

ARTICLES

METAL COMPLEXES OF 6-METHOXY-2-BENZOTHAZOLAMINE

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ABSTRACT

Complexes of Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) halides with 6-methoxy-2-benzothiazolamine (L) [ML_2X_2 (M = Co, Cu, Zn; X = Cl, Br; and M = Cd, Hg; X = Cl, Br, I)] were isolated and characterized by electrical conductivity, magnetic susceptibility, reflectance and infrared spectral data. Electronic spectra indicate a tetrahedral geometry for the Co(II) complexes and distorted octahedral structure for the Cu(II) complexes. The ligand is proposed to be coordinated through the ring nitrogen in all these complexes, except the mercury complexes, where linkage through the amino nitrogen is indicated.

INTRODUCTION

SUBSTITUTED benzothiazoles are biologically active compounds¹⁻². It has been observed that metal ion complexation improves their biological activities²⁻⁶. Benzothiazoles are also interesting ambidentate ligands. 2-Benzothiazolamine and its methyl and halogeno derivatives have been studied for their ligand characteristics⁷⁻¹³ but alkoxy-substituted derivatives have been little studied. We have initiated a study of the ligand behaviour of alkoxy derivatives of 2-benzothiazolamine¹⁴ and this paper deals with the coordination compounds of Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 6-methoxy-2-benzothiazolamine (L).

EXPERIMENTAL

Materials

6-Methoxy-2-benzothiazolamine (Koch-Light, pure grade) was used without further purification. Cobalt(II) chloride, cobalt(II) bromide and copper(II) chloride of BDH(LR); copper(II) bromide of Cieche, USSR; zinc(II) chloride of Loba(AR); cadmium(II) chloride of S.M.(LR); and cadmium(II) iodide and mercury(II) chloride of Glaxo Lab(AR) were used as such.

Preparation of the complexes

The complexes were prepared by mixing the respective metal salts and the ligand in 1:2 molar ratio in methanol, ethanol or acetone. However, ZnL_2Br_2 , CdL_2Br_2 and HgL_2Br_2 were isolated by adding 2 mmol of KBr to preformed solution of the

chloro complex obtained from the metal chloride and ligand. For HgL_2I_2 , $HgCl_2$ solution in acetone was treated with NaI and filtered to remove the precipitated NaCl, and the filtrate was then treated with the ligand.

Analysis of the complexes

C, H and N were microanalysed at the Central Drug Research Institute, Lucknow, and Regional Sophisticated Instrumentation Centre, Chandigarh. Sulphur and halogens were estimated as usual¹⁵. The metals were estimated volumetrically using EDTA¹⁵.

Physical measurements

IR spectra (caesium iodide discs) were recorded on a Perkin-Elmer 577 spectrophotometer in the 200–4000 cm^{-1} region. Molar conductivities were determined with a Philips conductivity meter, model PR 9500/90. Magnetic measurements were performed on a Gouy balance. Reflectance and nujol mull spectra were recorded in the 25000–5000 cm^{-1} (400–2000 nm) region on a Hitachi 330 UV VIS-NIR spectrophotometer (RSIC, Chandigarh) against a $BaSO_4$ disc. Electronic spectra in solution were recorded on a Pye-Unicam PU 8600 spectrophotometer in the 50000–11111 cm^{-1} (200–900 nm) region.

RESULTS AND DISCUSSION

The compounds synthesized, and the analytical, physical, spectral and IR data are given in tables 1–3. The analytical data indicate the composition of the complexes to be ML_2X_2 . The molar conductivity

Table 1 Analytical data, colour, molar conductivity and magnetic moment of 6-methoxy-2-benzothiazolamine (L) complexes with Co(II), Cu(II), Zn(II), Cd(II) and Hg(II)

Complex	Colour	Conductivity ohm ⁻¹ cm ² mole ⁻¹	Magnetic moment (BM)	% Found (% Calculated)					
				C	H	N	S	X	M
CoL ₂ Cl ₂	Blue	6.8	4.8	39.0 (39.1)	3.2 (3.2)	11.2 (11.4)	12.9 (13.0)	14.6 (14.4)	12.1 (12.0)
CoL ₂ Br ₂	Blue	9.3	4.4	33.5 (33.1)	2.6 (2.7)	8.9 (9.6)	10.8 (11.0)	2.4 (27.6)	10.1 (10.1)
CuL ₂ Cl ₂	Black	46.0	1.9	39.6 (38.8)	3.4 (3.2)	11.0 (11.3)	12.1 (12.9)	13.3 (14.3)	12.5 (12.8)
CuL ₂ Br ₂	Black	45.1	1.9	32.4 (32.9)	2.7 (2.7)	8.7 (9.5)	10.2 (10.9)	27.1 (27.4)	10.8 (10.8)
ZnL ₂ Cl ₂	White	16.9	—	39.4 (38.7)	3.4 (3.2)	11.2 (11.3)	12.4 (12.9)	13.8 (14.3)	13.1 (13.1)
ZnL ₂ Br ₂	Grey	20.3	—	32.1 (32.8)	2.9 (2.7)	9.9 (9.5)	10.5 (10.9)	27.2 (27.3)	11.3 (11.1)
CdL ₂ Cl ₂	Grey	48.8	—	35.0 (35.3)	2.9 (2.9)	9.2 (10.3)	10.3 (11.7)	13.7 (13.0)	20.7 (21.6)
CdL ₂ Br ₂	Grey	42.2	—	32.3 (30.3)	2.7 (2.5)	8.0 (8.8)	9.6 (10.1)	25.0 (25.3)	17.4 (17.7)
CdL ₂ I ₂	White	50.0	—	27.2 (26.4)	2.3 (2.2)	6.5 (7.7)	8.7 (8.8)	— (34.9)	15.4 (15.4)
HgL ₂ Cl ₂	White	23.3	—	30.8 (30.4)	2.6 (2.5)	8.1 (8.8)	9.9 (10.1)	11.1 (11.2)	31.5 (31.7)
HgL ₂ Br ₂	Grey	23.3	—	27.7 (26.6)	2.3 (2.2)	7.0 (7.7)	8.1 (8.8)	22.0 (22.2)	28.0 (27.8)
HgL ₂ I ₂	White	25.4	—	24.4 (23.5)	1.9 (1.9)	6.9 (6.8)	8.5 (7.8)	— (31.1)	24.7 (24.6)

values of all the complexes indicate their non-electrolytic behaviour in acetone or DMF. The magnetic moment of the cobalt chloro complex (4.74 BM) is on the borderline between the values for the tetrahedral (4.4–4.7 BM) and the octahedral (4.7–5.2 BM) structure, but the magnetic moment of the bromo complex (4.6 BM) indicates its tetrahedral geometry. However, the electronic spectra of these complexes definitely suggest that they are tetrahedral. For the Cu(II) complexes, the magnetic moments correspond to the normal one-electron case. The electronic spectra suggest that the Cu(II) complexes have a distorted octahedral approximating to square planar configuration.

ELECTRONIC SPECTRA

Cobalt complexes

The electronic spectra of the complexes were measured in acetone and the reflectance spectra in

the form of BaSO₄ disc. The reflectance spectra of the complexes exhibit bands around the 16000 cm⁻¹ region. The solution spectra also show bands in the 15873–15822 cm⁻¹ region. The presence of bands in the same region both in the solid state and in solution indicates that there is no change in the coordination number or stereochemistry due to solvation. The order of $\Sigma m (\approx 3 \times 10^2)$ appears to suggest a tetrahedral geometry. The tetrahedral complexes of Co(II) are expected to show three bands corresponding to ν_1 , ${}^4T_2(F) \leftarrow {}^4A_2(F)$; ν_2 , ${}^4T_1(F) \leftarrow {}^4A_2(F)$; and ν_3 , ${}^4T_1(P) \leftarrow {}^4A_2(F)$, but generally two bands for ν_2 and ν_3 corresponding to ${}^4T_1(F) \leftarrow {}^4A_2(F)$ and ${}^4T_1(P) \leftarrow {}^4A_2(F)$ are observed. The ν_1 band corresponding to ${}^4T_2(F) \leftarrow {}^4A_2(F)$ is expected to be in the 3000–5000 cm⁻¹ region. Duff *et al.*¹⁶ studied the magnetic moments and electronic spectra of halogeno complexes of cobalt with 2-thiazolamine and noted that the lower energy transition corresponding to ν_2 is split into three components, as expected for C_{2v} symmetry. We also

Table 2 Electronic spectral data for some 6-methoxy-2-benzothiazolamine (L) complexes

Complex (phase)	Observed (cm ⁻¹)			Calculated ²¹					
	ν_2	ν_3	10 Dq	ν_2	ν_3	15B'	$\beta = \frac{15B'}{15B}$	B%	ν_2/ν_1
CoL ₂ Cl ₂ (solid)	6250, 7353, 8696	15873, 17094 sh	4490	7695	16485	10710	0.67	32.4	1.7
CoL ₂ Cl ₂ (solid)	5882, 6849, 8928	15504, 16666 sh	4440	7600	16086	10365	0.65	34.5	1.7
(acetone)	15873 (Σm 274)								
CoL ₂ Br ₂ (solid)	—	5714, 6803, 8734	4335	7429	16025	10455	0.66	33.9	1.7
(acetone)	15822 (Σm 288)								
CuL ₂ Cl ₂ (nujol mull)	32786, 20000 br								
(acetone)	28328 (Σm 2923), 20408 br (Σm 680)								
CuL ₂ Br ₂ (nujol mull)	32786, 20000 sh								
(methanol)	27027 (Σm 1418), 20000 sh								

L' = 2-Thiazolamine

15B for free ion = 15840 cm⁻¹.

observed a prominent band at 15503 cm⁻¹ (sh 16666 cm⁻¹) and at 15384 cm⁻¹ (sh 16666 cm⁻¹) in the cobalt chloro and bromo complexes respectively, which may be assigned to ν_3 . The bands corresponding to ν_2 transitions are observed at 8928, 6849 and 5882 cm⁻¹ in the chloro and at 8733, 6802 and 5714 cm⁻¹ in the bromo complexes. The similarity in the reflectance spectra of the 6-methoxy-2-benzothiazolamine complexes and 2-thiazolamine complexes of Co(II) indicates similar geometry for the two series. In dichloro-bis(2-thiazolamine) Co(II), the metal atom is shown by X-ray studies to be tetrahedrally coordinated through the ring nitrogen atom¹⁷. The calculated values of β for the 2-thiazolamine and 6-methoxy-2-benzothiazolamine complexes are very close, which also indicates similar mode of linkage through the ring nitrogen atom in both cases.

Copper complexes

It is not possible to unambiguously assign the

stereochemistry of Cu(II) complexes only on the basis of electronic spectral data in a limited range^{18,19}. The electronic spectra of the chloro complex in acetone and the bromo complex in methanol show a band around 28328 cm⁻¹ (Σm , 2923) and 27027 cm⁻¹ (Σm , 1418) respectively, which can be assigned as charge-transfer transitions¹⁸. A broad band around 20408 cm⁻¹ (Σm , 680) in the chloro complex and a shoulder around 20000 cm⁻¹ in the bromo complex suggest a probable square planar configuration²⁰. However, as Cu(II) complexes frequently exist in a highly distorted stereochemistry¹⁹, and the spectra of the solid complexes in nujol mull also show a broad plateau around 20000 cm⁻¹ (along with the charge-transfer band at 32786 cm⁻¹), it appears more reasonable to assign a distorted octahedral stereochemistry for these mixed ligand complexes with CuN₂X₂ chromophore.

INFRARED SPECTRA

6-Methoxy-2-benzothiazolamine shows two bands

Table 3 Principal IR bands (cm^{-1}) of 6-methoxy-2-benzothiazolamine (L) and its complexes

Band assignment	L	CoL_2Cl_2	CoL_2Br_2	CuL_2Cl_2	CuL_2Br_2	ZnL_2Cl_2
$\nu_{\text{NH}_2(\text{asym})}$	3365 s, sp	3420, 3340 s, sp	3410, 3330 s, sp	3365 s, msp	3385 s, msp	3400, 3330 s, mbr
$\nu_{\text{NH}_2(\text{sym})}$	3272 s, msp	3265 s, msp	3255 vs, msp	3270 s, sp	3280 s, msp	3260 s, msp
δ_{NH_2}	1630 s, sp	1604 vs, msp	1600 vs, msp	1600 vs, msp	1604 s, sp	1600 s, msp
$\nu_{\text{C=N}}$	1538 s, msp	1510 s, mbr	1505 ms, mbr	1525 ms, mbr	1532 ms, mbr	1512 s, mbr
$\nu_{\text{C-S}}$	608 w, msp	615 ms, sp	615 s, sp	615 w, mbr	614 ms, msp	615 s, mbr
$\nu_{\text{M-N}}$	—	310 s, msp	322 w, mbr	312 w, br	318 w, mbr	298 ms, mbr
$\nu_{\text{M-X}}$	—	325 s, msp	235 w, mbr	330 w, mbr	250 w, mbr	322 ms, mbr

Band assignment	ZnL_2Br_2	CdL_2Cl_2	CdL_2Br_2	CdL_2I_2	HgL_2Cl_2	HgL_2Br_2	HgL_2I_2
$\nu_{\text{NH}_2(\text{asym})}$	3430 3330 s, sp	3375— 3335 s, br	3330 s, br 3375 sh	3330 s, msp 3375 sh	3355 s, msp	3330 s, br	3370 s, msp
$\nu_{\text{NH}_2(\text{sym})}$	3280 s, sp	3270 s, msp	3265 s, msp	3260 s, msp	3265 s, msp	3255 s, br	3280 ms, sp
δ_{NH_2}	1613 s, sp	1605 s, msp	1600 s, mbr	1597 s 1618 sh	1628 s, msp	1625 s, br	1631 s, sp
$\nu_{\text{C=N}}$	1520 s, sp	1518 s, mbr	1512 s, mbr	1510 s, mbr	1535 s, mbr	1532— 1520 s, br	1538 s, msp
$\nu_{\text{C-S}}$	610 ms, mbr	610 s, mbr	608 s, msp	600 s, mbr	612 s, msp	602 s, mbr	618 w, mbr
$\nu_{\text{M-N}}$	299 w, mbr	315 w, mbr	310 w, mbr	300 w, mbr	612 s, msp	602 s, mbr	618 w, mbr
$\nu_{\text{M-X}}$	240 w, mbr	260 w, msp	—	—	255— 270 w, br	—	—

at 3365 and 3275 cm^{-1} assigned to N–H asymmetric and symmetric stretching modes respectively. The asymmetric stretching band gets split and broadened in some of the complexes and appears in the 3420–3330 cm^{-1} region, whereas the symmetric stretching mode suffers a negative shift of only 7–17 cm^{-1} . Normally the asymmetric stretching frequency suffers a shift to lower frequency on complexation of the $-\text{NH}_2$ group. The positive shift may be due to hydrogen bonding in the ligand in the solid state, which is reduced in the complexes. The δ_{NH_2} of the ligand appears at 1630 cm^{-1} as a strong band, which shows a negative shift of 30 cm^{-1} in the complexes. The $\nu_{\text{C=N}}$ of the ligand at 1538 cm^{-1} suffers a decrease in frequency (6–33 cm^{-1}) as well as intensity in the complexes, indicating involvement of the ring nitrogen in coordination. The C–S stretching frequency of the ligand is at 608 cm^{-1} , but in the complexes this appears at higher frequencies, by about 10 cm^{-1} . This is also opposite to the generally observed change to lower frequencies on complexation. Therefore we propose that the ligand is linked through the ring nitrogen atom. A medium intensity band corresponding to $\nu_{\text{M-N}}$ is observed in the 322–294 cm^{-1} region in these complexes.

However, in the case of mercury complexes the IR spectra show a different pattern. The asymmetric

N–H stretching frequency shows a large negative shift of about 10–30 cm^{-1} , whereas the symmetric one shows only a small, 7–17 cm^{-1} negative shift. The bending N–H mode remains unshifted but gets slightly broadened. In contrast to the situation in the other complexes, the C=N stretching mode is negligibly affected in the Hg complexes; therefore bonding through ring nitrogen is less likely. Similarly $\nu_{\text{C-S}}$ also shows a negligible shift, indicating non-participation of ring sulphur in coordination. We therefore tentatively propose bonding of the metal through the exocyclic amino nitrogen in the Hg complexes. A weak intensity band in the 270–255 cm^{-1} region is attributed² to $\nu_{\text{Hg-Cl}}$.

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ANNOUNCEMENTS

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