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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Biochemically Relevant Complexes of Copper: Synthesis, Magnetic and Spectral Studies of Some Mixed-Ligand Chelates of Bis(O-Hydroxyacetophenonato)Copper(II with Benzothiazole and Related Ligands

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Version of record first published: 14 Apr 2008.

To cite this article: R. C. Maurya, S. Pillai, T. Singh, H. Singh & B. Shukla (1998): Biochemically Relevant Complexes of Copper: Synthesis, Magnetic and Spectral Studies of Some Mixed-Ligand Chelates of Bis(O-Hydroxyacetophenonato)Copper(II) with Benzothiazole and Related Ligands, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 28:7, 1053-1064

To link to this article: http://dx.doi.org/10.1080/00945719809349388

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SYNTH. REACT. INORG. MET.-ORG. CHEM., 28(7), 1053-1064 (1998)

BIOCHEMICALLY RELEVANT COMPLEXES OF COPPER: SYNTHESIS, MAGNETIC AND SPECTRAL STUDIES OF SOME MIXED-LIGAND CHELATES OF BIS(o-HYDROXYACETOPHENONATO)COPPER(II) WITH BENZOTHIAZOLE AND RELATED LIGANDS

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ABSTRACT

A series of novel mixed-ligand complexes of copper(II) of the compositions [Cu(o-haph)$_2$(L)$_2$], where o-haphH = o-hydroxyacetophenone and L = benzothiazole, 2-methylbenzothiazole, 2-(2'-hydroxyphenyl)benzothiazole, 2-(2'-tolyl)benzothiazole or 2-(3'-tolyl)benzothiazole, and [Cu(o-haph)$_2$(AMBZT)], where AMBZT = 2-aminobenzothiazole, have been prepared by the interaction of [Cu(o-haph)$_2$]$\cdot$H$_2$O with the ligands. The compounds so obtained were characterized by analytical data, molar conductances, magnetic measurements, electron paramagnetic resonance and infrared spectral studies. Suitable octahedral structures have been proposed for these complexes.

INTRODUCTION

The ligational behaviour of benzothiazole and its derivatives has been reported[1-4] previously. In the past few years there has been growing interest in the synthesis and characterization of some mixed-ligand complexes of bis(o-hydroxyacetophenonato)copper(II)

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and bis(o-hydroxyacetophenonato)nickel(II) with pyridine and related ligands[5-8]. Panda and Mahapatra[6] have reported the synthesis and characterization of some mixed-ligand adducts of copper(II), zinc(II), nickel(II), cadmium(II) and cobalt(II) involving o-hydroxyacetophenone and heterocyclic bases. In recent communications[9,10] from our laboratory, Maurya *et al*. have reported the synthesis, magnetic and spectral studies of some mixed-ligand hexa-coordinate complexes of diaquabis(o-hydroxyacetophenonato)-cobalt(II), diaquabis(o-hydroxyacetophenonato)nickel(II) and bis(o-hydroxyacetophenonato)copper(II) monohydrate with 2- or 3-pyrazoline-5-ones. However, there is no report on mixed-ligand complexes of bis(o-hydroxyacetophenonato)copper(II) involving heterocyclic donors such as benzothiazole and related ligands. We, therefore, have examined the ligational behaviour of benzothiazole (BZT), 2-methylbenzothiazole (MBZT), 2-aminobenzothiazole (AMBZT), 2-(2'-hydroxyphenyl)benzothiazole (HPBZT), 2-(2'-tolyl)benzothiazole (2'-TOBZT) and 2-(3'-tolyl)benzothiazole (3'-TOBZT) towards bis-(o-hydroxyacetophenonato)copper(II) monohydrate.

As the biological activity is often augmented[11] when the ligand forms complexes with metal ions, the resulting mixed-ligand complexes may be of potential biological importance. Additional interest for this investigation has been generated by the discovery[12] of the enzyme Galactose oxidase which contains a mixed-ligand monomeric copper(II) complex involving N/O donors in its active site. Benzothiazole and its derivatives are structurally shown in Fig. 1.

EXPERIMENTAL

Materials

o-Hydroxyacetophenone (B. D. H. Chemical, Bombay), o-toluic acid, m-toluic acid, 2-aminobenzothiazole and copper(II) chloride

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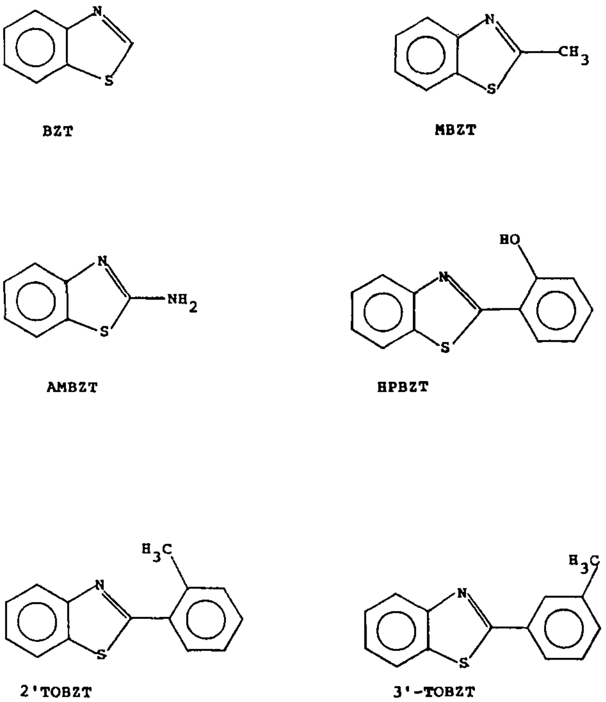

BZT

MBZT

AMBZT

HPBZT

2'TOBZT

3'-TOBZT

Fig. 1. Structures of Ligands.

dihydrate (Sisco-Chem Industries, Bombay), benzothiazole, 2-methylbenzothiazole (Aldrich Chemical Company, U. S. A.), salicylamide (E. Merck, India), were used as received. All other chemicals used were of A. R. grade.

Preparation of HPBZT, 2'-TOBZT and 3'-TOBZT

The benzothiazole derivatives were prepared by the usual method[13] of condensation of *o*-aminothiophenol with salicylamide for HPBZT, with *o*-toluic acid for 2'-TOBZT or with *m*-toluic acid for 3'-TOBZT in the presence of a sufficient quantity of polyphosphoric acid.

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Preparation of the Parent Compound [Cu(o-haph)$_2$].H$_2$O

The parent compound bis(o-hydroxyacetophenonato)copper(II) monohydrate was prepared by the method of Panda *et al.*[6].

Preparation of the Mixed-Ligand Chelates

A stoichiometric quantity of the parent compound, [Cu(o-haph)$_2$].H$_2$O (0.01 mole, 3.515 g), dissolved in a sufficient quantity of ethanol (~30 mL) was added to the solution of the appropriate ligand [0.02 mole for BZT (2.7 g), MBZT (3.0 g), HPBZT (4.5 g), 2'-TOBZT (4.5 g), 3'-TOBZT (4.5 g) and 0.01 mole for AMBZT (1.5 g)] dissolved in ethanol (~20 mL). The resulting mixture was refluxed for 6-7 h at 80°C over a hot plate. During this time a coloured solid separated out. It was filtered by suction, washed several times with ethanol and finally with ether and dried *in vacuo* to constant weight. The analytical data of the synthesised complexes are given in Table I.

Analyses

For the determination of copper, a weighed amount (~150 mg) of the synthesized complex was decomposed by digestion with perchloric acid and nitric acid, until the resulting residue gave a transparent solution in dilute HCl. Copper was determined[14] as copper salicylaldoximate, Cu$(C_7H_6O_2N)_2$. Carbon, hydrogen and nitrogen were determined microanalytically.

Physical Methods

Magnetic measurements were performed by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant at Central Salt and Marine Chemicals Research Institute, Bhavnagar. Electron paramagnetic resonance spectra were recorded on powdered

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Table I. Analytical Data and Important IR Spectral Bands (cm^{-1}) of the Synthesized Complexes

Sr. No.	Compound (Empirical Formula) (Formula Weight)	Found (Calc.), % C	H	N	S	Cu	ν(C=O) (acetyl carbonyl)	ν(C=N) + ν(C=C)
1.	[Cu(*o*-haph)$_2$(BZT)$_2$] ($C_{30}H_{24}N_2O_4S_2Cu$) (603.5)	59.25 (59.65)	3.68 (3.97)	4.30 (4.64)	10.92 (10.60)	10.98 (10.52)	1580	1605
2.	[Cu(*o*-haph)$_2$(MBZT)$_2$] ($C_{32}H_{28}N_2O_4S_2Cu$) (631.5)	60.27 (60.80)	4.30 (4.43)	4.62 (4.43)	10.52 (10.13)	10.65 (10.05)	1585	1600
3.	[Cu(*o*-haph)$_2$(AMBZT)] ($C_{23}H_{20}N_2O_4SCu$) (483.5)	57.29 (57.08)	4.30 (4.13)	5.60 (5.79)	6.38 (6.62)	13.68 (13.13)	1571	1602
4.	[Cu(*o*-haph)$_2$(HPBZT)$_2$] ($C_{42}H_{32}N_2O_6S_2Cu$) (787.5)	64.25 (64.00)	4.30 (4.06)	3.20 (3.55)	8.01 (8.12)	8.78 (8.06)	1575	1603
5.	[Cu(*o*-haph)$_2$(2'-TOBZT)$_2$] ($C_{44}H_{36}N_2O_4S_2Cu$) (783.5)	67.80 (67.39)	4.20 (4.59)	3.29 (3.57)	8.37 (8.16)	8.85 (8.10)	1570	1600
6.	[Cu(*o*-haph)$_2$(3'-TOBZT)$_2$] ($C_{44}H_{36}N_2S_2O_4Cu$) (783.5)	67.68 (67.39)	4.25 (4.59)	3.27 (3.57)	8.30 (8.16)	8.62 (8.10)	1575	1604

samples at Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Bombay. Conductance measurements were made at room temperature in DMF using a Toshniwal conductivity bridge and dip-type cell with a smooth platinum electrode of cell constant 1.3. Solid state infrared spectra were recorded in KBr at National Chemical Laboratory, Pune.

RESULTS AND DISCUSSION

The parent compound, $[Cu(\underline{o}\text{-haph})_2].H_2O$ and the mixed-ligand complexes of copper(II) were prepared according to the following equations.

$$CuCl_2.2H_2O + 2(\underline{o}\text{-haphH})_2 \xrightarrow[NH_4OH]{Ethanol} [Cu(\underline{o}\text{-haph})_2].H_2O + 2HCl + H_2O$$

$$[Cu(\underline{o}\text{-haph})_2].H_2O + 2L \xrightarrow[Reflux]{Ethanol} [Cu(\underline{o}\text{-haph})_2(L)_2] + H_2O$$

where L = BZT, MBZT, HPBZT, 2'-TOBZT or 3'-TOBZT

and

$$[Cu(\underline{o}\text{-haph})_2].H_2O + AMBZT \xrightarrow[Reflux]{Ethanol} [Cu(\underline{o}\text{-haph})_2(AMBZT)] + H_2O$$

The resulting compound under this investigation are non-hygroscopic, air stable solids. Some physical properties of these complexes are given in Table II. These compounds were characterised on the basis of the following studies reported below.

Infrared Spectral Studies

The important IR spectral bands and their tentative assignments are given in Table I. The IR spectrum of the parent compound shows the presence of lattice water as inferred by a broad band for ν(O-H) at 3600-3400 cm^{-1}. The resulting mixed-ligand complexes do not show an absorption in this region. This

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Table II. Some Physical Properties of the Synthesized Complexes.

Sr. No.	Compound	Colour	Decomp. Temp. (°C)	μeff (B.M.)	Yield %	Λ_M ($ohm^{-1} cm^2 mole^{-1}$)
1.	$[\mathrm{Cu}(\underline{o}\text{-haph})_2(\mathrm{BZT})_2]$	Brown	265	1.79	55	6.2
2.	$[\mathrm{Cu}(\underline{o}\text{-haph})_2(\mathrm{MBZT})_2]$	Light brown	252	1.76	57	7.9
3.	$[\mathrm{Cu}(\underline{o}\text{-haph})_2(\mathrm{AMBZT})]$	Greenish brown	275	1.81	60	8.2
4.	$[\mathrm{Cu}(\underline{o}\text{-haph})_2(\mathrm{HPBZT})_2]$	Brown	225	1.79	50	10.6
5.	$[\mathrm{Cu}(\underline{o}\text{-haph})_2(2'\text{-TOBZT})_2]$	Brown	246	1.82	56	5.8
6.	$[\mathrm{Cu}(\underline{o}\text{-haph})_2(3'\text{-TOBZT})_2]$	Brown	238	1.78	58	7.2

suggests that the resulting mixed-ligand complexes are not hydrated.

The significant absorption band for o-hydroxyacetophenone at 1640 cm^{-1}, assignable to ν(C=O) (acetyl carbonyl) is shifted to lower wave numbers[10,15] in the mixed-ligand complexes, and appears then at 1570-1585 cm^{-1}.

The ligands BZT, MBZT, 2'-TOBZT and 3'-TOBZT used in the present study possess two potential donor sites: (i) the benzothiazole nitrogen and (ii) the benzothiazole sulphur, while the ligands AMBZT and HPBZT are potentially tridentate: (i) the benzothiazole sulphur, (ii) the benzothiazole nitrogen, and (iii) the amino nitrogen in case of AMBZT or the phenolic oxygen in case of HPBZT. However, considering the planarity of the latter two ligands AMBZT and HPBZT, it is unlikely that these two ligands could be tridentate on a single metal. Hence, these two ligands are potentially bidentate: (i) the benzothiazole-nitrogen or sulphur, and (ii) the amino nitrogen in case of AMBZT or the phenolic oxygen in case of HPBZT.

The ν(O-H) band at 2540 cm^{-1} in free HPBZT is unaffected after complexation, suggesting thereby that the phenolic (O-H) group is not taking part in coordination. It is observed that the (CSC) band of all the ligands occurring at 700-720 cm^{-1} is not affected appreciably in the respective complexes. This indicates that the benzothiazole sulphur is not involved in bonding. The appearance of a band at 1600-1605 cm^{-1} attributable to ν(C=N) plus ν(C=C) vibrations indicates the bonding of benzothiazole tertiary nitrogen to copper in all the complexes[16].

The possibility of amino nitrogen coordination in the ligand AMBZT to copper was also examined. The ν_{as}(N-H) and ν_{s}(N-H) bands of the amino group in free AMBZT, observed at 3455 and 3330 cm^{-1},

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respectively, are shifted to lower wave numbers and appeared then at 3340 and 3190 cm^{-1}, respectively, in its complex. This suggests the coordination of the amino nitrogen to copper.

Conductance Measurements

The observed molar conductances of all the mixed-ligand complexes in DMF (in the range 5.2-10.6 $ohm^{-1} cm^{2} mol^{-1}$) are given in Table II. These values are indicative of the non-electrolytic nature[17] of these complexes. Such a non-zero molar conductance value for each of the complex in the present study is most probably due to the strong donor capacity of DMF which may leads to the displacement of anionic ligand and change of electrolyte[17] type.

Magnetic Measurements

The observed magnetic moments (1.76-1.82 B. M.) of the complexes correspond to one unpaired electron and give no specific information about their stereochemistry.

Electron Paramagnetic Resonance Spectra

The room temperature X-band EPR spectrum of a representative compound, $[Cu(\underline{o}\text{-haph})_2(AMBZT)]$, was recorded on a powdered sample at the microwave frequency 9.07 GHz. The electron spin resonance spectral studies have shown that 'g' values are sensitive to the covalent nature of the metal-ligand bond[18] and the values of $g < 2.3$ indicate strong covalent interaction between the ligand and the divalent metal ion, whereas values of $g > 2.3$ indicate ionic environment. The observed 'g' values of less than 2.3 (2.0678) in the present complex suggest the covalent nature of metal-ligand bonds in these complexes.

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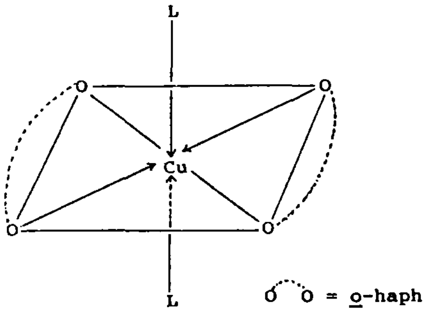

Fig. 2a. Proposed Trans- Octahedral Structure of [Cu(o-haph)$_2$(L)$_2$] (where L = BZT, MBZT, HPBZT, 2'-TOBZT or 3'-TOBZT.

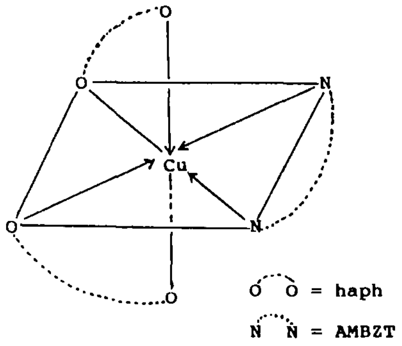

Fig. 2b. Proposed Cis- Octahedral Structure of [Cu(o-haph)$_2$(AMBZT)].

Electronic Spectra

The electronic spectra of the complexes were recorded in 10^{-3} M DMF. They exhibit three absorption bands at 275-290, 400-425 and 640-660 nm. The first UV band at 275-290 nm is comparable to a band observed for octahedral bis-adducts of the metal acetylacetonates[19]. The remaining two weak d-d transitions in the visible region at 400-425 and 640-660 nm are assigned to the transitions $^2A_{1g} \longleftarrow {}^2B_{1g}$ and $^2E_g \longleftarrow {}^2B_{1g}$, respectively, which suggest tetragonally distorted octahedral geometry[20] for these complexes.

CONCLUSION

The satisfactory analytical data and all the above studies indicate that the complexes may be formulated as $[Cu(\underline{o}\text{-haph})_2(L)_2]$ (where L = BZT, MBZT, HPBZT, 2-TOBZT or 3'-TOBZT) and $[Cu(\underline{o}\text{-haph})_2\text{-}(ABZT)]$. Keeping in view of the normal magnetic moments of all the complexes, and EPR result of the $[Cu(\underline{o}\text{-haph})_2(AMZT)]$ (involving a bidentate ABZT ligand, and wherein a singlit-triplet transition for a dimeric structure[10] near half field is absent in the EPR spectrum), a monomeric <u>trans</u>- octahedral structure (Fig. 2a) and a monomeric <u>cis</u>-octahedral structure (Fig. 2b) have been proposed, tentatively, for the complexes $[Cu(\underline{o}\text{-haph})_2(L)_2]$ and $[Cu(\underline{o}\text{-haph})_2\text{-}(ABZT)]$, respectively. The inclusion of a bidentate (ABZT) ligand spanning the <u>trans</u> position of the monomeric octahedron, is very unlikely.

ACKNOWLEDGEMENTS

We are grateful to Professor J. P. Shukla, Vice-Chancellor of this university and Professor M. C. Agrawal, Head, Department of Chemistry, for providing laboratory facilities and encouragements.

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Received: 31 December 1997
Accepted: 20 February 1998

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