766 **RESEARCH PAPER** DECEMBER, 766–768 JOURNAL OF CHEMICAL RESEARCH 2006

Complexes of zinc(II) with 1,2-disubstituted benzimidazoles

Ganganaika Krishnamurthy and Narasimhaiah Shashikala*

Department of Studies in Chemistry, Bangalore University, Central College Campus, Bangalore 560 001, India

The reactions of hydrated halides and perchlorate of divalent zinc with 1-*o*-hydroxybenzyl-2-*o*-hydroxyphenylbenzimidazole (L^1), 1-*m*-hydroxybenzyl-2-*m*-hydroxyphenylbenzimidazole (L^2),1-*p*-hydroxybenzyl-2-*p*-hydroxyphenylbenzimidazole (L^3) and 1-*o*-chlorobenzyl-2-*o*-chlorophenylbenzimidazole (L^4) ligands in 1:2 and 1:3 molar ratios in absolute ethanol/acetone at refluxing temperature produced white/pale yellow complexes of the formula $ZnX_2L_n.yH_2O$ [$L = L^1$, X = Cl, $n = 2$, $y = 1$; X = Br, $n = 2$, $y = 0$; X = I, $n = 3$, $y = 1$; X = ClO_4, n = 2, $y = 0$; $L = L^2$, X = Cl, Br, $n = 2$, $y = 1$, X = ClO_4, $n = 2$, $y = 2$; $L = L^3$, X = Cl, n = 2, $y = 0$; X = Br, I, $n = 3$, $y = 2$; X = ClO_4, $n = 2$, $y = 1$; $L = L^4$, X = Cl, $n = 3$, $y = 2$; X = Br, $n = 3$, $y = 5$; X = ClO_4, $n = 2$, $y = 0$]. The complexes are characterised by elemental analysis, conductivity, thermal analysis, IR, ^1H and ^{13}C NMR spectral studies.

Keywords: zinc complexes, 1,2-disubstituted benzimidazoles

Zinc is one the most important metals in the biological system. It is involved in the function of enzymes such as carboxypeptidase-A and carbonic anhydrase.[1] In the case of carboxypeptidase-A, zinc is coordinated nearly tetrahedrally to two histidine N-atoms, the carboxyl oxygen of a glutamate residue and a water molecule; the water molecule can be replaced by a donor atom. Thus, the coordination chemistry of zinc is of considerable importance. The complexes of zinc(II) are white/pale-yellow and diamagnetic, having the d^{10} electronic configuration. Zinc(II) salts form a variety of complexes with bisbenzimidazoles and 2-substituted benzimidazole derivatives.[2] Herein, we report the synthesis and characterisation of a number of new halo- and perchlorate-complexes of zinc(II) with 1,2-disubstituted benzimidazole derivatives, L^1 through L^4.

Experimental

Reagents

The hydrated zinc(II) chloride was used as supplied (BDH). *o*-Phenylenediamine, salicylaldehyde, *m*-hydroxybenzaldehyde, *p*-hydroxybenzaldehyde and *o*-chlorobenzaldehyde were Merck/SD's fine chemicals. The solvents used were Merck chemicals and they were purified according to literature methods.[3] Hydrated zinc(II) bromide, zinc(II) iodide and zinc(II) perchlorate salts were obtained by dissolving zinc carbonate in 1:1 hot aqueous hydrobromic, hydroiodic and perchloric acids respectively, followed by filtration and careful evaporation nearly to dryness under reduced pressure.

Measurements

C, H and N analyses were carried out on a Carlo Erba analyser. IR spectra (in nujol) were recorded on a Nicolet 4000D spectrophotometer. Molar conductivity measurements were made with 10^{-3} M solution in dimethylformamide (DMF) using a digital (SYSTRONICS) conductivity metre-304 with a conventional dip type conductivity cell with a cell constant 1.00 cm^{-1}. NMR spectra were recorded (in DMSO-d_6) on Bruker WH-270 or AMX-400 MHz spectrometers using TMS as the internal standard. Thermograms were recorded on a Shimadzu Thermal Analyser DT30 at a heating rate of 5°C/min.

Preparation of the ligands

The ligands were prepared according to the literature method.[4] A mixture of salicylaldehyde and o-phenylenediamine in the molar ratio of 2:1 in benzene was refluxed on a water bath for about an hour. The solution was cooled and kept overnight. After the evaporation of the solvent, a yellow crystalline solid separated. It was filtered to give 1-*o*-hydroxybenzyl-2-*o*-hydroxyphenyl benzimidazole (L^1). Similar reactions of *m*-/*p*-hydroxybenzaldehyde, *o*-chloro benzaldehyde and o-phenylenediamine taken in 2:1 mole ratio in benzene were carried out by refluxing the solutions for one hour, then keeping the reaction mixture overnight. The resulting precipitates were filtered to obtain a pale-yellow, 1-*m*-hydroxybenzyl-2-*m*-hydroxyphenylbenzimidazole (L^2), buff, 1-*p*-hydroxybenzyl-2-*p*-hydroxyphenylbenzimidazole (L^3) and pale-yellow, 1-*o*-chlorobenzyl-2-*o*-chlorophenylbenzimidazole (L^4) respectively.

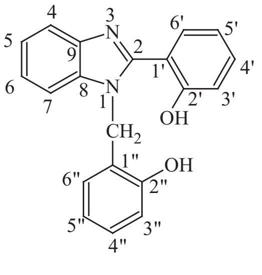
Preparation of the complexes

$[ZnX_2L_n].yH_2O$ ($L = L^1$, X = Cl, $n = 2$, $y = 1$; X = Br, $n = 2$, $y = 0$; X = I, $n = 3$, $y = 2$; $L = L^2$, X = Cl, $n = 2$, $y = 1$; X = Br, $n = 2$, $y = 2$; $L = L^3$, X = Cl, $n = 2$, $y = 0$; X = Br, $n = 3$, $y = 3$; X = I, $n = 3$, $y = 2$; $L = L^4$, X = Cl, $n = 3$, $y = 3$; X = Br, $n = 3$, $y = 5$).

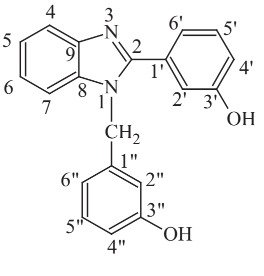
To a solution of zinc(II) halide (1 mmol) in ethanol-triethylorthoformate/acetone (1:19, 20 ml), the ligand (2 or 3 mmol) in ethanol/acetone (20 ml) was added and the mixture was refluxed for 6–8 hours, during which time a white or pale yellow solid separated. This was filtered, washed with ethanol/acetone (20 ml) and dried in a vacuum (yield 80%).

$[Zn(OClO_3)_2L_2]\ nH_2O$ ($L = L^1, L^4, n = 0; L = L^2, L^3, n = 1$)

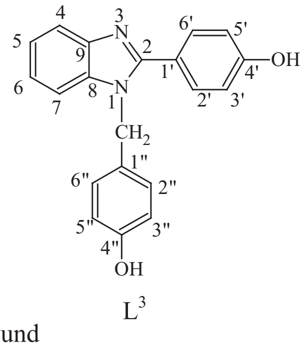
Zinc(II) perchlorate (1 mmol) was dissolved in triethylformate–ethanol/acetone(1:19, 20 ml), then the ligand (2 mmol) in ethanol/acetone (20 ml) was added. The resulting mixture was refluxed for 6 h when a yellow, buff or pale yellow coloured solid separated.



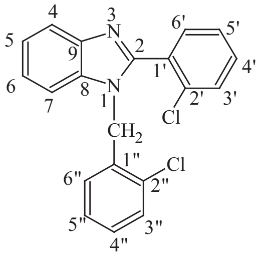
L^1



L^2



L^3



L^4

Compound

L^1	1-*o*-hydroxybenzyl-2-*o*-hydroxyphenylbenzimidazole
L^2	1-*m*-hydroxybenzyl-2-*m*-hydroxyphenylbenzimidazole
L^3	1-*p*-hydroxybenzyl-2-*p*-hydroxyphenylbenzimidazole
L^4	1-*o*-chlorobenzyl-2-*o*-chlorophenylbenzimidazole

---

* Correspondent. E-mail: ns_slg107@yahoo.co.in

The solid was filtered, washed with ethanol/acetone (20 ml) and dried in a vacuum (yield 60–80%).

Results and discussion

The physical and analytical data of the complexes are compiled in Table 1. The complexes are soluble in common organic solvents and are non-electrolytes in DMF except the iodo-complex of L^1, which exhibits 1:1 electrolytic behaviour in DMF as evidenced by its conductivity data. The bromo-complex of L^4 behaves as a 1:2 electrolyte in DMF. All the other complexes show low conductivity in DMF. This may arise from the replacement of the halide by DMF in solution and the existence of an equilibrium of the type below.[5]

$$ZnX_2L_n + DMF \leftrightarrow [ZnX(DMF)L_n]^+ + X^- \leftrightarrow [Zn(DMF)_2L_n]^{2+} + 2X^-$$

The IR spectra (in nujol mull) of the substituted benzimidazole complexes containing substituted benzimidazoles are similar to the spectra of the uncoordinated pro-ligands except for minor shifts in the positions of some of the bands and some changes in their intensities due to coordination.. In the case of L^1, the band due to νOH of the ligand, expected around 3100–3200 cm^{-1}, is absent due to intramolecular hydrogen bonding. However, it appears in the spectra of its complexes. The νOH of lattice water in the chloro- and iodo-complexes of L^1 occurs at 3412 and 3477 cm^{-1} respectively and νOH of the ligand is observed at 3183 and 3198 cm^{-1} respectively. In the case of L^2 complexes, the bands in the range 3170–3190 cm^{-1} and 3330–3370 cm^{-1} are due to the νOH of the ligand and lattice water molecules respectively. A broad band in the range 3170–3190 cm^{-1} in the complexes of L^3 is due to the OH stretching vibration.[6] The νOH of lattice water molecules in the bromo-, iodo- and perchlorate-complexes of L^3 are found in the range 3440–3359 cm^{-1}. In the case of $[Zn(L^4)_3(OH_2)_2]Br_2.2H_2O$, the peak due to hydroxyl stretching of the coordinated water is centreed around 3250 cm^{-1}, while that due to lattice water occurs in the range 3460–3550 cm^{-1}.[7-9] The νC=N and νC =C vibrations are very close to each other and occur around 1610 cm^{-1} as weak bands in the spectra of uncoordinated heterocycles and have been observed to shift to lower wavenumbers by about 5–10 cm^{-1} on complexation. The shift in the position of νC=N and νC=C are suggestive of coordination of the substituted benzimidazoles via the tertiary nitrogen of the imidazole moiety.[10] The C–N stretching vibration occurs around 1300 cm^{-1}. The bands due to *o*-disubstituted benzene ring vibrations occur around 1460, 1280 and 721 cm^{-1}. The peaks due to *m*-disubstituted benzene ring vibrations are observed around 1280 and 730 cm^{-1} while the band due to *p*-disubstituted benzene ring vibrations occur around 1300, 1250 and 760 cm^{-1}.[6,11] The bands around at 1200, 1010, 920 and 670 cm^{-1} are assigned to the benzimidazole ring vibrations. The C–Cl stretching vibration of uncoordinated L^4 and its complexes appear at around 760 cm^{-1}.[12] In the perchlorate complexes, in addition to the bands observed due to the ligand, the spectra also show peaks around 1100 and 620 cm^{-1} characteristic of ν_3 and ν_4 of the perchlorate ion. The peak around 1100 cm^{-1} is split, indicating the presence of at least one of the perchlorates coordinated to the metal ion.[13]

The ^1H NMR spectra of the complexes recorded in DMSO-d_6 exhibit resonances due to coordinated 1,2-disubstituted benzimidazoles. The spectra of the complexes are almost similar to those of the free ligands except for a slight shift in the positions of the signals. The spectra of the complexes display resonance signals in the range δ 9.0–10.0 ppm, which are due to the O–H protons of the phenolic and benzyl groups. The phenolic O–H group resonance signal appears in the down field region when compared to that of the benzyl group hydroxyl proton. The resonance signals due to the protons of the benzyl ring are observed in the range 6.4–7.8 ppm, and the protons of the phenolic group in the range 6.8–7.8 ppm. The resonance signals due to the aromatic protons of benzimidazole ring are found in the range

Table 1 Physical properties and analytical data of the complexes

Sl. no.	Complex	Colour	Yield /%	M.p. /°C	$\Lambda_M{}^a$ $\Omega^{-1}\,cm^2\,mol^{-1}$	Found (calcd %)		
						C	H	N
1	$[ZnCl_2L^1{}_2].H_2O$	Pale yellow	80	262	03	60.6 (61.1)	5.3 (4.4)	6.9 (7.1)
2	$[ZnBr_2L^1{}_2]$	Yellow	80	138	02	55.6 (56.0)	4.0 (3.8)	5.6 (6.5)
3	$[ZnIL^1{}_3]I.2H_2O$	White	70	208	67	55.5 (55.3)	4.8 (4.0)	6.8 (6.4)
4	$[Zn(OClO_3)_2L^1{}_2]$	Yellow	75	232	27	54.5 (53.6)	4.0 (3.6)	6.0 (6.2)
5	$[ZnCl_2L^2{}_2].H_2O$	White	80	158	19	60.4 (61.1)	5.0 (4.4)	6.4 (7.1)
6	$[ZnBr_2L^2{}_2].2H_2O$	White	85	192	11	53.9 (53.8)	3.2 (4.1)	6.8 (6.3)
7	$[Zn(OClO_3)_2L^2{}_2].H_2O$	Buff	80	196	32	52.3 (51.5)	3.0 (3.9)	6.8 (6.0)
8	$[ZnCl_2L^3{}_2]$	Pale yellow	70	166	11	63.6 (62.5)	5.0 (4.2)	6.9 (7.3)
9	$[ZnBr_2L^3{}_3].3H_2O$	Pale yellow	70	158	12	58.9 (58.7)	5.0 (4.4)	6.1 (6.8)
10	$[ZnI_2L^3{}_3].2H_2O$	Pale pink	75	172	20	55.2 (55.3)	3.8 (4.0)	6.6 (6.4)
11	$[Zn(OClO_3)_2L^3{}_2].H_2O$	Pale yellow	70	>260	12	53.2 (52.5)	4.0 (3.8)	7.1 (6.1)
12	$[ZnCl_2L^4{}_3(OH_2)].2H_2O$	Pale yellow	80	>260	12	57.7 (57.7)	3.6 (3.9)	6.7 (6.7)
13	$[ZnL^4{}_3(OH_2)_3]Br_2.2H_2O$	Pale yellow	70	>260	134	51.6 (52.4)	3.2 (3.8)	5.6 (6.1)
14	$[Zn(OClO_3)_2L^4{}_2$	Pale yellow	75	206	20	48.9 (49.5)	2.5 (2.9)	5.2 (5.8)

^{a}Molar conductance of ~ 10^{-3} M solutions in DMF at 25°C.

Table 2 Thermogravimetric analysis data of zinc(II) complexes

Complex	Stage	Temp. /°C	Weight loss /% (calcd)	Species lost
(1) $[ZnCl_2L^1{}_2].H_2O$	1	160	3.0 (2.2)	H_2O
	2	300	10.0 (9.0)	2Cl
	3	490	78.7 (80.3)	2L
(5) $[ZnCl_2L^2{}_2].H_2O$	1	133	2.6 (2.2)	H_2O
	2	341	9.0 (9.0)	2Cl
	3	597	53.9 (51.4)	2L
(6) $[ZnBr_2L^2{}_2].2H_2O$	1	140	2.0 (2.3)	H_2O
	2	540	68.5 (71.7)	2L
(9) $[ZnBr_2L^3{}_3].3H_2O$	1	170	2.0 (2.2)	$2H_2O$
	2	380	9.0 (9.0)	2Br
	3	540	72.2 (71.1)	2L
(12) $[ZnCl_2L^4{}_3(OH_2)].2H_2O$	1	262	1.0 (1.4)	H_2O
	2	400	51.5 (58.8)	$2L+H_2O$
	3	599	28.6 (29.1)	L
(13) $[ZnL^4{}_3(OH_2)_3]Br_2.2H_2O$	1	233	1.6 (2.6)	$2H_2O$
	2	558	57.4(56.1)	$3H_2O+2L$

6.8–7.5 ppm. Further the resonance signals due to the protons of $–CH_2–$ group shift downfield by 0.01–0.02 ppm. The coordination-induced shifts at the positions 4 and 6^l are higher because of polarisation of electron density towards the metal ion after complexation.[14] The coordination-induced shifts for various protons of the coordinated ligands are in the range 0.02–0.74 ppm. A similar observation was made earlier for the related complexes.[2,15]

The ^{13}C NMR spectra of the complexes recorded in DMSO-d_6 reveal distinct resonances that are in agreement with the expected carbon environments. The ^{13}C spectra of the complexes of L^4 could not be recorded due to their poor solubility in DMSO-d_6. The assignment of the signals is made based on those reported for benzimidazole and substituted benzimidazoles.[16] The resonance signal due to the $–CH_2–$ carbon is observed around 47.1 ppm. The coordination-induced shifts (c.i.s) are in the range 0.01–1.5 ppm. The carbons C-6', C-2 and C-1' are proximate to the coordinated nitrogen and show positive c.i.s. The resonance signals in the range 120–160 ppm correspond to the carbons of benzyl group and phenolic group carbons of L^1, L^2 and L^3. The resonance signals due to the benzimidazole ring carbons are observed in the range 127.0–158.0 ppm. The carbon atom of the C–OH group of the benzyl group resonates at around 120.0 ppm in L^1 and L^3 while in the complexes of L^2 it has been observed around 153.0 ppm. The C–OH peaks of the phenolic group of L^1 and L^3 are located in the range 119.0–123.0 ppm, while in the L^2 complexes the same peak is found in the range 157.0–170.0 ppm. Both positive and negative c.i.s. values are noted for the complexes point to considerable metal-to-ligand π-back donation and ligand-to-metal σ-donation respectively.[16-20]

Thermogravimetric analysis data of $ZnX_2L_n.yH_2O$ complexes are compiled in Table 2. The complexes show loss of water of hydration as noted from TGA curves. In the case of L^1, L^2 and L^3 containing-complexes the lattice water molecules are lost in the range 160–175°C. The weight loss corresponding to the loss of two halide ions takes place in the temperature range of 300–380°C. The weight loss in the temperature range 500–600°C corresponds to the loss of two benzimidazole molecules. In the case of $[ZnCl_2(L^4)_3].2H_2O$, there is loss of water of hydration around 260°C. In the case of $[Zn(L^4)_3(OH_2)_3]Br_2.2H_2O$ complex, the loss of two lattice water molecules takes place around 230°C, the loss of two benzimidazoles and three molecules of coordinated water occur around 560°C. All the complexes undergo decomposition in the temperature range 230-600°C, indicating that they are more thermally stable than the free ligands.[21,22]

Based on above discussion, the chloro-, bromo- and perchlorate-complexes of L^1, L^2, and chloro- and perchlorate-complexes of L^3 and perchlorate-complex of L^4 are proposed to possess tetrahedral geometry. The perchlorate ion in all these complexes is monodentately coordinated to the metal ion as supported by IR spectra. The iodo- complex of L^1 is suggested to have tetrahedral geometry while the bromo- and iodo- complexes of L^3 are suggested to have square pyramidal/ trigonal bipyramidal geometry. The molar conductivities in DMF for the chloro- and bromo-complexes of L^4 suggest non-electrolytic and uni-bivalent electrolytic behaviour respectively and indicate the ionic nature of the bromide ions, and the thermal data suggest the coordination of water molecules and hence an octahedral geometry is proposed for these complexes. In all the complexes, the ligands are monodentately coordinated through the tertiary imidazole nitrogen.

The authors are thankful to Professor D.N. Sathyanarayana, Indian Institute of Science, Bangalore, India, Professor B.K. Sadashiva, Raman Research Institute, Bangalore, India and the authorities of Central Drug Research Institute, Luknow, India for CHN analyses and the authorities of the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India for recording the NMR spectra. The authors are also thankful to UGC-DRS and FIST programme for financial assistance.

Supplementary information: Tables of ^1H and ^{13}C NMR are available from the authors on request.

Received 7 August 2006; accepted 11 October 2006
Paper 06/4128

References

1 R.H. Prince, *Adv. Inorg. Chem. Radiochem*., 1979, **22,** 349**.**

2 N. Donappa and S.B. Naikar, *Asian J. Chem.,* 1993, **3,** 617; N.M Shivakumaraiah and N.M. Nanje Gowda, Synth*, React. Inorg. Met. Org. Chem.,* 2003, **33,** 1207**;** S. Sathyanarayana and K.R, Nagasundara, *Synth. React. Inorg. Met. Org. Chem.,* 2004, **34**, 883; L. Mishra, A.K. Pandey and U.C. Agarwala, *Ind. J. Chem*., 1993, **32A**, 442; A.W. Addition, T. Nageswara Rao, J. Reedijk, J.C. Rijn and G.C. Verschoor, *J. Chem. Soc. Dalton Trans*., 1984, 1349.

3 D.D.Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966.

4 N.V. Subba Rao and C.V. Ratnam, *Curr. Sci*., 1955, **24,** 174**.**

5 W.J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

6 T.J. Lane., C.S.C., I. Nakagawa, J.L.Walter, C.S.C., and A.J. Kandathil, *Inorg. Chem.*, 1962, **1**, 267.

7 K.Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn. John Wiley, New York*,* 1978**.**

8 J. Dillen, A.T.H. Lenstra, J.G. Haasnoot and J. Reedijk, *Polyhedron*, 1983, **3**, 195.

9 E. Bermejo, R. Carballo, A. Castineiras, A. Lombao, W. Hiller and J. Strahle, *Polyhedron*, 1991, **13**, 1579.

10 E.W. Aniscough, A.M. Bridues and N.G. Larsen, *Inorg. Chim. Acta*, 1984, **60**, 25.

11 L.J.Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.

12 K. Nakanishi and P.H. Soloman, *Infrared Absorption Spectroscopy.* Holden-Day, Inc., Sydney, 1977.

13 N.M.N. Gowda, S.B.Naikar, and G.K.N. Reddy, *Advances in Inorganic Chemistry and Radio Chemistry*, 1984, **28**, 41

14 S.B. Sanni, H.J. Behm, P.T. Beurkens, G.A.V. Albada, J. Reedijk, A.T.W. Lenstra, A.W. Adison and M. Palaniandavar, *J. Chem. Soc. Dalton Trans.,* 1988, 1429.

15 Y.S. Ramaswamy, PhD Thesis, Synthesis and spectral studies of organo ruthenium, rhodium and iridium complexes with N-heterocycles*.* Bangalore University*,* 1991.

16 R.J. Pugmire and D.M. Grant, *J. Am. Chem. Soc*., 1971, **93**, 1880.

17 J. VanRijn, J. Reedijk, M. Dartmann and B. Krebs, *J.C.S. Dalton Trans.*, 1987, 2579.

18 L.J. Mathias and C.G. Overberger, *J. Org. Chem*., 1978, **43**, 3526.

19 Grundemann, D. Martin and A. Wenzel, *Org. Magn.Reson*., 1979, **12**, 95

20 E.P. Papadopoulos and U. Hollstein, *Org. Magn. Reson.,* 1982*,* **19**, 188.

21 S. Wang, Q. Luo, X. Zhou and Z. Zeng, *Polyhedron*, 1993,**15**, 1039; J.R. Allan, G.M. Baillie, N.S. Middlemist and M.J. Pendlowski, *J. Them. Anal*., 1981, **22**, 8.

22 J.R. Allan, J.G. Bonner, D.L. Gerrard and Birnie, *Thermo.Chim. Acta*, 1991, **185**, 295.