Synthesis and characterisation of mixed ligand complexes of Cu(II) containing optically active R-(+)- & S-(–)-1,1′-bi-2-naphthol (BINOL)

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The novel mixed ligand complexes of Cu(II) with optically active R-(+)- / S-(–)-1,1′-bi-2-naphthol and N, N′ – donor bidentate ligands have been synthesised and characterised by elemental analysis and various spectral studies.

Keywords: R-(+)/S-(–)-BINOL, R-(+)/S-(–)-1,1'-bi-2-napthol, Cu(II) complex, C_2–symmetry axial chiral ligand, mixed ligand complex

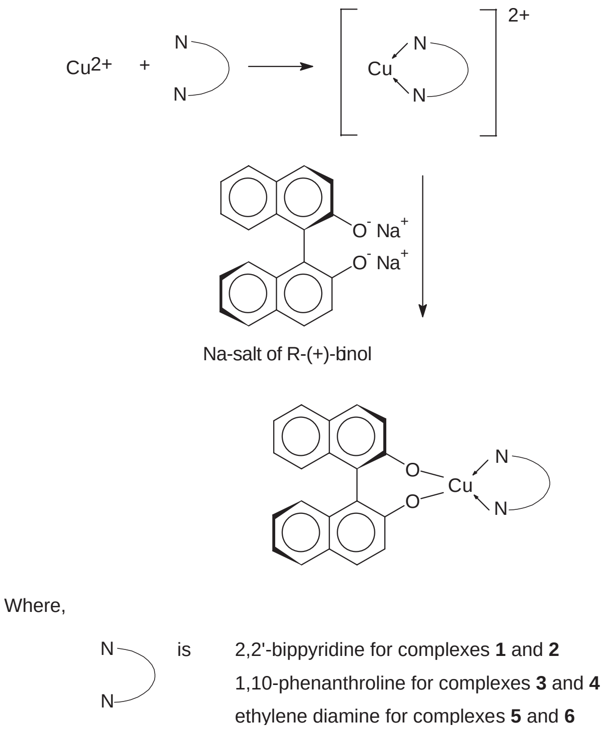
The synthesis of metal complexes with axially chiral ligands has attracted considerable interest,[1-4] This is because such compounds have been extensively used as catalysts for asymmetric synthesis. 1,1'-bi-2-naphthol (H_2binol) with restricted rotation about the C–C bond linking the two naphthyl units is chiral and has been used as a chiral auxiliary in many metal based enantioselective catalysts and reagents.[5,6] Shibasaki has developed hetrobimetallic derivatives with the binaphthol ligand coordinated both to a lanthanide and to an alkaline metal ion, which afford high asymmetric inductions for various reactions such as nitro-aldolisation[7] or Michael reactions.[8] Kobayashi obtained ytterbium or samarium compounds in presence of base and binaphthol which are enantioselective catalysts for cyclo-adddition reactions.[9] Samarium binaphthyliodo-complexes are reported to be highly enantioselective for the Diels-alder reaction.[10]

It is very well known that in the case of enantioselective catalysis using chiral metal complexes, the central metal ion provides catalytic activity for reaction, whereas the organic ligand or auxiliaries direct the steric course of the reaction. For designing highly enantioselective catalyst with a wide range of application, therefore, it is necessary to choose a proper central metal ion apart from selecting a ligand with an appropriate symmetry element and ability for chiral recognition. H_2binol is known to be a hard base and its complexes that are reported to date are also with metal ions having hard acid character. The complexes of binol with the Cu^{2+} ion, which is moderate acidic (border line) in character, are not known. With an aim to synthesise such complexes, the sodium salt of binol was treated with cupric ion that was already bounded to another N, N' – donor bidentate ligand (Scheme I). The resultant complexes were mixed ligand complexes with optically active binol as one of the ligands. The complexes have been characterised by elemental analysis and various spectral techniques like UV–visible, ESR and FAB mass spectra.

Result and discussion

The reaction of optically active H_2binol [R-(+)- / S-(–)-] with cupric ion coordinated to an N, N' – donor bidentate ligand in alcoholic solution at room temperature, yielded brown-coloured, mixed ligand complexes.

The IR spectra of the ligand H_2binol shows band at ~3650–3590 cm^{1-} indicating O–H stretching vibrations. The IR spectra of all the complexes show no band for the phenolic O–H group, which indicates coordination of the ligand binol to the metal ion. The >C=N stretching vibrations of free 2,2'-bipyridine and 1,10-phenanthroline at ~1660–1640 cm^{1-} are shifted to ~1610–1588 cm^{1-} in the corresponding complexes (**1–4**). This indicates coordination of the imine group of 2,2'-bipyridine and 1,10-phenanthroline to the metal ion. The N–H stretching band of the $-NH_2$ group of free ethylene diamine at ~3500 cm^{1-} is shifted to ~3435 cm^{1-} in the corresponding complexes (**5–6**). This confirmed coordination of $-NH_2$ group of the ethylene diamine ligand. All other bands corresponding to the binol, 2,2'-bipyridine, 1,10-phenanthroline and ethylene diamine were also observed. The elemental analysis of the complexes (Table 1) correspond to the expected molecular formula for mixed ligand complexes.



Scheme 1

The electronic spectra of the complexes in CH_2Cl_2, have a broad band with λ_{max} at ~520 nm as expected for Cu(II)–complexes.[11] In the ESR spectra of two of the complexes (**1** and **2**), hyperfine splitting is observed, indicating electron spin (S = 1/2) – nuclear spin (I = 3/2) interaction. The $g_{\parallel}$ and $g_{\perp}$ values are found to be different (Table 2) and $g_{\parallel} > g_{\perp} > 2$. The different values of g in parallel and perpendicular directions indicate distorted octahedral or tetragonal geometry around the Cu(II) ion. As the value for $g_{\parallel}$ is greater than 2, it indicates that the unpaired e^- resides in the $d_{x^2-y^2}$ orbital.

The FAB mass spectral data of complexes (**1** and **2**) confirmed formation of the mixed ligand complexes with the molecular ion peak at m/z = 504 (Table 3).

Thus, it can be concluded that mixed ligand complexes of binol with cupric ion can be prepared according to Scheme 1.

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Table 1 Analytical data of the complexes (**1–6**)

Complexes	Analysis found (calculated)/%			
	C	H	N	Cu
1	70.9	4.1	5.0	12.3
	(71.5)	(4.0)	(5.6)	(12.6)
2	71.0	4.0	4.9	13.0
	(71.5)	(4.0)	(5.6)	(12.6)
3	72.2	3.9	5.0	12.4
	(72.8)	(3.8)	(5.3)	(12.0)
4	72.4	4.0	5.0	12.1
	(72.8)	(3.8)	(5.3)	(12.0)
5	64.2	4.8	6.1	16.3
	(64.8)	(4.9)	(6.9)	(15.6)
6	64.3	5.1	6.2	16.0
	(64.8)	(4.9)	(6.9)	(15.6)

Table 2 ESR parameters of the complexes (**1** and **2**)

Complexes	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$
1	2.1714	2.0401	160
2	2.1714	2.0401	160

Table 3 FAB mass spectral data of the complexes (**1** and **2**)

Fragments	Molecular ion	*m/z* value
1	[Cu (bpy) (binol)]	504
2	[Cu (bpy) $]^{2+}$	219
3	binol	286

Experimental

Synthesis of H_2binol

H_2binol was prepared from β-naphthol, which gave the racemic mixture.[12] The resolution was carried out using (–)-N-benzyl cinchonidinium chloride.[13]

M.p. 218 ^{o}C. Found C, 84.0; H, 4.8; Calculated for $C_{20}H_{14}O_2$, C, 83.9 %; H, 4.9%. Specific rotation $[\alpha_D]^{21}$ = + 34 (c=1; THF) for R-(+)-H_2binol and $[\alpha_D]^{21}$ = –34 (c=1; THF) for S-(–)-H_2binol was found as reported earlier.

Synthesis of complexes

0.170 g (1 mmol) of $CuCl_2{\cdot}2H_2O$ was taken in 10 ml of water–alcohol (1:1 mixture) and to this was added 1 mmol of N, N' – donor ligand (diimine/diamine) (i.e. 2,2'-bipyridine or 1,10-phenanthroline or ethylene diamine) in 10 ml. of water–alcohol (1:1 mixture) dropwise with continuous stirring. The reaction was stirred for ~1 h at room temperature. To this was added 0.286 g (1 mmol) of R-(+)- or S-(–)-H_2binol and 2 mmol of NaOH in 20 ml of water–alcohol (1:1 mixture) dropwise with continuous stirring. The reaction mixture was again stirred for about ~1 h at room temperature. After completion of the reaction, the brown coloured solid formed was filtered, first washed with 10 ml of water–alcohol (1:1 mixture) and then with ether and dried in a vacuum.

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