Asian Journal of Chemistry Vol. 8, No. 3 (1996), 449–454

Synthesis and X-Ray Diffraction Studies on Some Copper(II) Complexes of Naphthalene Analogues of 2′-Hydroxychalcones

E.R. AGHARIA and S.S. DODWAD*
Post-Graduate Department of Chemistry
Ismail Yusuf College, Jogeshwari (East), Bombay-400 060, India

Some copper(II) complexes of naphthalene analogues of 2′-hydroxychalcones have been synthesised and characterised. The copper(II) complexes have the general formula CuL_2, where L is the deprotonated ligand, the naphthyl chalcone. In the present investigation, the lattice constants of the copper(II) complexes have been determined with the help of X-ray powder diffraction data. They all have the tetragonal unit cell. On the basis of cell parameters it has been concluded that (i) replacement of a phenyl ring by a naphthyl ring results in decrease of cell parameters, and (ii) *ortho* substituent tends to increase cell parameters.

INTRODUCTION

Chalcones and their derivatives are found to possess a wide spectrum biological activity. They usually exhibit multiprotecting biochemical activities. Chalcones are found to possess germicidal,[1–3] bactericidal,[4–6] fungicidal,[7, 8] carcinogenic,[9] analgesic[10, 11], anti-inflammatory[10, 11], sedative[10, 11], antifertility[12], etc. activities. Naphthalene and phenanthrene analogues of chalcones also possess potential bactericidal and carcinogenic[13–15] activity. Methoxy and hydroxy chalcones can arrest the destruction of adrenaline.[16] Chalcones and their derivatives find application[17] as artificial sweeteners, stabilizers against heat, visible light, ultraviolet light, aging, colour photography, scintillators, polymerisation catalysts, fluorescent whitening agents and organic brightening additives. The *ortho*-hydroxychalcones have good chelating properties and were exploited as analytical reagents for the estimation of different metal ions.[18] 2′-Hydroxychalcones and their heterocyclic and naphthalene analogues are reported to form coordination complexes.[18–20]

Literature survey reveals that so far no significant work has been carried out on characterisation of metal complexes of chalcones and their derivatives using X-ray diffraction technique. However, recently, some X-ray diffraction studies on Cu(II) complexes of 2′-hydroxychalcones have been reported.[21] This aroused our interest to carry out the present work in which the X-ray diffraction studies on some Cu(II) complexes of naphthalene analogues of 2′-hydroxychalcones are investigated.

EXPERIMENTAL

The naphthalene analogues of 2′-hydroxychalcones, 1-(1-hydroxy-2-naphthyl)-3-phenyl-2-propen-1-one (BenchaH), 1-(1-hydroxy-2-naphthyl)-3-(2-methoxy-

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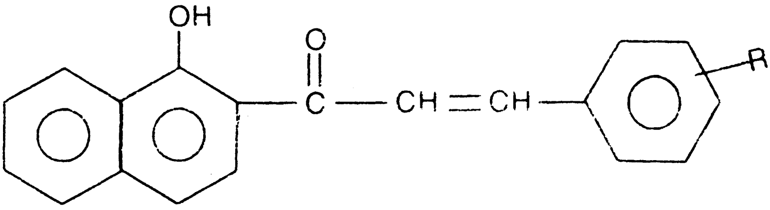
Present address for correspondence: Head, Physical Chemistry Division, The Institute of Science, 15, Madam Cama Road, Fort, Bombay-400 032.

phenyl)-2-propen-1-one [*o*-AnichaH], 1-(1-hydroxy-2-naphthyl)-3-(4-methoxyphenyl)-2-propen-1-one [*p*-AnichaH] and 1-(1-hydroxy-2-naphthyl)-3-(3,4-methylenedioxyphenyl) -2-propen-1-one [PipchaH] were prepared by condensing 2-acetyl-1-naphthol with either benzaldehyde or substituted benzaldehyde in ethyl alcohol in the presence of 40% (w/w) aqueous caustic potash solution by following the reported procedures[22] in detail. These naphthyl chalcones represented by the following general structure, were orange-red to orange-yellow in colour.



where, —R = —H, 2-OCH$_3$, 4-OCH$_3$, or 3,4-

The metal complexes of the naphthyl chalcones were prepared by refluxing aqueous solution of the required metal salt and the acetone solution of the corresponding naphthyl chalcone in 1 : 2 ratio for 3 to 4 h. The pH of the solution was then raised to ~8.00 with aqueous ammonia and further refluxed for about 1 h. The complexes obtained were filtered, washed with water, acetone and ethanol and dried at 110°C. These complexes are coloured, non-hygroscopic, highly stable solids, insoluble in water and have varying but low solubility in common organic solvents.

The X-ray diffraction patterns of the complexes in powder form were recorded on a Krystellofles, Model 810 (Germany), equipped with CuKα target tube (λ = 1.5418 Å). The diffraction patterns were recorded at a scanning rate of 2° (2θ)/min and at a chart speed of 2 cm/min using the scale, 1° = 1 cm.

RESULTS AND DISCUSSION

The X-ray powder diffraction patterns of the Cu(II) complexes have been indexed by standard methods,[23-26] keeping in mind the characteristics of various symmetry systems, till a good fit was obtained between the observed and calculated Bragg's spacings of interplanar spacings (d) values. They all could be successfully indexed[27, 28] for tetragonal crystal system. The unit cell parameters were calculated from the indexed data by using the equation[29, 30]

$$\sin^2 \theta_{hkl} = A(h^2 + k^2) + C \cdot l^2$$

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

All main peaks are indexed and the calculated values of Miller indices (hkl) along with observed and calculated d spacings (in Å) and relative intensities are reported in Tables 1-4.

TABLE-1
X-RAY DIFFRACTION DATA OF Cu(Bencha)$_2$

Sr. No.	2θ	d_{Obs} (Å)	d_{Cal} (Å)	hkl	Relative intensity $I/I_0 \times 100$
1	5.70	15.51	15.48	001	100.00
2	10.75	8.22	8.24	110	49.23
3	15.20	5.83	5.82	200	48.46
4	17.00	5.22	5.21	210	49.23
5	21.60	4.11	4.12	220	65.00
6	23.60	3.77	3.77	301	40.77
7	27.00	3.30	3.33	312	68.85
8	32.90	2.72	2.73	402	19.62

A = B = 0.0043811 C =0.0024787 a = b = 11.6468 Å c = 15.4841 Å
c/a = 1.3295 Crystal system = Tetragonal Cell volume = 2100.3864 (Å)^3

TABLE-2
X-RAY DIFFRACTION DATA OF Cu(*o*-Anicha)$_2$

Sr. No.	2θ	d_{Obs} (Å)	d_{Cal} (Å)	hkl	Relative intensity $I/I_0 \times 100$
1	6.70	13.18	13.15	100	55.00
2	9.00	9.82	9.80	002	26.25
3	10.52	8.40	8.40	111	35.42
4	13.45	6.57	6.57	200	100.00
5	16.24	5.46	5.46	202	50.83
6	18.99	4.67	4.65	220	20.00
7	21.38	4.16	4.16	310	87.50
8	22.90	3.88	3.83	312	32.50
9	26.00	3.43	3.42	322	44.58
10	28.80	3.10	3.10	330	17.92
11	31.75	2.82	2.82	422	14.58

A = B = 0.0034386 C = 0.0015468 a = b = 13.1464 Å c = 19.6011 Å
c/a = 1.4910 Crystal system = Tetragonal Cell volume = 3387.6155 (Å)^3

With the limits of experimental errors, the calculated and observed values of d are in good agreement. The crystal parameters and other characteristics of these Cu(II) complexes are given in Table 5. All the Cu(II) complexes under present X-ray diffraction studies are of tetragonal crystal system with their axial ratio c/a > 1.

Recently, the cell parameters of a = b = 12.98 Å, c = 16.06 Å and c/a = 1.24 with tetragonal crystal system have been reported[21] for Cu(II) complex of 2′-hydroxychalcone. However, in the present study, we have obtained cell parameters of a = b = 11.6468 Å, c = 15.4841 Å and c/ a = 1.3295 with tetragonal crystal system for Cu(Bencha)$_2$, the Cu(II) complex of BenchaH which is the naphthalene analogue of 2′-hydroxychalone. Thus, the replacement of a hydroxy phenyl ring by 1-hydroxy-2-naphthalene ring (in general, a phenyl ring by a naphthyl ring) has resulted in the decrease of all cell parameters indicating better packing efficiency in this complex which may be attributed to enhanced molecular interactions.

TABLE-3

X-RAY DIFFRACTION DATA OF Cu(*p*-Anicha)$_2$

Sr. No.	2θ	d_{Obs} (Å)	d_{Cal} (Å)	hkl	Relative Intensity $I/I_0 \times 100$
1	5.84	15.15	15.12	001	26.48
2	8.14	10.86	10.89	100	100.00
3	10.02	8.81	8.84	101	31.01
4	11.50	7.69	7.70	110	92.33
5	12.90	6.86	6.86	111	36.06
6	17.30	5.13	5.12	201	35.54
7	19.00	4.67	4.64	211	85.37
8	20.14	4.41	4.42	202	58.54
9	21.58	4.12	4.10	212	78.40
10	23.10	3.85	3.85	220	56.45
11	23.90	3.72	3.73	221	51.05
12	25.85	3.44	3.44	310	25.78
13	26.45	3.37	3.36	311	37.98
14	28.50	3.13	3.13	312	40.77
15	29.50	3.03	3.02	005	30.31
16	32.00	2.80	2.81	322	20.56
17	33.30	2.69	2.68	401	17.77
18	34.50	2.60	2.60	411	18.12
19	37.45	2.40	2.40	421	17.42
20	41.20	2.19	2.19	423	17.07

A = B= 0.0050078 C = 0.0025989 a = b = 10.8937 Å c = 15.1218 Å

c/a = 1.3881 Crystal system = Tetragonal Cell volume = 1794.5446 (Å)^3

As can be seen from the Table 5, Cu(o–Anicha)$_2$, the Cu(II) complex of the substituted naphthyl chalcone. *o*-AnichaH (with —OCH_3 group in the *ortho*-position of the phenyl ring of the aldehyde moiety), structurally deffers (as is evident from cell parameters, a, b and c) from Cu(Bencha)$_2$ and Cu(*p*-Anicha)$_2$, the Cu(II) complexes of the unsubstituted naphthyl chalcone BenchaH and the substituted naphthyl chalcone *p*-AnichaH (with —OCH_3 group in the *para*- position of the phenyl ring of the aldehyde moiety) respectively. This structural difference of this complex, Cu (*o*-Anicha)$_2$ in the solid state is further supported by its ESR studies made by us, in which the ESR spectra of this complex in its polycrystalline solid state, both at room temperature and at liquid nitrogen temperature yield an abnormal $g_\perp$ value of 1.99 each. However the ESR spectrum of this complex in its chloroform solution at liquid nitrogen temperature yields the normal $g_\perp$ value of 2.034. This distinct difference in the observed spectral and structural parameters (ESR and XRD) for this complex, Cu(*o*-Anicha)$_2$ as compared to the other Cu(II) complexes under present study may be attributed to the reflection of the *otho-* effect[31] of the —OCH_3 groups present in the *ortho-* positions of the phenyl rings fo the aldehyde moieties of this complex.

TABLE-4

X-RAY DIFFRACTION DATA OF Cu(Pipcha)$_2$

Sr. No.	2θ	d_{Obs} (Å)	d_{Cal} (Å)	hkl	Relative Intensity I/I × 100
1	6.10	14.49	14.55	100	37.09
2	7.84	11.29	11.26	101	24.91
3	9.90	8.93	8.91	111	34.18
4	12.20	7.25	7.26	200	100.00
5	13.60	6.51	6.51	210	28.18
6	14.98	5.92	5.93	003	89.45
7	18.00	4.93	4.94	221	32.00
8	19.92	4.45	4.45	311	36.00
9	21.75	4.08	4.09	312	46.73
10	24.40	3.65	3.64	400	32.18
11	25.65	3.47	3.46	411	55.09
12	27.40	3.26	3.25	420	77.64
13	30.20	2.96	2.96	006	30.55

A = B = 0.0028067 C = 0.0018795 a = b = 14.5512 Å c = 17.7818 Å

c/ a = 1.2220 Crystal system = Tetragonal Cell volume = 3765.0724 (Å)^3

TABLE 5

CRYSTAL PARAMETERS AND OTHER CHARACTERISTICS OF Cu(II) COMPLEXES

Compound	A = B	C	a = b (Å)	c (Å)	Cell volume (Å)^3	c/a	Crystal system
Cu(Bencha)$_2$	0.0043811	0.0024787	11.6468	15.4841	2100.3864	1.3295	Tetragonal
Cu(*o*-Anicha)$_2$	0.0034386	0.0015468	13.1464	19.6011	3387.6155	1.4910	Tetragonal
Cu(*p*-Anicha)$_2$	0.0050078	0.0025989	10.8937	15.1218	1794.5446	1.3881	Tetragonal
Cu(Pipcha)$_2$	0.0028067	0.0018795	14.5512	17.7818	3765.0724	1.2220	Tetragonal

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(*Received:* 30 October 1995; *Accepted*: 2 February 1996) AJC-1072