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Complexes of Copper (II), Cobalt (II) and Nickel (II) with Substituted Benzimidazoles

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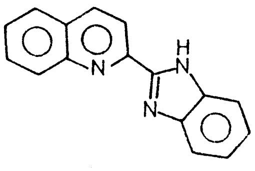
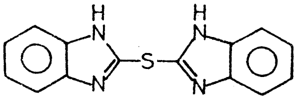
A series of complexes of the general formulae MLX_2(M = Cu; X = Cl, Br; L = 2–(2′–quinolyl) benzimidazole (2–QylBzIH), 2,2'–bis (benzimidazyl) sulphide ($bBzIH_2s$); 2,2'–bis (benzimidazyl) ethane ($bBzIH_2e$); M = Co; X = Cl, Br, I; L = $bBzIH_2s$, M = Co; X = Cl, Br; L = $bBzIH_2e$ and M = Ni; X = Cl, Br; L = $bBzIH_2e$) have been prepared and characterised by conductivity, magnetic susceptibility, electronic, IR and far-IR-spectra. The infrared spectral data support the involvement of pyridine nitrogen (s) rather than the imino nitrogen(s) in the complex formation. The results favour square planar structure for copper (II) and tetrahedral structure for cobalt (II) and nickel (II) complexes.

INTRODUCTION

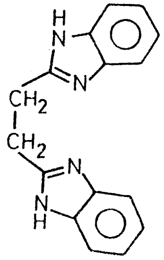
In recent years much attention has been paid on transition metal complexes containing nitrogen heterocycles because of their biological relevance and interesting spectral, magnetic and structural properties[1-11]. We have reported earlier from this laboratory some substituted benzimidazole complexes of Cu (II), Ag (I), Zn (II), Cd(II) and Hg (II) perchlorates[12,13]. The work has now been extended to the halo complexes of copper, cobalt and nickel with the following ligands are synthesised and their characterisation discussed.



2-QylBzIH



$bBzIH_2S$



$bBzIH_2e$

EXPERIMENTAL

Copper (II) chloride and bromide, cobalt (II) chloride, nickel (II) chloride and bromide were from B.D.H. Cobalt (II) bromide and cobalt (II) iodide were prepared by dissolving the corresponding carbonates in 1 : 1 aqueous hydrobromic and hydroiodic acids respectively and evoparating the resulting solutions to almost dryness under reduced pressure. The ligands were prepared according to the literature methods[14-18].

Preparation of Complexes

$[Cu(2\text{-}QylBzlK)X_2](X = Cl, Br)$: Copper (II) halide (1 mmol) in methanol (10 ml) were refluxed on a steam bath for 1hr. and then the ligand (1 mmol) in methanol (10 ml) was added and the refluxing was continued to nearly 1/2 hr when a brown crystalline solid got separated. It was washed with methanol and dried in vacuo.

$[Cu(bBzlH_2s)X_2](X = Cl, Br)$: The ligand $bBzIH_2s$ (1 mmol) in THF (10 ml) was refluxed on a steam bath for about 2 hrs and then copper (II) halide (1 mmol) in THF (5 ml) and triethylorthoformate (5 ml) was added. The refluxing was continued for 4 hrs. Three fourths of the solvent was removed under reduced pressure and the solution was allowed to stand for overnight. Light green cystalline solid that separated was washed with THF and dried in vacuo.

$[Cu(bBzlH_2e)X_2](X = Cl, Br)$: To a solution of the copper (II) halide (1 mmol) in ethanol (5 ml) was added $bBzIH_2e$ (1 mmol) in ethanol (10 ml); on refluxing the mixture for 1 hr dark green crystals separated out. It was washed with ethanol and dried in vacuo.

$[Co(bBzlH_2s)X_2](X = Cl, Br, I)$: The ligand $bBzIH_2s$ (1 mmol) in THF (10 ml) was refluxed on a steam bath for 1hr. and subsequently the metal halide (1 mmol) in THF (5 ml) and triethylorthoformate (5 ml) was added and the refluxing was continued for 1/2 hr. when blue crystalline solid separated out. It was washed with THF and dried in vacuo.

$[Co(bBzlH_2e)X_2](X = Cl, Br)$: A solution of coblat (II) halde (1 mmol) in alcohol (10 ml) was dehydrated by the addition of triethylorthoformate (5 ml) at the refluxing temperature for 15 min. To it was added the ligand (1 mmol) dissolved in alcohol (10 ml) and the refluxing was continued for 1hr. The resulting blue crystalline solid was washed with ethanol and dired in vacuo.

$[Ni(bBzlH_2e)X_2](X = Cl, Br)$: A solution of nickel (II) halide (1 mmol) and $bBzIH_2e$ (1 mmol) in ethanol (15–20 ml) was refluxed for 2 hrs. The resulting light green crystalline solid was washed with ethanol and dired under reduced pressure.

RESULTS AND DISCUSSION

The analytical results are given in Table-1. All the complexes melt with decomposition in the temperature range 280°–320°C. The complexes are not soluble in common organic solvents. However, they are soluble in DMF. The complexes have 1 : 1 stoichiometry with the general formula MLX_2. The molar conductivity values in DMF at 10^{-3} M concentration are too low to account for any dissociation of the complexes. Hence these complexes can be regarded as non-electrolytes. Due to the insolubility of the complexes in nitrobenzene, the determination of the molecular weights could not be carried out.

TABLE 1
ANALYTICAL AND MAGNETIC SUSCEPTIBILITY DATA OF Cu (II), Co (II) AND Ni (II) COMPLEXES

Complex/colour	m.pt or Dec. pt.(°C)	Found (Calc.)%				μ_{eff} B.M.
		M	C	H	N	
[Cu(2–QylBzIH)Cl$_2$] (Brown)	290	15.80 (16.73)	51.29 (50.60)	2.73 (2.89)	12.78 (11.87)	1.75
[Cu(2–QylBzIH)Br$_2$] (Brown)	280	14.40 (13.55)	41.93 (40.99)	2.29 (2.39)	8.83 (8.97)	1.74
[Cu(bBzIH$_2$s)Cl$_2$] (Light green)	300	16.40 (15.85)	40.91 (41.60)	1.85 (2.49)	14.50 (13.97)	1.91
[Cu(bBzIH$_2$s)Br$_2$] (Light green)	298	12.10 (12.97)	34.99 (34.29)	1.56 (2.04)	12.40 (11.43)	1.93
[Cu(bBzIH$_2$e)Cl$_2$] (Dark green)	293	15.20 (16.02)	48.74 (48.42)	3.55 (3.53)	14.14 (14.12)	1.96
[Cu(bBzIH$_2$e)Br$_2$] (Dark green)	295	15.20 (13.09)	38.70 (39.54)	2.94 (2.88)	10.85 (11.53)	1.95
[Co(bBzIH$_2$s)Cl$_2$] (Blue)	305	13.91 (14.87)	42.39 (42.43)	2.75 (2.53)	13.60 (14.40)	4.47
[Co(bBzIH$_2$s)Br$_2$] (Blue)	302	11.10 (12.14)	34.62 (33.95)	2.00 (2.06)	10.80 (11.54)	4.30
[Co(bBzIH$_2$s)I$_2$] (Blue)	301	10.10 (10.17)	30.01 (29.40)	1.70 (1.73)	9.78 (9.68)	4.53
[Co(bBzIH$_2$e)Cl$_2$] (Blue)	320	14.86 (15.04)	48.05 (48.98)	3.66 (3.57)	13.59 (14.29)	4.49
[Co(bBzIH$_2$e)Br$_2$] (Blue)	318	11.87 (12.25)	38.95 (39.90)	2.18 (2.91)	10.80 (11.64)	4.60
[Ni(bBzIH$_2$e)Cl$_2$] (Blue)	297	13.98 (14.90)	49.26 (49.01)	3.39 (3.37)	13.24 (14.20)	3.60
[Ni(bBzIH$_2$e)Br$_2$] (Blue)	294	11.37 (12.11)	40.47 (39.96)	3.05 (2.91)	11.92 (11.65)	3.90

The infrared spectra of the ligands in nujol mull do not show the expected νN–H band in the 3500–3200 cm^{-1} region presumably due to intermolecular hydrogen bonding. However, DMF solutions of the ligands show a strong and sharp peak around 3450 cm^{-1} attributable to νN–H indicating the dissociation of hydrogen bonding in the solution[19]. The νC=N and νC=C vibrations are very close and occur around 1620 cm^{-1} as weak bands. The N–H in-plane bending occurs around 1590 cm^{-1}, while the band appearing at 1540 cm^{-1} may be assigned to to νC=C and νC–H vibrations. νC–N and δN–H appear around 1320 cm^{-1}. The bands around 1410, 1270, 1000, 740, 625 and 430 cm^{-1} are assigned to ring vibrational modes. A weak band appears around 780 cm^{-1} and is ascribed as due to N–H out-of-plane bending vibtration.

The non particpation of the S – atom is evidenced[29] by the C–S stretching frequency in the complexes (bBzIH$_2$s) which appears at 740 cm^{-1}. It is observed for free ligand at the same position. Moreover the molecular models also revealed that the S-atoms cannot occupy the apical positions because of steric hindrance. These band assignments are tentative and have been made on the basis of similar assignments made in the case of benzimidazole and 2–α-pyridylbenzimidazole[20–22]. The infrared spectra of the CuLX$_2$, CoLX$_2$ and NiLX$_2$ complexes are similar to the spectra of the corresponding ligands. The N–H stretching vibration which is absent in the spectra of the ligands due to intermolecular hydrogen bonding, appears in the 3200–3100 cm^{-1} region in the spectra of the complexes and has considerably lower value as compared to that for free ligand. The other bands in the spectra of the complexes are almost unaffected except for slight shifts in their positions and changes in their intensities due to coordination.

The electronic spectra of copper (II), cobalt (II) and nickel (II) complexes in the solid state have been recorded in the region 50,000–12,500 cm^{-1}. The bands at 18,450 and 27,100 cm^{-1} in the electronic spectra of Cu (II) complexes are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions in the square planar geometry[23,24]. The electronic spectra of the cobalt (II) complexes exhibit high intensity and multicomponent bands in the region 16,000–14,500 cm^{-1} charateristic of cobalt (II) complexes having tetrahedral geometry and is attributed to $^4A_2 \rightarrow {}^4T_{1(p)}$ transition[25]. Hence cobalt (II) complexes are assigned tetrahedral structure. Nickel (II) complexes display two bands of high intiensity in the region 16,388–14,710 cm^{-1}. It is documented in the literature[25] that tetrahedral nickel (II) complexes show high intensity bands in the region 16,000–14,000 cm^{-1} and they are attributed to $^3T_{1(F)} \rightarrow {}^3T_{1(p)}$ transition.

The observed effective magnetic moments of the copper (II) complexs fall in the range 1.75–1.98 B.M. close to the spin only value for the one unpaired electron. The data suggest that the complexes are devoid of spin-spin interaction. However, it is difficult to predict the geometry from the magnetic moment in the case of copper (II) complexes. From the electronic spectra it may be concluded that the Cu (II) complexes have square planar geometry. The cobalt (II) complexes show magnetic moments varying from 4.3–4.6 B.M. It is documented in the literature[2,26] that tetrahedral cobalt (II) complexes display magnetic moments in the range 4.2–4.7 B.M. Hence it may be inferred that cobalt (II) complexes have tetrahedral geometry. Nickel (II) complexes exhibit magnetic moments in the range 3.6–3.9 B.M. These values are in the expected range *viz.* 3.4–4.0 B.M. for tetrahedral nickel (II) complexes[26-28]. Hence nickel (II) complexes are assigned tetrahedral structure.

Finally low frequency spectra (650–50 cm^{-1}) of the complexes were studied to obtain insight into the strength of the metal-ligand bond. The absorption bands that appear in the complexes are assigned to M–N and M–X vibrations. The assignment of metal-ligand modes is made according to the literature[30]. The characteristic infrared bands of the MLX_2 complexes, we have noticed medium intensity bands in the 280–255 cm^{-1} region attributable to the ν (M–N) vibrations. Appearance of strong intensity bands in the 320–300 (X=Cl), 260–230 (X=Br) and 215–180 (X=I) cm^{-1} regions may be regarded as due to the ν(M–X) vibrations.

It is evident from the results discussed above, the Cu (II), Co (II) and Ni (II) ions are surrounded by two halides and two nitrogens of the benzimidazole molecule. In the complexes of $bBzIH_2s$ also, the ligand coordinates bidentately and sulphur is not coordinated, probably due to steric hindrance. Thus Cu(II) complexes are suggested to have square planar geometry and Co (II) and Ni (II) complexes have tetrahedral coordination.

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