
33	1.37453	17.4	0.33715	0.33714	(666)
34	1.16441	13.8	0.43955	0.43953	(269)

$A=0.002615$ $C=0.004135$
 $a=17.3869\text{\AA}$ $c=11.9743\text{\AA}$
 Cell Volume[V] = 3619.9405\AA^3 $n=10$
 Density Observed = 3.169 gm cm^{-3}
 Density Calculated = 2.9549 gm cm^{-3}

Table IV
X - ray powder diffraction data of $\text{Cu}(\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_4\text{S})\text{MoO}_4 \cdot 4\text{H}_2\text{O}$ complex

Peak No.	d-spacing	Relative Intensity $I/I_0 \times 100$	Observed $\text{Sin}^2 \theta$	Calculated $\text{Sin}^2 \theta$	(hkl)
1	12.36693	80.3	0.00387	0.00387	(100)
2	9.33363	75.7	0.00681	0.00681	(110)
3	6.84180	64.0	0.01267	0.01267	(111)
4	5.75539	51.5	0.01936	0.01935	(201)
5	5.00741	74.9	0.02323	0.02322	(211)
6	3.56114	100.0	0.04634	0.04644	(222)
7	3.32851	61.5	0.05063	0.05031	(023)
8	3.22197	61.1	0.05429	0.05418	(123)
9	3.10843	52.7	0.06189	0.06192	(004)
10	3.01175	74.5	0.06589	0.06579	(223)
11	2.91562	47.3	0.06969	0.06966	(330)
12	2.86693	88.9	0.07352	0.07353	(331)
13	2.67766	100.0	0.08524	0.08514	(334)
14	1.78674	79.2	0.18963	0.18963	(007)
15	1.59336	58.3	0.22069	0.22059	(445)
16	1.56981	60.4	0.24769	0.24768	(008)
17	1.55468	58.3	0.25541	0.25542	(455)
18	1.43533	54.2	0.29026	0.29025	(555)
19	1.28762	45.1	0.34830	0.34930	(457)
20	1.20281	44.4	0.41022	0.41032	(934)

$A=0.00387$
 $a=12.3775$
 Cell Volume[V] = 1896.2941\AA^3 $n=3$
 Density Observed = 1.699 gm cm^{-3}
 Density Calculated = 1.7024 gm cm^{-3}

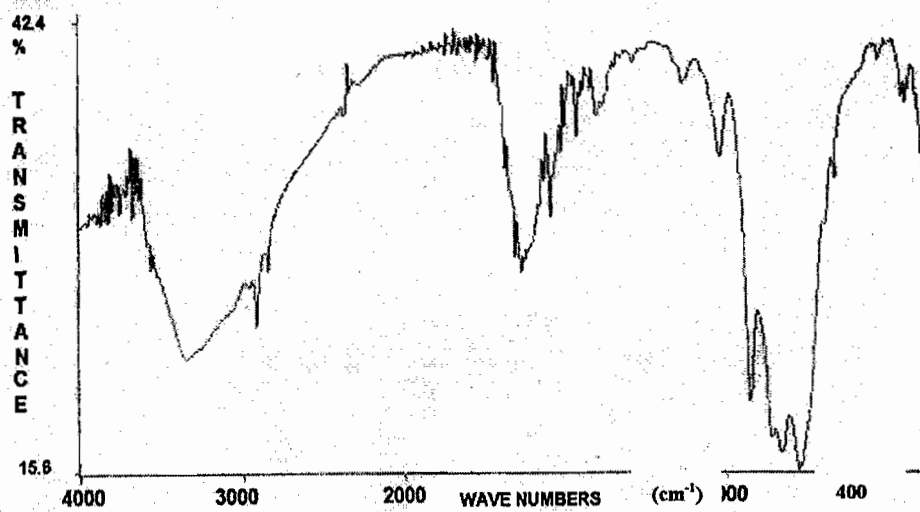


Fig 1: Infrared spectrum of Ni (C₁₆ H₁₉ N₃ O₄S) MoO₄·4H₂O complex

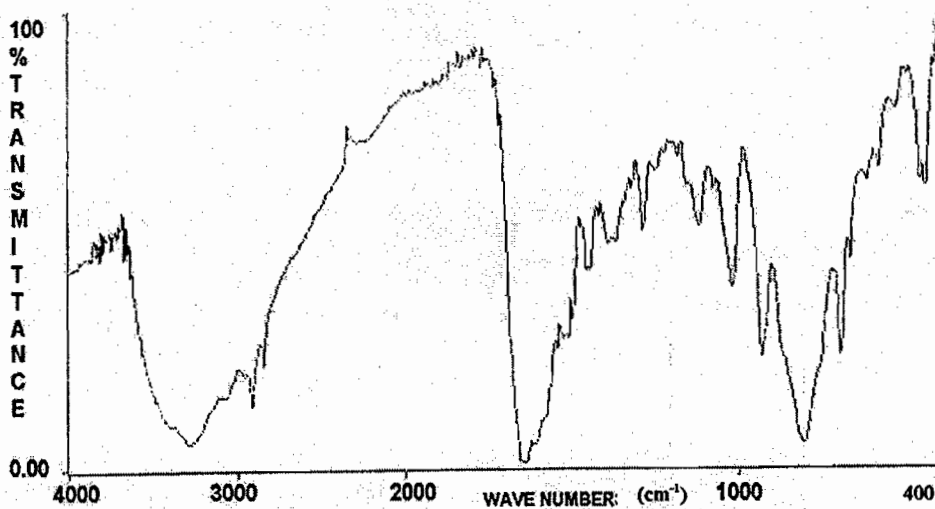


Fig 2: Infrared spectrum of Cu (C₁₆ H₁₉ N₃ O₄S) MoO₄·4H₂O complex

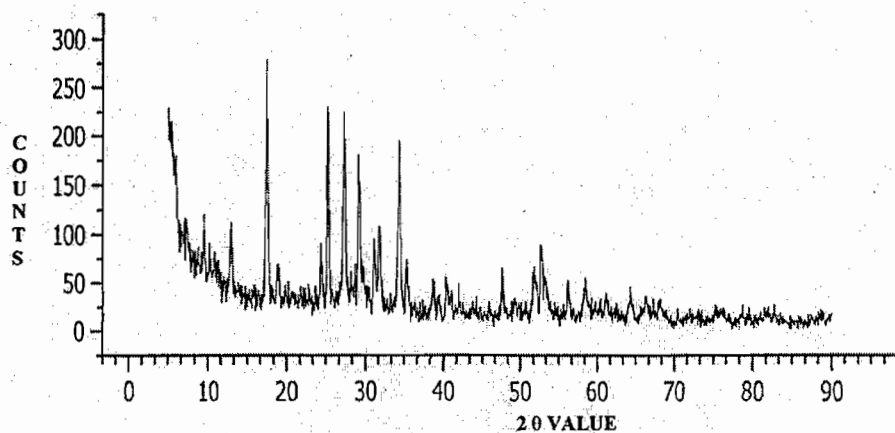


Fig 3 : X-Ray Diffractogram of Ni (C₁₆ H₁₉ N₃ O₄S) MoO₄·4H₂O complex

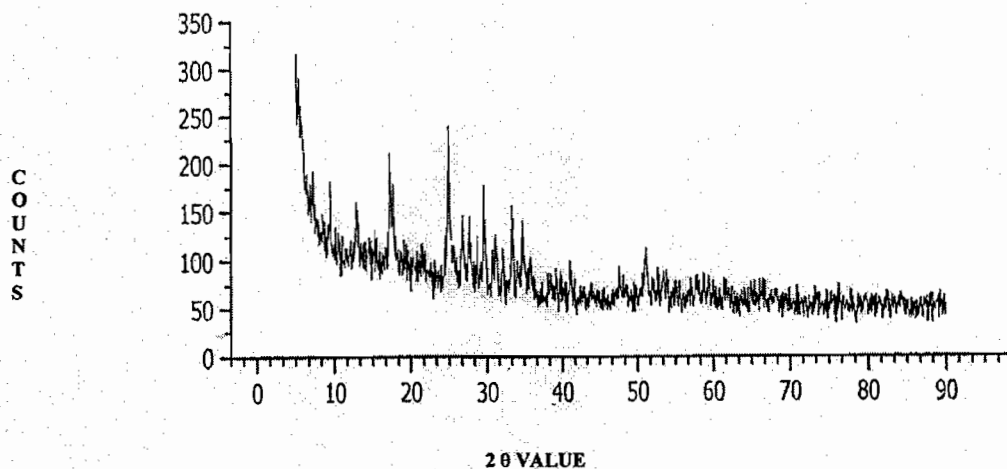
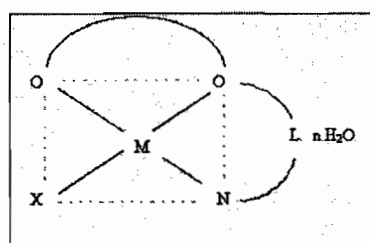


Fig 4 : X-Ray Diffractogram of Cu (C₁₆ H₁₉ N₃ O₄S) MoO₄·4H₂O complex



M=Cu(II)/Ni(II)
 L = Ampicillin
 N = 4
 X = Molibdate

Fig 5: Representative Structure of the Complexes.

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