Synthesis and Properties of Transition-metal Complexes of 5,5-Bis(*N*-8-quinolylcarbamoyl)nonane

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Several metal complexes of 5,5-bis(*N*-8-quinolylcarbamoyl)nonane (H_2L^1) and the copper(II) complex of 5,5-bis(*N*-2-methyl-8-quinolylcarbamoyl)nonane (H_2L^2) have been synthesised and their spectroscopic properties studied. Whereas complexes of Cu, Ni, Pd, Zn and Cd with H_2L^1 were obtained, no complex with Co and Pt could be isolated. On the other hand, the copper complex of H_2L^2 was readily obtained, but the nickel complex could not be isolated. These compounds can be formulated as [ML] in which the amide groups of H_2L^1 and H_2L^2 are fully deprotonated. They were characterized by mass, IR and ^1H NMR spectroscopy. Their ultraviolet–visible, luminescence and redox properties were also investigated.

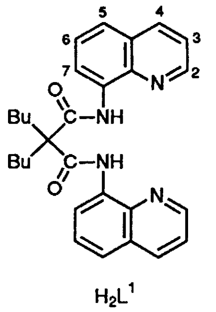
Amide-containing ligands are involved in a large variety of compounds with metal ions, *e.g.* oligopeptides[1] and their macrocyclic analogues polyoxocyclams,[2] complexes of cyclic amide ligands[3] [α-pyridone,[3a–d] 1-methylthymine(1,5-dimethylpyrimidine-2,4-dione),[3e,f] 1-methyluracil(1-methylpyrimidine-2,4-dione)[3g,h]], complexes containing the bridged bis(*N*-substituted)picolinamide[4] or 2-hydroxybenzamide tetradentate ligands,[5] or even simply acetanilide(*N*-phenylacetamide) in compounds with multiple metal–metal bonds.[6] In general, these ligands favour the square-planar geometry[7] and stabilize higher oxidation states of transition metals, *e.g.* Cu^{III},[5c,7,8] Ni^{III},[8] Co^{III},[4d,9] Co^{IV},[10] Cr^{III},[11] Mn^{III},[12a] Os^{III},[12b] Os^{IV} [5a,13] and Pt^{III}.[3a,b,d] Some of these complexes were used in catalytic oxidation reactions.[12]

5,5-Bis(*N*-8-quinolylcarbamoyl)nonane (H_2L^1) was shown selectively to extract Cu^{II} from aqueous solutions containing other divalent metal ions, *e.g.* Ni^{II}, Co^{II} and Zn^{II}, by formation of a 1:1 complex with Cu^{II} with simultaneous release of two amide protons. Additionally, this complex could be isolated as a microcrystalline compound.[14] By contrast, 5,5-bis(*N*-2-methyl-8-quinolylcarbamoyl)nonane (H_2L^2) showed poor extraction ability. These results prompted us to undertake a systematic study of the complexation ability of these compounds toward several divalent metal ions. In this paper, we report the synthesis, characterization and spectroscopic properties of the complexes of H_2L^1 with Cu, Ni, Pd, Zn and Cd, and the copper complex of H_2L^2.

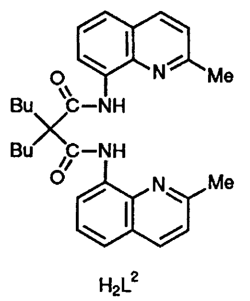
Experimental

Materials.—All reagents were supplied by Wako or Kanto Chemical Companies. Solvents for fluorometry were from Merck. Benzene was dried on molecular sieves (4 Å) or distilled from CaH_2 prior to use. Triethylamine was distilled from potassium hydroxide. All other reagents and solvents were used as received. Silica gel for column chromatography was Wakogel C300.

Physical Measurements and Instrumentation.—Proton NMR spectra were recorded at 60 MHz on a Varian EM 360 spectrometer and at 200 MHz on a Bruker AC 200P spectrometer. Chemical shifts are reported in ppm *vs.* $SiMe_4$, with multiplicity. Ultraviolet–visible absorption and fluorescence measurements were performed on a Hitachi 330 spectrophotometer and a Hitachi F-3000 spectrofluorometer, respectively. Infrared spectra were recorded either with a JASCO A-3 IR spectrometer (resolution 5 cm^{-1}) or with a Nicolet 20DXB FT-IR spectrometer (resolution 0.5 cm^{-1}) equipped with a 20DX data processor. Secondary ion mass spectroscopy (SIMS) was performed using a Hitachi M80BS mass spectrometer. Cyclic voltammetry experiments used a Nikko Keisoku NPGF2-2501-A potentiogalvanostat equipped with a XY Graphtec WX 1000 recorder. The working electrode was a platinum disk (0.79 mm^2), polished with diamond paste (Royal 1-W-47), rinsed with water, acetone and carefully wiped. The reference electrode was a saturated KCl, Ag–AgCl electrode, and the counter electrode was a platinum grid. Dichloromethane was distilled from P_2O_5 under N_2. Tetrabutylammonium perchlorate used as supporting electrolyte was recrystallized twice from acetone–diethyl ether and dried *in vacuo*. In all cases, ferrocene was added at the conclusion of the experiment as an internal potential standard. All potentials are quoted with respect to the formal potential of the ferrocenium–ferrocene couple which we found to be 0.55 V *vs.* our $Ag–Ag^+$ electrode [lit.,[5c] 0.48 V *vs.* saturated calomel electrode (SCE)]. Luminescence experiments were performed using a Schlenk cell and the solutions were degassed by nitrogen bubbling for a minimum of 15 min.



H_2L^1



H_2L^2

Melting points were measured with a Mitamura Riken microscope. Microanalyses were performed by one of us (K. H.).

Syntheses.—5,5-*Bis*(N-8-*quinolylcarbamoyl*)*nonane* (H_2L^1). Dibutylmalonic acid (2.2 g, 0.012 mol) and excess of thionyl chloride (5 cm^3, 0.0685 mol) were stirred at 60 °C for *ca.* 4 h under Drierite. After removal of excess of thionyl chloride under reduced pressure, the residue was dried *in vacuo*. It was then dissolved in benzene (20 cm^3) and 8-aminoquinoline (2.9 g, 0.0201 mol) was added. The resulting bright orange precipitate was stirred at room temperature under Drierite for 1 h. Then triethylamine (3 cm^3, 0.0216 mol) was added: the reaction mixture immediately bleached and became thicker. After stirring overnight at 60 °C, it was washed with water (3 × 20 cm^3). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated, leaving 5.42 g of oily residue. This was chromatographed on silica gel (200 g) with pure chloroform. A crystalline compound was obtained by crystallization from cyclohexane, yield 81%, m.p. 141.5–142.5 °C (Found: M^+ 468.251. $C_{29}H_{32}N_4O_2$ requires M 468.252); ν/cm^{-1}(NH) 3339 and 3306 (KBr). $\delta_H(CDCl_3)$ 0.89 (6 H, t, CH_3), 1.42 (8 H, m, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.31 (4 H, m, $C\mathit{H}_2CH_2CH_2CH_3$), 7.46 (2 H, m, H^3), 7.54 (4 H, m, $H^{5,6}$), 8.15 (2 H, d, H^4), 8.90 (4 H, m, $H^{2,7}$) and 11.32 (2 H, s, NH); $\delta_H[(CD_3)_2SO]$ 0.96 (6 H, t, CH_3), 1.30 (8 H, br, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.19 (4 H, br, $C\mathit{H}_2CH_2CH_2CH_3$), 7.61 (2 H, q, $H^{3,6}$), 7.69 (2 H, dd, H^5), 8.40 (2 H, dd, H^4), 8.63 (2 H, dd, H^7), 8.90 (2 H, dd, H^2) and 11.04 (2 H, s, NH).

5,5-*Bis*(N-2-*methyl*-8-*quinolylcarbamoyl*)*nonane* (H_2L^2). This compound was synthesised according to the same procedure. Yield 65%, m.p. 96.5–98.5 °C (Found: M^+ 496.280. $C_{31}H_{36}N_4O_2$ requires M 496.284); ν/cm^{-1}(NH) 3330 (KBr). $\delta_H(CDCl_3)$ 0.9 (6 H, t, CH_3), 1.2–1.8 (8 H, m, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.1–2.6 (4 H, m, $C\mathit{H}_2CH_2CH_2CH_3$), 2.7 (6 H, s, 2-$CH_3$ of quinolyl), 7.3 (2 H, d, aryl-H), 7.5 (2 H, d, aryl-H), 8.0 (2 H, d, aryl-H), 8.9 (4 H, m, aryl-H) and 11.5 (2 H, s, NH).

[NiL^1]. Nickel(II) acetate tetrahydrate (53.1 mg, 0.21 mmol) in ethanol (10 cm^3) was added to a solution of H_2L^1 (100.5 mg, 0.215 mmol) in ethanol (15 cm^3). The reaction mixture turned deep red. Evaporation of the solvent left a green solid residue which was recrystallized from hot ethanol. The green crystals were washed with cold ethanol and dried *in vacuo*. Another crop could be recovered from the mother-liquor (91.9 mg, 82%) (Found: M^+ 525.3. $C_{29}H_{30}N_4NiO_2$ requires M 525.4). $\delta_H(CDCl_3)$ 0.81 (6 H, t, CH_3), 1.32 (8 H, m, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.05 (4 H, t, $C\mathit{H}_2CH_2CH_2CH_3$), 7.29 (2 H, dd, H^5), 7.44 (2 H, dd, H^3), 7.57 (2 H, t, H^6), 7.83 (2 H, dd, H^2), 8.31 (2 H, dd, H^4) and 9.09 (2 H, dd, H^7).

[PdL^1]. Palladium(II) acetate (48.0 mg, 0.21 mmol) in acetone (8 cm^3) was added to a solution of H_2L^1 (100.4 mg, 0.215 mmol) in acetone (7 cm^3). The resulting solution was heated to reflux for 1 h. Upon cooling, crystallization occurred. The orange crystals were collected, washed with cold acetone and dried *in vacuo*. Another crop could be recovered from the mother-liquor (92.5 mg, 76%) (Found: M^+ 573.8. $C_{29}H_{30}N_4O_2Pd$ requires M 573.0). $\delta_H(CDCl_3)$ 0.86 (6 H, t, CH_3), 1.37 (8 H, m, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.17 (4 H, t, $C\mathit{H}_2CH_2CH_2CH_3$), 7.16 (2 H, d, H^5), 7.44 (2 H, t, H^6), 7.52 (2 H, dd, H^3), 8.26 (2 H, d, H^4), 8.39 (2 H, d, H^2) and 9.07 (2 H, d, H^7).

[CuL^1].[14] Copper(II) acetate monohydrate (43.1 mg, 0.22 mmol) in ethanol (7 cm^3) was added to a solution (15 cm^3) of H_2L^1 (101 mg, 0.22 mmol) in ethanol. The reaction mixture turned green-brown. Removal of the solvent under reduced pressure left a residue which was crystallized from cyclohexane–benzene.[14] The crystals were collected, washed three times with cyclohexane–benzene (1:1) and dried *in vacuo* (67 mg, 59%) (Found: C, 65.55; H, 5.95; N, 10.55%; M^+ 531.0. $C_{29}H_{30}CuN_4O_2$ requires C, 65.70; H, 5.70; N, 10.55%; M 531.1).

[ZnL^1]. Zinc acetate dihydrate (46.7 mg, 0.21 mmol) in ethanol (10 cm^3) was added to H_2L^1 (99.9 mg, 0.21 mmol) in ethanol (15 cm^3). Then triethylamine (0.24 cm,^{3} 1.7 mmol) was added, and the bright yellow solution was heated under reflux overnight. A microcrystalline yellow material precipitated. It was collected, washed with cold ethanol and dried *in vacuo* (77.3 mg, 68%) (Found: M^+ 531.5. $C_{29}H_{30}N_4O_2Zn$ requires M 531.9). $\delta_H[(CD_3)_2SO]$ 0.85 (6 H, t, CH_3), 1.26 (8 H, m, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.07 (4 H, m, $C\mathit{H}_2CH_2CH_2CH_3$), 7.42 (2 H, dd, H^5), 7.56 (2 H, t, H^6), 7.73 (2 H, q, H^3), 8.58 (4 H, m, $H^{4,7}$) and 8.69 (2 H, dd, H^2). Spectroscopic data showed that the compound contained minute traces of unreacted ligand. Further washing of the material with CH_2Cl_2 did not improve its purity.

[CdL^1]. Cadmium acetate dihydrate (56.3 mg, 0.21 mmol) in ethanol (10 cm^3) was added to H_2L^1 (100 mg, 0.21 mmol) in ethanol (10 cm^3). To the pale yellow solution, triethylamine (0.24 cm^3, 1.7 mmol) was added and a bright yellow colour developed. The reaction mixture was heated under reflux for 7 h. The microcrystalline yellow product which precipitated was collected, washed copiously with cold ethanol and dried *in vacuo* (30 mg, 25%). $\delta_H[(CD_3)_2SO]$ 0.87 (6 H, t, CH_3), 1.28 (8 H, m, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.14 (4 H, m, $C\mathit{H}_2CH_2CH_2CH_3$), 7.33 (2 H, d, H^5), 7.49 (2 H, t, H^6), 7.69 (2 H, dd, H^3), 8.50 (2 H, d, H^4), 8.57 (2 H, d, H^7) and 8.99 (2 H, dd, H^2). Spectroscopic data showed that the compound contained noticeable amounts of unreacted ligand. Further washing of the material with CH_2Cl_2 did not improve its purity.

[CuL^2]. Copper(II) acetate monohydrate (40.5 mg, 0.20 mmol) in ethanol (7 cm^3) was added to H_2L^2 (100.5 mg, 0.21 mmol) in ethanol (15 cm^3). The brown-orange reaction mixture was evaporated to dryness and redissolved in hot acetone (2–3 cm^3). The solution was filtered while hot and after cooling crystallization occurred. The crystals were collected, washed with cold acetone and dried *in vacuo*. Another crop could be recovered from the mother-liquor (86.9 mg, 77%) (Found: C, 64.70; H, 6.00; N, 9.55. $C_{31}H_{34}CuN_4O_2{\cdot}H_2O$ requires C, 64.60; H, 6.30; N, 9.70%).

Results and Discussion

Synthesis and Characterization.—The synthesis of the ligands has been described in a previous paper.[14] In the case of the complexes, all metal sources were the acetates, but experimental conditions differed from one metal to another. When H_2L^1 was used as ligand the complexes of Cu and Ni formed readily at room temperature in ethanol. Complexation of Pd requires heating in refluxing acetone (ethanol decomposes palladium acetate), but the platinum complex could not be obtained. Platinum(II) is kinetically inert,[15] but complexes of dioxocyclams have been described (dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-12,14-dione),[16] and in the case of tripeptides the ease of metal-promoted amide deprotonation increases in the order Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II}.[17] A reaction was shown to occur in the case of Co^{II}, but no pure compound could be isolated from the reaction mixture. Metals of the Group 2B triad require less mild conditions: complexes of both Zn and Cd form only upon heating in refluxing ethanol and in the presence of excess of triethylamine. The reaction is probably also driven out by the fact that the products are highly insoluble, even in boiling ethanol. Additionally, the cadmium complex is obtained in much lower yield (25%) than that of Zn (68%) and the mercury complex was not obtained at all. These synthetic results may be related to those obtained for oxalamide-*N*,*N*′-diacetate:[18] only in the case of Cu^{II} and Ni^{II} could complexes of the deprotonated ligand be obtained. In the case of Co^{II}, Zn^{II} and Cd^{II} weak complexation without deprotonation of the amide nitrogen was observed. The complexes of Zn and Cd with H_2L^1 are yellow microcrystalline materials, soluble in Me_2SO. By contrast, those of Cu, Ni and Pd are soluble in various organic solvents ($CDCl_3$, CD_2Cl_2, acetone). When H_2L^2 was used as ligand, the copper complex forms readily at room temperature. Complete disappearance of the ligand spot on TLC was observed in the case of Ni, when a mixture of nickel(II) acetate tetrahydrate, H_2L^2 and excess of triethylamine was heated in refluxing ethanol. A dark green solution was obtained, but no solid could be crystallized. The copper(II) complex of H_2L^2 is also soluble in common organic solvents. The characterization and study of this complex will be examined later. All other compounds were characterized by mass spectroscopy. In the case of the complexes of Ni, Pd, Cu and Zn the molecular peak corresponding to $[ML^1]^+$ is observed. In the case of the cadmium complex however only the peak corresponding to the free ligand is detected, suggesting that this compound decomposes during the ionization process. Of

Table 1 Infrared carbonyl bands (cm^{-1}) in KBr disks

Compound	ν(C=O)	Δν
H_2L^1	1677	—
H_2L^2	1670	—
[NiL^1]	1627	50
[PdL^1]	1626	51
[CuL^1]	1622	55
[ZnL^1]	1598	79
[CdL^1]	1583	94
[CuL^2]	1610	60

Table 2 UV–visible absorption and luminescence data

Compound	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})	λ_{em} (λ_{ex})/nm
H_2L^1 [a]	317 (14.6), 306 (13.8), 242 (83.6), 206 (54.0)	396 (327)
[NiL^1]	[a] 426 (10.7), 268 (40.7), 237 (21.6), 197 (82.4)	—
	[b] 442 (8.85), 277 (35.7), 246 (36.0)	—
[PdL^1] [b]	429 (8.20), 270 (36.8)	—
[CuL^1] [b]	406 (7.10), 268 (53.4)	—
[ZnL^1] [c]	397 (4.00), 324 (8.10), 268 (36.8)	546 (398)
[CdL^1] [c]	400 (3.70), 318 (6.70), 263 (25.00)	547 (401)
[CuL^2] [b]	391 (6.44), 322 (3.92), 271 (59.70)	—

[a] In MeCN. [b] In $CHCl_3$, the solvent absorbs below 250 nm. [c] In Me_2SO, the solvent absorbs below 250 nm.

Table 3 Cyclic voltammetry data [a]

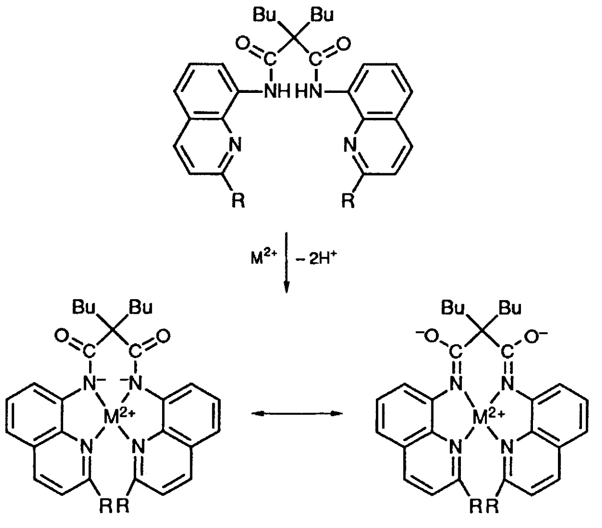
Compound	E_{ox}/V	E_{red}/V
H_2L^1	1.19	—
[NiL^1]	0.56	−2.15
[PdL^1]	0.96,[b] 0.60	−2.17
[CuL^1]	0.62	−1.68
[CuL^2]	0.71	−1.42 (180)

[a] Data obtained in CH_2Cl_2 (NBu_4ClO_4 as supporting electrolyte), at a platinum electrode, using an Ag–AgCl reference electrode. Potentials are quoted *vs.* the ferrocenium–ferrocene couple (0.55 V *vs.* Ag–Ag$^+$). Unless otherwise stated, each process is irreversible. [b] At 300 mV s^{-1}, ΔE_p = 190 mV (E = 0.9 V).

interest is the fact that in the case of the complexes of Ni, Cu and Zn a peak which might correspond to a [M_2L]$^+$ species is observed. It has the highest intensity (0.4 times that of the parent molecular peak) in the spectrum of [CuL^1]. In addition to their mass spectra, all diamagnetic compounds were characterized by ^{1}H NMR spectroscopy.

Spectroscopic and Cyclic Voltammetry Studies.—Infrared spectra provided the best means for evidencing the bonding fashion of H_2L^1. Upon complexation, the NH absorption bands (3339 and 3306 cm^{-1}) vanish, while that corresponding to C=O (1677 cm^{-1}) shifts to lower frequencies. The former results from ligand deprotonation, the latter from the partial loss of double-bond character of the carbonyl groups, due to the resonance exchange shown in Scheme 1. These data are collected in Table 1. The complexes [NiL^1] and [PdL^1] show the smaller shifts (*ca.* 50 cm^{-1}), whereas [ZnL^1] and [CdL^1] show the larger shifts (*ca.* 80–95 cm^{-1}). The shift observed for [CuL^1] (55 cm^{-1}) is smaller than that observed for the copper complex of dioxocyclam (75 cm^{-1}).[19] A broad band due to water is present in all the spectra, but is much more important in the case of the complexes of Zn and Cd.

Ultraviolet–visible and luminescence data are collected in Table 2. All complexes give coloured solutions. Those of Ni, Pd and Cu show a band whose maximum ranges from 406 [CuL^1] to 442 nm, [NiL^1], in $CHCl_3$. The magnitude of its molar absorption coefficient (7100–8850 dm^3 mol^{-1} cm^{-1}) suggests that it is metal-to-ligand charge transfer (m.l.c.t.) in nature, due to the π-accepting quinoline moieties. In the case of [NiL^1] the maximum is blue-shifted by 16 nm when a more polar solvent is used (MeCN). In addition to the m.l.c.t. band, the complexes show a very weak absorption band [NiL^1] and [PdL^1] or tail, [CuL^1], between 500 and 600 nm. Ligand-to-metal charge-transfer transitions originating from deprotonated amide nitrogen are to be found in the UV region of the spectrum. In the case of peptide complexes of Cu^{II} and Ni^{II}, they were shown to occur near 250 nm.[20] The spectra of [ZnL^1] and [CdL^1] were obtained in Me_2SO. In the visible, the maxima occur near 400 nm with molar absorption coefficients reaching 4000 dm^3 mol^{-1} cm^{-1}. These bands are likely to be due to ligand-centred transitions with a bathochromic shift due to complexation of the metal ion to the quinoline nitrogen atoms. Whereas the luminescence of the free ligand occurs at 396 nm, both complexes display intense luminescence near 545 nm when excited in their lowest-energy band. The large Stokes shift associated with this luminescence suggests that it is due to phosphorescence. That it does not depend on the nature of the metal suggests that it is ligand-centred phosphorescence. The complexes of Ni, Pd and Cu did not show any luminescence when excited in their m.l.c.t. band.



Scheme 1 R = H or Me

Compounds H_2L^1, [NiL^1], [PdL^1] and [CuL^1] were examined by cyclic voltammetry in CH_2Cl_2. Data are summarized in Table 3. Surprisingly all compounds showed irreversible behaviour in anodic as well as cathodic regions, at a scan rate of 100 mV s^{-1}. In the range of potentials examined no reduction of the free ligand could be observed. Reduction occurred near −2.16 V for [NiL^1] and [PdL^1]. It is probably localized on the quinoline moieties whose π-accepting character decreases upon complexation. By contrast, the reduction of [CuL^1] is likely to occur at the metal, since it is much less cathodic (−1.68 V). All three complexes show an irreversible oxidation wave near 0.60 V, which may be attributed to oxidation of the metal.* In the case of the copper complex it is suprising that it is irreversible given literature data on related compounds.[5c,21] In addition, examination of the reported oxidation potentials shows that the value measured for this complex (0.62 V) is unusually anodic, given that the complex contains a deprotonated N-amide ligand. In the case of bridged 2-hydroxybenzamide ligands the potentials range between −0.120 and 0.0825 V,[5c] the benzyldioxocyclam copper(II)

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* In the case of [PdL^1] only this wave is followed by a second one at 0.96 V. The latter becomes quasi-reversible as the scan rate is increased. For example at 300 mV s^{-1}, ΔE_p = 190 mV (E = 0.9 V).

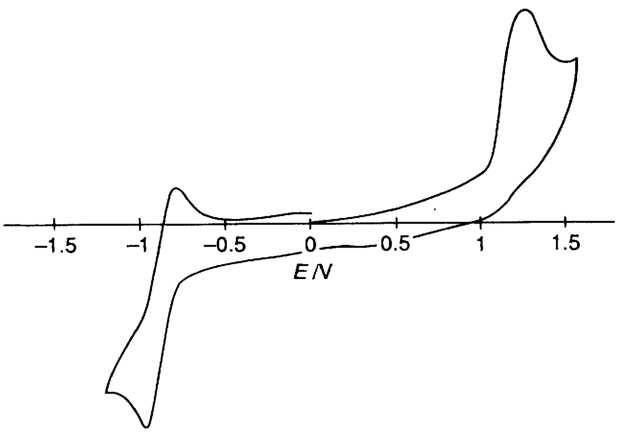

Fig. 1 Cyclic voltammogram of [CuL^2] in CH$_2$Cl$_2$, at a scan rate of 100 mV s^{-1}. The potential scale is referenced to the Ag–AgCl electrode

complex oxidizes at 0.15 V,[21] and the oxidation potential of [CuL^1] is closer to that of [Cu(cyclam)] (0.99 V[22]) (cyclam = 1,4,8,11-tetraazacyclotetradecane) which does not contain any deprotonated N-amide ligand. This behaviour may be explained by the fact that the π-accepting quinoline ligand fragments balance the σ-donating properties of the deprotonated N-amide functions, and thus reduce the charge density on the metal.[7]

Study of the Complex [CuL^2].—This complex was examined by IR and ultraviolet–visible absorption spectroscopies, and cyclic voltammetry. It seemed interesting to elucidate the effect of the steric hindrance induced by the introduction of methyl groups *ortho* to the nitrogen quinoline atoms. A similar study was reported for complexes of bis(picolinamide) tetradentate ligands.[23] In the IR spectrum the carbonyl frequency shifts from 1670 (free ligand H$_2$L^2) to 1610 cm^{-1}. This 60 cm^{-1} shift is slightly higher than that measured for [CuL^1] (55 cm^{-1}) or for a related sterically hindered complex (50 cm^{-1}).[23] The maximum of the absorption in the visible region occurs at 391 nm (ε = 6400 dm^3 mol^{-1} cm^{-1}). This band is probably m.l.c.t. in nature. It is blue shifted by 16 nm by comparison with [CuL^1]. A weak absorption tail between 500 and 600 nm is also observed. A cyclic voltammogram recorded at 100 mV s^{-1} is shown in Fig. 1. As in the previous cases, oxidation is irreversible. It occurs at a slightly more anodic potential than that of [CuL^1] (0.71 *vs.* 0.62 V). Unlike the previous cases, reduction is quasi-reversible (ΔE_p = 180 mV) and occurs at a less cathodic potential than that of [CuL^1] (−1.42 *vs.* −1.68 V). It has been noted that the deprotonated peptide or amide nitrogen atoms having high ligand field co-ordinate in a planar arrangement around the metal atom, even in sterically hindered complexes. In these cases the steric hindrance is relieved by deformation within the ligand.[23] Deviations from square-planar geometry are however observed. Our electrochemical data are consistent with these observations. Indeed the fact that the oxidation potential of [CuL^2] is higher than that of [CuL^1] indicates that the +1 oxidation state of Cu is more stabilized in the former than in the latter; the co-ordination geometry of copper in [CuL^2] is probably tetrahedrally distorted square-planar.

Conclusion

We have shown in this paper that the ligands H$_2$L^1 and H$_2$L^2 are able to complex various metal ions, Ni^{2+}, Pd^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} in the case of H$_2$L^1 and Cu^{2+} in the case of H$_2$L^2, while they are able to extract only Cu^{2+} from aqueous solutions containing Ni^{2+}, Cu^{2+} and Zn^{2+}. Spectroscopic studies as well as earlier titrations[14] show that all the complexes may be formulated as M^{II}L complexes were L is a tetradentate deprotonated N-amide ligand (H$_2$L is the neutral form), and where the redox state of the metal is +2.

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