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X-Ray Crystallographic Studies of Mononuclear and Binuclear Copper(II) Complexes with some Schiff-bases

S.S. DODWAD*, R.S. DHAMNASKAR and S.V. SALVI†
Department of Chemistry
The Institute of Science, 15 Madam Cama Road, Fort
Bombay-400 032, India

Some mononuclear and binuclear copper(II) complexes with Schiff bases have been synthesised and characterised. They have a general formula $[CuL_2]$ and $[(CuL)_2Cl_2]$ where $L = C_{17}H_{12}NOX$ and $X = H, CH_3, OCH_3, C_6H_5$ and Cl. The present investigation reports the crystal structure studies done by X-ray powder method. The observed reflection are indexed. All observed reflections indicate single phase for every complex. Lattice constants are determined within an accuracy of 0.01 Å. All the mononuclear complexes are tetragonal while binuclear complexes have orthorhombic geometry.

INTRODUCTION

Copper has been desctribed 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] Copper complexes are used as support to surface of an inorganic ion-exchanger. Bulky complexes have been incorporated between the layers of a smectite clay by an ion exchange process and the products have exhibited interesting catalytic[3] behaviour. Hydrogen peroxide reactions are catalysed by Cu(II) complexes[4]. Physico-chemical properties of Schiff base complexes have been studied by the authors[5–9] at large. 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 mononuclear and binuclear copper(II) complexes with some Schiff bases are reported.

EXPERIMENTAL

The Schiff bases were prepared by refluxing calculated quantities of 2-hydroxy-1-naphthaldehyde and the corresponding aryl amine in ethanolic

*Present Address: Principal S.I.WS. (Smt.) Thirumalai College of Science, Wadala, Bombay-400 031, India.
†Department of Physics, The Institute of Science, Bombay.

medium for 2 h. Solidification occured on cooling. The resulting compounds were purified by recrystallising from ethanol. The Schiff bases thus obtained were yellowish orange in colour (Fig.1).

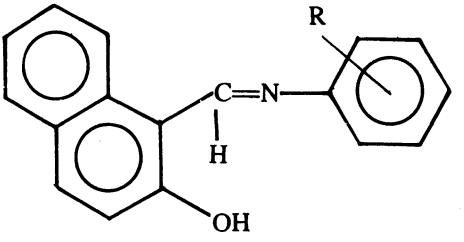

Fig. 1

Mononuclear complexes were prepared by refluxing for 1–2 h ethanolic solutions of copper nitrate and the corresponding Schiff base in 1:2 ratio at 7 pH. The binuclear complexes were prepared by refluxing for 1 h the ethanolic solutions of copper chloride and the corresponding Schiff base in 1:2 ratio at 11 pH. The precipitates obtained were filtered and washed with hot ethanol and dried in *vacuo*. The mononuclear complexes were red in colour and binuclear complexes were green in colour. Their molecular structures are characterised by studying their various physical properties. X-ray diffractograms of all these complexes were recorded on a D-500 siemens diffractometer at TIFR, Colaba, Bombay-400 005.

RESULTS AND DISCUSSION

The X-ray diffraction patterns show few intense reflections followed by reflections of rapidly decreasing intensities at higher angles and the background typical of material having low crystallinity. Similar observations have been reported by the author[6] and Brown[7] *et al.* All the observations are indexed and the lattice constants are determined. They indicate that the mononuclear complexes crystallize in a primitive tetragonal unit except complex No . C_2 which crystallize as orthorhombic, while all the binuclear complexes crystallize as orthorhombic. The unit-cell dimensions of mononuclear complexes range from 13 Å to 24 Å while for binuclear complexes the dimensions range from 13 Å to 19 Å. The crystallographic results such as 'd' values (observed and calculated), Miller indices and relative percentage intensities are reported in Table No-1(a) to 1(e) and 2(a) to 2(e) Table no 1(f) and 2(f) provides interesting comparision of lattice constants, volumes, and c/a ratios for the complexes studied.

A dramatic considerable difference in unit cell volumes of binuclear and mononuclear complexes may serve as a useful parameter in the catalytic and pharmaceutical applications.

TABLE-1(a)
CRYSTALLOGRAPHIC RESULTS OF MONONUCLEAR COPPER(II) COMPLEX OF 2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_1)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.56	5.56	003	37
5.12	5.10	200	65
4.55	4.55	210	36
4.40	4.40	113	22
4.21	4.17	004	25
3.78	3.76	203	100
3.64	3.61	114	28
3.53	3.52	213	35
3.48	3.51	221	73
3.40	3.39	300	31
3.33	3.33	301	25
3.08	3.08	214	29
2.72	2.72	224	22

TABLE-1(b)
CRYSTALLOGRAPHIC RESULTS OF MONONUCLEAR COPPER(II) COMPLEX OF 3'-METHOXY-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_2)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.32	5.32	120	34
5.13	5.13	121	49
4.81	4.81	004	61
4.45	4.45	200	46
4.22	4.22	210	100
4.08	4.09	123	40
3.99	3.96	130	56
3.83	3.83	005	42
3.65	3.65	203	69
3.51	3.52	213	39
3.15	3.01	106	58
2.90	2.89	310	24
2.83	2.83	302	33
2.75	2.76	135	29

TABLE-1(c)
CRYSTALLOGRAPHIC RESULTS OF MONONUCLEAR COPPER(II) COMPLEX OF 3-CHLORO-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_3)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.94	5.91	102	36
5.79	5.85	210	08
4.80	4.65	202	100
4.42	4.42	003	46
3.99	3.98	113	11
3.75	3.72	222	11
3.49	3.51	312	55
3.27	3.27	400	10
2.61	2.62	500	08

TABLE-1(d)
CRYSTALLOGRAPHIC RESULTS OF MONONUCLEAR COPPER(II) COMPLEX OF 3'-METHYL-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_4)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.71	5.71	130	21
5.56	5.56	131	36
5.41	5.42	042	21
5.20	5.16	132	100
4.84	132	005	46
4.66	4.66	133	33
4.42	4.42	142	27
4.22	4.15	134	40
3.80	3.82	221	43
3.68	3.69	153	31
3.50	3.46	070	64
3.28	3.29	233	59

TABLE-1(e)
CRYSTALLOGRAPHIC RESULTS OF MONONUCLEAR COPPER(II) COMPLEX OF 3'-PHENYL-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_5)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.89	5.95	110	100
5.63	5.68	111	89
4.32	4.32	113	24
4.14	4.11	201	11
3.85	3.84	202	19
3.77	3.77	210	07
3.70	3.69	211	08
3.51	3.50	212	20
3.32	3.23	213	19
3.10	3.14	204	18

TABLE-1(f)
STRUCTURAL DETAILS OF MONONUCLEAR COPPER(II) COMPLEXES

Complex	Lattice Constants				Volume $(Å)^3$
	a	b	c	c/a	
C_1	10.17	10.17	16.67	1.94	1724
C_2	8.06	8.06	24.18	3.0	1571
C_3	8.89	24.18	19.21	—	2266
C_4	8.42	8.42	18.83	2.24	1335
C_5	13.00	13.09	13.25	1.01	2270

TABLE-2(a)
CRYSTALLOGRAPHIC RESULTS OF BINUCLEAR COPPER(II) COMPLEXES OF 2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_6)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
4.94	4.94	030	100
4.82	4.80	300	68
4.42	4.46	131	57
4.20	4.18	023	59
3.99	3.99	213	51
3.54	3.54	033	58
3.49	3.48	303	53
3.40	3.39	313	53
3.15	3.15	323	62

TABLE-2(b)
CRYSTALLOGRAPHIC RESULTS OF BINUCLEAR COPPER(II) COMPLEXES OF 4′-METHYL-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_7)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
6.84	6.84	200	—
6.31	6.32	201	—
5.85	5.86	211	—
4.91	4.91	221	—
4.18	4.14	230	—
3.52	3.52	204	—
3.42	3.42	400	—
3.16	3.17	332	—
3.14	3.14	420, 242	—

TABLE-2(c)
CRYSTALLOGRAPHIC RESULTS OF BINUCLEAR COPPER(II) COMPLEXES OF 3'-METHYL-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_8)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.02	5.07	113	61
4.94	4.92	301	100
4.80	4.72	311	44
4.53	4.48	123	43.5
4.20	4.23	321	53.0
3.98	3.96	033	45.0
3.78	3.78	024	40.0
3.54	3.52	233	51
3.44	3.44	412	61
3.39	3.40	224	51
3.15	3.15	025	65
3.08	3.08	125	36
2.76	2.75	060	33

TABLE-2(d)
CRYSTALLOGRAPHIC RESULTS OF BINUCLEAR COPPER(II) COMPLEX OF 3'-METHOXY-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_9)

d in Å (obs)	d in Å (calc)	Miller indices	Relative % intensities
5.00	5.00	301	100
4.85	4.89	131	59
4.55	4.56	302	44
4.45	4.47	132	45.5
4.24	4.24	321	56
3.65	3.65	331	38
3.46	3.47	332	50
3.42	3.44	421	44
3.17	3.16	225, 340	56

TABLE-2(e)
CRYSTALLOGRAPHIC RESULTS OF BINUCLEAR COPPER(II) COMPLEX OF 2'-NAPTHYL-2-HYDROXY-1-NAPHTHALIDENE-ANIL (C_{10})

d in Å (obs)	d in Å (calc)	Miller indices	Reletive % intensities
4.97	4.97	030	100
4.55	4.55	300	47
4.23	4.21	032	58
4.01	4.02	230	50
3.95	3.94	302	54
3.45	3.44	303	52.5
3.41	3.41	400	52
3.16	3.16	005	58

TABLE-2(f)
STRUCTURAL DETAILS OF BINUCLEAR COPPER(II) COMPLEXES.

Complex	Lattice constants				Volume $(Å)^3$
	a	b	c	c/a	
C_6	14.40	14.81	15.20	1.05	3242
C_7	13.72	15.62	16.44	1.19	3523
C_8	15.43	15.53	17.03	1.10	4342
C_9	15.52	16.03	19.21	1.24	4781
C_{10}	13.65	14.92	15.79	1.16	3216

REFERENCES

1. C.R. Bhandari "*Vanaushadhi Chandrodaya*" (An Encyclopedia of Indian Botaniks and Herbs), Chaukhambha Sanskrit Sansthan, Varanasi, Part V, pp. 10–15 (1985).
2. G.D. Sen, "*Bheshajya Ratnavali*" (modified by V.S.L.H. Shanker), Ayurvedodharak Karyalaya, Moradabad, pp. 1063–64 (1936).
3. W.H. Quavle and T.J. Pinnavala, *Inorg. Chem.*, **18**, 2840 (1979).
4. H. Sigel, Angew. Chem., **81**, 161, (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 167 (1969).
5. S.S. Dodwad, M.G. Datar and I.R. Patil, *Indian J. Chem.*, **22A**, 83 (1983).
6. _____, *J. Indian Chem. Soc.*, **61**, 595 (1984).
7. S.S. Dodwad and P.S. Prabhu, *J. Indian Chem. Soc.*, **60**, 546 (1983).
8. _____, *J. Indian Chem. Soc.*, **63**, 475 (1986).
9. _____, *J. Indian Chem. Soc.*, **63**, 610 (1986).
10. S.S. Dodwad and D.K. Kulkarni, *Polyhedron*, **8**, 1790 (1989).
11. D. Brown and K.W. Begnall., *J. Chem. Soc., Dalton Trans.*, 1249 (1975).

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