SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 33, No. 8, pp. 1307–1318, 2003

Complexes of Copper(II) with 2,3-Dimethyl-4formyl(benzhydrazide)-1-phenyl-3pyrazolin-5-one

K. C. Raju and P. K. Radhakrishnan*

School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India

ABSTRACT

Copper(II) complexes of the Schiff base 2,3-dimethyl-4-formyl-(benzhydrazide)-1-phenyl-3-pyrazolin-5-one (L) of the general formula $[Cu(L)_2]X_2$ (X = ClO₄ or NO₃), $[Cu(L)Cl_2]$ and $[Cu(L)_2Br_2]$ have been synthesized and characterized by elemental analyses, electrical conductance in non-aqueous solvents, infrared, electronic and EPR spectra, as well as magnetic susceptibility measurements. In these complexes, the ligand acts as a neutral bidentate unit coordinating through the azomethine nitrogen atom and the carbonyl oxygen of the pyrazolone ring. In the perchlorate and nitrate complexes both anions remain ionic, while in the corresponding halide complexes both anions are coordinated to the metal ion. The perchlorate, nitrate and chloride complexes are of square-planar geometry while the bromide complex is of distorted octahedral geometry.

1307

DOI: 10.1081/SIM-120024311 Copyright © 2003 by Marcel Dekker, Inc. 0094-5714 (Print); 1532-2440 (Online) www.dekker.com

^{*}Correspondence: P. K. Radhakrishnan, School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, Kerala, India; E-mail: mgu@vsnl.com.

INTRODUCTION

The interesting and varied ligand behavior of hydrazines and hydrazones towards transition metal ions is well known.^[1] The pharmacological application of antipyrine-based ligands and their metal complexes have been extensively studied.^[2–4] As an extension of our studies on metal complexes with antipyrine derivatives,^[5–10] we report here the synthesis and structural investigation on copper(II) complexes of a new pyrazolone-hydrazide Schiff base ligand 2,3-dimethyl-4-formyl(benzhydride)-1-phenyl-3-pyrozolin-5-one (L). (Figure 1).

RESULTS AND DISCUSSION

The formation of the complexes can be represented by the general equation shown below:

$$CuCl_2+L \rightarrow Cu(L)Cl_2$$
 and CuX_2+2L
$$\rightarrow Cu(L)_2X_2 \ (X=ClO_4,NO_3 \ or \ Br)$$

All the complexes are light-yellow in color except the bromide complex which is brown. They are non-hygroscopic solids soluble in DMF, ethanol, methanol and nitrobenzene, but insoluble in benzene, chloroform, ethyl acetate and toluene. The analytical data (Table 1) indicate that the complexes have the general formulae $Cu(L)_2X_2$ (X = ClO₄, NO₃ or Br) and Cu(L)Cl₂.

The molar conductance values of the complexes (Table 2) in DMF, methanol and nitrobenzene (10^{-3} M solutions) are in the range expected for 1:2 electrolytes for perchlorate and nitrate complexes, while the corresponding chloride and bromide complexes behave as non-electrolytes.^[11]



Figure 1. 2,3-Dimethyl-4-formyl(benzhydrazide)-1-phenyl-3-pyrazolin-5-one (L).

	L	able I. Ana	lytical data ⁵	a of copper(II) complex	es of L.			
Complex	Molecular formula	Formula weight	Metal (%)	Anion (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Yield (%)	M.p. (°C)
L	$C_{19}H_{18}N_4O_2$	334.39	I	I	67.98 (68.25)	5.58 (5.43)	16.64 (16.76)	85	198
$[Cu(L)_2](ClO_4)_2$	$C_{38}H_{36}Cl_2CuN_8O_{12}$	931.22	6.79 (6.82)	21.42	48.98	(3.90)	11.94	92	223
$[Cu(L)_2](NO_3)_2$	$C_{38}H_{36}CuN_{10}O_{10}$	856.33	7.32		53.20 53.20	4.19 (4.24)	16.28 16.36)	88	201
$[Cu(L)Cl_2]$	$C_{19}H_{18}Cl_2CuN_4O_2$	468.84	13.48 13.48 (13.55)	15.08	48.67) (48.67)	(3.87) (3.87)	(11.95)	89	258
$[Cu(L)_2Br_2]$	$\mathrm{C}_{38}\mathrm{H}_{36}\mathrm{Br}_{2}\mathrm{CuN}_{8}\mathrm{O}_{4}$	892.14	7.01 (7.12)	(51.16)	51.08 (51.16)	4.01 (4.07)	12.48 (12.56)	84	218
^a Calculated values	in narentheses								



Molar conductance Complex DMF Methanol Nitrobenzene $[Cu(L)_2](ClO_4)_2$ 164.70 203.13 55.99 $[Cu(L)_{2}](NO_{3})_{2}$ 148.23 192.15 50.51 $[Cu(L)Cl_2]$ 38.43 8.78 43.92 $[Cu(L)_2Br_2]$ 45.01 49.41 10.98

Table 2. Molar conductance data^a of the copper(II) complexes of L (in ohm^{-1} cm² mol⁻¹).

^a10⁻³ M solutions used.

Thus, the complexes may be formulated as $[Cu(L)_2X_2]$ (X = ClO₄ or NO₃), $[Cu(L)Cl_2]$ and $[Cu(L)_2Br_2]$.

Infrared Spectra

The important infrared spectral data of the ligand and its complexes are presented in Table 3. The infrared spectral bands at 1674 and 1630 cm⁻¹ are characteristic of v(C=O) of the pyrazolone ring and the benzoyl moiety respectively.^[8] In all reported complexes, the band at 1674 cm⁻¹ is shifted to the region 1642–1654 cm⁻¹ indicating that the carbonyl oxygen is involved in coordination.^[8] The band corresponding to v(C=O) of the

Table 3. Important IR spectral bands (cm^{-1}) of L and its copper complexes.

L	$\begin{array}{c} [Cu(L)_2] \text{-} \\ (ClO_4)_2 \end{array}$	[Cu(L) ₂]- (NO ₃) ₂	[Cu(L)Cl ₂]	[Cu(L) ₂ Br ₂]	Assignment
1674 s	1654 s	1652 s	1642 s	1653 s	v(C=O) ring
1630 s	1630 s	1629 s	1629 s	1632 s	v(C=O)
1571 s	1551 s	1558 s	1560 s	1560 s	v(C=N)
998 w	1008 w	1008 w	1010 w	1007 w	v(N-N)
_	1986 s	-	-	_	v ₃ -ionic ClO ₂
_	623 m	_	-	-	v ₄ -ionic ClO ₄
_	_	1378 s	-	_	v ₃ -ionic NO ₃
_	_	821 m	-	_	v ₂ -ionic NO ₃
_	_	_	310 m	-	v(Cu-Cl)
_	_	_	-	292 m	v(Cu-Br)
_	458 w	459 w	458 w	460 w	v(Cu-N)
_	552 w	550 w	550 w	555 w	v(Cu-O)

s = strong, m = medium, w = weak.

benzoyl moiety remains practically unaltered in all of these complexes at about 1630 cm⁻¹, indicating the non-coordination of benzoyl carbonyl in these complexes.^[12] The strong band observed at 1571 cm⁻¹ in the ligand, attributed to the C=N stretching vibration, is shifted to 1551–1560 cm⁻¹, indicating coordination of the azomethine nitrogen in the complexes.^[8] The v(N–N) band at 998 cm⁻¹ in the ligand spectrum is shifted to higher frequency (1007–1010 cm⁻¹) in the complexes, which further supports the bonding through the azomethine nitrogen.^[13]

In the perchlorate complex, the band observed at 1086 cm⁻¹ is assigned to the v_3 vibration of uncoordinated perchlorate ion of T_d symmetry.^[14] This is supported by the presence of a medium intensity band at 623 cm⁻¹ due to v_4 vibration of perchlorate ion of T_d symmetry.^[14]

In the nitrate complex, a strong band at 1378 cm⁻¹ and a medium intensity band at 821 cm⁻¹ are attributed v_3 and v_2 vibration of uncoordinated nitrate ion of D_{3h} symmetry.^[15]

In the far-infrared spectrum of the chloride and bromide complexes the Cu-Cl and Cu-Br, stretching vibrations occur at 310 and 292 cm⁻¹, respectively, that are not present in the ligand spectrum.

The above observations, along with the conductance data, confirm that perchlorate and nitrate ions remain ionic in these complexes while chloride and bromide ions are coordinated to the metal ion. Further, v(Cu-N) and v(Cu-O) stretching vibrations are observed at about 460 and 550 cm⁻¹, respectively, in all these complexes.

Electronic Spectra

The electronic spectral data of the ligand and complexes in the solid state (using Nujol) with their tentative assignments are given in Table 4. In the complexes both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands were found to be red-shifted to the regions 22,123–22,471 and 39,682–40,816 cm⁻¹, respectively, compared to the ligand. The band observed in the region 13,477–13,820 cm⁻¹ is attributed to $2B_{1g}\rightarrow 2A_{1g}$ transitions consistent with a square-planar geometry^[16] around the copper(II) ion in all the complexes except in the bromide complex. In the bromide complex, the broad band at 19,608 cm⁻¹ indicates tetragonal configuration around copper(II) ions.^[17,18] The electronic spectra of all the complexes exhibit an intense absorption band in the region 33,222–33,444 cm⁻¹ which might be due to a charge transfer process.

Magnetic Moment Data

The molar magnetic moments of copper(II) complexes vary in the range 1.61 to 2.01 B.M. This clearly indicates that the complexes, except

Complex	Abs.max. (cm ⁻¹)	Tentative assignment	μ_{eff} (B.M.)
L	23,866	$n \rightarrow \pi^*$	
	41.153	$\pi \! ightarrow \! \pi^*$	
$[Cu(L)_2](ClO_4)_2$	22,123	$n \! \rightarrow \! \pi^*$	2.01
	40,485	$\pi \! ightarrow \! \pi^*$	
	33,444	Charge transfer	
	13,477	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$	
$[Cu(L)_2](NO_3)_2$	22,371	$n \rightarrow \pi^*$	1.95
	40,485	$\pi \! ightarrow \! \pi^*$	
	33,333	Charge transfer	
	13,386	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$	
$[Cu(L)Cl_2]$	22,471	$n \rightarrow \pi^*$	1.61
	40,816	$\pi \! ightarrow \! \pi^*$	
	33,333	Charge transfer	
	13,820	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$	
$[Cu(L)_2Br_2]$	22,172	$n \rightarrow \pi^*$	1.68
	39,682	$\pi ightarrow \pi^*$	
	33,222	Charge transfer	
	19,608	d-d transition	

Table 4. Electronic spectral data (in Nujol) and magnetic moments of the copper(II) complexes of L.

the chloride complex, are monomeric and any metal-metal interaction is absent in these complexes.^[17] The magnetic moment of the chloride complex is slightly lower than that expected which may be due to metal-metal interaction.^[19]

EPR Spectra

The X-band EPR spectra of the copper(II) complexes were recorded in 1:1 methanol-toluene mixture at liquid nitrogen temperature using DPPH free radical as the 'g' marker (Figure 2). All the complexes have a well-resolved g_{\parallel} and a broadened g_{\perp} region. In all the spectra, no superhyperfine splitting from the ligand part is observed.

The various spin Hamiltonian parameters computed are presented in Table 5. The trend $g_{\parallel} > g_{\perp} > 2.0023$ indicates that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital.^[20] The covalency parameter α^2 is calculated using the Kivelson and Neiman equation.^[21]

$$\alpha_{Cu}^2 \;=\; -(A_{\parallel}/0.036) + (g_{\parallel}-2.002) + \frac{3}{7}(g_{\perp}-2.002) + 0.04$$



Figure 2. EPR spectra of the complexes. $A = [Cu(L)_2](ClO_4)_2$, $B = [Cu(L)_2](NO_3)_2$, $C = [Cu(L)Cl_2]$, $D = [Cu(L)_2Br_2]$.

In the present case, α^2 is in the range 0.74 to 0.76 indicating the fairly covalent nature in the metal-ligand bonding.^[17] Furthermore, the shape of the EPR spectra indicates that the geometry around the copper(II) ion is square planar in the perchlorate, nitrate and chloride complexes with an elongated octahedron in the bromide complex as is evident from the less intense low-field side and high-intense high-field side.^[17]

Based on the results of the present study, the structure shown in Figure 3 may be assigned to these complexes.

Table 5. EPR bonding parameters of the copper(II) complexes of L at liquid nitrogen temperature.

Complex	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	$g_{\rm av}$	α^2
$[Cu(L)_2](ClO_4)_2$	2.30	2.05	140.00	86.66	2.13	0.75
$[Cu(L)_2](NO_3)_2$	2.30	2.06	140.00	86.66	2.14	0.75
$[Cu(L)Cl_2]$	2.31	2.07	140.00	83.33	2.15	0.76
$[Cu(L)_2Br_2]$	2.31	2.07	135.00	80.00	2.15	0.75

EXPERIMENTAL

The metal salts, Cu(ClO₄)₂·6H₂O, Cu(NO₃)₂·6H₂O, CuCl₂·2H₂O, and CuBr₂·4H₂O, were prepared from Analar BDH copper carbonate and the respective 50% acids and crystallized out by evaporating the solution on a steam bath. For example, CuCl₂·2H₂O was prepared as follows. Copper carbonate was dissolved in hot 50% hydrochloric acid. A slight excess of metal carbonate was used. The undissolved carbonate was removed by filtration. The filtrate was concentrated by evaporation when green crystals of CuCl₂·2H₂O separated.

Preparation of the Ligand

The ligand 2,3-dimethyl-4-formyl(benzhydrazide)-1-phenyl-3-pyrazolin-5-one (L) was prepared and characterized as reported earlier.^[8]

Preparation of the Complexes

Perchlorate Complex

A quantity of 0.371 g (1 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in ethyl acetate (10 mL) was added to a boiling suspension of 0.736 g (2.2 mmol) of the ligand in ethyl acetate (100 mL). The resulting solution was refluxed for about 4 h on a boiling steam bath. The complex precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was dried under vacuum over phosphorus(V) oxide.

Nitrate and Chloride Complex

A quantity of 0.256 g (1 mmol) of $Cu(NO_3)_2 \cdot 6H_2O$ or 0.170 g (1 mmol) of $CuCl_2 \cdot 2H_2O$ in acetone (10 mL) was added to a boiling suspension of 0.736 g (2.2 mol) of the ligand for $Cu(NO_3)_2 \cdot 6H_2O$ or 0.401 g (1.2 mmol) of the ligand for $CuCl_2 \cdot 2H_2O$ in acetone (100 mL). The mixture was refluxed for about 4 h on a steam bath. The precipitated complex was cooled, filtered and washed several times with hot benzene to remove the excess ligand. It was dried under vacuum over phosphorus(V) oxide.

Bromide Complex

A quantity of 0.295 g (1 mmol) of $CuBr_2 \cdot 4H_2O$ in acetonitrile (10 mL) was added to a boiling solution of 0.736 g (2.2 mmol) of the ligand in acetonitrile (100 mL). The solution was refluxed for about 3 h on a steam



C₆H₅ =0 C₆H₅ -H N Η CH₃ H₃C ₿r Cu br CH₃ H_3C N | C₆H₅ Η -H Ν **=**O Ċ₆H₅



Figure 3. $[Cu(L)_2]X_2$ (X = ClO₄ or NO₃), $[Cu(L)_2Br_2]$ and $[Cu(L)Cl_2]$.

bath. The complex precipitated on cooling was filtered and washed several times with hot benzene to remove the excess ligand. It was dried under vacuum over phosphorus(V) oxide.

Analyses and Physical Methods

All the complexes were analysed for metal and halide contents by the standard methods^[22] and the perchlorate content by the Kurz method.^[23] The molar conductances of the complexes in DMF, methanol and nitrobenzene (10^{-3} M) solutions were measured at room temperature using a Toshniwal conductivity bridge with a dip-type conductance cell (cell constant = 1.094). The infrared spectra of the ligand and complexes were recorded in the range 4000–400 cm⁻¹ on a Shimadzu IR-470 spectrophotometer. Electronic spectra of the ligand and complexes were measured in the solid state (paste with Nujol) on a Shimadzu UV 160A spectrophotometer in the range 1,100–200 nm. The EPR spectra of the complexes were recorded in methanol-toluene (1:1) at liquid nitrogen temperature using a Varian E-112 EPR spectrophotometer. DPPH free radical was the 'g' marker. C, H, and N analyses were carried out using a Heraeus CHNO rapid analyzer. Magnetic susceptibility measurements were done at room temperature by the Guoy method using mercury(II)tetrathiocyanatocobaltate(II) as the calibrant.

ACKNOWLEDGMENTS

We thank the Heads of the Regional Sophisticated Instrumentation Centers at the Indian Institute of Technology, Chennai, and the Indian Institute of Technology, Mumbai, for some instrumental analyses. We also thank the Mahatma Gandhi University, Kottayam, for providing laboratory facilities and the University Grants Commission for awarding a Teacher Fellowship to one of us (KCR) under the faculty improvement program. Also, we wish to express our heartfelt thanks to Dr. Siby Joseph and Dr. N.T. Madhu for some fruitful discussions.

REFERENCES

- 1. Pelizzi, E.; Pelizzi, G.; Predieri, G.; Resolva, S. Investigation into aroyl hydrazones as chelating agents. J. Chem. Soc. Dalton Trans. **1982**, 1349.
- 2. Singh, L.; Mohan, G.; Parashar, R.K.; Tripathi, S.P.; Sharma, R.C. Studies on antiinflammatory activity of some lanthanone complexes of bioactive organic molecules. Curr. Sci. **1986**, *55*, 846–848.

- Alice, C.J.; Prabhakaran, C.P. Synthesis and characterization and biological studies of Pd(II) complexes of some ON and NS donors. Ind. J. Chem. 1990, 29A, 491–493.
- Alaudeen, M.; Abraham, A.; Radhakrishnan, P.K. Synthesis and antibacterial activity of rare-earth-perchlorate complexes of 4-2¹hydroxynaphthylazo)antipyrine. Proc. Ind. Acad. Sci. (Chem. Sci.) 1995, 107, 123–126.
- Joseph, S.; Radhakrishnan, P.K. Yttrium and lanthanide perchlorate complexes of N,N¹-bis(4-antipyrylmethylidene)ethylenediamine. Synth. React. Inorg. Met.-Org. Chem. **1998**, 28 (3), 423–435.
- Madhu, N.T.; Radhakrishnan, P.K. Copper(II) complexes of 1,2-di(imino-4¹-antipyrinyl)ethane and 4-N-(4¹-antipyrylmethylidene)aminoantipyrine. Synth. React. Inorg. Met.-Org. Chem. 2001, 31 (2), 315–330.
- Madhu, N.T.; Radhakrishnan, P.K. Cobalt(II) complexes of 1,2-Di-(imino-4¹-antipyrinyl)ethane and 4-N-(4¹-antipyrylmethylidene) aminoantipyrine. Transition Met. Chem. 2000, 25, 287–292.
- Ajithkumar, G.; Radhakrishnan, P.K. Yttrium and lanthanide nitrate complexes of 2,3-dimethyl-4-formyl(benzhydrazide)-1-phenyl-3-pyrazolin-5-one. Synth. React. Inorg. Met.-Org. Chem. 2002, 32 (4), 831–842.
- Raju, K.C.; Radhakrishnan, P.K. Complexes of copper(II) with N,N¹-bis (4-antipyrylmethylidene)ethylenediamine. Synth. React. Inorg. Met.-Org. Chem. 2002, 32 (6), 1117–1128.
- Raju, K.C.; Radhakrishnan, P.K. Complexes of cobalt(II) with N,N¹-bis (4-antipyrylmethylidene)ethylenediamine. Synth. React. Inorg. Met.-Org. Chem. **2002**, *32* (10), 1719–1728.
- Geary, W.J. The use of conductivity measurements in organic solvents for the characterization of coordination compounds. Coord. Chem. Rev. 1971, 7, 81–115.
- Kumar, P.A. Synthesis and spectral studies of some seven-coordinated rare earth metal complexes. Synth. React. Inorg. Met.-Org. Chem. 1997, 27 (4), 577–588.
- Singh, B.; Narang, K.K. Rachana srivastava. Studies on complexes of cobalt(II), nickel(II), copper(II) and cadmium(II) with acetophenone oxalolyldihydrazones. Synth. React. Inorg. Met.-Org. Chem. 2001, 31 (8), 1387–1401.
- 14. Scholer, R.P.; Merbach, A.E. Raman and infrared study of hexamethylphosphoramide complexes of lanthanide perchlorates. Inorg. Chim. Acta **1975**, *15*, 15–20.
- Gatehouse, B.M.; Livingstone, S.E.; Nyholm, R.S. Infrared spectra of some nitrato and other oxyanion coordination complexes. J. Inorg. Nucl. Chem. 1958, 8, 75–78.
- 16. Nawar, N.; Khattab, M.A.; Hosny, N.M. Some metal(II) complexes of

Raju and Radhakrishnan

O-aminoacetophenonebenzoylhydrazone. Their preparation, characterization and antimicrobial activity. Synth. React. Inorg. Met.-Org. Chem. **1990**, *29* (8), 1365–1384.

- Shetty, S.N.; Murthy, A.S.R.; Timbe, G.L. Synthesis and spectral characterization of copper(II) complexes of dithiosemicarbazone. Ind. J. Chem. 1993, 32A, 3180322.
- 18. Dey, K.; Nandi, K.K. Transition and non-transition metal complexes with 1-formylferrocene-4-methoxybenzoyl hydrazone and 1-acetylferrocene-4-methoxybenzoylhydrazone. Synth. React. Inorg. Met.-Org. Chem. **1999**, *29* (3), 419.
- Dey, K.; Bandyopadhyay, D. Synthesis and characterization of complexes of nickel(II), cobalt(II) and cobalt(III) with morpholine Nthiohydrazones formed from salicylaldehyde and 2-hydroxyacetophenone. Ind. J. Chem. 1992, 31A, 34–38.
- Singh, B.; Yadav, B.P.; Aggarwal, R.C. Synthesis and characterization of 1-phenyl-5-benzol-4-thiobiuret complexes with oxovanadium(IV), cobalt(II) and (III), nickel(II), copper(II), cadmium(II) and mercury(II). Ind. J. Chem. **1984**, 23A, 441–444.
- 21. Kivelson, D.; Neiman, R. ESR studies on the bonding in copper complexes. J. Chem. Phys. **1961**, *35* (1), 149–155.
- 22. Bassett, J.; Denny, R.C.; Jeffrey, G.H.; Mendhen, J. Titrametric analysis. In *Vogel's Text Book of Quantitative Inorganic Analysis*, 5th Ed.; ELBS: London, 1961; 341–379.
- 23. Kurz, E.; Kober, G.; Berl, M. Determination of perchlorates by fusion with nitrite. Anal. Chem. **1958**, *30* (12), 1983–1986.

Received August 16, 2002 Accepted April 17, 2003 Referee I: M. Bayachou Referee II: J. Protasiewicz

Marcel Dekker, Inc.

270 Madison Avenue, New York, New York 10016

Copyright © 2003 EBSCO Publishing

Copyright of Synthesis & Reactivity in Inorganic & Metal-Organic Chemistry is the property of Marcel Dekker Inc. and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.