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HOMO-DINUCLEAR HEXADENTATE COPPER(II) AND NICKEL(II) CRYPTATES: SYNTHESIS, SPECTROSCOPIC AND ELECTROCHEMICAL CHARACTERIZATION OF THE PERCHLORATE SALTS

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Abstract—Two homo-dinuclear cryptates of Cu^{II} and Ni^{II} with a ditopic cryptand incorporating both hard and soft donors are described. The electronic and EPR spectral data for the dicopper cryptate are consistent with a distorted octahedral coordination geometry. The EPR spectra of this complex is axial in nature at 77 K corresponding to the $d_{x^2-y^2}$ ground state. A room temperature magnetic moment number (μ_{eff}/μ_B) of 1.98 per copper indicate that the two Cu^{II} centres are not magnetically coupled. Cyclic voltammetric experiments show a quasi-reversible ($\Delta E_p = 115$ mV) reductive response at $E_f = -0.17$ V (vs SCE) corresponding to the Cu^{II}/Cu^{I} couple. Exhaustive controlled potential coulometry on this cryptate at 295 K gives $n = 1.96\ e^-$, signifying that the cyclic response is a two-electron process involving two independent Cu^{II} centres. The dinickel cryptate, on the other hand, does not show any cyclic response in the range $+1.0$ to -1.0 V. However, the electronic spectral and magnetic susceptibility data obtained on this cryptate are consistent with a distorted octahedral geometry around each Ni^{II}. The Schiff base precursor of the cryptand also readily forms a dicopper cryptate having similar electronic spectral, EPR and magnetic properties as the dicopper cryptate described above. However, the Cu^{II}/Cu^{I} couple for this cryptate appears at $E_f = +0.14$ with $\Delta E_p = 95$ mV. The difference in E_f values for the two cryptates are attributable to the greater σ-donor ability of the amino nitrogens compared to the imino nitrogens.

Cryptands with more then one receptor site provide systems for studying polynuclear metal complexes.[1–4] Variation of ligand design can give systems where the distances between metal ions can be varied. In the case of short distances between the metal ions, interactions between them can be probed. On the other hand, when the distance between the metal ions is significant, small substrates may be introduced[5,6] between the two leading to its activation. The ligand described here has a slipped ellipsoidal cavity as illustrated in Fig. 1. Two metal ions may enter the cavity to form dinuclear cryptates. The present cryptand was synthesized and characterized earlier.[7] We have treated this cryptand with different Cu^{II} and Ni^{II} salts in excess to isolate dinuclear complexes. The Schiff base precursor of the cryptand, also having a slipped ellipsoidal cavity, forms a dimetallic cryptate. Synthesis and characterization of these complexes are described here.

EXPERIMENTAL

Materials

Sulphur monochloride, isobutyraldehyde and tris(2-aminoethyl)amine, $NaBH_4$, $[Cu(H_2O)_6](ClO_4)_2$ and $[Ni(H_2O)_6](ClO_4)_2$ (Aldrich) were reagent grade chemicals which were used without further purification. All the solvents (Glaxo, India)

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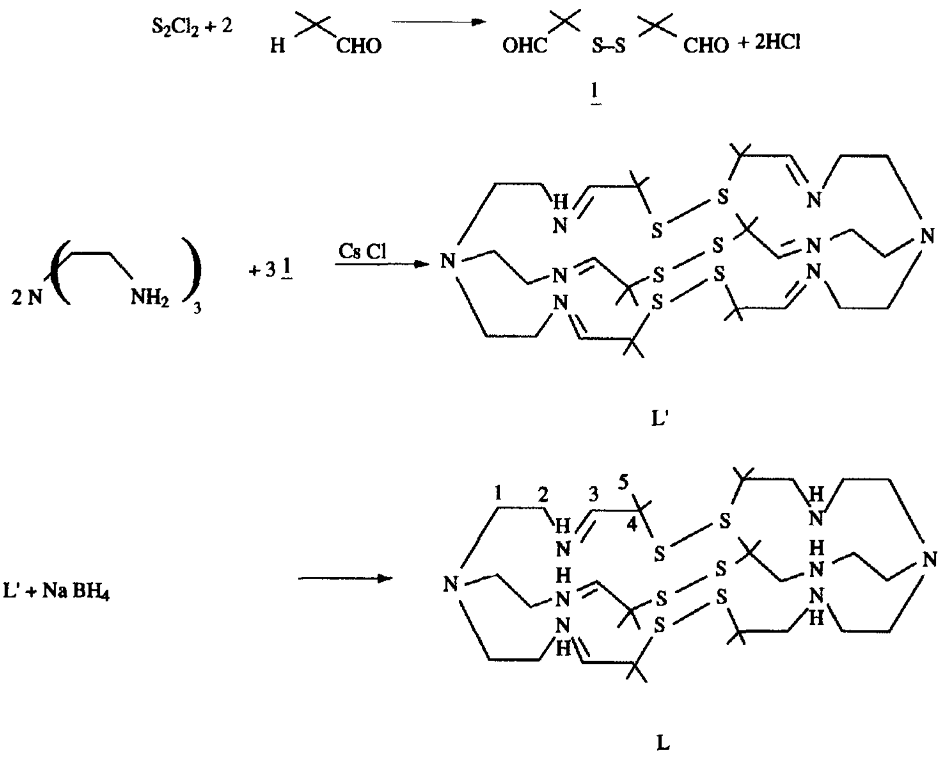

Fig. 1. Synthetic scheme for the cryptand.

were purified prior to use following standard procedures.[8]

Physical measurements were made as reported earlier.[9] Elemental analyses were done at the Central Drug Research Institute, Lucknow, India.

Synthesis of the cryptand, L

Synthesis of the precursor cryptand L′ and that of L have been reported by the authors[10] in a preliminary communication. The synthesis was achieved via several steps as illustrated schematically in Fig. 1. The diisobutyraldehyde was prepared by the thermally induced radical reaction between sulphur monochloride and isobutyraldehyde. The reaction was performed following a literature procedure.[11] Freshly distilled isobutyraldehyde (5.8 g; 0.08 mol) was mixed with CCl_4 (15 cm^3) and warmed to 40°C. To this warm solution, sulphur monochloride (5.4 g; 0.04 mol) in CCl_4 (15 cm^3) was added dropwise while stirring continuously. As soon as S_2Cl_2 came in contact with isobutyraldehyde, copious evolution of HCl gas took place which was driven out of the reaction vessel by the occasional passage of dinitrogen gas. Total addition time was 2 h and the temperature of the reaction mixture was maintained at 40°C for another 48 h, for completion of the reaction. CCl_4 was removed by distillation under reduced pressure and the resulting pale yellow thick liquid was washed several times with distilled water and the desired product was collected as a colourless liquid upon fractional distillation (15 mm; 95–100°C). Yield 72%. ^{1}H-NMR (80 MHz, $CDCl_3$, ppm) 1.4 (s, 12H, CH_3); 9.1 (s, 2H, CHO). The spectrum matches with the one reported.[11] The cryptand L′ was prepared via a [2 + 3] Schiff base condensation of tris (2-aminoethylamine) and the dialdehyde in the presence of Cs^+ ion as the template. The reaction did not give the desired product when another alkali metal ion was used. The experiment was performed as follows:

Tren (0.73 g; 5 mmol) and CsCl (0.42 g; 2.5 mmol) were dissolved in 3% aqueous tetrahydrofuran (400 cm^3) by stirring and warming to 40°C under argon. A solution of diisobutyraldehyde disulphide (1.5 g; 7.5 mmol) in tetrahydrofuran (150 cm^3) was then added over a period of 6 h and the resulting pale yellow solution was stirred at 40°C for a further 6 h. Then all of THF was removed at low pressure to obtain a colourless solid which was found to be unstable and decomposed to yellow flakes in contact with air. However, it could be used to synthesize the dicopper(II) cryptate (*vide infra*) which was found to be stable in air although highly hygroscopic. The Schiff base once formed was therefore reduced *in situ* by refluxing with excess $NaBH_4$. In a typical experiment, to the Schiff base formed using chemicals in the quantities mentioned above, solid $NaBH_4$ (0.6 g) was added in portions over a period of 15 min at RT. After the addition was complete, the solution was allowed to reflux for 8 h, THF was completely removed and the residue shaken with 20 cm^3 of water; the desired cryptand formed oily droplets which could be extracted with chloroform (2×50 cm^3). The crude cryptand was purified by passing through a neutral alumina column. The major impurities were removed by eluting with $CHCl_3$ and the pure product was eluted with the mixed solvent, $CHCl_3$ and MeOH (2 : 1 ratio by volume). Removal of the solvent gave a pale yellow oil in 42% yield. As reported in the literature,[12] $NaBH_4$ did not cleave the disulphide bond, as evidenced by the FAB-mass spectrum which shows the molecular ion peak at m/z 816. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) 1.35 (s, 36H, CH_3); 2.6 (t, 12H, 1); 2.7 (overlapped t and s, 24H, 2 and 3). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) 27.5 (C5); 47.5 (C1); 49.6 (C4); 53.0 (C2); 59.1 (C3).

Hexapicrate derivative of L

The picrate derivative was prepared to characterize the cryptand further. To a solution of L (0.2 g; 0.25 mmol) in chloroform (15 cm^3) was added a solution of picric acid (0.3 g; 1.5 mmol) in benzene (25 cm^3) with stirring at 40°C. A bright yellow precipitate appeared immediately which was collected by filtration and dried *in vacuo*. Yield 85%. Found: C, 39.8; H, 4.2; N, 16.5 and S, 8.9. $C_{72}H_{96}N_{26}O_{42}S_6$ requires: C, 39.5; H, 4.4; N, 16.6 and S, 8.8%. The elemental analysis indicates that it is a hexapicrate. It has been found by other[13] workers that an acid does not protonate the bridgehead nitrogens of a cryptand easily. ^{1}H-NMR (400 MHz, d_6-DMSO, ppm) 1.3 (s, 36H, 5); 2.9 (d, 12H, 1); 3.9 (overlapped t and s, 24H, 2 and 3) and 8.7 (s, 12H, aromatic).

Synthesis of $[Cu_2L'](ClO_4)_4$, **1**

A solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.37 g; 1 mmol) in methanol (15 cm^3) was added to a solution of L′ (0.4 g; 0.5 mmol) in methanol (15 cm^3) and stirred for 10 min. Then chloroform (50 cm^3) was added to the green solution and the resulting solution kept at 5°C overnight. The green solid deposited was collected by filtration and dried *in vacuo*. Yield 40%. This complex was found to be very hygroscopic.

Synthesis of $[Cu_2L](ClO_4)_4$, **2**

The freshly prepared ligand (0.2 g; 0.25 mmol) dissolved in dry EtOH (10 dm^3) was treated with a solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.18 g; 0.5 mmol) in EtOH (10 dm^3) at RT under nitrogen. On stirring the solution at RT for 30 min, a green solid precipitated which was collected by filtration and dried *in vacuo*. Yield 62%.

Synthesis of $[Ni_2L](ClO_4)_4$, **3**

The freshly prepared ligand (0.2 g; 0.25 mmol) in EtOH (10 dm^3) was treated with $[Ni(H_2O)_6](ClO_4)_2$ (0.17 g; 0.5 mmol) dissolved in EtOH (10 dm^3). After stirring at RT for 30 min, EtOH was completely removed, the residue washed several times with water and finally dried at 40°C *in vacuo* to obtain a purple solid in 54% yield. Analytical data for the complexes are given in Table 1.

RESULTS AND DISCUSSION

The cryptand or its precursor Schiff base does not include the Cs^I ion. Complexation by transition metal ions by these ligands can be easily achieved. Under no circumstances can a mononuclear cryptate be isolated.

The molar conductivities of the complexes in acetonitrile (*ca* 1×10^{-3} M) lie in the range 490–510 $\Omega^{-1}cm^2\,mol^{-1}$ at room temperature (RT). This range is higher than the one found[14] in the case of 1 : 3 electrolytes. In that case, the complexes can be formulated as $[M_2L]\cdot 4ClO_4$ in acetonitrile. Each complex exhibits a strong and broad absorption band centred around 1100 cm^{-1} in the infrared spectrum attributable to the presence of anionic perchlorates.[15] Absorptions due to coordinated perchlorate are not seen.

Electron transfer properties of the cryptates were probed by cyclic voltammetry in acetonitrile at 295 K (Table 1). The cyclic voltammogram (Fig. 2) of the dicopper cryptate **1** shows a quasi-reversible response at $E_f = +0.14$ V with $\Delta E_p = 95$ mV. In case of **2**, the response (Fig. 2) occurs at $E_f = -0.17$ V with $\Delta E_p = 115$ mV. The following characteristics were observed: ΔE_p value increases by 35 (for **1**) and 40 mV (for **2**) with the increase in the scan rate from 50 to 200 mV s^{-1}; $i_{pa}/i_{pc} = 1.1$ at all the scan rates employed (20, 50, 100, 200 mV s^{-1}). The corresponding dinickel complex, **3**, does not show any cyclic response in the range -1.0 to $+1.0$ V. Also, the free ligand does not show any response in the same region. An exhaustive controlled potential coulometric experiment done only on complex **2** at -0.4 V gives $n = 1.96$ e^-. This indicates that

Table 1. RT magnetic moments, electrochemical and analytical data of the cryptates[a]

		Cu^{II}/Cu^{I} couple		Analysis (%)[b]			
Cryptate	μ_{eff}/μ_B	E_f(V)	ΔE_p(mV)	C	H	N	S
1	2.01	0.14	95	31.7(32.6)	5.3(5.0)	8.0(8.4)	14.1(14.5)
2	1.98	−0.17	115	32.4(32.3)	5.7(5.8)	8.5(8.4)	14.3(14.4)
3	2.93	—	—	32.7(32.5)	5.9(5.9)	8.7(8.4)	14.2(14.5)

[a] All results reported were obtained at 295 K at a scan rate of 100 mV s^{-1} and referenced to SCE; $E_f = 0.5(E_{pc}+E_{pa})$; E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively.

[b] Calculated values are given in parentheses.

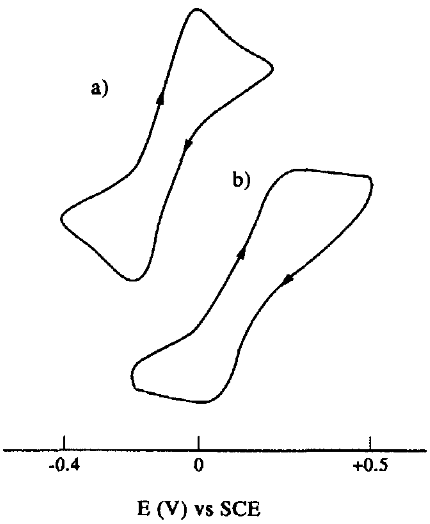

Fig. 2. Cyclic voltammograms for the Cu(II) complexes: (a) **1** and (b) **2**.

the cyclic response is associated with the transfer of two electrons. We, therefore, assign the cyclic response as due to the Cu^{II}/Cu^{I} couple associated with the two independent Cu^{II} centres as shown in the following redox reactions:

$$[Cu_2L']^{4+}\ (\mathbf{1})\ +2e^- = [Cu_2L']^{2+}$$
$$[Cu_2L]^{4+}\ (\mathbf{2})+2e^- = [Cu_2L]^{2+}.$$

The lower E_f value in **1** compared to that observed in the case of **2** can be accounted for by the lower σ-donor ability of the imino nitrogens compared to that of the amino nitrogens.[16]

Electronic spectral studies were carried out further to investigate the coordination geometry around each metal ion inside the cavity. The data for the complexes at RT in acetonitrile are collected in Table 2 with probable assignments. The free ligands do not absorb significantly at wavelengths longer than 280 nm. The spectral band positions do not change to any noticeable extent when the solvent was changed from methanol to DMF, implying no coordination by the solvent molecules. The electronic spectrum of the complex **1** shows five bands (Table 2). In the case of hexacoordinated Cu^{II} complexes with moderate Jahn–Teller distortions, the lowest energy, $d_{z^2} \rightarrow d_{x^2-y^2}$ transition occurs[17] around 750–900 nm. For **1**, the band at 750 nm is similarly assigned. Therefore, the broad band at 630 nm is attributable to the transitions from the components of t_{2g} to $d_{x^2-y^2}$. The strong band at 275 nm is due to the $\sigma(N) \rightarrow Cu^{II}$ LMCT transition[18] and the intra-ligand absorptions. The bands at 385 and 465 nm are therefore originating from the disulphide groups. Theoretical studies[19] suggest that the energy difference between the two highest occupied MOs of a disulphide depend upon the substituents in the α-carbon atoms. Accordingly, with the α-carbon atoms bearing two methyl substituents, the energy difference between the HOMO and the SHOMO as in the present cryptand should be about 0.65 eV. Taking this number at its face value, the two bands at 385 and 465 nm are attributable[20] to the LMCT transitions from the SHOMO and the HOMO respectively to the *d*-vacancy. The dicopper cryptate, **2**, shows five bands at nearly the same positions (Table 2) as in **1** except the *d–d* bands which are slightly red-shifted. The five bands are assigned as in the case of **1**.

Three ligand field bands are observed for the dinickel complex, **3**. The peak positions vary slightly with the nature of the solvent indicating interference of the solvent with the chromophore. For an octahedral (trigonal antiprismatic) arrangement of donor atoms around Ni^{II}, three spin allowed transitions[21] are expected: ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. Intensities of these transitions usually lie below 30 $dm^3\ mol^{-1}\ cm^{-1}$. Complexes with trigonal prismatic geometry, however, show ligand field transitions with intensities more than 30 $dm^3\ mol^{-1}\ cm^{-1}$. Therefore, the geometry around Ni^{II} is closer to trigonal prismatic. X-Ray crystallographically characterized trigonal prismatic NiS_3N_3 chromophores[22] show similar

Table 2. Electronic spectral data for the cryptates

Cryptate	λ_{max}(nm)	ε_{max}(dm^3 mol^{-1} cm^{-1})	Assignment
1	745	376	$d_{z^2} \longrightarrow d_{x^2-y^2}$
	605	516	$t_{2g} \longrightarrow d_{x^2-y^2}$
	465	1010	$(S_2) \longrightarrow$ Cu^{II} LMCT
	385	2010	$(S_2) \longrightarrow$ Cu^{II} LMCT
	275	5400	$\sigma(N) \longrightarrow$ Cu^{II} LMCT + intra-ligand absorption
2	776	420	$d_{z^2} \longrightarrow d_{x^2-y^2}$
	633	502	$t_{2g} \longrightarrow d_{x^2-y^2}$
	460	1339	$(S_2) \longrightarrow$ Cu^{II} LMCT
	385	1922	$(S_2) \longrightarrow$ Cu^{II} LMCT
	288	5370	$\sigma(N) \longrightarrow$ Cu^{II} LMCT + intra-ligand absorption
3	925	63	$^3A_{2g} \longrightarrow {}^3T_{2g}$
	856	63	$^3A_{2g} \longrightarrow {}^3T_{1g}$
	552	60	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$
	405	102	$(S_2) \longrightarrow$ Ni^{II} LMCT
	262	8925	$\sigma(N) \longrightarrow$ Ni^{II} LMCT + intra-ligand absorption

ligand field transitions. The shoulder which appears at 405 nm is assigned as due to LMCT transitions involving the disulphides and Ni^{II} by comparing with the spectra of the two dicopper cryptates.

Effective room temperature magnetic moment (μ_{eff}/μ_B) values are presented in Table 1. The values are typical of discrete Cu^{II} and Ni^{II} hexadentate complexes.[23] There is no magnetic interaction ($2J \rightarrow 0$) between the two metal ions in any of the complexes although they are bridged by three disulphide groups. For a noticeable magnetic interaction, the orbitals of the two metal ions and the disulphide moiety should have a significant overlap. However, due to the slipped ellipsoidal nature of the cavity, the possibilities for magnetic interaction either by super exchange pathway or by direct overlap of orbitals of Cu^{II} or Ni^{II} centres are absent.

To probe the possible existence of magnetic interactions further between the two Cu^{II} centres in **1** and **2**, they were studied by EPR spectroscopy at 298 and 77 K. The EPR spectral data are collected in Table 3. No signal near $g = 4$ is found either in the solid state or in solutions of **1** or **2** which indicates that there is no interaction between the metal centres.[24] In the solid state at 298 or 77 K, both **1** and **2** show only broad bands with $g_{av} = 2$ and are not indicative of the stereochemistry of these cryptates. At 298 K, the spectra in acetonitrile show characteristic four-line signals for both **1** and **2**. When cooled to 77 K, each spectrum changes to an axial one indicating the presence of three-fold symmetry around each metal ion. The $A_{\parallel}^{Cu}$ values are small (Table 3) as each Cu^{II} is bonded to three sulphurs which are known[25] to reduce hyperfine coupling.

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Table 3. EPR spectral data of the dicopper cryptates

Cryptate	g_{av}	$A_{av}^{Cu\,a}$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Cu\,a}$	
1	2.09	—	—	—	—	(298 K solid sample)
	2.08	—	—	—	—	(77 K solid sample)
	2.10	60	—	—	—	(298 K in MeCN)
	—	—	2.35	2.09	110	(77 K in MeCN)
2	2.08	—	—	—	—	(298 K solid sample)
	2.07	—	—	—	—	(77 K solid sample)
	2.11	63	—	—	—	(298 K in MeCN)
	—	—	2.36	2.09	114	(77 K in MeCN)

[a] Unit of A^{Cu} is cm^{-1} × 10^{-4}.

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