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Some high-potential trithioether chelates of copper

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Abstract

The linear quadridentate ligand 1,8-bis(2′-quinolyl)-3,6-dithiaoctane and the three quinquedentate ligands 1,9-bis(2′-pyridyl)-2,5,8-trithianonane, 1,9-bis(6′-methyl-2′-pyridyl)-2,5,8-trithianonane and 1,11-bis(2′-quinolyl)-3,6,9-trithiaundecane have been prepared. The deep green–blue copper(II) chelates have been characterized by optical and ESR spectroscopy and cyclic voltammetry. The two pyridyl chelates have similar tetragonal coordination about the copper, with an equatorial N_2S_2 donor set, plus the third thioether sulfur bound axially. The most marked consequence of the pyridine α-methylation is that the $Cu^{2+/+}$ reduction potential is raised by about 200 mV; otherwise, the $E_{1/2}$ is consonant with previously advanced models for correlating redox potentials with ligand structural features. The pyridyl copper(II) complexes have been isolated as the tetrafluoroborate salts, whereas the quinolyl–copper(II) chelates are rather redox unstable, in association with even more positive $Cu^{2+/+}E_{1/2}$ values, similar to that for dibromine reduction.

Introduction

There is continuing interest in coordination complexes of copper(II) with various combinations of heterocyclic nitrogen, thiolate, phenolate and thioether donors [1–5], because of the increasing amount of detailed information becoming available regarding the active sites of copper-containing proteins, in which such groups act as the protein's donors [6–11]. In this regard, we have been interested mainly in the properties of thioether chelates incorporating benzimidazole donors, while other research groups have paid attention to macrocycles [1], and to imidazyl- [3] and pyridyl–thioether [12] systems as well as some 8-quinolyl [13] analogues of the latter. Goals of these efforts include elucidation of structure/function and structure/spectra relationships for such biomimetic systems.

We report here on some complexes of copper(II) incorporating the linearly oligodentate ligands shown in Fig. 1.

Experimental

Reagents and solvents for syntheses were obtained commercially and used without further purification. Butyronitrile (PrCN) and acetonitrile (MeCN) for electrochemistry and spectroscopy were distilled off sodium and calcium hydride under N_2, respectively. Tetraalkylammonium salts (tetra-n-butylammonium hexafluorophosphate, TBAH; tetraethylammonium perchlorate, TEAP), used at the 0.1 M levels as electrochemical supporting electrolytes, were prepared by metathesis from NR_4Br and HPF_6 or $NaClO_4$ in aqueous solution, recrystallized from water and dried *in vacuo* over P_4O_{10}. ^1H NMR spectra were taken on a 250 MHz Bruker Aspect 2000 instrument at room temperature, and mass spectra on a Finnigan-4500 instrument; the spectral data are truncated below 8% or $m/e = 65$, and only the most intense member of an isotope multiplet is given. Molecular models were constructed on a Macintosh-II platform using Chem3D Plus™ software, and minimized using the angles of the ideal tetragonal pyramid as optimal angles for the coordination core, without constraining the bond lengths. For the optimal bond length and bond angle values in the organic fragment the internally defined values were used. Extended Hückel calculations were performed using the program ICON8, provided by the Quantum Chemistry Program Exchange (Bloomington, IN) using the predefined orbital parameters for all atoms involved. EPR spectra were obtained from a Varian E-12 X-band spectrometer calibrated near $g = 2$ with diphenylpicrylhydrazyl radical, and optical spectra using Perkin-Elmer 320 and 330 spectrophotometers. Rotating disc electrode polarography and cyclic voltammetry (at scan rates of 0.02–1 V s^{-1}) were performed under N_2 (boil-off from Air Products liquid N_2) in a three-electrode cell utilizing a PAR-173 potentiostat and a PAR-176 *i*/*E* converter,

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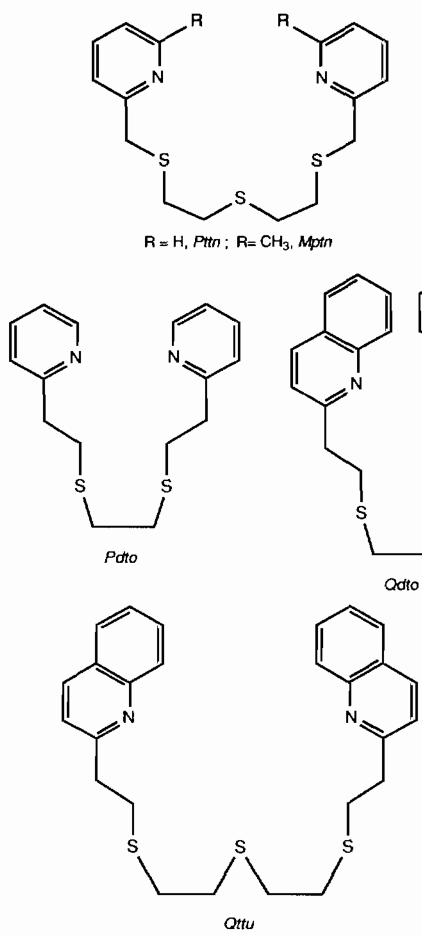

Fig. 1. The ligands reported herein.

the various platinum wire and disc working electrodes being referred to an Ag^+ (0.01 M, 0.1 M NEt_4ClO_4, CH_3CN)/Ag electrode. Voltammograms were corrected for *IR* drop by a modification of Parker's procedure [14]. Elemental microanalyses were performed by Robertson Microanalytical Laboratories (Madison, NJ).

1,8-Bis(2'-quinolyl)-3,6-dithiaoctane (Qdto)

To ethane-1,2-dithiol (Aldrich, 0.81 g, 8.6 mmol) and 0.25 mmol NaOH in ethanol (10 ml) under dinitrogen were added 2.86 g (18.4 mmol) of 2-vinylquinoline (Eastman Kodak). The solution was refluxed overnight, and the tan solid produced from the cooled solution was recrystallized from 95% ethanol (charcoal) and air-dried, to give white flakes of product in 30% yield. MS: 405 (*M*H^+, 47%), 248 (9%), 216 (77%), 188 (89%), 156 (100%), 143 (56%), 128 (47%), 105 (11%), 101 (10%), 77 (11%).

Anal. Calc. for $C_{24}H_{24}N_2S_2\cdot\frac{1}{2}H_2O$: C, 69.7; H, 6.09; N, 6.77. Found: C, 69.7; H, 5.99; N, 6.99%.

1,11-Bis(2'-quinolyl)-3,6,9-trithiaundecane (Qttu)

To bis(2-mercaptoethyl)sulfide (Aldrich, 1.22 g, 8.75 mmol) in ethanol (10 ml) under dinitrogen were added 2.72 g (17.5 mmol) of 2-vinylquinoline. The solution was refluxed overnight, and the tan solid produced from the cooled solution was recrystallized from 95% ethanol (charcoal) and air-dried, to give a white powdery product in 20% yield. MS: 465 (*M*H^+, 35%), 310 (23%), 276 (20%), 216 (37%), 188 (100%), 156 (90%), 143 (33%), 129 (43%), 115 (9%), 105 (21%), 101 (16%), 87 (8%), 77 (21%).

Anal. Calc. for $C_{26}H_{28}N_2S_3\cdot\frac{1}{2}C_2H_5OH\cdot H_2O$: C, 64.1; H, 6.58; N, 5.54. Found: C, 64.2; H, 5.78; N, 5.39%.

1,9-Bis(2'-pyridyl)-2,5,8-trithianonane (Pttn)

2.12 g (13 mmol) of 2-chloromethylpyridine hydrochloride (Aldrich) dissolved in 25 ml of ethanol were slowly added, under nitrogen and vigorous stirring, to a solution of 1.46 g (26 mmol) KOH and 1.00 g (6.5 mmol) bis(2-mercaptoethyl)sulfide (Aldrich) in 25 ml of nitrogen-flushed ethanol. A white precipitate of KCl formed immediately. The reaction mixture was stirred for 30 min and refluxed 1 h, after which it was cooled to room temperature, and the solvent removed by rotary evaporation. Water was then added, followed by enough KOH to bring the pH to 13, following which the product was extracted with dichloromethane. After the dichloromethane solution was dried with magnesium sulfate and stripped of solvent by rotary evaporation, the product was obtained as a yellowish oil (yield 1.9 g, 93%).

Characterization by ^1H NMR (δ ppm versus TMS, $CDCl_3$): 8.52 (doublet $J=4$ Hz, 2H; 6-pyr), 7.67 (doublet $J=8$ Hz of doublets $J=8$ Hz, 2H; 4-pyr), 7.38 (doublet $J=8$ Hz, 2H; 3-pyr), 7.18 (doublet $J=8$ Hz of doublets $J=4$ Hz, 2H; 5-pyr), 3.87 (singlet, 4H; pyr-CH_2-S) and 2.68 (singlet, 8H; S-C_2H_4-S).

6-Chloromethyl-2-methylpyridine hydrochloride

Thionyl chloride was added with stirring and cooling to 3.36 g of 6-methyl-2-pyridinemethanol (Aldrich/Bader) in 40 ml of dichloromethane until no effervescence was seen upon further addition. Methanol was then added to consume any excess thionyl chloride. Following addition of 1 ml of concentrated hydrochloric acid, the solution was concentrated on a steam bath, and subsequently further evaporated to dryness under reduced pressure, to yield 4.91 g (100%) of tan solid. This product was used immediately for further syntheses, without additional purification or characterization.

1,9-Bis(6'-methyl-2'-pyridyl)-2,5,8-trithianonane (Mptn)

This synthesis was done analogously to that of 1,6-bis(2'-pyridyl)-2,5,8-trithianonane, i.e. by adding 2 mol equiv. of 6-chloromethyl-2-methylpyridine hydrochloride in ethanol to a solution of 1 mol equiv. of bis(2-mercaptoethyl)sulfide and 4 mol equiv. of KOH in ethanol, under a nitrogen atmosphere. The work-up procedure was the same and the yield comparable.

Characterization by ^1H NMR (δ ppm versus TMS, $CDCl_3$): 7.62 (doublet $J=8$ Hz of doublets $J=8$ Hz, 2H; 4-pyr), 7.24 (doublet $J=8$ Hz, 2H; 3-pyr), 7.08 (doublet $J=8$ Hz, 2H; 5-pyr), 3.90 (singlet, 4H; pyr-CH_2-S), 2.70 (singlet, 8H; S-C_2H_4-S) and 2.59 (singlet, 6H; CH_3-6-pyr).

Cu(Pttn)(BF₄)₂

1.41 g Pttn (4.2 mmol) dissolved in 10 ml of methanol was slowly added, under vigorous stirring, to 4.2 ml of a 1.0 M solution of $Cu(BF_4)_2$ (Alfa-Ventron) in MeOH/H_2O. The solution immediately turned dark blue and the blue product started to precipitate. Saturated sodium tetrafluoroborate in methanol was added to the reaction mixture to induce further precipitation of the product, which was filtered off and dried *in vacuo*. Yield 1.63 g (68%) of deep blue crystals, which after standing for several days, either *in vacuo* or exposed to air, slowly turned deep green.

Anal. Calc. for $C_{16}H_{20}B_2CuF_8N_2S_3$: C, 33.5; H, 3.51; N, 4.88. Found: C, 33.5; H, 3.45; N, 4.81%.

Cu(Mptn)(BF₄)₂

4.59 g Mptn (27 mmol) dissolved in 10 ml of methanol was slowly added, under vigorous stirring, to 13.5 ml of a 1.0 M solution of $Cu(BF_4)_2$ in MeOH/H_2O. The solution immediately turned green and the green product started to precipitate. Saturated sodium tetrafluoroborate in methanol was added, and the resulting product was filtered off, washed with methanol and water and dried *in vacuo*. Yield 4.71 g (57%) of dark green solid.

Anal. Calc. for $C_{18}H_{24}B_2CuF_8N_2S_3$: C, 35.9; H, 4.02; N, 4.66. Found C, 35.1; H, 3.99; N, 4.44%.

Cu(Qdto)PF₆

Qdto (0.20 g, 0.5 mmol) in warm ethanol were added to 0.5 mmol of copper(II) chloride (Fisher Scientific) in ethanol/trimethyl orthoformate, and the resulting turbid green solution was refluxed briefly. Addition of KPF_6 and filtering of the now greenish yellow solution resulted in the eventual formation of small lemon–yellow crystals, in rather low yield. This copper(I) product was filtered off, washed with ethanol and dried *in vacuo*.

Anal. Calc. for $C_{24}H_{24}CuF_6N_2PS_2$: C, 47.0; H, 3.95; N, 4.57. Found: C, 46.0; H, 3.96; N, 4.42%.

Results and discussion

The optical spectra in acetonitrile (Table 1) are generally consistent with tetragonal N,S-coordination of the type common for copper(II), there being no indication of trigonal coordination. The pyridyl complexes have two ligand field bands, one centred near 600 nm, and the other, less intense, around 950 nm, but the latter is absent from the Qdto–Cu(II) spectrum. There is some enhancement of the shorter wavelength d–d band's absorption, as is often seen with sulfur donors. In each copper(II) complex, the strong band in the near-UV region (355–370 nm) is clearly assignable to a thioether-S → Cu(II) charge-transfer transition [15].

The cryogenic electron spin resonance spectra from butyronitrile/nitromethane solution are fairly clearly indicative of essentially tetragonal coordination. The $g_{\parallel}$ values are similar to those for $Cu(Pdto)^{2+}$ (2.164, $A_{\parallel}=174\times10^{-4}$ cm^{-1}; Pdto = 1,8-bis{2'-pyridyl}-3,6-dithiaoctane [16], Fig. 1) and generally akin to those observed for tetragonal CuN_2S_2 systems [17, 18]. The g values in particular are higher than one would expect for a $CuNS_3$ equatorial coordination core. Our assignment is therefore of CuN_2S_2 equatorial cores and consequently, the remaining S-donor is presumed to be axially coordinated in each case. This also applies for the two quinolyl complexes, which have ESR spectra identical to each other, and for which the higher value of the ratio $(g_{\parallel}\text{-}2)/A_{\parallel}$ indicates a modest pseudotetrahedral distortion of their CuN_2S_2 cores. Figure 2 illustrates how the geometric considerations which normally govern the construction of a tetragonal coordination sphere from such NSSSN ligands, most favourably generate a CuN_2S_2 equator (a) reflected by the ESR. Disregarding the possibility of a 'dangling' donor, the alternatives (b)–(d) involve a meridianal arrangement of donors. In a weak (e.g. O–) donor solvent D, (c) would default to a CuN_2DS equatorial core. While (d) would also yield a CuN_2S_2 equator, it fails (as do (b) and (c)) to accede to the model of Bosnich *et al.* [19] regarding the manner in which adjacent five-membered chelate rings joined at thioether sulfur tend to fold onto the face of a coordination polyhedron, rather than unfolding along a meridian. Nonetheless, extended Hückel calculations on the Chem3DPlus-minimized methylated structures showed a minimum in total energy for the configuration (d). Examination of the corresponding model (Fig. 2(e)) reveals a potent influence of the α-methyl groups on the ligand conformation, which supercedes the folding criterion noted above.

It was initially a little surprising to us, that the α-methylated and the non-methylated pyridyl chelates display such closely matched cryogenic ESR spectra, indicating that under these conditions, structural distortions of the coordination core due to the steric demands of these methyl groups are noteworthily minimal. However, (a) and (d) are indeed expected to have very similar resonances, and we also noted that the ambient temperature MeCN solution of $Cu(Pttn)^{2+}$ is deep blue, while the other chelates are all deep

TABLE 1. Properties of the complexes

	Complex						
	$Cu(Pttn)(BF_4)_2$	$Cu(Mptn)(BF_4)_2$	$Cu(Qdto)^{2+}$[a]	$Cu(Qttu)^{+}$[a]	$Cu(Qttu)^{2+}$[a]	$Cu(ClO_4)_2 \cdot xH_2O$	Br_2
Electrochemistry							
Medium[b]	MeCN/TBAH	MeCN/TBAH	MeCN/TBAH	MeCN/TBAH		MeCN/TEAP	MeCN/TEAP
$E_{1/2}$ (*obs.*)[c]	+0.195	+0.40	+0.60	+0.62		+0.74	+0.61[d]
$E_{1/2}$ (SHE)	+0.74	+0.945	+1.15	+1.17		+1.28	+1.16
$\Delta E_p°$ (mV)[e]	71	70	230	290		78	105
$D\eta$ (g cm s^{-2})	2.9×10^{-8}	1.4×10^{-8}	[f]	[f]		3.3×10^{-8}	2.4×10^{-8}
ESR[g]							
Medium[b]	NM/PrCN	NM/PrCN	C_7H_8/PrCN		C_7H_8/PrCN	MtyOH	
g_0	2.088	2.086	[h]		[h]		
$10^4\times A_0$ (cm^{-1})	70	66	[h]		[h]		
$g_\parallel$	2.159	2.159	2.202		2.205	2.408	
$10^4\times A_\parallel$ (cm^{-1})	165	163	161		162	137	
$g_\perp$	2.04	2.04	2.03		2.03	2.08	
$10^4\times A_\perp$ (cm^{-1})	23	18					
Optical spectra							
Medium[b]	MeCN/TBAH	MeCN/TBAH	MeCN/TBAH	MeCN/TBAH	[h]		
λ_{max} (nm)	960 [210]	920 [130]	630 [>295]	326 [12600]			
[ϵ (l mol^{-1} cm^{-1})]	595 [450]	620 [410]	367 [>2600]	318sh [11100]			
	358 [4200]	370 [2750]		313sh [10700]			

[a] Solution prepared from copper(II) perchlorate (Fluka) and ligand; the Cu(I)–Qttu chelate via reduction with ethanol. [b] MeCN = acetonitrile; PrCN = butyronitrile; NM = nitromethane; C_7H_8 = toluene; MtyOH = 2-methoxyethanol. [c] Referred to the non-aqueous electrode defined in 'Experimental'. The SHE E_f value is estimated by adding 545 mV. [d] $n=1$ process. [e] $\Delta E_p°$ is the peak potential separation extrapolated to zero scan rate. [f] A diffusion-controlled limiting current could not be estimated. [g] g_0, A_0 from ambient-T spectra; $g_\parallel$, $A_\parallel$, $g_\perp$ at 77 K; $A_\perp$ via $3A_0=A_\parallel+2A_\perp$; g_0, $g_\parallel \pm 0.003$; $10^4\times A \pm 3$; $g_\perp \pm 0.01$. [h] Redox instability prevented measurement; ESR data are from quickly frozen solutions of metal salt with excess ligand.

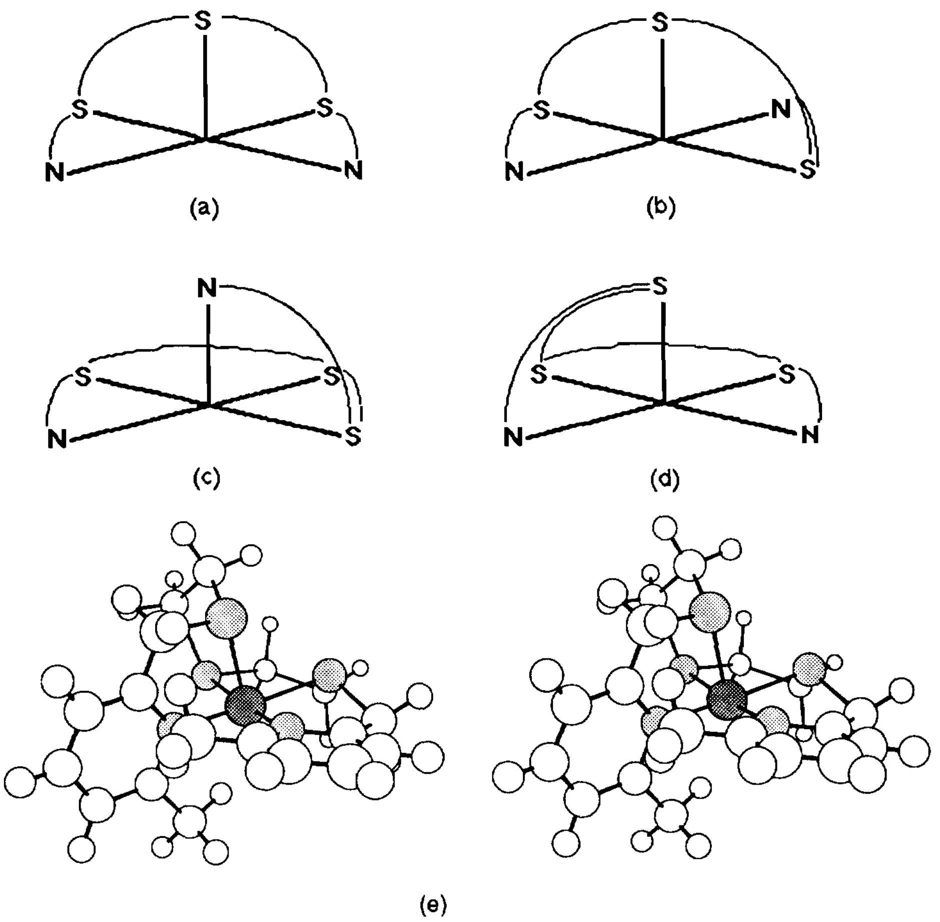

Fig. 2. (a)–(d) Various modes for wrapping a quinquedentate NSSSN ligand about a tetragonally pentacoordinate copper centre. (e) A molecular model (cross-eyed stereo) of Cu(Mptn)$^{2+}$. Note the manner in which one α-methyl group tends to force the positioning of the pyridine rings, while the other (lower left) leads to some shielding of the putative solvent coordination site.

green. In addition, it is likely that at 77 K, there is increased tetragonalization of the coordination in each case [20], so that there must be a caveat regarding the dependence of these details of the coordination on temperature and solvent. For example, when acetone/toluene is used as solvent for Cu(Mptn)(BF$_4$)$_2$, a difficultly resolvable ESR spectrum is obtained at 77 K, apparently containing two species, while the solution in CH$_2$Cl$_2$/nitromethane yields a spectrum ($g_\parallel = 2.169$, $10^4 \times A_\parallel = 163$ cm^{-1}) similar to that in nitromethane/PrCN. On the other hand, in 2-methoxyethanol the deep green ambient temperature solution gives rise to a markedly different spectrum at 77 K (pale blue glass, $g_\parallel = 2.391$, $10^4 \times A_\parallel = 143$ cm^{-1}) which is close to that for Cu^{2+} in 2-methoxyethanol (Table 1). We also observed the deep colour of the Mptn and Qttu chelates to be dispelled by *N*,*N*-dimethylformamide. That this is again due to displacement of ligand from the metal ion by these strong donicity solvents, and not to reduction to Cu(I) is evidenced by the still intense ESR spectrum, which for the Cu^{2+}–Qttu case ($g_\parallel = 2.398$, $10^4 \times A_\parallel = 140$ cm^{-1} in DMF) again matches that of free Cu^{2+} in this solvent [15].

In comparison with the N$_2$S$_2$ chelate Cu(Pdto)$^{2+}$, addition of the third sulfur donor and its attendant five-membered chelate ring in Pttn is expected to raise the $E_{1/2}$ by about 95 mV [21]. Taking a mean $E_{1/2}$ of +0.62 V (versus the SHE) for Cu(Pdto)$^{2+/+}$ in MeCN [12, 16], we arrive at an experimental $E_{1/2}$ difference between the Cu(Pttn)$^{2+/+}$ and Cu(Pdto)$^{2+/+}$ couples of about 120 mV, which is within 1.6 standard errors [21] of the difference 'predicted' on the bases of prior aqueous and methanolic solution results [19, 21]. Although the limiting peak-to-peak potential separations ($\Delta E_p{}^\circ$) for both compounds approach 70 mV rather than 60 mV, this does not predicate against their being Nernstian in their behaviour, because of the small radii of electrode curvature [22]. The reader might also find interest in the notably high reduction potential for the acetonitrile–Cu$^{II/I}$ couple itself.

The steric (rather than inductive [23, 24]) effects of pyridyl α-methylation (Mptn versus Pttn) are quite apparent in the redox behaviour, as the Cu(II)/Cu(I) reduction potential is about 200 mV higher for the methylated chelate. In correlation with this, the optical spectra in this instance show that with pyridine methylation, the copper $3d_{x^2-y^2}$ CT-acceptor orbital moves about 0.11 eV lower in energy with respect both to the sulfur CT-donor orbital and to the origin of the visible region d–d band. As with many other chelates of this class, solutions allowed to stand eventually become reductively bleached, either thermally or photochemically [25].

The structural origins of the above $E_{1/2}$ shifts are neither uniformly nor blatantly apparent in the other copper(II) spectroscopy, so if the α-methyl groups exert any significant effect in destabilizing the copper(II) state as opposed to stabilizing the copper(I), then their more important influence may through their effect in hindering solvation of the copper(II), rather than with distorting the copper(II) structure. Indeed, the model (e) in Fig. 2 reveals a highly relevant feature of the $Cu(Mptn)^{2+}$ structure, in that the α-methyl group of one of the pyridyl units would indeed have a shielding effect on the sixth coordination position of the copper ion. In any case, the α-methylation of these pyridine rings raises the $E_{1/2}$ by almost an order of magnitude more than we have observed ring methylation to do in some pyrazole–amine chelates [24], in which the geometry presumably directs the methyl substituents less tightly toward the metal centre. The redox potentials of structurally similar methylated pyrazolyl–thioether chelates would be of interest in this regard.

In the case of the 2-quinolyl complexes, the effects resulting from the replacement of pyridine α,β-hydrogens by benzo units (Pdto versus Qdto) are even more marked, so that the $E_{1/2}$ values approach those of the halogens and the acetonitrile–Cu^{II}/Cu^{I} couple itself (Table 1). We presume that the features combining to elevate the redox potentials to these quite high levels are that the quinolyl termini are (i) more sterically demanding than 2-picolyl groups [26], and (ii) less σ-basic than (alkyl)pyridines, as measured by their pK_As. However, differences in π-acceptor capabilities are apparently not important, as it is pyridine which has the lower energy LUMO (by about 0.3 eV) [27]. The Qdto–Cu^{II}/Cu^{I} potential is about half a volt more positive than that for Pdto–Cu^{II}/Cu^{I}. The elevation in $E_{1/2}$ associated with incorporation of the third sulfur donor (Qdto to Qttu, 20 mV) is considerably less than we should have expected, but we note that these two are not really Nernstian systems. Although it is possible that equilibrium ligand dissociation from Cu(I) may contribute to this characteristic, the voltammetric peak potentials are, in the equilibrium sense, quite different from those of Cu^{II}/Cu^{I} in acetonitrile (Table 1). Regardless of the precise mechanism, the large $\Delta E_p°$ values clearly indicate considerable reorganization of the coordination spheres during electron transfer.

One significant consequence of the quite positive reduction potentials is that thermal reduction by solvent (particularly alcohols) causes experimental difficulty in generating long-lived copper(II) species, particularly with Qttu and Qdto, so that physical measurements (Table 1) on their copper(II) complexes were made immediately after generating these by mixing solutions of their constituent.

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