DALTON
FULL PAPER

Evidence for the localisation of electronic charge in electrochemically reduced copper(I) complexes with electron deficient ligands: a structural and spectroelectrochemical study ‡

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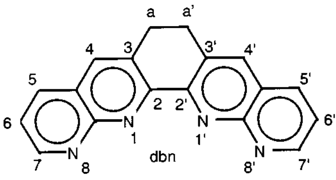
The electrochemical and spectral properties of copper(I) complexes with binaphthyridine ligands, bn and tbn (where bn = 2,2′-1,8-binaphthyridine, tbn = 3,3′-trimethylene-2,2′-1,8-binaphthyridine), have been studied. The complexes are [Cu(bn)$_2$]$^+$ **1**, [Cu(tbn)$_2$]$^+$ **2**, [Cu(bn)(PPh$_3$)$_2$]$^+$ **3** and [Cu(tbn)(PPh$_3$)$_2$]$^+$ **4**. Reduction of **1**–**3** results in the formation of radical anion species involving the ligands. Reduction of **4** results in decomposition. For **3**$^-$ strong near infrared absorptions (1000 nm) are observed suggesting a bn$^{\bullet -}$ radical anion species, in which the redox MO extends across the entire ligand. For **2**$^-$ absorptions at 750 nm suggest a redox MO which is much less extensive and localised on a single naphthyridine unit of the tbn ligand. Reduction of **1** is complicated by the presence of two closely lying reduction waves. Application of a reducing potential resulted in spectral features similar to those observed for **3**$^-$. However, further reduction showed spectral features similar to those of **2**$^-$. The crystal structure of **3**·BF$_4$ was determined by single-crystal X-ray diffraction.

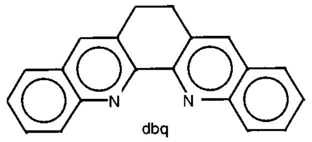
Copper(I) complexes with polypyridyl ligands are of interest because of their novel photophysical and electrochemical properties.[1,2] The electrochemical reduction of copper(I) complexes is often characterised by the reduction of Cu^I to Cu^0 and subsequent dissociation of the complex.[3] This clearly limits the utility of such complexes in supramolecular photochemical devices. In such species electron transfer at metal and ligand sites, subsequent to initial photoexcitation, is likely. It is possible to mitigate this dissociation pathway by either ligand topology, in which the ligands wrap around the copper centre to hold it in place after it has been reduced,[4] or by using highly electron deficient ligands which accept the reducing electron into a π* MO of the ligand.[5] A recent study showed that binaphthyridine-based ligands could be used to ensure copper(I) complexes would store charge on ligand MOs rather than dissociating with reduction.[3] We have used copper(I) complexes with substituted binaphthyridine ligands to investigate the charge storage as a function of ligand geometry. The bn ligand in [Cu(bn)(PPh$_3$)$_2$]$^+$ shows a dihedral angle between the naphthyridine moieties of about 17°. The tbn ligand has the naphthyridine units connected by a three carbon chain. The dihedral angle between the naphthyridine units is estimated to be almost 50°.§,[6] Thus, for the tbn ligand the redox MO may not extend across both ring systems.

Experimental

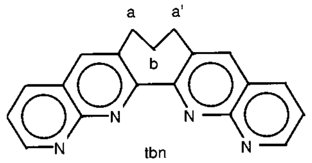
Synthesis



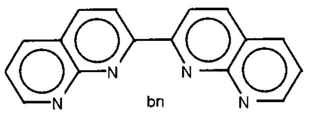
dbn



dbq



tbn



bn

The ligands were prepared by literature methods.[7] Complexes were prepared as described previously.[4a,9] Samples for analysis were obtained by recrystallisation from CH$_2$Cl$_2$ for [Cu(tbn)$_2$]$^+$ **2** and [Cu(tbn)(PPh$_3$)$_2$]$^+$ **4**, from CHCl$_3$ for [Cu(bn)$_2$]$^+$ **1** and from MeOH for [Cu(bn)(PPh$_3$)$_2$]$^+$ **3**. Ligand NMR spectra and microanalyses (SUP 57409) were in agreement with those of previous studies.[7,8]

Complex **1**·BF$_4$·CHCl$_3$ (Found: C, 49.98; H, 3.11; N, 14.37. Calc.: C, 50.43; H, 2.67; N, 14.25%): yield 56%; ^{1}H NMR [(CD$_3$)$_2$CO] δ 8.96 (d, 2 H, H^7 and H$^{7'}$), 7.57 (dd, 2 H, H^6 and H$^{6'}$), 8.58 (br d, 4 H, H^5 and H$^{5'}$, H^3 and H$^{3'}$), 9.04 (d, 2 H, H^4 and H$^{4'}$) and 7.27 (s, CHCl$_3$). Complex **2**·BF$_4$·CH$_2$Cl$_2$ (Found: C, 56.44; H, 3.43; N, 13.58. Calc.: C, 56.32; H, 3.63; N, 13.47%): yield 37%; ^{1}H NMR (CDCl$_3$) δ 8.85 (br d, 2 H, H^7 and H$^{7'}$), 7.50 (dd, 2 H, H^6 and H$^{6'}$), 8.28 (dd, 2 H, H^5 and H$^{5'}$), 8.22 (s, 2 H, H^4 and H$^{4'}$), 5.30 (s, CH$_2$Cl$_2$), 2.90 (t, 4 H, CH$_2^a$ and CH$_2^{a'}$) and 2.40 (q, 2 H, CH$_2^b$). Complex **3**·BF$_4$·MeOH (Found: C, 67.28; H, 4.23; N, 5.85. Calc.: C, 67.63; H, 4.60; N, 5.95%): yield 69%; ^{1}H NMR (CDCl$_3$) δ 8.42 (br d, 2 H, H^7 and H$^{7'}$), 7.50

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‡ *Supplementary data available*: ligand analyses and NMR data, resonance Raman spectra. Available from BLDSC (No. SUP 57409, 4 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

§ Calder *et al.*[6] reported the estimated dihedral angles between the phenyl rings in 2,2′-(bridged)-biphenyl. Thummel *et al.*[7] predicted that these would not change significantly for the binaphthyridine systems. The crystal structure of the *fac*-bromotricarbonyl(3,3′-trimethylene-2,2′-bi-1,8-naphthyridine)rhenium(I) complex has the dihedral angle of the ligand at 23.4° which is still significantly twisted given the π acid properties of the Re(CO)$_3$Br moiety.[8]

(dd, 2 H, H^6 and $H^{6'}$), 8.27 (dd, 2 H, H^5 and $H^{5'}$), 8.64 (br d, 2 H, H^4 and $H^{4'}$), 8.78 (br d, 2 H, H^3 and $H^{3'}$), 7.18 (t, 10 H, PPh_3), 7.01 (t, 5 H, PPh_3) and 3.35 (s, MeOH). Complex **4**·BF_4·$0.66CH_2Cl_2$ (Found: C, 67.32; H, 4.30; N, 5.97. Calc.: C, 67.27; H, 4.60; N, 5.64%): yield 57%; ^1H NMR ($CDCl_3$) δ 8.80 (dd, 2 H, H^7 and $H^{7'}$), 8.33 (dd, 2 H, H^5 and $H^{5'}$), 8.49 (s, 2 H, H^4 and $H^{4'}$), 7.5–6.8 (m, 17 H, PPh_3, H^6 and $H^{6'}$), 2.96 (t, 4 H, $CH_2{}^a$ and $CH_2{}^{a'}$), 2.60 (q, 2 H, $CH_2{}^b$) and 5.30 (s, CH_2Cl_2).

Physical measurements

Apparatus for spectral studies has been described elsewhere.[3,10–12] For electrochemical and spectroscopic measurements solvents of spectroscopic grade were used. These were further purified by distillation and stored over 5 Å molecular sieves. The supporting electrolyte used in the electrochemical measurements was tetrabutylammonium perchlorate which was further purified by repeated recrystallisations from ethanol–water.[13]

Cyclic voltammetry (CV) was performed on argon-purged degassed solutions of compound (*ca.* 1 mM) with 0.1 M NBu_4ClO_4 present. The electrochemical cell consisted of a 1.6 mm diameter platinum working electrode embedded in a Kel-F cylinder with a platinum auxiliary electrode and a saturated potassium chloride calomel reference electrode. The potential of the cell was controlled by an EG&G PAR 273A potentiostat with Model 270 software.

The electronic absorption spectra of reduced species were measured using an optically transparent thin layer electrode (OTTLE) cell with a platinum grid as the working electrode.[14] For Raman spectra of reduced species a similar cell was employed.

Crystallography

Single crystals of complex **3**·BF_4 were grown by the slow diffusion of diethyl ether into a solution of it dissolved in dichloromethane. A red rod shaped crystal with approximate dimensions 0.8 × 0.5 × 0.4 mm was secured to the end of a glass fibre with cyanoacrylate glue and data collection, reduction, solution and refinement were performed as previously described.[15]

Crystal data. $C_{52}H_{40}BCuF_4N_4P_2$, $M = 933$, orthorhombic, space group *Pbca* (no. 61), $a = 18.849(11)$, $b = 20.303(9)$, $c = 23.301(9)$ Å, $U = 8917(7)$ Å^3, $T = 273$ K, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 0.620$ mm^{-1}, 30 415 reflections measured, 7884 unique ($R_{int} = 0.0736$) which were used in all calculations. The final $R'(F_o{}^2) = 0.0812$, $R(F_o) = 0.0369$, where $R'(F_o{}^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2]/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$, $w^{-1} = [\sigma^2(F_o{}^2) + (aP)^2 + bP]$ $\{a = 0.0536, b = 0$ and $P = [\max(F_o{}^2,0) + 2F_c{}^2]/3\}$. The structure was refined of $F_o{}^2$ using all data; the $R(F_o)$ value is given for comparison with older refinements based on F_o with a threshold of $F > 4\sigma(F)$ and $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; R factors based on F^2 are statistically about twice as large as those based on F.[16]

The BF_4 anion was disordered and modelled as a single boron site with two sets of tetrahedrally arranged fluorides with partial occupancies of 70 and 30% respectively.

CCDC reference number 186/1064.

See http://www.rsc.org/suppdata/dt/1998/2873/ for crystallographic files in .cif format.

Results

All of the complexes were stable in solid and solution phases for prolonged periods. The molecular structure of the cationic portion of **3**·BF_4 is shown in Fig. 1. The copper is held in a distorted tetrahedral environment with the Cu–P and Cu–N bond lengths being within the range reported for related complexes.[18] However, one of the Cu–N bonds is slightly shorter at 2.095(2) Å than the other at 2.126(2) Å (Table 1). While the bn is a bulky ligand there is no indication of significant steric interactions with the PPh_3 moieties that would explain the differing Cu–N distances. Compound **3** is the first example of a structurally characterised complex containing the bn ligand. A few complexes containing similar ligands have been structurally characterised. With the limited number of reported structures comparisons between **3** and other complexes is difficult as the distortions enforced by the linkage in dbn, dbq and tbn will have to be separated from the other geometrical requirements of the complex. However, there are a number of crystal structures of complexes formed by the more closely related 2,2′-biquinoline (biq) ligand.[19] One of the notable features associated with complexes of the biq ligand is a tendency for the ligand to take on a banana shape. This is not apparent in **3**. The ligand is not planar, with an angle of 16.8(1)° between the planes of the two co-ordinated pyridyl rings and the angle between the extreme pyridyl rings is 16.8(1)°. In addition, the angles between the fused pyridyl rings in the naphthyridine ring systems are 1.0(2) (N1,N2) and 1.6(2)° (N3,N4), respectively. Analysis of the crystal packing reveals no stacking interactions between neighbouring molecules. As this is the only reported crystal structure of a complex containing the bn ligand it is too early to determine if the differences between biq and bn are the result of the $[Cu(PPh_3)_2]^+$ co-ordination or the differing nature of the two ligands.

Table 1 Selected bond lengths (Å) and angles (°) for complex **3**·BF_4

Cu–N(3)	2.095(2)	Cu–P(2)	2.2753(9)
Cu–N(2)	2.126(2)	Cu–P(1)	2.2806(9)
N(3)–Cu–N(2)	77.43(8)	N(3)–Cu–P(1)	104.74(6)
N(3)–Cu–P(2)	116.89(6)	N(2)–Cu–P(1)	119.29(6)
N(2)–Cu–P(2)	102.61(6)	P(2)–Cu–P(1)	126.08(4)

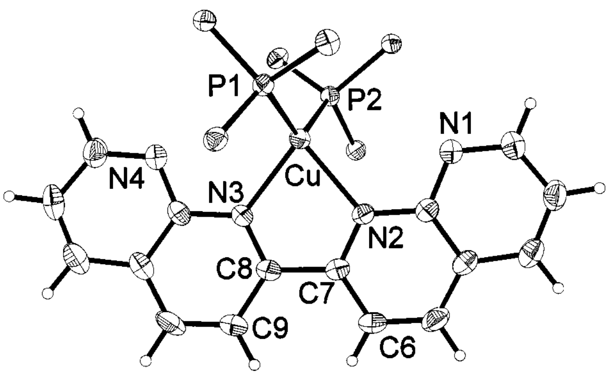

Fig. 1 An ORTEP[17] drawing of complex **3**. Thermal ellipsoids are shown at 30% probability. For clarity only the *ipso*-carbons of the phenyl rings are depicted

The NMR data are informative as to the disposition of ligand geometries in the complexes. The spectra of the ligands agree closely with those previously reported by Thummel *et al.*[7] On complexation to Cu^I the chemical shifts of H^7 and $H^{7'}$ shift upfield. A similar shift pattern is observed for the H^7 and $H^{7'}$ protons in $[Cu(dbn)_2]^+$.[3] Jahng *et al.*[20] have studied the biquinoline counterparts of these complexes. They attribute the observed upfield resonance shifts to shielding by the aromatic ring current of the orthogonal ligand. This appears to occur for the naphthyridine based complexes as well.

Electronic spectral data for ligands and complexes and reduced species are shown in Table 2. The complexes show strong absorptions in the visible region (λ > 400 nm) attributed to metal-to-ligand charge-transfer (MLCT) transitions. These transitions lie further to the red for **1** and **3** than **2** and **4**, consistent with a more planar structure for the bn than tbn ligand in the complexes.[6]

Table 2 Electronic spectral data for ligands and complexes at room temperature

Compound	λ/nm (10^{-3} ε/M^{-1} cm^{-1})				
bn[a]	329 (17)	342 (18.2)			
tbn[b]	329 (16.5)	344 (19.1)			
1[c]	340 (26)	356 (18)	441 (3.6)	687 (2.6)	817 (1.8)
2[c]	350 (21)	373 (13)	449 (3)	700 (2)	
$\mathbf{2}^{-}$ [c]		390 (11)	661 (9)	724 (12)	790 (8)
3	346 (20)	361 (22)	479 (2)		
$\mathbf{3}^{-}$	445 (8)	487 (6)	975 (7)	1069 (7)	1150 (8)
4	358 (22)	379 (17)	484 (2)		

[a] Spectrum measured in MeOH. [b] Spectrum measured in EtOH. [c] Spectrum measured in acetone.

Table 3 Electrochemical data for complexes and ligands in dichloromethane at 298 K[a]

	$E^{\circ\prime}$/V	
Compound	Oxidation	Reduction
1[b]	0.72	−1.41, −1.70
2[b]	0.65 (i)	−1.51
3	0.72 (i)	−1.48
4[c]		−1.56 (i)
bn[b]		−1.38
tbn		−1.55

i = Irreversible process. [a] $E^{\circ\prime}$ *versus* SCE, $E^{\circ\prime} = (E_a + E_c)/2$ where E_a and E_c are the anodic and cathodic peaks observed in the cyclic voltammogram. Potentials *vs.* SCE ± 0.02 V. Supporting electrolyte 0.1 M NBu_4ClO_4, scan speed 200 mV s^{-1}. Reversibility defined by peak separation for E_a and E_c of ≈60 mV and by $i_a = i_c$, where i_a and i_c are the current heights for the anodic and cathodic waves in the cyclic voltammogram. [b] Owing to solubility reasons the compound was run in acetone. [c] No oxidation was observed on scanning up to +1.7 V *vs.* SCE.

Electrochemical data for ligands and complexes are presented in Table 3.

Changes in the electronic absorption spectrum of bn with application of a reducing potential are shown in Fig. 2. A depletion of the ligand-centred (LC) bands in the UV with an increase in intensity of visible absorptions is observed. An isosbestic point is observed at 352 nm indicating a clean conversion from the neutral into the reduced ligand. The electronic absorption spectra for $\mathbf{3} \longrightarrow \mathbf{3}^{-}$ are shown in Fig. 3(a). The $\mathbf{3}^{-}$ species is characterised by strong absorptions at 1150, 975 and 445 nm. Isosbestic points are observed at 330 and 369 nm. Attempts to generate $\mathbf{4}^{-}$ were unsuccessful with permanent decomposition occurring on the timescale of the spectroelectrochemical experiment. The electronic absorption spectra showing the conversion of $\mathbf{2} \longrightarrow \mathbf{2}^{-}$ are shown in Fig. 3(b). The $\mathbf{2}^{-}$ state shows a strong absorption at 724 nm. Two reductions are observed in the cyclic voltammogram of **1**, at −1.4 and −1.7 V *vs.* SCE. When the OTTLE cell has a reducing potential applied across it spectral changes are observed for **1**, as shown in Fig. 3(c), and new bands grow in at 1070, 914 and 444 nm. When a more negative potential, sufficient to cause reduction of $\mathbf{1}^{-}$ to $\mathbf{1}^{2-}$, is applied a second set of spectral changes are observed [Fig. 3(d)] with a band growing in at 745 nm.

Resonance Raman spectra of the ligands and complexes are dominated by naphthyridine vibrations (SUP 57409).[21] Resonance Raman spectroelectrochemistry was successful for $\mathbf{3} \longrightarrow \mathbf{3}^{-}$ only. The spectra are shown in Fig. 4. Complex $\mathbf{3}^{-}$ shows strong bands at 1592, 1484 and 1439 cm^{-1}. The spectrum of $\mathbf{3}^{-}$ is much more intense than that of **3**, consistent with its greater absorption at the excitation wavelength of 514.5 nm.

Discussion

The electronic absorption data show that the MLCT transitions for the bn complexes are lower in energy than those for tbn. This suggests, assuming the metal donor orbitals are unchanged between the bn and tbn complexes, that the π* ligand acceptor MO is lower in energy for the bn complexes **1** and **3**. This is supported by the electrochemical data which indicate that the bn complex **1** is easier to reduce than its corresponding tbn analogue **2**. This is also the case for the corresponding mixed-ligand complexes **3** and **4**.

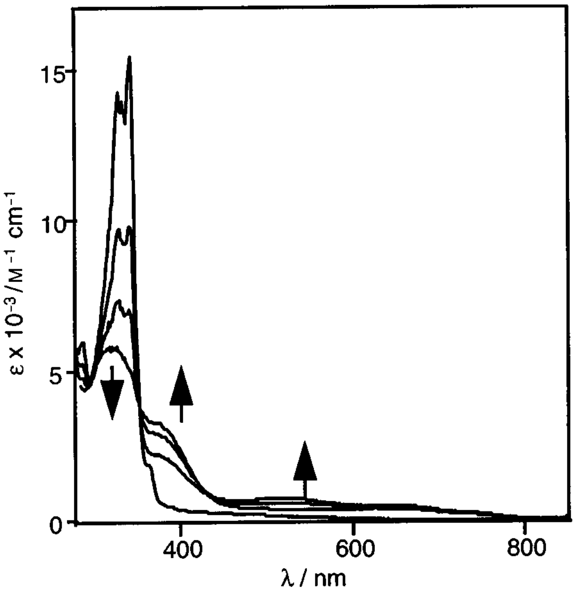

Fig. 2 Electronic absorption spectra of bn in MeOH measured in an OTTLE cell at varying potentials. Arrows indicate spectral changes on stepping through 0.0 to −1.4 V applied potential *versus* Ag^{+}–AgCl

The electronic absorption spectra for the reduced species are strikingly different from those of the corresponding parent complexes. In cases where a reversible reduction is present strong transitions are observed in the visible region. When the complexes are reduced both metal- and ligand-based MOs will be perturbed thus shifts in parent complex absorptions may be possible. The new features that grow in are intense (ε > 4000 M^{-1} cm^{-1}) which rules out ligand field transitions as giving rise to the observed absorptions. Alternately we may be observing metal-to-ligand charge-transfer bands which have been shifted as a consequence of reduction.[22] This behaviour is common in ruthenium(II) complexes of the type $[Ru(bpy)_2L]^{2+}$ (bpy = 2,2′-bipyridine, L = a ligand with a more extensive π system, which is normally easier to reduce than bpy). In these complexes the Ru→bpy MLCT transition is shifted from 450 to 480 nm upon reduction of the complex when the reducing electron occupies an MO based on L. However, the electronic absorption spectrum for $\mathbf{3}^{-}$ is very similar to that of $[Cu(dbn)_2]$ and $[Cu(dbn)(PPh_3)_2]$ which show intense absorption features at 1100 and 950 nm.[3] For $[Cu(dbn)_2]$ and $[Cu(dbn)(PPh_3)_2]$ there is strong evidence that the species formed in the reduced state is $dbn^{\bullet -}$. This would support the assignment of a $bn^{\bullet -}$ species being present in $\mathbf{3}^{-}$. The resonance Raman spectrum of $\mathbf{3}^{-}$ is supportive of this in that the bands at 1592 and 1484 cm^{-1} correspond closely to those for $dbn^{\bullet -}$ which lie at 1602 and 1490 cm^{-1}. This is reasonable in view of the fact that the dbn and bn ligands adopt similar geometries in complexation with copper(I). The dihedral angle in $[Cu(dbn)_2]^{+}$ is 21°.[3]

The electronic absorption spectrum of complex $\mathbf{2}^{-}$ differs significantly from that of $\mathbf{3}^{-}$ and $[Cu(dbn)(PPh_3)_2]$.[3] The bands observed for $\mathbf{2}^{-}$ are significantly blue-shifted consistent with the formation of a reduced species in which the redox orbital occupied is much less extensive than in $\mathbf{3}^{-}$. A plausible explanation for this is that the redox MO is localised on only one of the two naphthyridine moieties because of the extreme non-planar geometry of the tbn ligand.[7] Furthermore electronic absorption

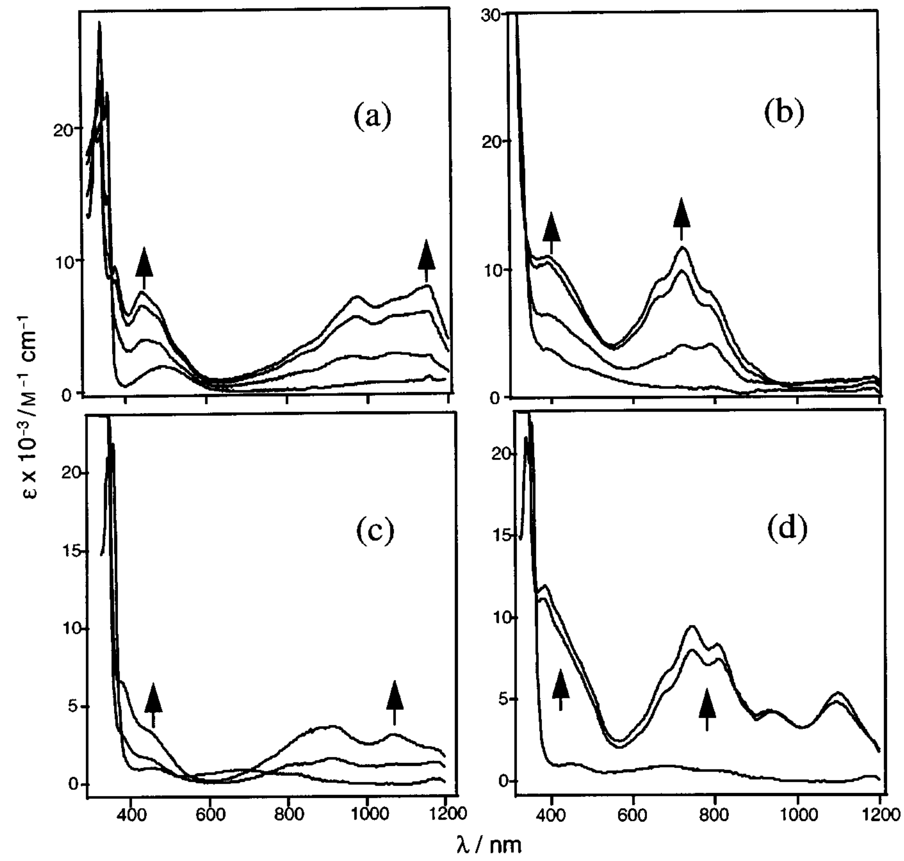

Fig. 3 Electronic absorption spectra of complexes measured in an OTTLE cell at varying potentials: (a) changes in the electronic absorption spectrum of **3** (CH_2Cl_2 solution with 0.1 M NBu_4ClO_4 supporting electrolyte) upon electrochemical reduction; (b) changes in the electronic absorption spectrum of **2** (acetone solution with 0.1 M NBu_4ClO_4 supporting electrolyte) upon electrochemical reduction; (c) changes in the electronic absorption spectrum of **1** (acetone solution with 0.1 M NBu_4ClO_4 supporting electrolyte) upon electrochemcial reduction; arrows indicate spectral changes on stepping through 0.0 to −1.1 V applied potential *versus* Ag^+–AgCl; (d) changes in the electronic absorption spectrum of $\mathbf{1}^-$ (CH_2Cl_2 solution with 0.1 M NBu_4ClO_4 supporting electrolyte) upon electrochemical reduction; arrows indicate spectral changes on stepping through −1.1 to −1.3 V applied potential *versus* Ag^+–AgCl

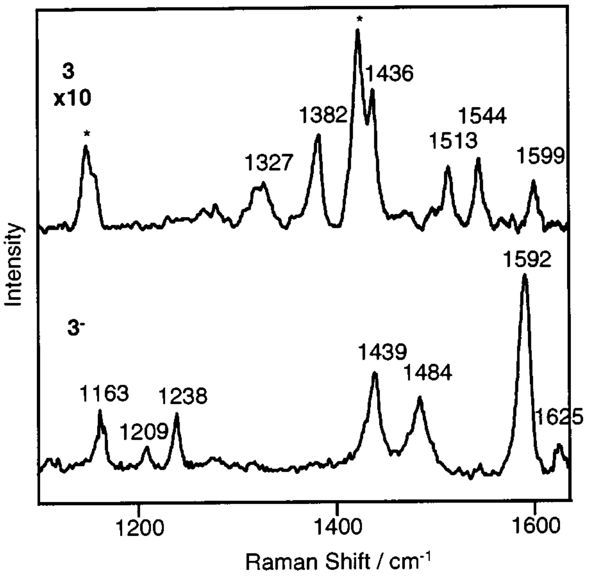

Fig. 4 Resonance Raman spectra (λ_{exc} = 514.5 nm, 10 mW at sample) of 5 mM solutions of complexes in CH_2Cl_2 measured in a spectroelectrochemical cell with 0.1 M NBu_4ClO_4 supporting electrolyte

spectra of the radical anions of diazanaphthalene systems show absorptions at *ca.* 710 nm.[23]

The electronic spectral changes upon reduction of complex **1** show both types of behaviour described above. The first reduction shows a spectral signature like that of $\mathbf{3}^-$; however at more reducing potentials new bands appear. These lie close to those observed for $\mathbf{2}^-$. The changes that occur in the reduction of **1** do not show clean isosbestic points. A clean isobestic point would indicate the conversion of one set of reactants into one set of products. However, in this complex, the application of a reducing potential sufficient to produce significant amounts of $\mathbf{1}^-$ across the platinum working electrode will also cause formation of $\mathbf{1}^{2-}$. In essence the OTTLE cell contains consecutive equilibria of **1**, $\mathbf{1}^-$ and $\mathbf{1}^{2-}$.

It appears that for this complex the first reduction occupies an MO like that of $bn^{\bullet -}$ or $dbn^{\bullet -}$ but with a second reduction a new type of redox MO is accessed with a more localised character. There are two possible formulations for $\mathbf{1}^{2-}$. First, the second reducing electron may occupy the same ligand as the first. The reduced species would by $[Cu(bn)(bn^{2-})]^-$. Alternatively the second reducing electron may lie on the other ligand, $[Cu(bn^-)_2]^-$. In this formulation the two bn^- species are not the same, as evidenced by their differing spectral signatures. However, the introduction of the first reducing electron to form $\mathbf{1}^-$ will result in a distortion of the complex and this may cause localisation of the MO occupied by the second reducing electron. It is unclear, with the present data, which of these two possible formulations is that of $\mathbf{1}^{2-}$.

Conclusion

Copper(I) complexes with tbn and bn ligands reduce at the ligand site and do not demetallate. However, that nature of the reduced species is rather different with the two ligands; for the bn ligand the reduction appears to extend across the entire bn ligand framework whereas for the tbn ligand, at least in **2**, the redox MO is localised at only one of the naphthyridine units.

The complex **1** shows initial reduction of bn$^{\bullet -}$ character but the second reduction shows spectral features which are consistent with a redox molecular orbital which is localised on one of the naphthyridine units.

Acknowledgements

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