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X-Ray Crystallographic Studies of Copper(II) Complexes with Few Drugs

RACHNA KESHARWANI* and PRAMILA SINGH
Department of Chemistry
Dr. H.S. Gour University, Sagar-470 003, India

Few drugs, *viz.*, diclofenac sodium, phenytoin sodium and amodiaquine hydrochloride complexes with Cu(II) have been synthesised and characterised. The present investigation reports the crystal structure studies done by X-Ray powder diffraction method. Lattice constants have been determined. The complexes of phenytoin sodium and amodiaquine-hydrochloride have tetragonal while diclofenac sodium has orthorhombic geometries.

INTRODUCTION

Copper has been described in Indian Ayurvedic system to possess strong antileprotic activity[1] and its compounds are frequently used in pharmaceutical preparations for the treatment of various skin diseases including psoriasis and leprosy[2]. Physico-chemical properties of drug complexes have been studied by authors at large[3–6]. X-ray diffractometric study of metal complexes provides information about their crystallization and effect of ligands on unit cell dimensions. In this communication XRD studies of few drug complexes of Cu(II) are reported.

RESULTS AND DISCUSSION

The analytical and physical data of the complexes are presented in Table-1. On the basis of elemental analysis, the molecular formulae of complexes are worked out to be $[CuL_2]$ where L = amodiaquine hydrochloride ($C_{20}H_{21}N_3OCl$) and $[CuL_2{\cdot}(H_2O)_2]$ where L= phenytoin sodium ($C_{15}H_{11}N_2O_2$), and diclofenac sodium ($C_{14}H_{10}NO_2Cl_2$).

TABLE–1
ANALYTICAL AND PHYSICAL DATA

Compound (colour)	Ana lysis %, found (calcd.)				μ_{eff} (B.M.)	M (Ω^{-1} cm^2 mol^{-1})
	Cu	C	H	N		
$[Cu(C_{15}H_{11}N_2O_2)_2{\cdot}(H_2O)_2]$ (Dark brown)	10.16 (10.56)	60.18 (59.34)	4.45 (4.32)	9.45 (9.30)	1.90	5.40
$[Cu(C_{20}H_{21}ClN_3O)_2]$ (Dark brown)	8.96 (8.82)	60.88 (62.36)	5.57 (5.43)	11.09 (10.88)	1.82	2.60
$[Cu(C_{14}H_{10}NCl_2O_2)_2{\cdot}(H_2O)_2]$ (Cascade green)	9.28 (9.21)	47.56 (48.72)	3.48 (3.18)	4.06 (3.73)	1.70	9.84

The low value of molar conductance indicates that complexes are non-electrolytic in nature. The complexes are paramagnetic at room temperature. Their magnetic moments values (μ_{eff}) lie in the range 1.7–2.0 B.M. which are in

agreement with the reported values for distorted ocahedral geometry of Cu(II) complexes corresponding to one unpaired electron.

The Cu(II) complexes of the drug showed characteristic X-ray powder diffraction pattern in Tables 2–4. The unit cell for phenytoin sodium and amodiaquin hydrochloride complexes has been found to be of tetragonal type with lattice constants a = b = 18.6419 Å and c = 30.8642 Å; a = b = 14.1294 Å and c = 19.3733 Å respectively while the unit cell for diclofenac sodium complex possesses the orthorhombic type with lattice constant a = 16.3734 Å, b = 32.2888 Å and c = 25.8886 Å. The cell parameters have been calculated using the equation[7]

For tetragonal: $\sin^2 \theta_{hkl} = A(h^2 + k^2) + C\,l^2$

where $A = B = \frac{\lambda}{4a^2}$ and $C = \frac{\lambda}{4c^2}$

For orthorhombic: $\sin^2 \theta_n kl = Ah^2 + Bk^2 + C\,l^2$

where $A = \frac{\lambda}{4a^2}$, $B\ \frac{\lambda}{4b^2}$ and $C = \frac{\lambda}{4c^2}$.

TABLE-2
X-RAY DATA OF $[Cu(C_{15}H_{11}N_2O_2)_2(H_2O)_2]$

Peak No.	d spacing Å	Relative Intensity I/I_0 (%)	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	(hkl)
1.	18.2513	.4.42404	0.0027	0.00270	(100)
2.	10.1976	18.03000	0.0089	0.00882	(003)
3.	7.7515	100.00000	0.0155	0.01550	(004)
4.	6.7802	50.75125	0.0203	0.01962	(203)
5.	5.3184	68.94824	0.0332	0.03312	(303)
6.	5.1096	41.90317	0.0360	0.03530	(205)
7.	4.8551	31.30217	0.0397	0.03998	(304)
8.	4.5754	9.01502	0.0448	0.04418	(401)
9.	3.3439	92.23706	0.0498	0.04880	(305)
10.	3.9523	47.24540	0.0602	0.05958	(306)
11.	3.8796	14.02337	0.0622	0.06272	(008)
12.	3.4368	13.60601	0.0793	0.07938	(009)
13.	3.4303	13.68948	0.0797	0.07938	(009)
14.	3.4027	34.05676	0.0810	0.08200	(109)
15.	3.3962	49.16527	0.0816	0.08200	(109)
16.	3.3707	11.43572	0.0826	0.08310	(504)
17.	3.3145	6.42737	0.0845	0.08310	(504)
18.	3.2973	8.68113	0.0865	0.08700	(308)
19.	3.2041	20.03338	0.0914	0.09120	(407)
20.	2.9895	7.42904	0.1049	0.10600	(603)
21.	2.6765	11.93656	0.1309	0.13020	(508)

A = B = 0.0027, C = 0.000985; a = b = 18.641972 Å, c = 30.864243 Å
Cell volume = 10726.037 $Å^3$, n = 14; D_{cal} = 1.2522 g/cm^3; D_{obs} = 1.2522 g/cm^3

TABLE–3
X-RAY DATA OF $Cu(C_{20}H_{21}ClN_3O)_2]$

Peak No.	d Spacing Å	Relative intensity I/I_0 (%)	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	(hkl)
1.	8.1360	20.80924	0.0140	0.0147	(102)
2.	7.0740	57.80346	0.0186	0.0188	(200)
3.	6.0635	40.75144	0.0256	0.0260	(211)
4.	6.0315	42.77456	0.0256	0.0260	(211)
5.	5.7115	61.84971	0.0284	0.0288	(202)
6.	5.6702	100.00000	0.0290	0.0288	(202)
7.	5.1579	0.31503	0.0351	0 0335	(212)
8.	4.9805	36.12716	0.0377	0.0376	(220)
9.	4.6987	50.00000	0.0425	0.0423	(300)
10.	4.3445	12.13872	0.0498	0.0495	(311)
11.	4.1989	82.54335	0.0529	0.0523	(302)
12.	4.0620	36.70520	0.0569	0.0570	(312)
13.	4.0364	30.05780	0.0577	0.0588	(204)
14.	3.8492	20.80924	0.0629	0.0625	(005)
15.	3.6545	13.29479	0.0705	0.0711	(322)
16.	2.4114	19.07514	0.1616	0.1622	(514)

A = B = 0.0047, C = 0.0025; a = b = 14.129435 Å, c = 19.373306 Å
Cell volume = 3867.70 $Å^3$, n = 4; D_{obs} = 1.28895 g/cm^3, D_{cal} = 1.38844 g/cm^3

The values of $\sin^2\theta$ for each peak have been calculated with the help of the cell parameters, and the corresponding hkl in all cases are in good agreement with observed $\sin^2\theta$ values.

Densities of the complexes have been calculated by using the formula $\rho = n\frac{M}{VN}$ where ρ is the density, n the number of molecules per unit cell, M the molecular weight, V the unit cell volume and N the Avogadro number. The calculated density values are in good agreement with the experimental values. The densities of the examined complexes have been measured by making a pellet under pressure 8 ton per sq. inch.

TABLE–4
X-RAY DATA OF $[Cu(C_{14}H_{10}NCl_2O_2)(H_2O)_2]$

Peak No.	d Spacing Å	Relative intensity I/I_0	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	(hkl)
1.	16.2718	39.50617	0.0035	0.0035	(100)
2.	14.6262	20.06172	0.0044	0.0044	(110)
3.	12.7380	17.28395	0.0056	0.0056	(002)
4.	12.4559	11.41975	0.0059	0.0058	(111)
5.	8.1594	15.43209	0.0140	0.0140	(200)
6.	6.7738	14.81481	0.0203	0.0205	(212)
7.	6.5012	12.65432	0.0218	0.0224	(004)
8.	6.1223	9.25925	0.0250	0.0259	(104)
9.	5.4445	49.07407	0.0314	0.0315	(300)
10.	4.5588	7.40740	0.0450	0.0450	(313)
11.	4.4490	20.67901	0.0472	0.0476	(160)
12.	4.2281	14.50617	0.0524	0.0520	(262)
13.	4.1876	13.58024	0.0533	0.0539	(304)
14.	4.0836	100.00000	0.0563	0.0560	(400)
15.	3.8887	9.56790	0.0620	0.0616	(402)
16.	3.6597	10.49382	0.0700	0.0704	(440)
17.	3.3916	14.81481	0.0816	0.0812	(372)
18.	3.3735	26.54320	0.0826	0.0826	(207)
19.	2.9528	12.65432	0.1076	0.1075	(542)
20.	3.9182	6.79012	0.1096	0.1099	(504)

A = 0.0035, B = 0.0009, C= 0.0014; a = 16.373432 Å, b = 32.288843 Å, c = 25.8886 Å
Cell volume = 13686.763 $Å^3$; n = 15, D_{obs} = 1.2539 g/cm^3, $D_{cal.}$ = 1.2547 g/cm^3

EXPERIMENTAL

All chemicals used were of AnalaR grade. The complexes were isolated from double distilled water. Concentrated aqueous solution of the drug (L) in slight excess over stoichiometric M : L : : 1 : 2 ratio was added slowly with constant stirring to an aqueous solution of metal salt (M). pH of the solution was so adjusted as to get the indication of complex formation by colour change or by precipitation. All the complexes prepared were obtained in pH range 4–6.5. After adjusting the pH the content was refluxed over steam bath for 1 h. The precipitate so obtained was filtered and washed many times with hot distilled water. It was dried in an oven at about 110°C and stored in a desiccator over anhydrous $CaCl_2$.

Carbon, hydrogen and nitrogen were analysed at C.D.R.I., Lucknow. The magnetic moments of complexes at room temperature were determined by Gouy's method using $Hg[Co(NCS)_4]$ as standard. The X-ray powder diffraction patterns were recorded on a Philips X-ray machine attached with Pw 1700 diffractometry

system, using FeK_{α} radiation at R.S.I.C., Nagpur. The single monochromator was obtained at scanning speed of 0.04 deg (2θ)/sec and chart speed 5 mm/deg (2θ).

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