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Synthesis, characterization and antifungal activity of complexes of 2-(1H-benzothiazol-2-yl) thioacetic acid with some bivalent metal ions

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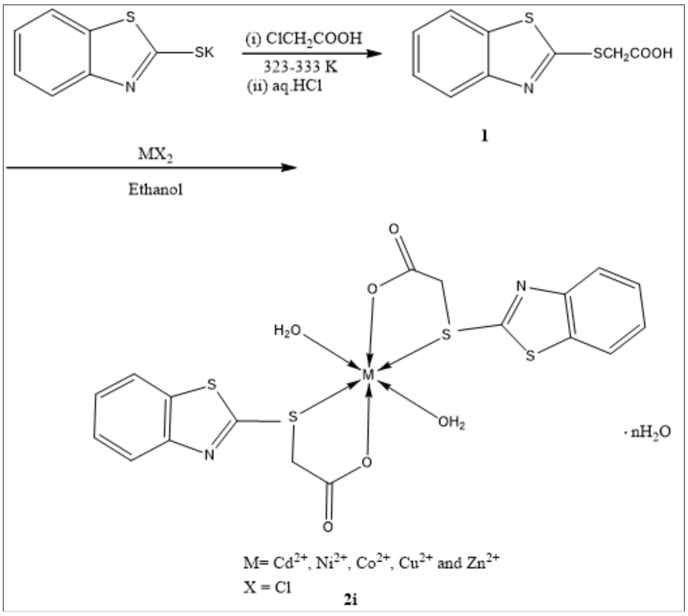
Abstract
Heterocyclic compounds, usually benzimidazole and benzothiazole derivatives, are essential for life system and extensively distributed in nature. Imidazole ring systems display a significant role in the metabolism of all living cells. Owing to the therapeutic properties of benzthiazole, we have prepared stable bis ligated complexes [ML_2]nH_2O [(M=Co(II), Ni(II), Mn(II), Cu(I), Zn(II) and Cd(II) involving benzthiazole moiety using potassium salt of 2-(1H- benzolthiazol-2-yl) thioacetic acid and studied their structures and magnetic susceptibility along with screening of their antifungal activity.

Keywords: Bivalent metal complexes, 2-(1H- benzolthiazol-2-yl) thioacetic acid, antifungal activity, magnetic susceptibility and electrical conductance

Introduction

Imidazole ring systems display a significant role in the metabolism of all living cells. Besides this, benzthiazole derivatives play an important role as therapeutic agents like antiviral, anticancer, antihelmintics, anticonvulsants, anti-inflammatory, analgesics, antiparasitics, antiulcer, antihypertensives, antifungal, anticoagulants [1-8] etc.

Considering a wide range of applications of the benzthiazole derivatives, the metal complexes of a number of benzimidazole and benzothiazole derivatives have been reported in literature [9-15]. Herewith we have prepared stable bis ligated complexes [ML_2]nH_2O [(M=Co(II), Ni(II), Mn (II), Cu (I), Zn (II), or Cd (II) and n=o, 2 and 4)] involving benzthiazole moiety using potassium salt of 2-(1H- benzolthiazol-2-yl) thioacetic acid.



Scheme

Experimental Section: Materials and Methods

Purity of the compounds was checked by thin layer chromatography (TLC) on silica gel using ultraviolet light and/or iodine vapour as visualizing agents. Compounds were purified by column chromatography using silica gel column. Yields are quoted for recrystallized compounds. Elemental analysis was carried out on a Perkin-Elmer CHNS analyzer (Model-2400). Infrared spectra were recorded on a Perkin-Elmer-FTIR spectrophotometer (KBr discs). UV visible spectra were recorded using shimadzu UV-vis 160 Spectrophotometer at IIT Patna. The magnetic properties of the complexes were studied by Gouy method. Proton nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz spectrophotometer.

Synthesis of 2-(1H-benzothiazole-2-yl) thioacetic acid

Potassium salts of a mixture of 2-mercaptobenzothiazole 1 (0.1 mole) and chloroacetic acid (0.1 mole) was refluxed for one hour at 50-60 °C and left overnight at room temperature. Then the mixture was treated with aq. HCl. The residue obtained was filtered, dried, purified by column chromatography (petroleum ether) and recrystallized with ethanol.

Synthesis of complexes

5 milli mole of ethanolic solution of the suitable metal chloride (Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) was slowly treated with an ethanolic solution of potassium salt of 2-(1H-benzothiazole-2-yl) thioacetic acid in 2:1 (ligand-metal) molar ratio. The resulting solution was refluxed for half an hour whereby the crystalline coloured precipitates of metal complexes separated slowly. The resulting solids were filtered, washed with distilled water and recrystallized from ethanol-acetone (50:50) mixture and dried in a desiccator over anhydrous $CaCl_2$.

Result and discussion

Physical data for ligands and the complexes

Table 1: Analysis found (Calculated) %

Compound	C	H	N	S	Metal
1, LH	47.98 (48.01)	3.80 (3.11)	5.89 (6.22)	28.23 (28.44)	-
2a, $NiL_2.4H_2O$	37.50 (37.32)	3.18 (3.45)	4.99 (4.83)	21.98 (22.11)	10.89 (10.14)
2b, ZnL_2	41.90 (42.07)	2.05 (2.33)	5.05 (5.45)	24.50 (24.93)	12.50 (12.73)
2c, $CuL_2.2H_2O$	39.05 (39.44)	2.80 (2.92)	5.03 (5.11)	23.10 (23.37)	11.20 (11.60)
2d, $CoL_2.4H_2O$	37.10 (37.31)	2.99 (3.45)	4.60 (4.83)	21.80 (22.10)	9.80 (10.17)
2e, $CdL_2.4H_2O$	38.10 (38.54)	1.53 (2.14)	4.10 (4.99)	22.16 (22.84)	19.68 (20.05)

From the result of elemental analysis it has been found that 2-(1-Hbenzimidazol-2-yl) thioacetic acid (LH) form bivalent metal complexes of compositions ML_2 nH_2O 2a, 2c and 2d (M= Ni^{2+}, Cu^{2+} and Co^{2+} respectively) and ML_2 2b and 2e (M= Zn^{2+} and Cd^{2+}).

Infrared spectra

Table 2: IR bands of 2-(1H-benzothiazol-2-yl) thioacetic acid and its complexes in cm^{-1}.

Compound	ν (OH) of (OOH) or ν(H_2O)	ν(C=O)	ν(C=N)	ν(C-S-C)	ν(M-O) cm^-
LH	3435 br	1710 str	1573 s	721 w	—
$NiL_2.4H_2O$	3350 br	1595 str	1575 s	705 w	446 m
$CuL_2.2H_2O$	3360 br	1620 str	1580 s	690 w	412 m
ZnL_2	—	1595 str	1578 s	695 w	438 m
$CdL_2.$ $4H_2O$	—	1590 str	1570 s	688 w	432 m
$CoL_2.4H_2O$	3320 br	1585 str	1576 s	697 w	442 m

br = broad, str = strong, s = sharp, w = weak, m = medium

The ligand shows prominent bands at 3435, 1573 and 690 cm^{-1} assignable to (COOH) hydroxyl (OH) groups stretching vibration, imidazole ring ν(C=N) band and ν(C-S-C) of thio group respectively.

The IR band of ν (C=O) of carboxyl group was observed at 1710 cm which shifted to lower frequency in complexes and observed in the range 1585-1620 cm^{-1}.The large shift in ν (CO) vibration on complexation is due to coordination of both carboxyl group (COO) oxygen to metal atoms and delocalization of (COO) group. The disappearance of ν (OH) band at 3435 cm^{-1} of ligand in complexes suggested the deprotonation of carboxyl group (COOH) proton and thus ligand (COO) is coordinating as monobasic bidentate group. In far infrared region the IR band between 412-446 cm^{-1} can tentatively be assigned to (M-O) stretching band. The ν(C-S-C) vibration of ligand is shifted to lower wave number, suggesting an environment sulfur in bond formation. The broad IR band in complexes between 3350-3320 cm^{-1} is attributed to ν (OH) of water group in CuL_22H_2O, CoL_24H_2O and NiL_24H_2O.

UV spectra

Table 3: For 2-(1H-benzothiazol-2-yl) thioacetic acid and it complexes in DMSO solvent.

Compound	Colour	Absorption bands (nm)	Assigned transition
LH	Yellow	282 301 328 223 and 252	π→π* σ→σ*
$NiL_2.4H_2O$	Pale green	281 301 460	π→π* $^3A_{2g}$→$^3T_{1g (F)}$
$CuL_2.2H_2O$	Green	290 338 610	π→π* $^2B_{1g}$→$^2A_{1g}$
ZnL_2	Pale yellow	290 301 343	π→π*
$CdL_2.4H_2O$	White	280 290 300	π→π*
$CoL_2.4H_2O$	Light pink	280 320 480	π→π* $^4T_{2g}$→$^4A_{2g}$

The electronic absorption spectra of complexes and ligands were recorded in DMSO. The strong electronic transition of ligands located at 223 and 252 nm is assigned to σ-σ* transition while bands at 282,301 and 328 nm can be assigned to π-π*of different groups present in ligands. These bands are slightly shifted to higher and lower wave lengths of coordination in metal complexes with enhanced intensity.

The ligand field electronic transition of the metal d-d bands were observed in Co^{2+}, Ni^{2+} and Cu^{2+} complexes in visible region. The UV band at 460 nm for NiL_24H_20 is assigned to the transition $^3A_{2g}\rightarrow{}^3T_{1g}$ and band at 610 nm for $CuL_2.2H_2O$ could be assigned to the $^2B_{1g}\rightarrow{}^2A_{1g}$ transition. The UV band at 480 nm observed in Co (ll) complexes $CoL_2.4H_2O$ can be assigned as $^4T_{2g}\rightarrow{}^4A_{2g}$ transition in octahedral field. As expected $Cd^{2+1}(d^{10})$ and Zn^{2+} (d^{10}) complexes did not show d-d transition due to filled d-orbital. The spectral characteristics of complexes are similar to reported distorted octahedral structure for Co^{2+}, NI^{2+} and Cu^{2+} complexes.

Table 4: Magnetic movement conductivity measurement in DMF solvent

Compound	Conductivity Ohm^{-1} mol^{-1} cm^2	Magnetic moment in BM at 304 k
$NiL_2.4H_2O$	12	3.28
$CuL_2.2H_2O$	16	1.89
$CoL_2.4_2O$	13	4.86
$CdL_2.4H_2O$	15	Diamagnetic
ZnL_2	10	Diamagnetic

The experimental values of magnetic moment for each metal complex after making correction for pascal constant are listed in Table 4. The magnetic moment value 3.28 BM for $NiL_2.4H_2$ at 304k occurs in the range of a distorted octahedral environment. The magnetic moment values 1.89 BM observed for CuL_2. $2H_2O$ and 486 BM at 304k for $CoL_2.4H_2O$ also occur in the approximately distorted octahedral structure of these metal complexes. The magnetic moment values also supported the proposed structure of complexes. As expected CdL_2 and ZnL_2 are diamagnetic (d^{10}) electronic system. The molar conductance value in DMF at 30±0.5 ^{0}C were found in the range 10-16 ohm^{-1} mol^{-1} cm^2 which indicated that complexes are non-electrolyte (Table 4).

Table 5: NMR Spectra

Compound	δ (OH) (δ-ppm)	δ(CH_2)aliphatic (δ-ppm)	δ (H)aromatic (δ-ppm)
CdL_2	—	4.22 ppm (s)	6.45-7.87 (m)
ZnL_2	—	4.24 ppm (s)	6.35-7.94 (m)
LH	12.22S	4.15S ppm (s)	7.35-8.12 (m)

(s = singlet, m = multiple)

Table 6: ^{13}C NMR spectra

Compound	C=O (^{13}C) (δ-ppm)	Aliphatic C (δ-ppm)	Aromatic C (δ-ppm)
$Zn(L)_2$	159.61	29.48	121.07-144.43
$Cd(L)_2$	159.64	28.58	121.15-115.17
L_H	169.61	30.39	121.22-114.2

Observed changes in ^{1}H NMR signals are evidence of coordination due to the chemical shift. The ^{1}H NMR spectrum of Zn^{2+} and Cd^{2+} complexes shows the disappearance of the -OH proton signal at (12.22 ppm) due to deprotonation of (OH) protons in complexes. The ^{1}H NMR signals of protons between 7.35-8.14ppm were assigned to aromatic ring protons and that shifted to a slightly higher field upon complexation. Similarly the H^1 NMR signal of the-CH_2 aliphatic group was shifted to a higher field (4.22-4.26 ppm). The ^{13}C NMR signals of the ligand and its complexes are presented in Table 6. The carboxyl group (C=O) ^{13}C NMR signal of ligand was observed at 169.61 ppm which shifted down field position in the complexes (158.46-159.61 ppm). The shift is due to the decrease of electron density at the carbon atom when oxygen is bonded to the metal atom in Zn (II) and Cd (II) complexes.

Antifungal activity of ligand and complexes

Antifungal activity of ligand and its complexes were screened by using radial growth technique. The fungi Aspergillus nigar, Aspergillus flavus, Rhizoctonia, Candida albicans and Candida tropicalis were screened by cup and plate method at concentration of 100 ppm and 200 ppm in DMSO +ethanol (50%) medium using the standard Griscoflavin (10 ppm). The nutrient medium was prepared by dissolving 6 gram peptone, 3 gram yeast extract, 1.5 gram beef extract, 3.0 gram Agar-Agar and 20 gram dextrose in one litre of double distilled water for bacterial growth. And for fungi screening, 10 gram peptone, 20.5 gram Agar-Agar and 20 gram dextrose in one liter of double distilled water was used. The organisms were examined under septic condition and incubated at 35 ºC for 40 hours. The radial growth was measured but it was found that no appreciable growth was seen for examined fungi.

Conclusion

The formation of stable bis ligated complexes $[ML_2\ ]nH_2O$ [(M=Co (II), Ni (II), Mn (II), Cu (I), Zn (II) and Cd (II) n=o, 2 or 4)] involving benzthiazole moiety using potassium salt of 2-(1H- benzolthiazol-2-yl) thioacetic acid and their characterization was achieved successfully. On the basis of UV and magnetic moment values, the distorted octahedral geometry has been proposed for the Cu^{2+}, Ni^{2+} and Co^{2+} complexes while tetrahedral geometry for Zn^{2+} and Cd^{2+} complexes. The screening of microbial studies observed for 100 ppm and 200 ppm concentrations showed no appreciable antifungal activity as was expected for the complexes in concerned.

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