Electrochemical Synthesis of Neutral Complexes with N_2SO Tetradentate Ligands

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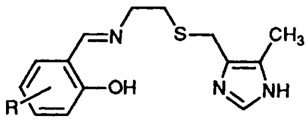
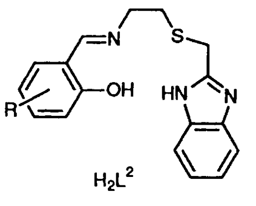
The electrochemical synthesis and physicochemical properties of neutral divalent transition-metal complexes of reduced N_2SO Schiff-base ligands are reported. The reduction of the imine bond provides novel flexible ligands whose complexes have geometries differing from those derived from the unreduced Schiff bases.

In a previous paper[1] we reported the synthesis and structural characteristics of neutral copper, zinc, cadmium and nickel complexes involving Schiff-base ligands derived from aminothioether imidazoles and salicylaldehydes H_2L^1 and H_2L^2.

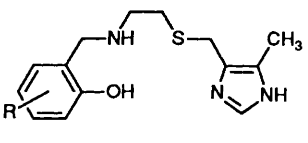
The reduction of the imine bond in these Schiff bases provides the more flexible ligands H_2L^3 and H_2L^4. Herein we describe the synthesis of these new ligands and the electrochemical synthesis of their complexes with Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}. As we have reported previously,[1,2] the electrochemical procedure facilitates the deprotonation of benzimidazole- or imidazole-containing ligands.



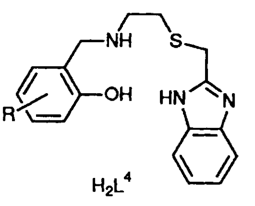
H_2L^1



H_2L^2



H_2L^3



H_2L^4

Results and Discussion

The Schiff-base ligands were prepared as described in previous papers.[1,3,4] The reduction of the imine bond was carried out with sodium tetrahydroborate, with yields of about 70% for the benzimidazole ligands, H_2L^4 [R = H, 3-OEt, 5-OMe or 4,6-$(OMe)_2$], and 80% for the imidazole ligands, H_2L^3 (R = H, 3-OEt or 5-Br). All these ligands were characterized by IR and ^1H NMR spectroscopy. The IR spectra of the ligands do not show any strong absorptions at *ca.* 1630 cm^{-1} attributable to the imine bond and the only absorption in this region shows up at *ca.* 1600 cm^{-1} as a very weak band attributed to the imine group of the (benz)imidazole ring. As expected, the ^1H NMR spectra of the ligands (Tables 1 and 2) have no azomethine hydrogen peaks at δ 8.2–8.5, but show new peaks at δ 3.6–3.8 attributable to the methylene group.

The neutral divalent transition-metal complexes (M = Cu, Zn, Cd, Ni or Co) were prepared by an electrochemical route[1,2,4] using the appropriate metal as the sacrificial anode. The solvent was acetonitrile and other experimental conditions are given in Tables 3 and 4. The reaction involved in the preparation of the complexes can be represented by equation (1). The electrochemical efficiency, defined as the quantity of

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

metal dissolved per Faraday of charge, had the expected value in each case.[1,2]

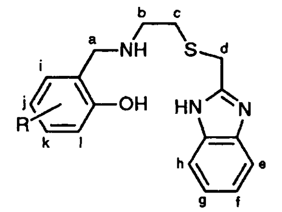
Benzimidazole-derived Complexes.—All the complexes obtained were recovered as powders and characterized by elemental analysis (Table 5), IR and mass spectroscopy. The copper, nickel and cobalt complexes were also studied by visible spectroscopy (Table 6). It must be stated that the great insolubility of these neutral systems limits their study in solution, particularly in the case of the zinc and cadmium compounds.

All the complexes contained lattice water, which showed up in the IR spectra as broad bands around 3400 cm^{-1}.

The close similarities in spectroscopic and magnetic behaviour of the three nickel complexes, [NiL^4] [R = H, 3-OEt or 4,6-$(OMe)_2$], suggest similarities in their geometry. The mass spectra show the molecular ion peak but, unlike those of nickel complexes with unsaturated ligands,[1] no peak corresponding to a dimeric species is observed. The solid-state electronic spectra give bands at *ca.* 1050 and 600 nm. These values are well within the range for tetrahedral nickel(II) complexes,[5] and the bands can accordingly be attributed to $^3A_2 \longleftarrow {}^3T_1(F)$ and $^3T_1(P) \longleftarrow {}^3T_1(F)$ transitions; the spectroscopic parameters are listed in Table 7. It has been impossible to calculate these parameters for the complex [NiL^4] [R = 4,6-$(OMe)_2$] because the third spin-allowed transition appears as a very broad band.

The magnetic moment of [NiL^4] (R = H) at 300 K is 3.24 (θ = 6.5 K), and that of [NiL^4] (R = 3-OEt), 3.40. The theoretical values for tetrahedral Ni^{II} at 300 K lie in the range 3.3–3.8 (*cf.* observed values of 3.5–4.0 for regular tetrahedral complexes and 3.0–3.5 for more distorted systems).[6] It can therefore be concluded that the nickel complexes are monomers with possibly distorted tetrahedral geometries in contrast to

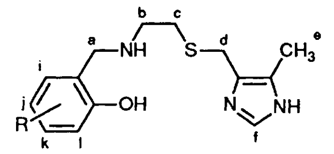
Table 1 Proton NMR data for the ligands H_2L^4 in $(CD_3)_2SO$



R	H^a	H^bH^c	H^d	R	H^e–H^h	H^i–H^l
H	3.80 (s)	2.74 (br s)	3.93 (s)	—	7.49 (m), 7.14 (m)	7.08 (m), 6.71 (m)
3-OEt	3.95 (s)	2.71 (br s)	3.98 (s)	3.91 (m) OCH_2 1.29 (t) CH_3	7.47 (m), 7.13 (m)	6.79 (m), 6.64 (m)
5-OMe*	3.86 (s)	2.77 ($A'_2B'_2$)	3.97 (s)	3.73 (s) OCH_3	7.52 (m), 7.24 (m)	6.76 (m), 6.51 (m)
4,6-$(OMe)_2$*	—	2.81 ($A'_2B'_2$)	3.98 (s)	—	7.55 (m), 7.25 (m)	6.08 (m)

* Solvent $CDCl_3$.

Table 2 Proton NMR data for the ligands H_2L^3 in $(CD_3)_2SO$



R	H^a	H^bH^c	H^d	H^e	H^f	R	H^i–H^l
H	3.59 (s)	2.62 ($A'_2B'_2$)	3.78 (s)	2.08 (s)	7.38 (s)		7.05 (m), 6.70 (m)
3-OEt	3.58 (s)	2.61 ($A'_2B'_2$)	3.77 (s)	2.07 (s)	7.38 (s)	3.94 (q) OCH_2 1.92 (t) CH_3	6.79 (m), 6.63 (m)
5-Br	3.58 (s)	2.60 ($A'_2B'_2$)	3.74 (s)	2.07 (s)	7.38 (s)		7.23 (m), 6.66 (d)

Table 3 Experimental conditions for the electrochemical synthesis of $[ML^4]\cdot nH_2O$

M	R	*n*	Amount of ligand (g)*	Initial potential (V)	Current (mA)	Time (s)	Metal used (mg)	E_f/mol F^{-1}
Cu	H	3.5	0.1771	12.60	10	8100	50.00	0.94
	3-OEt	3.5	0.1649	7.35	10	6600	41.90	0.96
Zn	H	1.5	0.2439	15.70	20	7260	44.80	0.46
	3-OEt	3.5	0.2604	15.00	9	9600	29.20	0.50
	5-OMe	2.5	0.2215	15.80	20	6180	37.30	0.44
Cd	H	1	0.1352	12.60	10	6300	37.40	0.51
	3-OEt	2.5	0.1952	13.65	10	7800	45.60	0.50
	5-OMe	2.5	0.1946	12.60	10	9300	52.10	0.48
Ni	H	2.5	0.2380	18.00	20	7200	42.40	0.48
	3-OEt	3.5	0.2349	8.50	9	9900	25.20	0.46
	4,6-$(OMe)_2$	3.5	0.2870	21.20	19	7200	34.70	0.42
Co	H	2.5	0.2602	24.70	20	7680	46.10	0.49
	3-OEt	4	0.2733	18.40	20	7200	46.70	0.53

* Plus NMe_4ClO_4 (*ca.* 10 mg).

their Schiff-base analogues which present strong interactions among the molecules giving, as a result, pseudo-octahedral geometries at the metal.

The ESR spectra of both copper complexes are the same. The spectra were run in the solid state and show quite broad signals, possibly because of exchange interactions in the pure materials. Hyperfine features corresponding to $A_{\parallel}$ appear on the low-field side; $g_{\parallel}$ may be estimated as 2.136, $g_{\perp}$ as 2.089 and $A_{\parallel}$ as 150 G, albeit with considerable uncertainty. Square planar complexes with nitrogen-donor atoms generally have $g_{\parallel} > 2.2$ and $g_{\perp} \approx 2.05$–2.08. There are a few complexes with $g_{\parallel} < 2.2$, but low $g_{\parallel}$ is generally accompanied by low $g_{\perp}$. The observed values might well be consistent with a non-planar ligand arrangement. The fast atom bombardment mass spectra of these compounds show peaks corresponding to the molecular weight of dimeric species as well as the molecular ion peak $[M + 1]$. These results suggest that the copper complexes are, at least, dimeric, with bridging occurring either through the phenolic oxygen or the imidazole nitrogen.[1,7]

The magnetic moments of the cobalt complexes at 300 K are 3.50 {$[CoL^4]$ (R = H)} and 3.36 {$[CoL^4]$ (R = 3-OEt)}. The magnetic moments of high-spin cobalt(II) complexes fall in the range 4.4–5.2; low-spin cobalt(II) complexes have magnetic moments of *ca.* 2. Five-co-ordinate cobalt(II) complexes containing benzimidazole or imidazole groups with magnetic moments in the range 3.20–3.60 at room temperature have been reported.[8] Such compounds show a gradual incomplete spin-crossover with a large residual high-spin fraction even at low temperatures. The magnetic susceptibility of our cobalt compounds was studied in the range 10–300 K. Plots of the temperature dependence of the magnetic susceptibility and the reciprocal magnetic susceptibility for $[CoL^4]$ (R = H) are shown in Fig. 1. The plot of χ_M^{-1} *vs.* T is linear and obeys the Curie–Weiss law with a Weiss constant of $\theta = 15.96$ K and very

Table 4 Experimental conditions for the electrochemical synthesis of $[ML^3]\cdot nH_2O$

M	R	*n*	Amount of ligand (g)*	Initial potential (V)	Current (mA)	Time (s)	Metal used (mg)	E_f/mol F^{-1}
Cu	H	5	0.1632	31.70	20	5100	64.30	0.96
Zn	H	3.5	0.1550	15.00	10	9600	30.20	0.48
	3-OEt	2.5	0.1000		10	6060	18.80	0.46
	5-Br	2	0.2450	12.70	20	6600	41.70	0.47
Cd	H	3	0.1548	11.00	10	9120	50.80	0.48
	3-OEt	4	0.1013	9.50	9	7500	34.70	0.44
	5-Br	3.5	0.1054	12.00	10	5700	33.10	0.50
Ni	H	2	0.1741	29.80	15	7200	31.10	0.47
	3-OEt	3.5	0.2020	35.30	20	6060	36.20	0.50
	5-Br	1.5	0.1092	20.50	11	5920	21.00	0.53
Co	H	2	0.1697	26.10	15	6120	27.40	0.49
	3-OEt	3	0.1932	18.00	13	8800	36.80	0.53
	5-Br	3	0.2445	23.50	20	6600	43.30	0.54

* Plus NMe_4ClO_4 (*ca.* 10 mg).

Table 5 Analytical data for the complexes $[ML^4]\cdot nH_2O$ and $[ML^3]\cdot nH_2O$

				Analysis (%)*		
L	M	R	*n*	C	N	H
L^4	Cu	H	3.5	45.85 (46.60)	9.40 (9.60)	4.05 (5.50)
		3-OEt	3.5	47.70 (47.35)	8.20 (8.70)	4.70 (5.80)
	Zn	H	1.5	50.45 (50.55)	10.30 (10.40)	4.60 (4.95)
		3-OEt	3.5	46.60 (47.15)	8.80 (8.70)	5.55 (5.80)
		5-OMe	2.5	47.45 (47.85)	8.75 (9.30)	4.50 (5.35)
	Cd	H	1	46.25 (46.20)	9.45 (9.50)	3.95 (4.30)
		3-OEt	2.5	44.95 (44.50)	7.65 (8.20)	4.20 (5.05)
		5-OMe	2.5	43.10 (43.35)	8.85 (8.40)	4.35 (4.80)
	Ni	H	2.5	48.50 (49.20)	9.95 (10.15)	4.85 (5.30)
		3-OEt	3.5	47.95 (47.85)	8.60 (8.80)	5.40 (5.85)
		4,6-$(OMe)_2$	3.5	45.75 (46.25)	8.20 (8.50)	4.85 (5.70)
	Co	H	2.5	49.15 (49.15)	9.60 (10.10)	4.55 (5.30)
		3-OEt	4	46.80 (46.90)	8.80 (8.65)	5.25 (5.95)
L^3	Cu	H	5	38.50 (39.20)	9.75 (9.80)	6.05 (6.30)
	Zn	H	3.5	41.40 (41.65)	10.20 (10.40)	5.40 (5.95)
		3-OEt	2.5	44.90 (44.70)	9.70 (9.80)	5.90 (6.05)
		5-Br	2	37.25 (36.90)	8.90 (9.20)	3.95 (4.40)
	Cd	H	3	38.25 (38.05)	9.30 (9.50)	4.95 (5.20)
		3-OEt	4	37.75 (38.15)	8.10 (8.35)	4.25 (5.75)
		5-Br	3.5	31.50 (31.75)	7.95 (7.95)	4.15 (4.35)
	Ni	H	2	45.40 (45.45)	11.40 (11.35)	5.30 (5.70)
		3-OEt	4	42.10 (42.70)	8.80 (9.35)	5.50 (6.45)
		5-Br	1.5	38.75 (38.20)	9.30 (9.55)	5.05 (4.30)
	Co	H	2	44.50 (45.40)	11.50 (11.35)	5.55 (5.65)
		3-OEt	3	43.75 (44.45)	9.60 (9.70)	5.40 (6.25)
		5-Br	3	35.80 (36.00)	8.70 (9.00)	4.35 (4.70)

* Calculated values in parentheses.

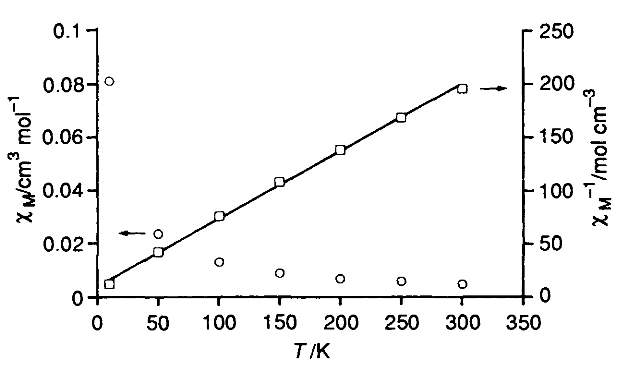


Fig. 1 Plots of the temperature dependence of the magnetic susceptibility χ_M and the reciprocal magnetic susceptibility χ_M^{-1} for $[CoL^4]\cdot 2.5H_2O$ (R = H)

Table 6 Ligand-field maxima* for the nickel(II), cobalt(II) and copper(II) complexes

Complex	λ_{max}/nm
$[CuL^4]\cdot 3.5H_2O$ (R = H)	647 (br)
$[CuL^3]\cdot 5H_2O$ (R = H)	617
$[NiL^4]\cdot 2.5H_2O$ (R = H)	1075, 617
$[NiL^4]\cdot 3.5H_2O$ (R = 3-OEt)	1042, 595
$[NiL^4]\cdot 3.5H_2O$ [R = 4,6-$(OMe)_2$]	1064
$[NiL^3]\cdot 2H_2O$ (R = H)	1075, 595
$[NiL^3]\cdot 4H_2O$ (R = 3-OEt)	1041
$[NiL^3]\cdot 1.5H_2O$ (R = 5-Br)	1105, 625, 480
$[CoL^4]\cdot 2.5H_2O$ (R = H)	1351, 1100, 585 (br)
$[CoL^4]\cdot 4H_2O$ (R = H)	1370, 1100
$[CoL^3]\cdot 2H_2O$ (R = H)	1149
$[CoL^3]\cdot 3H_2O$ (R = 3-OEt)	1163
$[CoL^3]\cdot 3H_2O$ (R = 5-Br)	1163

* Diffuse reflectance spectra, (br) broad.

Table 7 Spectral parameters for the nickel(II) complexes*

Complex	ν_2	ν_3	D_q	*B*	β	ν_1(Calc.)
$[NiL^4]$ (R = H)	1075	617	506	843	0.81	2325
$[NiL^4]$ (R = 3-OEt)	1042	595	524	874	0.84	2273
$[NiL^3]$ (R = H)	1075	595	490	892	0.86	2381
$[NiL^3]$ (R = 5-Br)	1105	625	500	833	0.80	2381

* Units: ν_1, ν_2, ν_3/nm; D_q, B/cm^{-1}.

slight temperature dependence, which rules out spin-crossover. The presence of strong magnetic interactions among molecules must also be ruled out because it would imply much stronger temperature dependence of the magnetic moments than was observed. The great ease with which cobalt(II) complexes are oxidized to low-spin cobalt(III) complexes is well known, and it may be suggested that our cobalt(II) complexes are contaminated with low-spin cobalt(III) impurities.

Imidazole-derived Complexes.—These complexes were also recovered as powders and characterized by elemental analysis (Table 5), and by IR, mass and visible spectroscopy (Table 6). The solid-state electronic spectra of the nickel compounds show bands at *ca.* 1075 and 600 nm similar to those observed in the benzimidazole-derived complexes; the spectroscopic parameters are listed in Table 7. The magnetic moment of $[NiL^3]$ (R = 5-OMe) is 3.22; tetrahedral geometries can be suggested for these complexes, as for the benzimidazole-derived complexes.

The diffuse reflectance spectra of the cobalt complexes (Table 6) are similar to that of the $[CoL^1]\cdot 2.5H_2O$ (R = H) complex with the Schiff base, which has bands at 1163 and 581 nm. The magnetic susceptibility of $[CoL^3]\cdot 2H_2O$ (R = H) was measured over the temperature range 2–300 K. The plot of χ_M^{-1} *vs.* T is linear and obeys the Curie–Weiss law with a Weiss constant $\theta = 9.7$ K. The magnetic moment at 300 K is 2.13, a value indicative of low-spin cobalt(II); it falls within the range 2.1–2.7 (300 K) of square-planar cobalt(II) complexes.[9,10] Its analogue $[CoL^1]\cdot 2.5H_2O$ (R = H), with the Schiff-base ligand, also presents a typical magnetic moment for square-planar cobalt(II) compounds (2.63) and so, these reduced ligands from Schiff bases do not provide a different geometry with respect to the Schiff-base ligand in cobalt complexes as occurs in the copper or nickel complexes. Nevertheless, it does not seem likely that there is an ideal square-planar geometry in these compounds owing to the electronic characteristics of the sulfur atom. Instead the geometry probably shows deviation from square-planar symmetry with the large sulfur donor atom lying out of the plane in a similar manner as found in cationic copper complexes with this type of Schiff-base ligand.[3]

Experimental

Microanalyses were determined using a Perkin Elmer 240B microanalyser. Infrared spectra were recorded as KBr discs or Nujol mulls using a Perkin Elmer 180 spectrometer, diffuse reflectance spectra of solids using a Philips Scientific SP 700 spectrometer, proton NMR using a Bruker WM 250 FT spectrometer, fast atom bombardment mass spectra on a Kratos MS50TC spectrometer and ESR spectra using a Bruker ER 200D-Scr. spectrometer. Magnetic moments were determined on a SQUID MPMS QUANTUM DESIGN apparatus. All reagents and solvents were of commercial reagent grade quality.

The Schiff-base ligands were prepared by the method described in ref. 1. In order to reduce the imine bond, 1 mmol of the base was dissolved in absolute ethanol (30 cm^3) and 2 mmol of sodium tetrahydroborate added. The solution was stirred at room temperature for *ca.* 3 h during which time it changed colour. Dilute hydrochloric acid (2 cm^3) followed by *ca.* 20 cm^3 of water were then added in order to destroy any unreacted sodium tetrahydroborate. The solvent was removed under vacuum and the new ligand was extracted from the residue with CH_2Cl_2. The organic phase was concentrated under vacuum and the resulting residue was washed with diethyl ether and stirred with hexane until it was transformed into a solid powder.

The electrochemical method used in the syntheses of the metal complexes is similar to that described by Tuck and co-workers.[11] The cell was a tall-form beaker (100 cm^3) fitted with a rubber bung through which the electrochemical leads entered into the cell. The anode, in foil form, was suspended from a platinum wire, and the cathode was another platinum wire. The ligand was dissolved in acetonitrile, and tetramethylammonium perchlorate (10 mg) was added to the solution as supporting electrolyte. The cell used can be summarized as $Pt(-)|MeCN + H_2L|M(+)$. Upon completion of the reaction, the compounds were collected, washed with acetonitrile, and dried *in vacuo*.

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