Inorganica Chimica Acta, *82* (1984) 27–29

Group IIB Metal Chloride Complexes with Some 2-(Methylpyridyl or -quinolyl)benz-X-azoles

M. MASSACESI*, M. BIDDAU

Istituto di Chimica Generale, Inorganica ed Analitica, Università, Cagliari, Italy

G. DEVOTO

Cattedra di Chimica, Facoltà di Medicina e Chirurgia, c/o Istituto Medicina del Lavoro, Università, Cagliari, Italy

E. BARNI and P. SAVARINO

Istituto di Chimica Organica Industriale, Università, Turin, Italy

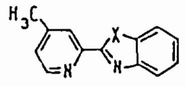
Received May 27, 1983

The complexes formed by Zn(II), Cd(II) and Hg(II) chlorides with benzimidazole, benzoxazole and benzothiazole linked to 4-methylpyridine and 4-methylquinoline have been prepared and characterized by chemical analysis, infrared spectra and conductivity data.

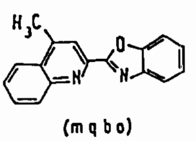
The coordination behaviour of these ligands toward the metal salts and the stereochemistry of the obtained complexes have been investigated.

Introduction

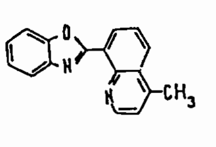
In earlier reports [1, 2] we prepared and studied in view of their interest as dye intermediates, the following compounds: 2-(4′-methyl,2′-pyridyl)benzimidazole (mpbi), 2-(4′-methyl,2′-pyridyl)benzothiazole (mpbt), 2-(4′-methyl,2′-pyridyl)benzoxazole (mpbo), 2-(4′-methyl,2′-quinolyl)benzoxazole (mqbo) and 2-(4′-methyl,8′-quinolyl)benzoxazole (mq′bo).



X = NH = (mpbi)
X = S = (mpbt)
X = O = (mpbo)



(mqbo)



(mq′bo)

These compounds are also suitable as ligands, owing to the presence of two nitrogen atoms, three in the (mpbi) molecule, one of which is in the five-membered ring. As is well known [3] this atom is in a less favourable position for the coordination to the metal ion than the nitrogen of the pyridine or quinoline ring. The substitution of an oxygen or sulphur atom for the NH group in the benzimidazole ring can give rise to electronic effects with an alteration of the chelating ability of the α-diiminic nitrogen atoms.

Other authors have reported [4] that introducing a methyl group in the 6-position of the pyridyl ring in the pyridylbenzothiazole, causes a steric hindrance which sometimes inhibits the coordination mode of this ligand with some metal salts.

In this paper we report the synthesis and characterization of the complexes of zinc(II), cadmium(II) and mercury(II) chlorides with the ligands, (mpbi), (mpbt), (mpbo), (mqbo) and (mq′bo), where the methyl group is in the 4-position of the pyridyl and quinolyl ring.

The aim of this work is to gain information on the coordination behaviour of these ligands and on the stereochemistry of the complexes obtained.

Results and Discussion

The compounds which were isolated have general formula $M(L)Cl_2$, where M = Zn(II), Cd(II) and Hg(II); L = (mpbi), (mpbt), (mpbo), (mqbo) and (mq′bo). These complexes are listed in Table I, along with the conductivity data. The most important far i.r. bands are reported in Table II. The compounds are powder-like or microcrystalline, white or yellowish-green, diamagnetic, generally soluble in DMF and $EtNO_2$, insoluble in $CHCl_3$. $Cd(mpbi)Cl_2$ and $Cd(mpbt)Cl_2$ are also slightly soluble in water. All the derivatives obtained are non-conductors in DMF: they melt above 250 °C. The near and mid i.r. spectra of the studied complexes are similar to the spectra of the corresponding ligands, in agreement with reported data [5].

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. Analytical and Physical Data.[a]

Compound	Colour	Found (Calc.)			Λ_M[b] in DMF ($cm^2\ \Omega^{-1}\ mol^{-1}$)
		C%	H%	N%	
Zn(mpbi)Cl$_2$	white	45.0(45.2)	3.3(3.2)	12.2(12.2)	10.0
Cd(mpbi)Cl$_2$	white	39.4(39.8)	3.0(2.8)	10.7(10.7)	13.7
Hg(mpbi)Cl$_2$	white	32.7(32.5)	2.5(2.3)	8.8(8.7)	6.0
Zn(mpbt)Cl$_2$	green	43.0(43.1)	2.7(2.8)	7.7(7.8)	6.1
Cd(mpbt)Cl$_2$	pale-green	37.6(38.1)	2.3(2.4)	6.6(6.8)	20.4
Hg(mpbt)Cl$_2$	green	30.7(31.4)	1.9(2.0)	5.2(5.6)	2.3
Zn(mpbo)Cl$_2$	pale-yellow	45.1(45.0)	3.2(2.9)	7.8(8.1)	3.0
Cd(mpbo)Cl$_2$	white	39.4(39.7)	2.6(2.6)	7.1(7.1)	17.2
Hg(mpbo)Cl$_2$	pale-yellow	32.1(32.4)	2.0(2.1)	6.1(5.8)	2.0
Zn(mqbo)Cl$_2$	dark-yellow	52.0(51.5)	3.3(3.1)	7.5(7.1)	4.1
Cd(mqbo)Cl$_2$	yellow	45.5(46.0)	2.5(2.7)	5.0(5.3)	17.6
Hg(mqbo)Cl$_2$	yellow	39.0(38.4)	2.3(2.3)	5.0(5.3)	2.6
Zn(mq'bo)Cl$_2$	white	51.9(51.5)	3.1(3.1)	7.3(7.1)	5.5
Cd(mq'bo)Cl$_2$	white	46.2(46.0)	2.7(2.7)	6.4(6.3)	16.3
Hg(mq'bo)Cl$_2$	pale-yellow	38.9(38.4)	2.4(2.3)	5.0(5.3)	1.0

[a] The names of the ligands listed above are: 2-(4'-methyl,2'-pyridyl)benzimidazole, (mpbi); 2-(4'-methyl,2'-pyridyl)benzothiazole, (mpbt); 2-(4'-methyl,2'-pyridyl)benzoxazole, (mpbo); 2-(4'-methyl,2'-quinolyl)benzoxazole, (mqbo); 2-(4'-methyl,8'-quinolyl)-benzoxazole, (mq'bo). [b] The refs. values in DMF, under the same conditions, are 70–90 for 1:1 electrolytes and 140–150 for 1:2 electrolytes [16].

TABLE II. Far I.r. Spectra (400–100 cm^{-1}).

Compound	ν(M–X)	ν(M–N)	Other bands
(mpbi)			307w, 274mw, 216vw, 140w
Zn(mpbi)Cl$_2$	328vsbr	248w, 220m	195w
Cd(mpbi)Cl$_2$	233sbr, 206s	174sbr	318w
Hg(mpbi)Cl$_2$	267vsbr	150w	323wbr, 203sbr
(mpbt)			364m, 306vwbr, 285w, 200mw
Zn(mpbt)Cl$_2$	340vsbr	248w, 209s	279mw, 157m
Cd(mpbt)Cl$_2$	222sbr, 198sbr	158s	
Hg(mpbt)Cl$_2$	266sbr	154w	325m, 212mbr, 170vw
(mpbo)			307w, 264mw, 224mw, 140vw
Zn(mpbo)Cl$_2$	310vs	242ms	200sh, 177m
Cd(mpbo)Cl$_2$	215vsbr, 208sh	156vsbr	277vw
Hg(mpbo)Cl$_2$	324vs	150w	120m
(mqbo)			264w, 218w
Zn(mqbo)Cl$_2$	351vs, 327vs	248mw, 218ms	195m, 172wbr
Cd(mqbo)Cl$_2$	246sh, 229vs	151m	229vs, 190s
Hg(mqbo)Cl$_2$	326vsbr, 321sh	168w, 148w	274m, 205m
(mq'bo)			314w, 200wbr, 182mw
Zn(mq'bo)Cl$_2$	326sbr	217m	280w, 192mw, 163m
Cd(mq'bo)Cl$_2$	210s, 188sbr	142m	220sh
Hg(mq'bo)Cl$_2$	310vs	160w, 150w	289m, 273m, 238w

In the i.r. spectra of the (mpbi) solid complexes, insoluble in $CHCl_3$, the NH stretching absorption is shifted to a higher frequency (3230–3180 cm^{-1}) than that of the free ligand (3040 cm^{-1}); this indicates that an intermolecular hydrogen bonding in the complexes in the solid state is not present [6, 7]. The NH is not involved in the coordination.

Coordination via S is excluded in all the (mpbt) complexes because the ν(CS) stretching vibration in the range 710–680 cm^{-1} does not change on going from the free ligand to the complexes [8].

The ν(CO) absorption band (1150–1050 cm^{-1}) of (mpbo), (mqbo) and (mq'bo) does not shift upon coordination with the metal salts used [8].

The bands at 1605–1590 cm^{-1}, attributed to the C=N stretching frequency ring of all ligands, shift to lower frequencies (1595–1570 cm^{-1}); this is expected if nitrogen coordination is involved [9].

The Zinc(II) complexes are of the 1:1 type and are non-conductors in DMF. The strong bands present at 351–310 cm^{-1} in the far i.r. region are typical of terminal zinc-chloride vibrations in a tetrahedral C_{2v} stereochemistry [10, 11]. All the complexes show bands in the 248–209 cm^{-1} range, attributed to the ν(Zn–N) vibrations according to the literature data [10, 12, 13]. No absorption bands were found for the ligands themselves in this region. These derivatives can be considered tetrahedral with the ligands bidentate, N-bonded, and terminal chlorides.

The $Cd(L)Cl_2$ compounds show a band, absent in the far i.r. spectra of the free ligands, at 174–142 cm^{-1}, which we attribute to metal–ligand vibration. These values are in the ranges expected for cadmium–nitrogen vibrations [14]. The two bands present at 246–188 cm^{-1} can be assigned to ν(Cd–Cl) bridging in accord with previous work on metal–chlorine infrared stretching frequencies involving six-coordinated cadmium halide complexes, *e.g.* $CdCl_2 \cdot 2py$ [15]. Therefore a distorted polymeric octahedral structure with bridging halogen and N-bonded chelating ligand molecules may be suggested for our $Cd(L)Cl_2$ complexes.

In the $Hg(L)Cl_2$ derivatives the strong bands present at 326–310 cm^{-1} have been assigned to terminal ν(Hg–Cl) [14]. In the spectra of all these complexes new bands, at 154–148 cm^{-1}, are present: these have been assigned to a metal–ligand interaction through the nitrogen atoms [11, 14]. These complexes can be considered tetrahedral with a C_{2v} stereochemistry.

We found that $\nu(Hg–Cl) > \nu(Cd–Cl)$; this must be attributed to the increase of coordination number of Cd(II) complexes [14]. From the above reported data, the Zn(II) and Hg(II) derivatives can be considered monomeric tetrahedral with terminal halogen; the Cd(II) compounds polymeric octahedral with bridging halogen; the ligands behave always as N-bonded chelate bidentate in all complexes. The introduction of a methyl group in 4-position of the ligands does not interfere with the coordination behaviour, but seems to enhance the heterocyclic α-diiminic nitrogen atoms.

Experimental

Preparation of the Ligands

The ligands (mpbi), (mpbt), (mpbo), (mqbo) were prepared as indicated in reference [1]; the ligand (mq'bo) was described in reference [2].

Preparation of the Complexes

All the compounds were prepared by reaction of the metal salts and the ligands in a hot ethanolic or methanolic solution in the required stoichiometric ratio. The complexes obtained by concentrating the solution were washed with chloroform and petroleum ether and dried over P_4O_{10}.

Analyses

Carbon, nitrogen and hydrogen were determined using a Perkin Elmer 240 analyzer. Melting points were uncorrected and determined by a capillary electrothermal apparatus.

I.R. Measurements

The i.r. spectra have been recorded in the range 4000–100 cm^{-1} with Perkin Elmer 983 and 180 spectrophotometers, calibrated for frequency with polystyrene film and with the far i.r. bands of the water molecule respectively. The spectra in the range 4000–400 cm^{-1} were measured on KBr pellets. The far i.r. spectra were recorded in Nujol mulls supported between polyethylene sheets.

Conductivity Measurements

These measurements were carried out with a WTW (Wiss.-Techn. Werkstätten) LBR/B conductivity meter at 25 °C for 10^{-3} *M* solutions in DMF.

References

1 E. Barni and P. Savarino, *J. Heterocyclic Chem., 14,* 937 (1977).
2 E. Barni and P. Savarino, *J. Heterocyclic Chem., 16,* 1579 (1979).
3 L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta, 2,* 119 (1968).
4 P. S. K. Chia and S. E. Livingstone, *Inorg. Chim. Acta, 2,* 427 (1968).
5 I. S. Ahuja and A. Garg, *Inorg. Chim. Acta, 6,* 453 (1972).
6 T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *J. Am. Soc., 78,* 270 (1956).
7 T. J. Lane, C. S. C., I. Nakagawa, J. L. Walter, C. S. C. and A. J. Kandathil, *Inorg. Chem., 1,* 267 (1962).
8 L. J. Bellamy, 'The infrared spectra of complex molecules', Methuen, London (1966).
9 B. Chiswell, F. Lions and B. S. Morris, *Inorg. Chem., 3,* 110 (1964).
10 J. R. Ferraro, 'Low frequency vibrations of inorganic and coordination compounds', Plenum Press, New York (1971).
11 C. Preti and G. Tosi, *J. Inorg. Nucl. Chem., 38,* 1125 (1976); and refs. therein.
12 R. J. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965).
13 C. W. Frank and L. B. Rogers, *Inorg. Chem., 5,* 615 (1966).
14 J. E. Douglas and C. J. Wilkins, *Inorg. Chim. Acta, 3,* 635 (1969).
15 G. E. Coates and D. Ridley, *J. Chem. Soc.,* 166 (1964).
16 R. C. Dutta, D. W. Meek and D. M. Bush, *Inorg. Chem., 9,* 1215 (1970); and refs. therein.