Asian Journal of Chemistry Vol. 5, No. 3 (1993), 617–624

Complexes of Zinc(II), Cadmium(II) and Mercury(II) Perchlorates with Substituted Benzimidazoles

N. DONAPPA and S.B. NAIKAR*
Department of Chemistry, Central College
Bangalore University
Bangalore-560 001, India

A series of zinc(II), cadmium(II) and mercury(II) perchlorate complexes of the general formulae $ML_n(ClO_4)_2$ (M = Zn(II), Cd(II) and Hg(II); L = 2,6-bis(2-bezimidazyl) pyridine-(bBzIH$_2$Py), 2-(2′-quinolyl) benzimidazole (2-QylBzIH), 2,2′-bis-(benzimidazyl) sulphide (bBzIH$_2$S), and 2,2′-bis(benzimidazyl)-ethane (bBzIH$_2$e) (n = 1 or 2) have been prepared and characterised by conductivity, IR and proton NMR spectra. IR spectra give evidence for co-ordination of perchlorate in most of these complexes.

INTRODUCTION

Though the coordinating ability of perchlorate to metal ions has been well established[1-3], only a few cationic complexes of copper(I) and silver(I) with ionic perchlorate have been reported earlier.[4-7] Moers and OpHetveld[8] have reported a complex $Cu(Cy_3P)_2ClO_4$ having an ionic perchlorate. However Ferguson and coworkers[9] have confirmed the coordination of perchlorate to copper(I) in this compound by X-ray diffraction analysis. Similarly Dikhoff and Goel[10] have isolated a few complexes of Ag(I) of the type $Ag(R_3P)ClO_4$ (R = alkyl or aryl group) with a monodentately coordinated perchlorate. We reported earlier from this laboratory a series of tertiary arsine and phosphine complexes of Cu(I), Ag(I), Zn(II),Cd(II) and Hg(II) with coordinated perchlorates[11,12]. We have also recently reported the isolation of some substituted benzimidazole complexes of Cu(II) and Ag(I) with coordinated perchlorate[13]. The work has now been extended to examine the coordinating ability of perchlorate to zinc(II), cadmium(II) and mercury(II) in the presence of some substituted benzimidazoles. In recent years much attention has been paid to transition metal complexes containing nitrogen heterocycles because of their interesting catalytic activity and biological importance and these aspects have been highlighted in several review articles.[14,15]

EXPERIMENTAL

The metal perchlorates of zinc and cadmium were prepared by dissolving a known amount of the corresponding metal oxide in minimum quantity of 1 : 1 hot perchloric acid. Mercuric perchlorate was prepared by treating a known amount of an aqueous solution of mercuric chloride with conc. NaOH and subsequently dissolving the yellow brown oxide in dil $HClO_4$. The $BzIH_2Py$, 2-QylBzIH, $bBzIH_2S$ and $bBzIH_2e$ were synthesised according to the literature methods[16–20]

Preparation of Complexes

$[ZnL_2](ClO_4)_2$ (L = $bBzIH_2Py$, $bBzIH_2e$), $[M(bBzIH_2e)_2](ClO_4)_2$ (M = Cd, Hg)

The metal perchlorate (1 mmol) in ethanol (5 ml) was refluxed on a steam bath for 2 hrs and then the ligand (2 mmol) in ethanol (10 ml) was added and the refluxing was continued for nearly 4 hrs when a white crystalline solid got separated. It was washed with water and ethanol and dried in vacuo.

$[ML](ClO_4)_2$ (M = Cd, Hg ; L = $bBzIH_2Py$)

The compounds were isolated as white crystalline solids following the above procedure.

$[M(2\text{-}QylBzIH)_2](ClO_4)_2$ (M = Zn, Cd,Hg)

2-(2′-Quinolyl) benzimidazole (2 mmol) in methanol (10 ml) was added to the metal perchlorate (1 mmol) in methanol (10 ml) and the mixture was refluxed for about 3 hrs. The resulting mixture was concentrated to a small volume under reduced pressure and kept overnight. When a white crystalline solid got separated, it was washed with methanol and dried in vacuo.

$[M(bBzIH_2S)_2](ClO_4)_2$ (M = Zn, Cd, Hg)

The ligand (2 mmol) in THF (10 ml) was refluxed on a steambath for about 4 hrs and then the metal perchlorate (1 mmol) in THF (10 ml) and triethylorthoformate (5 ml) was added and the refluxing was continued for 6 hrs. The (3/4th) solvent was removed under reduced pressure and the solution was allowed to stand for 8 hrs. A white crystalline solid that separated was washed with THF and dried in vacuo.

The IR spectra of the samples were recorded on a Carl-Zeiss SPECORD-75 infrared spectrophotometer using nujol mull method. The molar conductivity measurements of the complexes in nitrobenzene, nitromethane and acetonitrile for 10^{-3} M solutions were made on a Toshniwal conductivity bridge. The ^{1}Hnmr spectra were recorded on a Bruker WH 270 MHz instrument using tetramethylsilane as an internal standard and DMSO as solvent.

RESULTS AND DISCUSSION

The analytical results are given in Table 1 and all the complexes melt with decomposition in the temperature range of 200–320°C. The IR frequencies of the complexes are listed in Table 2 together with their assignments.

TABLE 1
ANALYTICAL AND MOLAR CONDUCTIVITY DATA OF Zn(II), Cd(II) AND Hg(II) COMPLEXES

Complex	Colour	M.pt. or dec.pt. (°C)	Found (Calc.)* %				Molar conductivity (ohm^{-1} cm^{2} mol^{-1})		
			M	C	H	N	PhNO$_2$	MeNO$_2$	MeCN
[Zn(bBzIH$_2$Py)$_2$OClO$_3$]ClO$_4$	White	295	7.89 (7.09)	49.90 (49.51)	3.04 (2.80)	16.16 (15.20)	55	176	275
[Zn(2-QylBzIH)$_2$OClO$_3$]ClO$_4$	White	288	9.04 (8.67)	50.55 (50.90)	2.55 (2.91)	12.07 (11.14)	57	178	280
[Zn(bBzIH$_2$S)$_2$OClO$_3$]ClO$_4$	White	299	8.14 (8.20)	41.35 (41.22)	2.56 (2.45)	12.81 (13.20)	54	169	259
[Zn(bBzIH$_2$e)$_2$OClO$_3$]ClO$_4$	White	259	7.76 (8.19)	49.20 (48.90)	3.18 (3.50)	13.69 (14.02)	56	174	271
[Cd(bBzIH$_2$Py)OClO$_3$]ClO$_4$	White	278	16.85 (17.55)	34.87 (35.60)	2.58 (2.03)	11.36 (10.93)	25	82	140
[Cd(2-QylBzIH)$_2$](ClO$_4$)$_2$	White	275	15.10 (14.03)	46.90 (47.89)	2.35 (2.74)	11.21 (10.48)	56	173	284

TABLE 1 (*Contd.*)

Complex	Colour	M.pt. or dec.pt (°C)	Found (Calc.)* %				Molar conductivity (ohm^{-1} cm^{2} mol^{-1})		
			M	C	H	N	$PhNO_2$	$MeNO_2$	MeCN
$[Cd(bBzIH_2S)_2](ClO_4)_2$	White	296	14.26 (13.33)	39.93 (39.81)	2.82 (2.37)	12.86 (13.27)	57	170	279
$[Cd(bBzIH_2e)_2](ClO_4)_2$	White	248	12.86 (13.46)	46.54 (45.97)	3.21 (3.35)	11.76 (12.21)	54	168	271
$[Hg(bBzIH_2Py)OClO_3]ClO_4$	Pale Yellow	221	26.78 (27.60)	30.96 (31.36)	1.57 (1.79)	10.20 (9.63)	26	85	148
$[Hg(2\text{-}QylBzIH)_2](ClO_4)_2$	Pale Yellow	268	21.78 (22.27)	43.00 (43.15)	2.01 (2.47)	8.58 (9.20)	53	160	277
$[Hg(bBzIH_2S)_2](ClO_4)_2$	White	315	20.86 (21.70)	40.82 (40.56)	2.90 (3.30)	13.10 (12.12)	55	169	281
$[Hg(bBzIH_2e)_2](ClO_4)_2$	White	298	20.89 (21.72)	40.78 (41.62)	2.96 (3.03)	11.79 (12.14)	52	171	275

*The values in the parentheses are calculated values.

TABLE 2
IR SPECTRAL DATA OF Zn(II), Cd(II) AND Hg(II) PERCHLORATE COMPLEXES

Complex	Perchlorate absorption (cm^{-1})		
	ν_1	ν_3	ν_4
$[Zn(bBzIH_2Py)_2OClO_3]ClO_4$	921	1130 1092 1031	620 618
$[Zn(2\text{-}QylBzIH)_2OClO_3]ClO_4$	920	1132 1089 1033	622 619
$[Zn(bBzIH_2S)_2OClO_3]ClO_4$	922	1133 1091 1032	624 620
$[Zn(bBzIH_2e)_2OClO_3]ClO_4$	920	1135 1090 1030	621 618
$[Cd(bBzIH_2Py)OClO_3]ClO_4$	921	1130 1088 1032	622 619
$[Cd(2\text{-}QylBzIH)_2](ClO_4)_2$	—	1089	621
$[Cd(bBzIH_2S)_2](ClO_4)_2$	—	1092	620
$[Cd(bBzIH_2e)_2](ClO_4)_2$	—	1088	619
$[Hg(bBzIH_2Py)OClO_3]ClO_4$	921	1134 1091 1032	622 618
$[Hg(2\text{-}QylBzIH)_2](ClO_4)_2$	—	1095	621
$[Hg(bBzIH_2S)_2](ClO_4)_2$	—	1088	619
$[Hg(bBzIH_2e)_2](ClO_4)_2$	—	1092	620

The ionic perchlorate of T_d symmetry exhibits two infrared active vibrations[21] around 1100 (ν_3) and 620 cm^{-1} (ν_4). When perchlorate coordinates as a monodentate ligand, the local symmetry is lowered to C_{3v} and the triply degenerate vibrations ν_3 and ν_4 are split into two componets each. Further the ν_1 and ν_2

vibrations near 920 and 450 cm^{-1} respectively become active. If perchlorate is bonded in a bidentate manner, its local symmetry is reduced to C_{2v} and each of the ν_3 and ν_4 are split into three components. The nondegenerate ν_1 and the doubly degenerate ν_2 which splits into two components appear as a single band as other component of ν_2 is infrared inactive.[22]

In the IR spectra of cadmium and mercury complexes of the type $ML_2(ClO_4)_2$ only unsplit broad bands around 1090 and 620 cm^{-1} respectively are observed implying that both the perchlorates are ionic in nature. Further the ν_1 band near 920 cm^{-1} is absent in the spectra of these complexes[12,23]

The IR spectra of $[ZnL_2OClO_3]ClO_4$, $[Cd(bBzIH_2Py)OClO_3]ClO_4$ and $[Hg(bBzIH_2Py)OClO_3]ClO_4$ exhibit three bands centred at 1130, 1090 and 1030 cm^{-1} in the ν_3 region. The band near 1090 cm^{-1} is assigned to ionic perchlorate. The ν_4 band near 620 cm^{-1} is split indicating coordination of perchlorate. Further ν_1 appears as a weak but sharp band at 920 cm^{-1} in the spectra of all the complexes. It was noted that the band due to ionic perchlorate (1090 cm^{-1}) is fairly broad and it partly overlaps with the 1130 and 1030 cm^{-1} bands of the coordinated perchlorate. The ν_2 band expected near 450 cm^{-1} is generally obscured by the ligand bands appearing in this region. The results suggest that the perchlorate group is monodentately coordinated to the metal ion in the complexes. Zinc(II) is thus coordinated to four nitrogens of the benzimidazole ligand and one of the two perchlorates acting as a monodentate ligand. The complexes of zinc with $bBzIH_2Py$, 2-QylBzIH, $bBzIH_2S$ and $bBzIH_2e$ are suggested to have a square-pyramidal structure. The complexes $[Cd(bBzIH_2Py)OClO_3]ClO_4$ and $[Hg(bBzIH_2Py)OClO_3]ClO_4$ have the three nitrogens from the bezimidazole molecule coordinated to metal atom and one of the perchlorates coordinating as a monodentate ligand. The complexes of Cd(II) and Hg(II) with $bBzIH_2Py$, 2-QylBzlH, $bBzIH_2S$ and $bBzIH_2e$ are suggested to have tetrahedral coordination.

The conductivity data are also listed in Table 1. The complexes of cadmium and mercury of the composition $ML_2(ClO_4)_2$ behave as 1 : 2 electrolytes[24] in nitrobenzene, nitromethane and acetonitrile as expected. The complexes of $[Cd(bBzIH_2Py)OClO_3]ClO_4$ and $[Hg(bBzIH_2Py)OClO_3]ClO_4$ behave as univalent electrolytes in all the solvents. This reveals that the coordinated perchlorate is apparently displaced in solution by a solvent molecule. The zinc(II) complexes behave as 1 : 2 electrolytes indicating that the coordinated perchlorate is similarly displaced in solution by a solvent molecule[25,26]. The results demonstrate the rather weak nature of coordination of ClO_4^- to the metal.

To ascertain the bonding of the ligand ^{1}Hnmr spectra of zinc, cadmium and mercury complexes of $bBzIH_2Py$, 2-QylBzIH, $bBzIH_2S$ and $bBzIH_2e$ were recorded in DMSO-d_6. The signals due to aromatic protons are observed in the range 7.5–9.2 ppm as a complex multiplet. The signal due to the –NH proton appears in the range of 11.5 to 14.5 ppm and it remains unshifted in the complexes showing the non-involvement of –NH in bonding. It is known that the –NH resonance occurs over a wide range and it is concentration dependent. The broadness of the peak may be attributed to the presence of strong hydrogen bonding.

From the results discussed above, the stereochemistry for the Zn(II), Cd(II) and Hg(II) complexes may be inferred. Four nitrogens from the benzimidazole molecules are coordinated to Zn(II) and one of the two perchlorates acts as a monodentate ligand. In the complexes of $bBzIH_2S$ also, the ligand coordinates bidentately and sulphur is not coordinated, probably due to steric hindrance. Thus the Zn(II) complexes are suggested to have square-pyramidal geometry and Cd(II) and Hg(II) complexes have tetrahedral coordination.

ACKNOWLEDGEMENT

The authors are grateful to Prof. D.N. Sathyanarayana, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore for their helpful discussion and to Prof. P.S. Veerabhadrappa, Head of the Chemistry Department, Bangalore University, Bangalore for providing necessary laboratory facilities.

REFERENCES

1. E.C. Aleya, S. Das, G. Ferguson and M. Khan, *Can. J. Chem.,* **57**, 2217 (1979).
2. C. Belin, M. Chaobouni, J.L. Pascal, J. Potier and Roziere, *J. Chem. Commun.*, 105 (1980).
3. A.N. Speca, C.M. Mikulski, F.J. Iaconianni, L.L Pytlewski and N.M. Karayannis, *J. Inorg. Nucl. Chem.*, **43**, 2271 (1981).
4. R.S. Nyholm, *J. Chem. Soc.*, 1257 (1952).
5. F.A. Cotton and D.M.L. Goodgame, *J. Chem. Soc.*, 5267 (1960).
6. R.N. Dash and D.V. Ramana Rao, *Z. Anorg. Allg. Chem.*, **393**, 309 (1972).
7. F.H. Jardine and F.J. Young, *J. Chem. Soc.* (A), 2444 (1971).
8. F.G. Mores and P.H. OpHetveld, *J. Inorg Nucl. Chem.*, **32**, 3225 (1970).
9. R.J. Restivo, A. Costin, G. Ferguson and A.J. Carty, *Can. J. Chem.*, **53**, 1949 (1975).
10. T.G.M.H. Dikhoff and R.G. Goel, *Inorg. Chim. Acta*, **44**, L72 (1980).
11. S.B. Naikar, N.M. Nanjegowda and G.K.N. Reddy, *Indian. J. Chem.*, **23A**, 133 (1984).
12. ________, *Indian J. Chem.*, **20A**, 436 (1981).
13. N. Donappa and S.B. Naikar, *Asian J. Chem.*, **4**, 879 (1992).
14. R.E. Harmon, S.K. Gupta and D.J. Brown, *Chem. Rev.*, **83**, 21 (1973).
15. S.S. Kukalenko, B.A. Bovykin, S.I. Shestakova and A.M. Omelchenko, *Russ. Chem. Rev.*, **54**, 676 (1985).
16. A.W. Addison and P.J. Burke, *J. Heterocycl. Chem.*, **18**, 803 (1981).
17. D.M. Heim, R.I. Altheilm and J.J. Leavitt, *J. Am. Chem. Soc.*, **79**, 427 (1957).
18. L.Lt. Yenwang and M.M. Jullie, *J. Am. Chem. Soc.*, **79**, 5706 (1957).
19. L. Harison T.J. Ralph and A.C.B. Smith, *J. Chem. Soc.*, Part III, 2930 (1963).

20. M.A. Phillips, *J. Chem. Soc.*, Part II, 2393 (1928).
21. Cohn Henry, *J. Chem. Soc.*, 4282 (1952).
22. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.* 309 (1961).
23. C. Henry, *J. Chem. Soc.*, 4282 (1952).
24. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
25. J. Peone (Jr) and L. Vaska, *Angew. Chem.*, **10**, 511 (1971).
26. I.V. Gavrilova, M.I. Gelfanan, N.V. Ivannikova and V.V. Razumovskii, *Russ. J. Inorg. Chem.*, **16**, 358 (1971).

(*Received*: 30 December 1991; *Accepted*: 15 October 1992) AJC–496