This article was downloaded by: [North Dakota State University] On: 16 November 2014, At: 13:20 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt19</u>

Synthesis and Physico-Chemical Studies of Some Mixed-Ligand Complexes of bis(Benzoylacetonato)copper(II) with Some Biologically Active Heterocyclic Chelating Donors

R. C. Maurya^a, R. Verma^a & H. Singh^a

^a Coordination Chemistry Laboratory , Department of P. G. Studies and Research in Chemistry , R. D. University , Jabalpur, 482 0019, India Published online: 15 Feb 2007.

To cite this article: R. C. Maurya, R. Verma & H. Singh (2003) Synthesis and Physico-Chemical Studies of Some Mixed-Ligand Complexes of bis(Benzoylacetonato)copper(II) with Some Biologically Active Heterocyclic Chelating Donors, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 33:6, 1063-1080

To link to this article: <u>http://dx.doi.org/10.1081/SIM-120021938</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 33, No. 6, pp. 1063–1080, 2003

Synthesis and Physico-Chemical Studies of Some Mixed-Ligand Complexes of bis(Benzoylacetonato)copper(II) with Some Biologically Active Heterocyclic Chelating Donors

R. C. Maurya,* R. Verma, and H. Singh

Coordination Chemistry Laboratory, Department of P. G. Studies and Research in Chemistry, R. D. University, Jabalpur, India

ABSTRACT

Six new mixed-ligand complexes of copper(II) of the compositions $[Cu(bzac)_2(L)_2]$, where bzacH = benzoylacetone and L = 3-methyl-2pyrazoline-5-one (MP) (1), 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (DMPHP) (3), benzimidazole (BZL) (4) or benzothiazole(BZT) (5) and $[Cu(bzac)_2(L-L)]$, where L-L = 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (ADMPHP) (2) or 2-aminobenzothiazole (ABZT) (6), have been synthesized by the interaction of bis(benzoylacetonato)copper(II) with the ligands L and L-L. The compounds so obtained were characterized by analytical data, molar conductances, magnetic measurements,

1063

DOI: 10.1081/SIM-120021938 Copyright © 2003 by Marcel Dekker, Inc. 0094-5714 (Print); 1532-2440 (Online) www.dekker.com

^{*}Correspondence: R. C. Maurya, Coordination Chemistry Laboratory, Department of P. G. Studies and Research in Chemistry, R. D. University, Jabalpur 482 001, India; E-mail: rcmaurya@sancharnet.in.

ESR, IR, and electronic spectral studies. Monomeric structures are suggested for these compounds.

Key Words: Keto-enol tautomerism; Mixed-ligand β -diketone complexes; Heterocyclic chelating donors; *cis*-Octahedral.

INTRODUCTION

 β -Diketones and related compounds capable of exhibiting keto-enol tautomerism^[1] react with metal cations to form complexes, in which the metal replaces the enolic hydrogen and a six-membered chelate ring is produced. Since the enolate ion carries a single negative charge, divalent metal atoms reacts with two enolate ions to give neutral molecules, ML₂ (LH = β -diketone), in which there are four donor oxygen atoms to each metal atom. If the normal coordination number of the metal towards ligand oxygen atoms is four, the result is an inner complex, or neutral molecule. The larger divalent ions of transition metals usually have coordination numbers towards oxygen ligands which are greater than four. The neutral molecules, ML₂, then behave as Lewis acids and form addition compounds with Lewis bases.^[2,3]

The chemistry of β -diketone complexes has aroused much interest in many areas, *viz.*, spectral studies, gas chromatography, solvent extraction, column and thin layer chromatography, NMR shift reagents, laser technology and in the polymer industry.^[4,5]

In the past few years there has been continuing interest in the synthesis and characterization of some mixed-ligand β -diketone complexes^[2,3,6-13] of Co(II), Ni(II), Cu(II) and Zn(II) involving tetra-, penta- and hexa-coordination. Mahapatra and Das^[14] have recently reported the synthesis and characterization of some mixed-ligand chelates of Co(II), Zn(II), Cd(II) and Hg(II) with a monobasic bidentate oxygen donor (acetoacetanilide) and a neutral monodentate N-donor (isoquinoline). In earlier communications Maurya et al.^[9-13] have described the isolation and characterization of hexa-coordinated mixed-ligand Co(II), Ni(II) and Zn(II) derivatives of β-diketones or β-diketoesters with heterocyclic nitrogen donors and 2- or 3-pyrazoline-5-one derivatives. A series of new mixed-ligand complexes of Co(II) of the composition $[Co(Cl)(A-A)(L)(H_2O)_2]$, where $(A-A)(L)(H_2O)_2$ A)H = acetoacetanilide, o-acetoacetanisidide or o-acetoactotoluidide and L = 3-methyl-1-phenyl-2-pyrazoline-5-one, 2,3-dimethyl-4-dimethylaminomethanesulphonatesodium-1-phenyl-3-pyrazoline-5-one, 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one have been synthesized and characterized by Maurya et al.^[15] In a recent communication^[16] from our coordination chemistry laboratory, we have reported the synthesis, magnetic and spectral studies of some mixed-ligand chelates of bis(2-hydroxyacetophenonato)-

Downloaded by [North Dakota State University] at 13:20 16 November 2014

copper(II) with 2- or 3-pyrazoline-5-one derivatives. The crystal structure of the *trans* form of bis(benzoylacetonato)copper(II)has been determined^[17] by three-dimensional X-ray diffraction data. However, there is no previous report on mixed-ligand complexes of bis(benzoylacetonato)copper(II) with biologically active heterocyclic chelating molecules. We, therefore, have examined the ligational behaviour of some heterocylic chelating donors, *viz.*, 3-methyl-2-pyrazoline-5-one (MP), 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (DMPHP), 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (DMPHP), benzimidazole (BZL), benzothiazole (BZT), 2-aminobenzothiazole (ABZT) towards bis(benzoylacetonato)copper(II). The present paper describes the results of such a study. The benzoylacetone and heterocyclic chelating donors are structurally shown in Figure 1.



Figure 1. Structures of ligands.

EXPERIMENTAL

Materials Used

Copper(II) sulfate pentahydrate (B. D. H. Chemicals, Bombay), benzoylacetone and 2-aminobenzothiazole (Sisco-Chem. Industry, Bombay), 3-methyl-2-pyrazoline-5-one and 4-amino-2,3-dimethyl-1-phenyl-3pyrazoline-5-one (Aldrich Chemical Co., U. S. A.), 2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (B. D. H. Chemicals, England), benzimidazole (Wilson Laboratories, Bombay) and benzothiazole (E. Merck, Germany) were used as supplied.

Preparation of bis(Benzoylacetonato)copper(II)

This compound was prepared by the method of Hon et al.,^[17] and used as the parent compound.

Synthesis of Mixed-Ligand Complexes

A stoichiometric quantity of the appropriate heterocyclic organic donors (0.02 mole for MP (1.96 g), DMPHP (3.76 g), BZL (2.36 g) or BZT (2.70 g), and 0.01 mole for ADMPHP (2.03 g) or ABZT (1.50 g) dissolved in an excess of ethanol (~ 20 mL) was added to the solution of parent compound, bis(benzoylacetonato)copper(II) (0.01 mole, 3.85 g) dissolved in ethanol (~ 25 mL). The resulting mixture was refluxed for 3–4 hours at 80 °C over a hot plate equipped with a magnetic stirrer. During this time coloured solids separated. In the case of ADMPHP and DMPHP separation of the coloured solids took place immediately. The precipitates were filtered by suction, washed several times with ethanol and dried in vacuo to constant weight.

Analyses and Physical Methods

Carbon, hydrogen and nitrogen were determined microanalytically at the Central Salt and Marine Chemicals Research Institute, Bhavnagar. Copper was determined as copper salicylaldoximate.^[18] Conductance measurements of the synthesized complexes were measured in analytical grade DMF (10^{-3} M solution) on an APX 185 digital conductivity meter, using a diptype cell (cell constant: 1.0 cm^{-1}). Magnetic susceptibility measurements were made at room temperature by the Gouy method. The apparatus was calibrated using mercury(II) tetrathiocyanatocobaltate(II), Hg[Co(NCS)₄], as the standard. Infrared spectra ($4000-450 \text{ cm}^{-1}$) of the uncoordinated ligands

and of the synthesized complexes were recorded in Nujol mulls supported between sodium chloride plates on a FT-IR spectrophotometer. Electronic spectra of the complexes were recorded in 10^{-3} molar dimethylformamide solutions on a Shimadzu model UV-160 spectrophotometer at the Central Salts and Marine Chemical Research Institute, Bhavnagar. The X-band EPR spectra of the complexes were measured at room temperature on a Bruker ESP X-band spectrometer using powdered samples at the microwave frequency of 9.46–9.47 GHz at the Regional Sophisticated Instrumentation Center, Indian Institute of Technology, Madras. The 1,1-diphenyl-2picrylhydrazyl (DPPH) free radical was used as an internal standard. Thermogravimetric analysis was done by heating the sample at the rate of 15 °C min⁻¹ up to 800 °C on a thermal analyzer at the Regional Sophisticated Instrumentation Center, Nagpur University Campus, Nagpur. The decomposition temperatures of the parent compound as well as the synthesized mixed-ligand complexes were recorded by an electrically operated Kumar Industries, Bombay, melting point apparatus with a heating capacity up to 360 °C.

1067

RESULTS AND DISCUSSION

Bis(benzoylacetonato)copper(II) reacted with heterocyclic chelating donors in ethanol to yield stable hexa-coordinated complexes. The copper(II) mixed-ligand complexes were prepared according to the following equations:

$$[Cu(bzac)_2] + 2L \xrightarrow[Reflux]{Reflux} [Cu(bzac)_2(L)_2]$$

L = MP(1), DMPHP(3), BZL(4) or BZT(5)

and

$$[Cu(bzac)_2] + LL \xrightarrow{Ethanol} [Cu(bzac)_2(LL)]$$

L-L = ADMPHP (2) or ABZT (6)

The resulting compounds are air-stable coloured solids (see Table 1 for colours). The analytical data, percentage yields and decomposition temperatures of these compounds are given in Table 1. The solubilities of these complexes in different solvents are recorded in Table 2.



	Table 1. Ana	lytical data ar	nd some phy	ysical proper	ties or the sy	inthesized complexes		
	Complex (emnirical formula)		Found (c	alc., %)			Vield	Dec temn
Sr. no.	(mol. wt.)	С	Н	N	Cu	Color	(%)	(°C)
I	[Cu(bzac) ₂]	61.82	4.67	I	16.18	Bluish grey	I	180
	$(C_{20}H_{18}CuO_4)$ (385 54)	(62.25)	(4.66)	I	(16.48)			
(1)	$[Cu(bzac)_2(MP)_2]$	57.32	5.42	9.27	11.13	Light grey	50	175
с. г	$(C_{28}H_{30}CuN_4O_6)$ (581-54)	(57.77)	(5.16)	(9.63)	(10.92)	• • •		
(2)	[Cu(bzac) ₂ (ADMPHP)]	63.70	5.38	7.29	10.43	Shiny Prussian	55	180
~	$(C_{31}H_{31}CuN_3O_5)$ (588.54)	(63.20)	(5.26)	(7.14)	(10.79)	blue		
(3)	$[Cu(bzac)_2(DMPHP)_2]$	66.52	5.30	7.12	8.76	Dark grey	55	165
	$(C_{42}H_{42}CuN_4O_6)$ (761.54)	(66.18)	(5.15)	(7.35)	(8.34)			
(4)	$[Cu(bzac)_2(BZL)_2]$	65.30	4.49	9.27	10.56	Shiny black	50	195
	$(C_{34}H_{30}CuN_4O_4)$ (621.54)	(65.64)	(4.82)	(9.01)	(10.22)			
(5)	$[Cu(bzac)_2(BZT)_2]$	62.24	4.38	4.10	9.48	Light blue	55	175
	$(C_{34}H_{28}CuN_2O_4S_2)$ (655.54)	(62.23)	(4.27)	(4.27)	(69.6)			
(9)	[Cu(bzac) ₂ (ABZT)]	60.78	4.25	5.62	11.60	Parrot green	60	170
	(C ₂₇ H ₂₄ CuN ₂ O ₄ S) (535.54)	(60.49)	(4.48)	(5.23)	(11.86)			

1068

Maurya, Verma, and Singh

	Table 2.	Solubility of 1	the synthesize	ed complexes	in various solv	/ents. ^a		
Sr. no.	Compound	Chloroform	Acetone	Ethanol	Methanol	Acetonitrile	DMF	DMSO
(1)	$[Cu(bzac)_2(MP)_2]$	IS	IS	Sd	IS	Sd	s	S
(2)	[Cu(bzac) ₂ (ADMPHP)]	IS	IS	IS	IS	PS	S	S
(3)	[Cu(bzac) ₂ (DMPHP) ₂]	IS	IS	PS	IS	S	S	S
(4)	[Cu(bzac) ₂ (BZL) ₂]	PS	IS	IS	SS	S	S	S
(2)	$[Cu(bzac)_2(BZT)_2]$	IS	SS	IS	PS	S	S	S
(9)	[Cu(bzac) ₂ (ABZT)]	IS	PS	IS	SS	S	S	S
^a Abbreviat	ion: $S = $ soluble (80–100%);	SS = sparingly	v soluble (5-	10%); PS =	partially solubl	e (40-50%); IS	= insoluble	0

Solubility of each compound was tested by taking 20 mg of each compound in 1 mL of the solvent.

1069

Mixed-Ligand Complexes of Copper(II)



Sr. no.	Complex	v(C=O) (bzac)	v(C=C) (bzac)	v(C=O) ^a / (C=N)	$v(NH_2)/\delta(NH_2)$	Λ_{M} (Ohm ⁻¹ cm ² - mole ⁻¹)	μ _{eff} (B.M.)
I	[Cu(bzac) ₂]	1588 s	1566 s	I	I	I	I
(1)	$[Cu(bzac)_2(MP)_2]$	1592 s	1555 s	1565 ^a s	I	5.2	1.82
(5)	[Cu(bzac) ₂ (ADMPHP)]	1600 s	1550 s	$1570^{\rm a} {\rm s}$	3300–3200 br	7.5	1.77
(3)	[Cu(bzac) ₂ (DMPHP) ₂]	1598 s	1560 m	1575 ^a m	I	3.2	1.79
(4)	$[Cu(bzac)_2(BZL)_2]$	1592 s	1555 s	1633 m	I	5.0	1.78
(5)	$[Cu(bzac)_2(BZT)_2]$	1592 m	1558 m	1648 s	I	3.1	1.81
(9)	$[Cu(bzac)_2(ABZT)]$	1590 s	1533 s	1616 s	3300, 3200 m	18.1	1.76
^a v(C=O) (cyclic) of the pyrazolone ligar	nds, MP, ADM	PHP and DMI	PHP.			

Table 3. Important IR spectral bands (cm⁻¹), molar conductances, and magnetic moments of the synthesized complexes.

1070

Maurya, Verma, and Singh

The compounds so obtained were characterized by various physicochemical techniques, *viz.*, IR, electronic, ESR, TGA, magnetic and conductance measurements as described below in detail.

Conductance Measurements

The molar conductances of the synthesized complexes in 10^{-3} molar DMF solutions are in the range 3.12-18.1 ohm⁻¹ cm² mol⁻¹ (Table 3). These results are indicative of the non-electrolytic nature of these complexes. The non-zero molar conductances of these complexes are most probably due to the strong donor capacity of DMF which may lead to the displacement of bzac and change of electrolyte type.^[19]

Magnetic Measurements

Copper(II) has a d⁹ electronic configuration and its complexes contain one unpaired electron in the d-shell. The majority of complexes are formed by involvement of d-orbitals and they are square-planar or distortedoctahedral. The Jahn-Teller distortion contributes a major role in the distortion of the geometry of the complexes. The formation of tetrahedral complexes of Cu(II) without using d-orbital was also reported to be formed.^[20] When the Cu(II) complexes display magnetic moment values equivalent to one unpaired electron, the complexes are referred to as magnetically dilute. In such complexes the paramagnetic metal centers are situated apart and metal ions are surrounded by ligand molecules in such a way that unpaired spins to neighbouring metal ions remain unaffected. In case of tetrahedral or distorted-octahedral Cu(II) complexes the room temperature magnetic moment values are usually observed in the range of 1.8-2.2 B.M., and are not affected appreciably by the temperature and magnetic field. In case of square-planar dimeric or polynuclear species, the complexes display subnormal magnetic moments. In practice, compounds whose geometry approaches octahedral usually exhibit magnetic moments at the lower end of the range, while those approaching tetrahedral geometry are at the higher end. In the present investigation the Cu(II) complexes exhibit magnetic moments in the range 1.77-1.83 B.M. (Table 2). These data suggest octahedral geometry for these compounds.

Infrared Spectra

The important IR spectral bands and their tentative assignments are presented in Table 3. The IR spectra of the parent compound and the mixed-ligand complexes derived from it do not show characteristic band(s) due to lattice or coordinated water.

Maurya, Verma, and Singh

The significant absorption bands due to coordinated benzoylacetone are v(C=O) and v(C=C), and these have been observed in the regions 1588–1600 and 1533–1566 cm⁻¹, respectively, in all of the synthesized complexes. These results are comparable to the data reported elsewhere.^[8,9]

The ligands MP and DMPHP used in the present study contain three potential donor sites, 1) the ring carbonyl oxygen, 2) and 3) the ring N^1 and N^2 , while the ligand ADMPHP possesses four potential donor sites, 1) the cyclic carbonyl oxygen, 2) and 3) the ring N^1 and N^2 , and 4) the exocyclic amino nitrogen.

The ligand benzimidazole used in this study contains two potential donor sites, 1) the imidazole NH nitrogen and 2) the imidazole tertiary nitrogen. Benzothiazole has two potential donor sites, 1) the benzothiazole 'S' and 2) the benzothiazole 'N', whereas the 2-aminobenzothiazole possesses three potential donor sites, 1) and 2) are the same as in benthiazole, and 3) the amino nitrogen. However, considering the planarity of the latter ligand, ABZT, it is unlikely that this ligand could be tridentate on a single metal. Hence, this ligand is potentially bidentate: 1) the benzothiazole-N or -S, and 2) the amino nitrogen as the donor sites. For the sake of convenience the present discussion is divided in to three parts.

Complexes of MP, ADMPHP, and DMPHP

The coordination of the ring N^1 in the ligand MP is unlikely because of possible zwitterion formation^[21] due to the presence of cyclic amide and thereby reduction of electron density. The v(C=N²) band in the MP appearing at 1585 cm⁻¹ remains almost unchanged and merged with v(C=O) (carbonyl group of benzoylacetone) and thus suggests that the ring nitrogen N^2 is not taking part in coordination.

The coordination of N^1 and N^2 in ADMPHP and DMPHP is also unlikely because of possible zwitterion formation^[21] due to cyclic amide alone (plus the steric demand of the phenyl ring), and zwitterions formations due to the presence of conjugation only, respectively.

The v(N–H) bands of free ADMPHP observed at 3430 and 3320 cm⁻¹, respectively, are shifted to lower^[22] wave numbers and then appear as a broad band at 3300-3200 cm⁻¹. This indicates coordination of the amino nitrogen of ADMPHP to copper upon complex formation.

For carbonyl donors,^[23] a significant shift to lower wave numbers of v(C=O) takes place because of the coordination through carbonyl oxygen. A comparison of the IR spectra of MP, ADMPHP and DMPHP and their complexes shows that the v(C=O) bands observed at 1620, 1670 and 1665 cm⁻¹, respectively, in uncoordinated MP, ADMPHP and DMPHP, respectively, are shifted to lower wave numbers in the respective complexes (see

Table 3). This suggests the bonding of the cyclic carbonyl oxygen to copper(II) in the complexes (1)-(3).

BZL Complex

The v(N–H) band occurring at 3050 cm⁻¹ in benzimidazole remains unchanged in its complex. This suggests that the NH-nitrogen of the imidazole nucleus is not involved in coordination. However, the v(C=N) mode occurring at 1605 cm⁻¹ in benzimidazole, undergoes a shift to higher frequency in the complex (4) and then appears at 1633 cm⁻¹. This suggests coordination of the benzimidazole via the imidazole tertiary nitrogen.^[24,25]

Complexes of BZT and ABZT

It is found that the CSC band of BZT and ABZT appearing at \sim 720 cm⁻¹ is almost unchanged in the respective complexes, indicating that the thiazole-S is not involved in the bonding. However, the appearance of a band at 1616–1648 cm⁻¹ attributable v(C=N) plus v(C=C) vibrations,^[26] suggests the involvement of the thiazole nitrogen in the coordination to copper(II) in the complexes (**5**) and (**6**). The v_{as}(N–H) and v_s(N–H) bands of the amino group in free ABZT, observed at 3455 and 3220 cm⁻¹, respectively, are shifted to lower wave numbers and then appeared at 3300 and 3200 cm⁻¹ in the complex (**6**); this suggests coordination of the amino nitrogen to copper.

Electronic Spectra

The electronic spectra of two representative compounds, [Cu-(bzac)₂(ADMPHP)] (2) and [Cu(bzac)₂(BZT)₂ (5) (Figures 2 and 3), were recorded in 10^{-3} M DMF solutions. The electronic spectra of these complexes show two spectral peaks at 371-375 and 652-690 nm. The second broad peak at 652-690 nm ($\varepsilon = 59-94$ L M⁻¹ cm⁻¹) is most probably due to the ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$ transition, suggesting distorted-octahedral geometry for these complexes.^[27] The first spectral peak at 371-375 nm of relatively higher intensity ($\varepsilon = 1316-1426$ L M⁻¹ cm⁻¹) is due to the M \leftarrow L charge transfer transition.

Electron Paramagnetic Resonance Spectra

The room temperature X-band EPR spectra of two compounds, $[Cu(bzac)_2(ADMPHP)]$ (2) and $[Cu(bzac)_2(ABZT)]$ (6) (Figures 4 and 5), were recorded using powdered samples at the microwave frequency

Copyright @ 2003 by Marcel Dekker, Inc. All rights reserved





Figure 2. Electronic spectrum of [Cu(bzac)₂(ADMPHP)] (2).



Figure 3. Electronic spectrum of $[Cu(bzac)_2(BZT)_2]$ (5).



Figure 4. ESR spectrum of [Cu(bzac)₂₍ADMPHP)] (2).

9.46–9.47 GHz. The $g\perp$, $g\parallel$ and g_{av} values for these complexes were observed at 2.062/2.068, 2.196/2.178 and 2.106/2.105, respectively.

The fact that both parallel and perpendicular features of 63 Cu are resolved in the spectrum is characteristic of axial symmetry. Nuclear hyperfine coupling is observed in the g|| region with only one component clearly visible. It appears, therefore, that the second, third and fourth components are obscured by the g \perp component.^[28]



Figure 5. ESR spectrum of [Cu(bzac)₂(ABZT)] (6).

Marcel Dekker, Inc. 270 Madison Avenue, New York, New York 10016



The trend g|| (2.196/2.178) > g \perp (2.062/2.068) > g_e (2.0036, free spin value) observed in these two complexes shows that the unpaired electron is in the d_{x²} - y² orbital of Cu(II).^[29] The g|| and g \perp values in the complexes deviate considerably from the free-spin value, and are close to those reported for a number of distorted-octahedral Cu(II) complexes.^[29]



 $[Cu(bzac)_{2}(L)_{2}]$ L = MP (1), DMPHP (3), BZL (4) or BZT (5)

 $[Cu(bzac)_2(ADMPHP)]$ (2)



 $[Cu(bzac)_2(ABZT)]$ (6)



Thermogravimetric Analysis

The thermogravimetric curve of a representative compounds, complex (6), was recorded in the temperature range from ambient to 600 °C. An observation of this curve shows that there is no mass loss of the compound up to 170 °C. It does show a mass loss of 58.08% in the temperature range 180 to 228 °C corresponding to the loss of one molecule of benzoylacetone and one molecule of 2-aminobenzothiazole per molecule of the complex (calc. 58%). Further decomposition occurs in the temperature range 230–480 °C corresponding to the elimination of one molecule of benzoylacetone. The final residue was found to be CuO. Thus the thermogram of this compound corroborates some of the assumptions made on the basis of the infrared spectral studies (vide supra).

CONCLUSIONS

The satisfactory analytical data and the physical studies presented above suggest that the complexes are of the general formulas [Cu(bzac)₂(L)₂] (where L = MP, DMPHP, BZL or BZT), and [Cu(bzac)₂(L-L)] (where L-L = ADMPHP or ABZT). Keeping in view the normal magnetic moments of all the complexes, ESR results of [Cu(bzac)₂(ADMPHP)] and [Cu(bzac)₂(ABZT)] (involving bidentate ligands, and wherein a singlettriplet transition for a dimeric structure near half-field is absent in each spectrum), and the well established *cis*-octahedral structure^[30] of [Cu(hfa)₂ (py)₂] and [Cu(hfa)₂(bpy)] (hfaH = hexafluoroacetylacetone and bpy=bipyridine), it is reasonable to propose a similar structure for these complexes as shown in Figure 6. The inclusion of the bidentate ligands (ADMPHP or ABZT) spanning the *trans*-position of the monomeric octahedron, is very unlikely.

ACKNOWLEDGMENTS

We are thankful to Professor S. D. Tripathi, Vice-chancellor of this University, for encouragement, and Professor K. K. Mishra, Head, Department of Chemistry, for laboratory facilities and helpful discussion. Analytical facilities provided by the Central Drug Research Institute, Lucknow, India, and the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, India, are gratefully acknowledged. Thanks are also due to Referee I for constructive suggestions regarding structures of the complexes.

1077

Copyright @ 2003 by Marcel Dekker, Inc. All rights reserved

REFERENCES

- 1. Graddon, D.P. Divalent transition metal β -keto-enolate complexes as Lewis bases. Coord. Chem. Rev. **1969**, *4*, 1–28.
- Maurya, R.C.; Mishra, D.D.; Mukherjee, S.; Trivedi, P.K. Novel mixedligand derivatives of bis(acetylacetonato)-, bis(methylacetoacetato)- and bis(ethylacetoacetato)-nickel(II) with some potentially mono-, bi- and tridentate 2/3-pyrazoline-5-one. Transit. Met. Chem. 1991, 16, 524–527.
- Maurya, R.C.; Mishra, D.D.; Choubey, V.; Khan, I.B. Studies on some novel mixed-ligand derivatives of bis(acetylacetonato)-, bis(methylacetoacetato)- and bis(ethylacetoacetato)cobalt(II) with 8-hydroxyquinolinesulphonamides and pyrazolone. Synth. React. Inorg. Met.-Org. Chem. 1990, 20, 1103–1113.
- Joshi, K.C.; Pathak, V.K. Metal chelates of fluorinated 1,3-diketones and related compounds. Coord. Chem. Rev. 1977, 22, 37–122, and references therein.
- Maurya, R.C.; Mishra, D.D.; Trivedi, P.K.; Gupta, A. Synthesis, magnetic and spectral studies of some mixed-ligand chelates of mercury(II) with acetoacetanilide/o-hyroxyacetophenone and 2/3-pyrazoline-5-one derivatives. Synth. React. Inorg. Met.-Org. Chem. 1994, 24, 17–28.
- Mahapatra, B.B.; Mahapatra, B.K.; Guru, S. Base adducts of bis(chloroacetylacetonato)zinc(II) with nitrogen donors. J. Indian Chem. Soc. 1979, 56, 836–837.
- Mahapatra, B.B.; Pujari, S.K.; Chiranjeevi, A. Penta-coordinated base adducts of bis(chloroacetoacetylanilido)copper(II). J. Indian Chem. Soc. 1981, 58, 742–743.
- Mahapatra, B.B.; Panda, D. Base adducts of bis(chloroacetoacetanilido)zinc(II) and -copper(II) with heterocyclic amines. Indian J. Chem. 1983, 22A, 898–899.
- Maurya, R.C.; Mishra, D.D.; Wadhawan, D.M.; Trivedi, P.K. Synthesis, magnetic and spectral studies of some mixed-ligand derivatives of Co(II)-β-diketone and β-diketoesters with 2-pyrazoline-5-one and benzimidazole derivatives. Proc. Indian Natl. Sci. Acad. **1991**, *57A*, 631–637.
- Maurya, R.C.; Mishra, D.D.; Shrivastava, D.K.; Trivedi, P.K.; Khan, I.B. Studies on some novel mixed-ligand derivatives of Co(II), Ni(II) and Zn(II) chelates of oxygen donors with 2/3-pyrazoline-5-ones. Natl. Acad. Sci. Lett. **1991**, *14*, 379–382.
- 11. Maurya, R.C.; Mishra, D.D.; Trivedi, P.K.; Khan, I.B. Mixed-ligand chelates of Co(II) involving β -diketone or β -diketoesters along with some biologically active O- or N-donors. J. Inst. Chem. (India) **1991**, 63, 85–88.

Downloaded by [North Dakota State University] at 13:20 16 November 2014

- Maurya, R.C.; Trivedi, P.K.; Singh, H. Synthesis, magnetic and spectral studies of some mixed-ligand derivatives of bis(acetoacetanilido)-, bis(*o*-acetoacetanisidido)- and bis(*o*-acetoacetotoluidido)nickel(II) with some heterocyclic nitrogen donors involving benzimidazole nucleus. Natl. Acad. Sci. Lett. **1997**, 20, 148–151.
- Maurya, R.C.; Pillai, S.; Singh, T.; Shukla, B. Biochemically relevant complexes of copper: synthesis and characterization of some copper(II) heterochelates involving acetoacetanilide, anthanilic acid and heterocyclic nitrogen donors. Natl. Acad. Sci. Lett. **1998**, *21*, 70–75.
- Mahapatra, B.B.; Das, D.K. Mixed-ligand complexes of Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) with acetoacetanilide and isoquinoline. Indian J. Chem. **1987**, 26A, 173–174.
- Maurya, R.C.; Mishra, D.D.; Pillai, S. Studies on some mixed-ligand chelates of cobalt(II), involving acetoacetylarylamides and biologically active heterocyclic oxygen donor. Synth. React. Inorg. Met.-Org. Chem. 1997, 27, 1453–1466.
- Maurya, R.C.; Verma, R.; Trivedi, P.K.; Singh, H. Synthesis, magnetic and spectral studies of some mixed-ligand chelates of bis(2-hydroxyacetophenonato)copper(II) with 2- or 3-pyrazoline-5-one derivatives. Synth. React. Inorg. Met.-Org. Chem. **1998**, 28, 311–329.
- 17. Hon, P.; Pfluger, C.E.; Belford, R.L. The molecular and crystal structure of bis(1-phenyl-1,3-butanedionato)copper. Inorg. Chem. **1966**, *5*, 516–521.
- Vogel, A.I. A Text book of Quantitative Inorganic Analysis; E. L. B. S., Longman Green & Co. Ltd., 1962; 498.
- Geary, W.J. The use of conductivity measurements in organic solvents for the characterization of coordination compounds. Coord. Chem. Rev. 1971, 7, 81–122.
- Patel, K.S.; Woods, J.A.O. Synthesis and physico-chemical properties of bis(3-alkyl-2,4-pentanedionato)copper(II) complexes and their adducts with 2,2'-bipyridine and 1,10-phenanthroline. Synth. React. Inorg. Met.-Org. Chem. **1990**, 20, 909–922.
- 21. Maurya, R.C.; Singh, T.; Shukla, B.; Dubey, J. Metal cyanonitrosyl complexes: synthesis and characterization of some novel mixed-ligand cyanonitrosyl {CoNO}⁸ complexes of Co(I) with biologically active heterocyclic donors. Synth. React. Inorg. Met.-Org. Chem. **1997**, *27*, 1467–1482.
- Maurya, R.C.; Pillai, S.; Singh, T.; Singh, H.; Shukla, B. Biochemically relevant complexes of copper: synthesis, magnetic and spectral studies of some mixed-ligand chelates of bis(*o*-hydroxoacetophenonato)copper(II) with benzothiazole and related ligands. Synth. React. Inorg. Met.-Org. Chem. **1998**, 28, 1053–1064.
- 23. Maurya, R.C.; Mishra, D.D. Synthesis and characterization of some

novel hexa-coordinated mixed-ligand cyanonitrosyl $\{CrNO\}^5$ complexes of chromium with some potentially mono- and bidentate-5-pyrazolone derivatives. Synth. React. Inorg. Met.-Org. Chem. **1989**, *19*, 533–544.

- 24. Gosh, S.P.; Bhattacharjee, P.; Dubey, L.; Mishra, L. Complexes of some platinum metals with imidazole and benzimidazole. Indian J. Chem. **1977**, *54*, 230–238.
- 25. Maurya, R.C.; Mishra, D.D. Synthesis and characterization of chromium(I) cyanonitrosyl hetero complexes with benzimidazole and related ligands. Indian J. Chem. **1991**, *30*, 551–553.
- Lane, T.J.; Nakagawa, I.; Walter, J.L.; Kandathil, A.J. Infrared investigation of certain imidazole derivatives and their metal chelates. Inorg. Chem. 1962, 1, 267–276.
- Nigam, S.; Patel, M.M.; Ray, A. Normal coordinate analysis and CNDO/II calculations of diacetyl monoxime. Its semicarbazone and thiosemicarbazone derivatives: synthesis and characterization of their metal chelates. Synth. React. Inorg. Met.-Org. Chem. 1989, 19, 533– 544.
- 28. Garcio-Lozano, J.; Martinez, M.A.; Escriva, E.; Ballestero, R. Synthesis and spectroscopic characterization of bis-complexes of cobalt(II), nickel(II) and copper(II) with N,N,N',N'-tetraethylpyridinecarboxamide. Synth. React. Inorg. Met.-Org. Chem. **1994**, *24*, 365–376.
- 29. Neiman, R.; Kivelson, D. ESR studies on the bonding in copper complexes. J. Chem. Phys. **1961**, *35*, 149–154.
- Izumi, F.; Kurosawa, R.; Kawamoto, H.; Akaiwa, H. Adducts of bis(hexafluoroacetyacetonato)metal(II) with uni- and bidentate nitrogenous bases. Bull. Chem. Soc. Jpn. 1975, 48, 3188–3192.

Received May 14, 1998 Accepted March 6, 2003 Referee I: R. P. Hotz Referee II: K. Moedritzer