Electrochemical Synthesis of Neutral Divalent Transition-metal Complexes with Tetradentate Thioether–Benzimidazole-containing Ligands†

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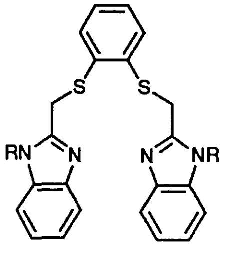
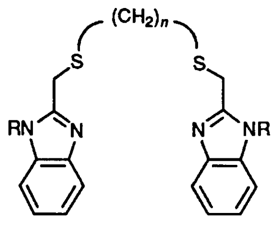
The electrochemical synthesis and physicochemical properties of neutral divalent transition-metal complexes [ML][H_2L = 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane or 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane] of tetradentate N_2S_2 donor ligands are presented. The dianionic ligands act as tetradentate ligands with both thioether sulphurs and both deprotonated benzimidazole nitrogens co-ordinating. All compounds are four-co-ordinated in tetrahedral or distorted tetragonal geometries with the exception of the nickel complexes, in which magnetic interactions are operating, indicating that they are polymeric with a distorted-octahedral geometry around the metal.

In order to understand the mechanisms that rule the physiological behaviour of metalloproteins it is necessary to know their structures or, at least, the structure of the active site. In accordance with the structural, chemical, and spectroscopic characteristics, there are several types of copper(II) ions present in copper proteins and there are two main factors to be considered in relation to the co-ordination of the metal ion: first, the imidazole group of histidine is a ligand apparently present in all proteins that contain copper and, secondly, it is certain that distortions in the co-ordination geometry around the metal, due to the structure of the protein, have a great importance because they control the redox properties of the particular protein. From this point of view, a logical step to synthetic models should be to design and synthesise ligands which contain one or more imidazole groups and so might impose a distorted co-ordination around the Cu^{II}.

Ligands such as (1)—(3) have two imidazole-nitrogen atoms and two thioether sulphur atoms available as potential donors. Consequently, these ligands are useful in the synthesis of metal complexes that, in the case of copper, may be considered as models for the type 1 sites present in blue proteins.

To date, several cationic copper, nickel, and cobalt complexes have been synthesised from these types of ligands.[1–8] Herein we report an extension of the electrochemical procedure to facilitate the synthesis of electrically neutral complexes [ML]·$n$$H_2O$ with copper, nickel, cobalt, zinc, and cadmium. The ligands L result from deprotonation of 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane (2; $n = 3$, R = H), H_2bbdhp, and 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane (2; $n = 2$, R = H), H_2bbdhx. The syntheses of mixed-ligand neutral complexes [ML(L′)] [L′ = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)] are also discussed.


(1)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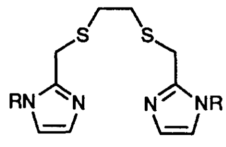
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Results and Discussion

The ligands were prepared by means of a Phillips acid-catalysed condensation as described in the Experimental section. The neutral metal complexes were obtained by the electrochemical route also detailed in the Experimental section and all compounds were recovered as powders. The reaction involved in the preparation of the complexes can be represented according to equation (1), and the process involved in the synthesis can be established by the value of the electrochemical efficiency defined as the quantity of metal dissolved per Faraday of charge and calculated from the relationship (2) where I is the

$$E_f = \frac{\text{Metal used} \times 96\,500}{I \times A \times \text{Time}} \qquad (2)$$

current intensity in mA and A is the atomic weight of the metal.

$$M + H_2L \longrightarrow [ML] + H_2 \qquad (1)$$

When E_f is close to 0.5 mol F^{-1} the process involved can be represented by reactions (3) and (4), on the other hand if E_f is

$$\text{Cathode:} H_2L + 2e^- \longrightarrow L^{2-} + H_2 \qquad (3)$$

$$\text{Anode:} L^{2-} + M \longrightarrow [ML] + 2e^- \qquad (4)$$

close to 1 mol F^{-1} the synthesis involves steps (5) and (6) followed by the oxidation reaction (7). The experimental conditions are given in Table 1 and it can be observed that only

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† *Non-S.I. units employed:* B.M. ≈ 9.27 × 10^{-24} J T^{-1}, G = 10^{-4} T.

Table 1. Experimental conditions for the electrochemical synthesis of the complexes [ML] (L = bbdhp or bbdhx)

Complex	Amount of ligand (g)[a]	Initial potential (V)[b]	Time (s)	Metal used (mg)	E_f/mol F^{-1}
[Cu(bbdhp)]·3H_2O	0.2082	14.0	10 800	60.7	0.89
[Cu(bbdhx)]·4H_2O	0.1980	31.5	10 800	60.1	0.84
[Ni(bbdhp)]·3H_2O	0.1745	10.5	8 100	24.5	0.50
[Ni(bbdhx)]·2H_2O·CH_3CN	0.1981	24.5	9 900	21.5	0.36
[Co(bbdhp)]·3H_2O	0.2081	16.5	10 800	29.1	0.44
[Co(bbdhx)]·3H_2O	0.1980	37.0	10 800	32.0	0.48
[Zn(bbdhp)]·3.5H_2O	0.1913	24.3	9 000	29.8	0.49
[Zn(bbdhx)]·3.25H_2O	0.1917	37.8	10 800	46.8	0.64
[Cd(bbdhp)]·3H_2O	0.2025	17.4	10 020	58.9	0.50
[Cd(bbdhx)]·3.5H_2O	0.1981	27.5	10 800	56.9	0.45

[a] Plus NMe_4ClO_4 (*ca.* 10 mg). [b] Voltage to produce a current of 10 mA.

Table 2. Analytical[a] and mass spectral[b] data for the complexes [ML] (L = bbdhp or bbdhx)

Complex	Analysis (%) C	N	H	M	$M + 1$
[Cu(bbdhp)]·3H_2O	46.15	10.95	3.95		431
	(47.15)	(11.60)	(4.95)		
[Cu(bbdhx)]·4H_2O	43.40	11.20	3.65	13.85	417
	(44.30)	(11.50)	(4.90)	(13.05)	
[Ni(bbdhp)]·3H_2O	46.80	12.05	5.15	11.25	425
	(47.60)	(11.70)	(5.00)	(12.25)	
[Ni(bbdhx)]·2H_2O·CH_3CN	49.65	14.10	4.10	11.30	411
	(49.20)	(14.35)	(4.70)	(12.05)	
[Co(bbdhp)]·3H_2O	47.60	11.70	5.00		426
	(47.60)	(11.70)	(5.00)		
[Co(bbdhx)]·3H_2O	45.45	12.05	3.95	13.65	412
	(46.45)	(12.05)	(4.75)	(12.65)	
[Zn(bbdhp)]·3.5H_2O	45.40	11.40	4.60	14.10	431
	(46.10)	(11.30)	(5.00)	(13.20)	
[Zn(bbdhx)]·3.25H_2O	44.90	11.75	3.95		417
	(45.40)	(11.75)	(4.75)		
[Cd(bbdhp)]·3H_2O	42.20	10.50	3.50	22.05	479
	(42.80)	(10.60)	(5.35)	(21.10)	
[Cd(bbdhx)]·3.5H_2O	41.00	10.50	3.50	21.50	465
	(40.95)	(10.60)	(5.35)	(21.30)	

[a] Calculated values in parentheses. [b] Fast atom bombardment.

Table 3. Ligand-field maxima for the nickel(II), cobalt(II), and copper(II) complexes

Complex	$\lambda_{max.}$*/nm
[Ni(bbdhp)]·3H_2O	1 042, 645, 454
[Ni(bbdhx)]·2H_2O·CH_3CN	1 000, 610, 400
[Ni(bbdhp)(phen)]·4H_2O	1 000, 625, 475
[Ni(bbdhx)(bipy)]·3H_2O·CH_3CN·0.5EtOH	893 (br), 588, 476 (sh), 435
[Co(bbdhp)]·3H_2O	1 316, 1 163, 602, 540 (sh), 375
[Co(bbdhx)]·3H_2O	1 280, 1 110, 602, 570 (sh), 380
[Co(bbdhp)(phen)]·4H_2O	1 330, 1 110, 588, 375
[Cu(bbdhp)]·3H_2O	665 (br), 420 (sh), 375
[Cu(bbdhx)]·4H_2O	655, 400

* Diffuse reflectance spectra; sh = shoulder, br = broad.

copper compounds show efficiencies close to 1 mol F^{-1}; for the other compounds (M = Ni, Co, Zn, or Cd) E_f has values close to 0.5 mol F^{-1}.

$$\text{Cathode}: H_2L + e^- \longrightarrow HL^- + \tfrac{1}{2} H_2 \quad (5)$$

$$\text{Anode}: HL^- + M \longrightarrow [M(HL)] + e^- \quad (6)$$

$$[M(HL)] \longrightarrow [ML] + \tfrac{1}{2} H_2 \quad (7)$$

All complexes were characterised by elemental analysis and mass spectra (Table 2) and i.r. spectroscopy. Copper, nickel, and cobalt complexes were also studied by visible spectroscopy (Table 3). It must be stated that the great insolubility of these neutral systems limits their study in solution, particularly for zinc and cadmium compounds.

One of the most representative changes, when i.r. spectra of ligands and complexes are compared, occurs in the region between 1 620 and 1 530 cm^{-1}. The spectra of the ligands show three bands in this region attributable to the ν(C=N) and ν(C=C) of the benzimidazole group. In the spectra of the complexes these absorptions undergo a shift and a single band at *ca.* 1 600 cm^{-1} is observed. Lattice water absorptions are detected in the spectra of the complexes as broad bands around 3 400 cm^{-1}.

The molecular ion peak is always present in the fast atom bombardment mass spectra of these compounds and only for [Cd(bbdhp)]·3H_2O and [Zn(bbdhx)]·3.5H_2O is it very weak in intensity. In the mass spectra of the complexes breakdown peaks were found due to fragments involving co-ordination of M^{II} to the species produced by cleavage of the ligand on either side of the ethylene or propylene link. It is therefore possible to find peaks corresponding to metal bound to the thioether-sulphur atom onto the imidazole-nitrogen atom. Other peaks may be assigned to the fragments $[MS_2(CH_2)_n]^+$ (n = 2 or 3), $[MN_2C_8H_6]^+$, $[M(N_2C_8H_6)_2]^+$, and $[MN_2C_8H_6S_2(CH_2)_n]^+$ (n = 2 or 3).

Because of the insolubility of these compounds, optical spectra were only recorded in the solid state (by diffuse reflectance). Both blue cobalt compounds present similar electronic spectra with two multiple bands one of which is situated in the near-i.r. region and the other in the visible region at *ca.* 600 nm. These absorptions are typical for tetrahedral or pseudo-tetrahedral cobalt(II) complexes and can be assigned to $^4T_1(F) \longleftarrow {}^4A_2$ and $^4T_1(P) \longleftarrow {}^4A_2$ transitions.[9] These spectra are similar to that observed when apotyrosinase is remetallated with Co^{II} generating a tetrahedral chromophore.[10] The magnetic moment was determined for [Co(bbdhx)]·3H_2O (4.41 B.M.); this value falls inside the range predicted, by theoretical considerations, for high-spin tetrahedral cobalt(II) complexes.[11]

The diffuse-reflectance spectra for the green nickel complexes give bands at *ca.* 1 000 and *ca.* 620 nm. These values are well within the range for typical octahedral nickel complexes and so the bands can be assigned to $^3T_{2g} \longleftarrow {}^3A_{2g}$ and $^3T_{1g} \longleftarrow {}^3A_{2g}$ transitions.[12,13] Bouwman *et al.*[5] have described the structure of [1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane]-di-isocyanatonickel(II) where it is suggested that the N_4S_2 chromophore around the metal ion leads to absorptions at *ca.* 970 and 571 nm. The magnetic susceptibility of the nickel compounds was studied in the range 20—300 K. Plots of the temperature dependence of the magnetic susceptibility and the reciprocal magnetic susceptibility are shown in the Figure. The plot of $1/\chi_M$ *vs.* T is linear and obeys the Curie–Weiss law $[1/\chi_M = C(T + \theta)]$ with a Weiss constant of θ = 35.0 K for [Ni(bbdhp)] and of θ = 24.5 K for [Ni(bbdhx)] obtained by a least-squares method, giving magnetic moments of 3.10 and 2.99 B.M. respectively, at 300 K. The experimental magnetic susceptibility increases as the temperature is lowered and the magnetic susceptibility shows a field dependence such that, when the magnetic field changes from 5 000 to 500 G, the magnetic moment also changes {from 2.99 to *ca.* 4 B.M. at 300

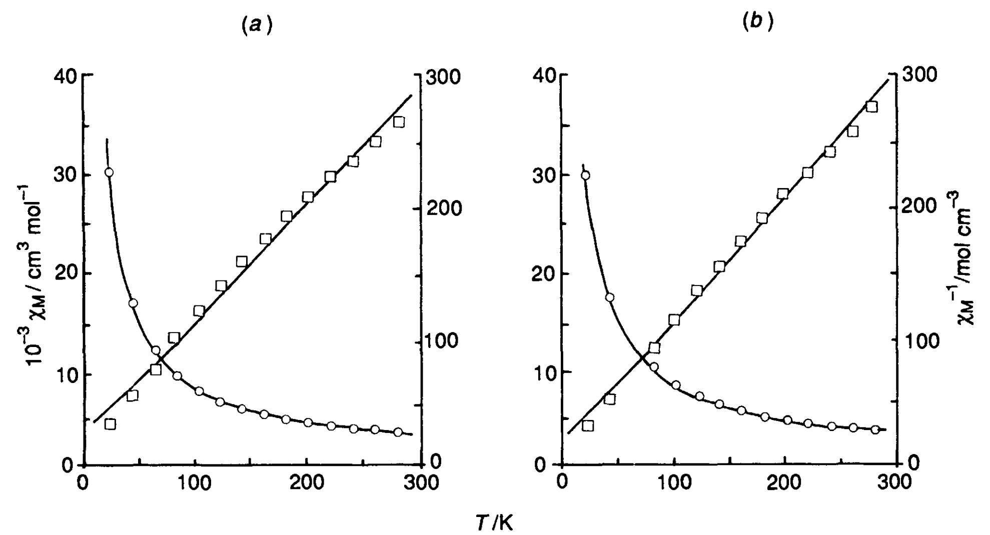

Figure. Plots of χ_M *vs.* T and $1/\chi_M$ for (*a*) [Ni(bbdhp)] and (*b*) [Ni(bbdhx)]

Table 4. Analytical data (%)* for the complexes [ML(L′)]

Complex	C	N	H	M
[Ni(bbdhx)(bipy)]·$3H_2O$·CH_3CN·0.5EtOH	54.95	14.45	5.65	9.00
	(54.35)	(14.30)	(5.25)	(8.55)
[Ni(bbdhp)(phen)]·$4H_2O$	54.10	13.05	3.95	8.75
	(54.95)	(12.40)	(5.00)	(8.65)
[Zn(bbdhp)(phen)]·$3.5H_2O$	54.20	12.75	4.10	10.15
	(55.15)	(12.45)	(4.90)	(9.70)
[Cd(bbdhp)(phen)]·$4H_2O$	51.35	10.70	4.80	17.70
	(51.05)	(11.40)	(4.65)	(17.05)
[Co(bbdhp)(phen)]·$4H_2O$	54.10	12.20	3.85	9.35
	(54.95)	(12.40)	(5.00)	(8.70)

* Calculated values in parentheses.

K for [Ni(bbdhx)]}. These results suggest that magnetic interactions are operating[14,15] and therefore the nickel complexes are likely to be polymeric through the benzimidazole nitrogen with a distorted-octahedral geometry around the metal. This is also supported by the observed ligand-field parameters: $B = 952$ cm^{-1}, $Dq = 1\,000$ cm^{-1} for [Ni(bbdhx)]; $B = 800$ cm^{-1}, $Dq = 960$ cm^{-1} for [Ni(bbdhp)]. The theoretical calculation for the ν_3 absorption, corresponding to a $^3T_{1g}(P) \longleftarrow {}^3A_{2g}$ transition, suggests that this band will fall in the energy region where charge-transfer bands are sited thus making its assignment difficult. The band at *ca.* 400—450 nm, which also appears in the spectra of the cobalt (*ca.* 380 nm) and copper (*ca.* 400 nm) compounds, may be associated with thioether $S(\sigma) \longrightarrow M^{II}$ ligand-to-metal charge transfers (l.m.c.t.s). This has been studied in copper complexes where this transition is expected to occur somewhere between 320 and 400 nm[7,8,16,17] and can overlap with some l.m.c.t. bands $\pi(N) \longrightarrow M^{II}$ and $M^{II} \longrightarrow \pi^*$ (ligand).[16]

The *d–d* transition in copper complexes at *ca.* 650 nm suggests a geometry distorted from square planar or tetragonal.[18] In the cationic complexes of H_2bbdhx the bulky nature of the ligand prevents planar four-co-ordination of Cu^{II} and a distorted trigonal-bipyramidal co-ordination geometry is achieved *via* the ligand donor set with a halide anion providing the fifth donor.[8] The use of space-filling models has suggested that the geometric requirement of bbdhp prevents all of the four donor atoms from co-ordinating to one copper atom at the same time,[7] however, the *X*-ray structure of a cationic copper(II) complex derived from bis-N-methylated bbdhp reveals a distorted trigonal-bipyramidal co-ordination *via* the ligand donor set and a water molecule.[1] Th e.s.r. spectra of the neutral complexes run at room temperature and 110 K are not particularly informative, showing only a single line with the maximum absorption corresponding to $g = 2.10$. The line is slightly asymmetric, being broadened on the low-field side. Whilst this does not help define a co-ordination geometry, it is not compatible with the distorted trigonal-bipyramidal geometry found in the cationic complexes.[8] The extreme insolubility of the neutral complexes is perhaps indicative of polymerisation. This could involve the deprotonated benzimidazole as a bridging ligand, or members of the donor set if they are not involved with a single copper atom due to steric inhibition.

In order to prepare mixed-ligand complexes [ML(L′)] nitrogen-containing Lewis bases (L′ = bipy or phen) were introduced into the electrochemical cell. In all cases a product began to precipitate after some minutes. This was filtered off, washed, and dried under vacuum. Analytical data were only successful for [M(bbdhp)(phen)] (M = Ni, Co, Zn, or Cd) and [Ni(bbdhx)(bipy)] (Table 4). In the other cases, the precipitate was found to be a mixture of [ML(L′)], [ML], and the additional ligand L′; these formulations were determined with the help of mass spectra. Successful complexation was also characterised by mass spectroscopy for [Co(bbdhp)(phen)] (*m*/*z* 607), [Ni(bbdhp)(phen)] (*m*/*z* 605), and [Ni(bbdhx)(bipy)] (*m*/*z* 567), where the molecular ion peak was observed.

The i.r. spectra of [M(bbdhp)(phen)] show bands corresponding to co-ordinated 1,10-phenanthroline and bbdhp. A surprising change is noted in the spectra of the brilliant green complex [Ni(bbdhx)(bipy)] where the three bands at 1 600—1 530 cm^{-1} of the free protonated ligand H_2bbdhx undergo a significant shift to higher frequency resulting in a broad medium-intense band at 1 660 cm^{-1}, and three intense bands of co-ordinated 2,2′-bipyridyl are noted[19] at 1 595, 1 470, and 780 cm^{-1}. Absorptions in the diffuse reflectance spectra for nickel and cobalt complexes are given in Table 3; these are typical for octahedral geometries at the metal ion with the added nitrogen-containing Lewis base leading to a N_4S_2 chromophore. The magnetic moment for [Ni(bbdhx)(bipy)] is independent of temperature with a value of 3.10 B.M., providing additional evidence in favour of an octahedral geometry. Copper did not give adducts of the type [CuL(L′)].

Experimental

Microanalyses were determined using a Perkin-Elmer 240B

Table 5. Experimental conditions for the electrochemical synthesis of [ML(L′)]

M	H_2L	L′	Amount of H_2L (g)[a]	Amount of L′ (g)[a]	Initial potential (V)[b]	Time (s)	Metal used (mg)	E_f/mol F^{-1}
Ni	H_2bbdhx	bipy	0.1951	0.0861	10.0	10 620	31.0	0.48
Ni	H_2bbdhp	phen	0.1764	0.0942	16.0	9 000	21.6	0.40
Zn	H_2bbdhp	phen	0.1913	0.1029	18.0	9 600	31.3	0.48
Cd	H_2bbdhp	phen	0.2029	0.1089	31.5	9 600	46.1	0.42
Co	H_2bbdhp	phen	0.2081	0.1119	21.7	10 800	35.8	0.54

[a] Plus NMe_4ClO_4(*ca.* 10 mg). [b] Voltage to produce a current of 10 mA.

microanalyser. I.r. spectra were recorded, as Nujol mulls or KBr discs, using a Perkin-Elmer 180 spectrophotometer, diffuse reflectance spectra of solids using a Pye Unicam SP700 spectrometer, proton n.m.r. spectra on a Bruker WH250FT spectrometer, mass spectra on a Kratos MS50TC, and e.s.r. spectra using a Bruker ER200D-Src spectrometer. Magnetic moments were determined by the Faculty of Physics at the University of Santiago. All reagents and solvents were of commercially reagent grade quality.

The protonated ligands H_2bbdhp and H_2bbdhx were prepared by means of a Phillips condensation reaction. The corresponding acid (3,7-dithianonanedioic or 3,6-dithia-octanedioic) (50 mmol) was refluxed during 24 h with 1,2-diaminobenzene (100 mmol) in 4 mol dm^{-3} HCl (250 cm^3). The resultant solution was filtered while warm and, after some hours, a white solid precipitated. This powder was filtered off, dissolved in water, and treated with sodium hydroxide. The white solid which precipitated was recrystallised from ethanol by addition of cold water.[7,8] Both ligands were filtered off, dried under vacuum, and characterised by elemental analysis, ^1H n.m.r. and i.r. spectroscopy: H_2bbdhp (Found: C, 61.05; H, 5.65; N, 14.95. Calc. for $C_{19}H_{20}N_4S_2$: C, 61.95; H, 5.45; N, 15.20%); ^1H n.m.r. [$(CD_3)_2SO$], δ 1.80 (q), 2.60 (t), 3.70 (s), 7.15 (m), 7.45 (m), and 12.30 (s); H_2bbdhx (Found: C, 60.35; H, 4.95; N, 15.50. Calc. for $C_{18}H_{18}N_4S_2$: C, 61.05; H, 5.10; N, 15.80%); ^1H n.m.r. [$(CD_3)_2SO$], δ 2.78 (s), 3.97 (s), 7.18 (m), and 7.50 (m).

The electrochemical method used in the synthesis of the metal complexes is similar to that described by Habeeb *et al.*[20] The cell was a tall-form beaker (100 cm^3) fitted with a rubber bung through which the electrical leads entered the cell. The anode, in foil form, was suspended from a platinum wire; the cathode was also a platinum wire. The ligand(s) were dissolved in the appropriate solvent and tetramethylammonium perchlorate (*ca.* 10 mg) added as the supporting electrolyte. Acetonitrile was used as solvent to prepare [M(bbdhp)] and [M(bbdhp)L′] when the additional ligand L′ = 1,10-phenanthroline. All complexes [M(bbdhx)] were prepared in absolute ethanol solution with the exception of [Ni(bbdhx)] which was obtained in acetonitrile. The remaining complexes were synthesised in acetonitrile–absolute ethanol (2:1) as solvent. In all cases the electrolysis was carried out under ambient conditions with magnetic stirring and the insoluble compounds were visible within a few minutes. At the completion of the reaction, the powdered compounds were collected, washed with the solvent used for the synthesis, and dried under vacuum.

The cell used can be summarised as Pt(−)|solvent + H_2L|M(+) in the case of [ML] complexes and Pt(−)|solvent + H_2L + L′|M(+) for the experiments to produce mixed-ligand complexes (L′ = bipy or phen). The experimental conditions are given in Tables 1 and 5.

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