Asian Journal of Chemistry Vol. 4, No. 4 (1992), 879-885

Studies on Perchlorate Complexes of Cu(II)and Ag(I) with Substituted Benzimidazoles

N. DONAPPA AND S. B. NAIKAR*

Department of Chemistry, Central College
Bangalore University, Bangalore-560 001, India

A series of perchlorate complexes of copper(II) and silver(II) of the compositions $CuL_2(ClO_4)_2$ L=2-(2'-quinolyl) benzimidazole (2-QylBzIH) 2,2'-bis(benzimidazyl) sulphide ($bBzIH_2s$), 2,2'-bis (benzimidazyl) ethane ($bBzIH_2e$) and $AgLClO_4$ (L=2,6-bis (2-benzimidazyl) pyridine ($bBzIH_2Py$), 2-QylBzIH, $BbzIH_2s$ and $BbzIH_2e$ have been prepared and characterised by conductivity, magnetic susceptibility, electronic, IR and proton NMR spectra. IR spectra give evidence for coordination of perchlorate in most of these complexes.

INTRODUCTION

Though perchlorate generally behaves as a non-coordinating ion, there have been several examples of complexes where it binds covalently to the metal though often the binding is rather weak and is termed *semi coordination*[1-9]. Recently the X-ray crystal structure determination of a tin compound where both monodentate as well as bidentate perchlorate groups are present has been reported[10,11], complexes of copper, cobalt, rhodium , iridium and other transition metals containing coordinating perchlorate groups are also known [12,13]. We have 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[15,16]. The studies have now been undertaken to investigate the coordinating ability of perchlorate to copper(II) and silver(I) in the presence of some substituted benzimidazoles. In recent years much attention has been paid on transition metal complexes containing nitrogen heterocycles because of their interesting catalytic activity and biological importance and this has been highlighted in several review articles[26,27]. Addison and coworkers[14] have reported the characterisation of copper complex $Cu(bBzIH_2Py)_2(ClO_4)_2$. Except for this study there are no reports on copper(II) and silver(I) perchlorate complexes of substituted benzimidazoles. The copper(II) and silver(I) perchlorate complexes with the following ligands are synthesised and their characterisation discussed.

EXPERIMENTAL

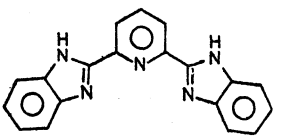
The metal perchlorates were prepared by dissolving a known amount of the corresponding metal oxide in a minimum quantity of 1 : 1 hot

perchloric acid and evaporating the resulting solution to almost dryness under reduced pressure. The ligands were prepared according to the literature methods[17–21].

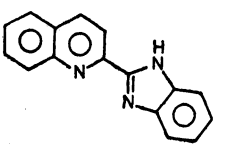
[*Ag*(*bBzIH*$_2$*Py*)]*ClO*$_4$: Silver(I) perchlorate (1 mmol) in ethanol (10 ml) was refluxed on a steambath for 1 hr and then the ligand (1 mmol) in ethanol (10 ml) was added and the refluxing was continued to nearly 2 hrs when a white solid got separated. It was washed with ethanol and dried in vacuo.

[*Ag*(2-QylBzIH)]ClO_4: 2-(2′-Quinolyl) benzimidazole (1 mmol) in methanol (10 ml) was added to the silver perchlorate (1 mmol) in methanol (10 ml) and the solution was refluxed for 2 hrs. The reaction mixture was concentrated to a small volume under reduced pressure and kept overnight during which a white solid got separated. The compound was washed with methanol and dried in vacuo.

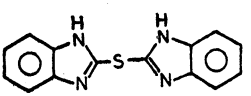
[*Ag*(*bBzIH*$_2$*s*]*ClO*$_4$: The ligand (1 mmol) in THF (10 ml) was refluxed on a steam bath for about 4 hr and then silver(I) perchlorate (1 mmol) in THF (10 ml) and triethylorthoformate (5 ml) was added and the refluxing was continued for another 3 hrs. Three fourths of the solvent was removed under reduced pressure and the solution was allowed to stand for a few



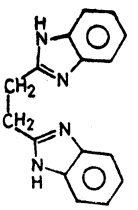
bBzIH$_2$Py



2-QylBzIH



bBzIH$_2$S



bBzIH$_2$e

hrs. A white solid that separated was washed with THF and dried in vacuo.

[*Ag*(*bBzIH*$_2$*e*)]*ClO*$_4$: To a solution of silver(I) perchlorate (1 mmol) in ethanol (10 ml) was added bBzIH$_2$e (1 mmol in ethanol (10 ml), on refluxing the mixture for 4 hrs, a white solid gets separated. This was washed with ethanol and dried in vacuo.

[*Cu*(2-*QylBzIH*)$_2$](ClO_4)$_2$: A solution of copper(II) perchlorate

(1 mmol) in methanol (10 ml) was added to 2-QylBzIH (2 mmol) in methanol (5 ml) and the mixture was refluxed for about 3 hrs. The resulting mixture was concentrated to a small volume under reduced pressure and was kept overnight. The brown crystals that separated were washed with water and methanol and dried in vacuo.

$[Cu(bBzIH_2s)_2](ClO_4)_2$: The ligand (2 mmol) in THF (10 ml) was refluxed on a steam bath for about 2hrs and then copper(II) perchlorate (1mmol) in THF (5 ml) and triethylorthoformate (5 ml) was added and the refluxing was continued for 3 hrs. Three fourths of the solvent was removed under reduced pressure and the solution was allowed to stand for 4 hrs. The light green crystalline solid that separated was washed with THF and dried in vacuo.

$[Cu(bBIH_2e)_2](ClO_4)_2$: To a solution of copper(II) perchlorate (1 mmol) in alcohol (10 ml) was added $bBzlH_2e$ (2 mmol) in alcohol (5 ml) on refluxing the mixture for 4 hrs, brown crystals separated out, it was washed with water and alcohol and dried in vacuo.

RESULTS AND DISCUSSION

The analytical results are given in Table 1 and all the complexes melt with decomposition in the temperature range of 250–300°C.

The IR frequencies of the complexes are listed in Table 2 together with their assignments. An examination of the IR spectra of the copper complexes $Cu(2\text{-}QylBzIH)_2(ClO_4)_2$, $Cu(bBzIH_2s)_2(ClO_4)_2$ and $Cu(bBzIH_2e)_2(ClO_4)_2$ reveals that in the 1100 cm^{-1} region, the spectrum is fairly complex. However, it is possible to assign the peaks in this region to ionic and coordinated perchlorate groups. the peak around 1090 cm^{-1} is assigned to ionic perchlorate and peaks around 1030cm^{-1} and 1130 cm^{-1} (Table 2) to monodentately coordinated perchlorate groups, some weak bands due to ligand also appear in this region. However, it is possible to identify them by comparison with the spectrum of the corresponding ligand, the spectra of the complexes also show a weak but sharp absorption around 915 cm^{-1} which is clearly due to the ν_1 mode and it has become infrared active due to lowering of the local symmetry of ClO_4 from T_d to C_{3v}. The band at 620 cm^{-1} is also split supporting coordination of one of the perchlorates. The extent of splitting is, however too small and in several cases the peak due to ionic perchlorate overlaps with one of the two peaks due to coordinated perchlorate with the result that only two peaks are observed. The ν_2 band expected around 450 cm^{-1} is generally obscured by the ligand bands in this region.

In the IR spectra of silver (I) perchlorate complexes $Ag(bBzIH_2Py)ClO_4$ and $Ag(bBzIH_2s)ClO_4$ only unsplit bands due to ν_3 and ν_4 modes of perchlorate are observed. Suggesting the ionic nature of perchlorate[16,22].

Spectra of complexes of 2-QylBzIH and $bBzIH_2e$ however, show the ν_3 and ν_4 mode are split in to doublets. In addition to ν_1 appears as a sharp low intensity band near 920 cm^{-1}. The ν_2 band could not be identified and is probably masked by the ligand absorption. These results indicate that the perchlorate group is monodentately coordinated to the metal ion in the complexes $Ag(2\text{-}QylBzIH)ClO_4$ and $Ag(bBzIH_2e)ClO_4$. Silver (I) (d^{10} system) is thus coordinated to two nitrogens of the benzimidazole ligand and one of the two perchlorates acting as a monodentate ligand.

The conductivity data are listed in Table 1. The complexes $Ag(bBzIH_2Py)\ ClO_4$ and $Ag(bBzIH_2s)\ ClO_4$ behave as a 1 : 1 electrolytes[25] in nitrobenzene, nitromethane and acetonitrile as expected. The other complexes $Ag(2\text{-}QylBzIH)ClO_4$ and $Ag(bBzIH_5e)ClO_4$ also behave as uni-univalent electrolytes in all the solvents. This shows that the coordinated perchlorate is apparently displaced in solution by a solvent molecule. The copper (II) complexes behave as 1 : 2 electrolytes indicating that the coordinated perchlorate is similarly displaced in solution by a solvent molecule[12,23]. The results demonstrate the rather weak nature of coordination of perchlorate to the metal.

The observed effective magnetic moment of all the copper complexes varies from 1.73 to 1.78 B.M. Close to the spin only value for one unpaired electron and as expected for the copper (II) complexes.

The electronic spectra of copper(II) complexes in the solid state have been recorded in the region 50,000–12,500 cm^{-1}. The complexes $[CuL_2OClO_3]ClO_4$ (where L=2-QylBzIH, $bBzIH_2s$ and $bBzIH_2e$) show two bands around 18,180 cm^{-1} and 14,880 cm^{-1}. The position and the intensities reveal that the band arises from energy levels associated with complexes of square pyramidal geometry.

To ascertain the bonding of ligand, ^{1}Hnmr spectra of the silver complexes of $bBzIH_2Py$, 2-QylBzIH, $bBzIH_2s$ and $bBzIH_2e$ have been recorded in dmso-d_6. The signal due to aromatic protons is observed in the range 7.1–8.6 ppm as a complex multiplet. Signal due to –NH proton appears in the range of 12.5–14.5 ppm and it does not show any shift from its position in ligand. This observation clearly shows 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 peak may be attributed to the presence of strong hydrogen bonding.

From the results discussed above, the stereochemistry for the Cu(II) and Ag(I) complexes may be derived. Four nitrogens from the two benzimidazole molecules are coordinated to Cu(II) and one of the two perchlorates act as a monodentate ligand. In the complex of $bBzIH_2s$ also, the ligand coordinates bidentately and sulphur is not coordinated probably due to steric hindrance. Thus the Cu(II) complexes are suggested

TABLE 1

ANALYTICAL AND MOLAR CONDUCTIVITY DATA OF Cu(II) AND Ag(I) 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
$[Cu(2\text{-}QylBzIH)_2OClO_3]ClO_4$	Brown	250	9.30 (8.44)	50.97 (50.96)	3.46 (2.95)	11.48 (11.15)	45	140	228
$[Cu(bBzIH_2s)_2OClO_3]ClO_4$	Light green	260	8.56 (7.99)	41.39 (42.25)	1.78 (2.52)	15.10 (14.08)	41	178	223
$[Cu(bBzIH_2e)_3OClO_3]ClO_4$	Brown	255	9.00 (8.07)	49.50 (48.82)	3.72 (3.56)	13.64 (14.24)	45	169	217
$[Ag(bBzIH_2Py)]ClO_4$	White	290	20.67 (19.95)	41.60 (42.50)	3.72 (3.56)	13.64 (14.24)	26	83	139
$[Ag(2\text{-}QylBzIH)OClO_3$	White	300	24.75 (23.83)	41.66 (42.42)	2.93 (2.43)	9.39 (9.28)	27	90	110
$[Ag(bBzIH_2s)]ClO_4$	White	300	23.65 (22.77)	36.20 (35.49)	2.56 (2.11)	10.90 (11.83)	26	84	149
$[Ag(bBzIH_2e)OClO_3]$	White	280	24.00 (23.05)	39.92 (40.91)	2.96 (2.98)	12.35 (11.91)	24	74	118

*The values in the parentheses are calculated values.

TABLE 2

IR SPECTRAL AND MAGNETIC MOMENT DATA OF COPPER(II) AND SILVER(I) PERCHLORATE COMPLEXES

Complex	Perchlorate absorption (cm^{-1})			μ_{eff} (B.M.)
	ν_1	ν_3	ν_4	
$[Cu(2\text{-}QylBzIH)_2OClO_3]ClO_4$	918	1130 1095 1030	620 617	1.73
$[Cu(bBzIH_2S)_2OClO_3]ClO_4$	920	1125 1085 1035	623 621	1.78
$[Cu(bBzIH_2e)_2OClO_3]ClO_4$	922	1135 1086 1030	622 619	1·74
$[Ag(bBzIH_2Py)]ClO_4$	—	1089	621	—
$[Ag(bBzIH_2S)]ClO_4$	—	1091	621	—
$[Ag(2\text{-}QylBzIH)OClO_3]$	918	1130 1095 1035	624 622	—
$[Ag(bBzIH_2e)OClO_3]$	923	1126 1089 1034	620 621	—

to have square pyramidal geometry and Ag(I) complexes have a trigonal planar structure.

ACKNOWLEDGEMENTS

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. C. H. Krishna, C. Mohapatra and K. C. Dash, *J. Inorg. Nucl. Chem.*, **29**, 1253 (1977).
2. M. Ciampollini, Cariomaahalli, and N. Tanardi, *J. Chem. Soc. Dalton Trans.*, 376 (1980).
3. A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta*, **37**, 551 (1979).

4. D. F. Christian and W. R. Roper, *Chem. Commun*, 1271 (1971).
5. N. M. Karayannis, C. M. Mikulski, L. L. Pytleweski and M. M. Labes, *Inorg. Chem.*, **9**, 582 (1970).
6. N. M. Karayannis, C. M. Mikulski, M. J. Strock, L. L. Pytleweski and M. M. Labes, *J. Inorg. Nucl. Chem.*, **33**, 3185 (1971).
7. B. J. Hathaway, D. G. Holah and M. Hudson, *J. Chem. Soc.*, 4586 (1963).
8. R. P. Scholer and A. E. Merbatch, *Inorg. Chim. Acta*, **15**, 15 (1975).
9. J. R. Roderic, A. Costin, G. Furguson and A. J. Carty, *Can. J. Chem.*, **33**, 1949 (1975).
10. C. Berlin, M. Chaabouri, J. Luis, J. Potier and J. Roziere, *J. Chem. Soc. Chem. Commun.*, 105 (1980).
11. N. M. N. Gowda, S. B. Naikar and G. K. N. Reddy, *Adv. Inorg. Chem. Radiochem.*, **28**, 255 (1984).
12. J. Peone (Jr.) and L. Vaska, *Angew-chem.*, **10**, 511 (1971).
13. B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
14. A. W. Addison, T. H. Albert, Lenstra and S. Bamidele, *J. Chem. Soc. Dalton Trans.*, 1429 (1988).
15. S. B. Naikar, N. M. Nanjegowda and G. K. N. Reddy, *Indian J. Chem.*, **23A**, 133 (1984)
16. S. B. Naikar, N. M. Nanjegowda and G. K. N. Reddy, *Indian J. Chem.*, **20A**, 436 (1981).
17. A. W. Addison and P. J. Burke, *J. Heterocycl. Chem.*, **18**, 803 (1981).
18. D. M. Heim, R. I. Altheim and J. J. Leavitt, *J. Am. Chem. Soc.*, **79**, 427 (1957).
19. L. Lt. Yenwang and M. M. Joullie, *J. Am. Chem. Soc.*, **79**, 5706 (1957).
20. D. Harison, J. T. Ralph and A. C. B. Smith, *J. Chem. Soc.*, Part III, 2930 (1963).
21. M. A. Phillips, *J. Chem. Soc.*, Part II, 2393 (1928).
22. C. Henry, *J. Chem. Soc.*, 4282 (1952).
23. I. V. Gavrilova, M. I. Gelfanan, N. V. Ivannikova and V. V. Razumovskii, *Russ. J. Inorg. Chem.*, **16**, 358 (1971).
24. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd edn,, Interscience, New York, p. 296 (1972)
25. W. J. Geary, *Coord. Chem. Rev.* **7**, 81 (1971).
26. R. E. Harmon, S. K. Gupta and D. J. Brown, *Chem. Rev.*, **83**, 21 (1973)
27. S. S. Kukalenko, B. A. Bovykin, S. I. Shestakova and A. M. Omelchenko, *Russ. Chem. Rev.*, **54**, 676 (1985).

(*Received*: 21 June 1991; *Accepted*: 2 August 1991) AJC-365