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Synthesis, structure, spectra and redox interconversions in copper(II) complexes of 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine†

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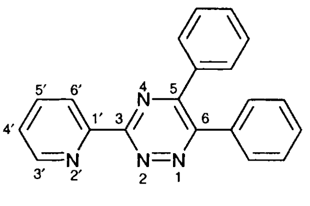
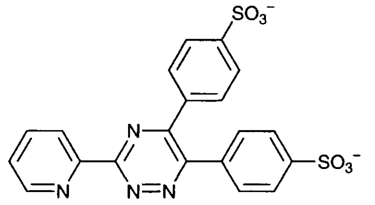
Copper(II) complexes of 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) with ClO_4^-, BF_4^-, NO_3^-, Cl^- and Br^- as counter ions have been prepared. The crystal structure of the complex $[Cu(dppt)_2(H_2O)_2][ClO_4]_2$ has been determined. The co-ordination geometry of the copper ion is elongated octahedral, the equatorial plane being formed by the N(2) nitrogens of both the triazine units and two pyridyl nitrogens and the axial positions being occupied by water molecules. The copper ion can be best described as centrosymmetric with the two dppt ligands being strictly coplanar to each other. The electronic and EPR spectral properties illustrate the strong axial interaction by solvent molecules with the weakly ligated CuN_4 plane. The markedly positive redox potential (0.57–0.34 V *vs.* NHE) of these complexes is ascribed to the π-acceptor properties of the ligand rather than to steric effects of the phenyl substituents. The $E_{\frac{1}{2}}$ and ΔE_p values are significantly dependent on the solvent and the anions. The spectral and electrochemical behaviour of the copper(II) complex of 3-(2-pyridyl)-5,6-bis(*p*-sulfonatophenyl)-1,2,4-triazine, the sulfonato derivative of dppt, in aqueous solution at various pH revealed that it could not act as an efficient catalytically active redox agent.

It is well known that factors like a low-symmetry environment, tetrahedral distortion caused by bulky ligand substituents[1] and π bonding[2] lead to high Cu^{II}–Cu^{I} redox potentials. Thus the high redox potentials of bis complexes of diimines such as 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) and substituted derivatives thereof are ascribed to destabilisation of Cu^{II} in the otherwise square-planar environment through interligand steric interactions. The methyl substituents in $[Cu(dmphen)_2]^{2+}$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) boosted the redox potential relative to the unsubstituted $[Cu(phen)_2]^{2+}$ and so the water-soluble complex anion[2a] $[Cu^{II}(dmsphen)_2(H_2O)]^{2-}$ [dmsphen = 2,9-dimethyl-4,7-bis(sulfonatophenyl)-1,10-phenanthroline] acts as a redox catalyst with potentials intermediate between the reacting species' oxidised and reduced states. Since such reagents are scarce, we became interested in the report[3] that a 1:2 solution of a copper(II) salt and dppt [dppt = 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine] exhibits a relatively high redox potential (0.43 V *vs.* normal hydrogen electrode, NHE). The latter may be rationalised on the basis of co-ordination of either N(2) involving π bonding[4] or N(4) sterically hindered by a bulky phenyl group. A ^1H NMR study[5] of $[Ru(bipy)_2(dppt)]^{2+}$ has also suggested the co-ordination of N(2) to Ru^{III}.

In the present study we have isolated copper(II) complexes of dppt with different anions and determined the crystal structure of the perchlorate salt to understand the mode of co-ordination of dppt to copper(II) and hence the origin of the high redox potential. Our detailed investigation on the structural, spectral and electrochemical properties of these complexes constitutes the present report. Also discussed are the spectra and redox chemistry of 1:2 Cu^{II}:pbspt [pbspt = 3-(2-pyridyl)-5,6-bis(sulfonatophenyl)-1,2,4-triazine] in aqueous solution.



dppt



pbspt

Experimental

Materials

All reagents and solvents were used as received from Aldrich (dppt, pbspt), Fluka $[Cu(ClO_4)_2\cdot6H_2O]$, G. F. Smith (tetra-*n*-hexylammonium perchlorate, tetra-*n*-butylammonium perchlorate BDH, India $(CuCl_2\cdot2H_2O)$, and Sisco, India (sodium tetrafluoroborate, tetra-*n*-ethylammonium bromide). The supporting electrolytes $N(C_6H_{13})_4ClO_4$ and $NBu^n{}_4ClO_4$ were recrystallised twice from aqueous ethanol and tetra-*n*-ethylammonium tetrafluoroborate thrice from ethyl acetate–water (3:1). For electrochemical studies, dimethylformamide (dmf) was refluxed with P_4O_{10}, the phosphoric acid generated neutralised using dry powdered NaOH and then distilled under reduced pressure. Methanol was distilled from $Mg(OMe)_2$.

Preparation of complexes

$[Cu(dppt)_2(H_2O)_2][ClO_4]_2$. To dppt (0.310 g, 1 mmol) in dioxane–methanol (1:1 v/v, 15 cm^3) was added $Cu(ClO_4)_2\cdot6H_2O$ (0.185 g, 0.5 mmol) in methanol (5 cm^3). The pale green precipitate formed immediately was filtered off, washed

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† *Supplementary data available* (No. SUP 57132 3 pp.): Electrochemical investigation of $[Cu(pbspt)_2]^{2-}$ at various pH. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Non-SI unit employed: G = 10^{-4} T.

with methanol and dried over P_4O_{10} *in vacuo*. Yield 0.34 g, 85% (Found: C, 52.45; H, 3.60; Cu, 7.00; N, 12.45. $C_{40}H_{32}Cl_2CuN_8O_{10}$ requires C, 52.25; H, 3.50; Cu, 6.90; N, 12.20%).

A bright green solution of the compound in acetonitrile was filtered, a few drops of light petroleum (b.p. 80–100 °C) added and kept at room temperature for 1 week when tiny flat blocks of bright green crystals separated. The latter were found suitable for X-ray diffraction. **CAUTION**: perchlorate salts are potential explosives!

$[Cu(dppt)_2(H_2O)_2][BF_4]_2 \cdot 2H_2O$. This complex was obtained as a light green crystalline product by following the above procedure except that $Cu(BF_4)_2 \cdot 4H_2O$ was employed. A solution of this complex in a MeCN–MeOH mixture was kept for slow evaporation. The fine square plate-like green crystals formed were collected. Yield 0.37 g, 80% (Found: C, 52.60; H, 4.30; Cu, 7.45; N, 11.95. $C_{40}H_{36}B_2CuF_8N_8O_4$ requires C, 52.55; H, 3.95; Cu, 7.55; N, 12.25%).

$[Cu(dppt)_2(H_2O)_2][NO_3]_2$. This was obtained as light green soft needle-shaped crystals by employing a similar procedure to that for the perchlorate. Yield: 0.35 g, 82% (Found: C, 57.30; H, 4.20; Cu, 7.60; N, 16.75. $C_{40}H_{32}CuN_{10}O_8$ requires C, 56.90; H, 3.80; Cu, 7.53; N, 16.60%).

$Cu(dppt)_2Cl_2 \cdot H_2O$. This was isolated as a green crystalline solid by mixing dppt (0.310 g, 1 mmol) in dioxane–methanol (1:1 v/v, 15 cm^3) and $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) in methanol (2 cm^3) and allowing the reaction mixture to stand for 5 d. Yield 0.29 g, 75% (Found: C, 62.40; H, 4.15; Cl, 9.45; Cu, 7.85; N, 14.40. $C_{40}H_{30}Cl_2CuN_8O$ requires C, 62.15; H, 3.90; Cl, 9.20; Cu, 8.20; N, 14.50%).

$Cu(dppt)_2Br_2$. This was obtained as a buff yellowish green precipitate by following a similar method to that for $Cu(dppt)_2Cl_2$. Yield 0.31 g, 74% (Found: C, 56.65; H, 3.75; Cu, 7.75; N, 13.20. $C_{40}H_{28}Br_2CuN_8$ requires C, 56.90; H, 3.35; Cu, 7.55; N, 13.30%).

Physical measurements

Elemental analyses were performed at City University, London. The copper content was determined by a titration method using ethylenediaminetetraacetate. Infrared spectra (400–4000 cm^{-1}) were recorded as KBr discs and Nujol mulls on a Shimadzu 435 spectrophotometer, diffuse-reflectance and solution spectra on a Hitachi U-3400 double-beam UV-Vis-NIR spectrophotometer. The UV/VIS spectral measurements were used to ascertain the formation of 1:2 Cu^{II}: pbspt complexes in solution. The EPR spectra were obtained on a Varian E-112 X-band spectrometer. The field was calibrated with diphenylpicrylhydrazyl (dpph). The values of g_0 and A_0 were measured at ambient temperature and $g_{\parallel}$ and $A_{\parallel}$ at 77 K.

Cyclic voltammetry and differential-pulse voltammetry (DPV) on a platinum-sphere electrode were performed at 25.0 ± 0.2 °C. A three-electrode cell configuration was used. The reference electrode was Ag(s)–$AgNO_3$ (0.01 mol dm^{-3}), $N(C_6H_{13})_4ClO_4$ (0.1 mol dm^{-3}) in acetonitrile (for non-aqueous solutions) or a saturated calomel electrode (for aqueous solutions). The temperature of the electrochemical cell was maintained by a cryocirculator (Haake D8 G). The solutions were deoxygenated by bubbling research-grade nitrogen. The instrument utilised included an EG&G PAR 273 potentiostat/galvanostat and an IBM PS-2 computer; EG&G M270 software was employed to carry out the experiments and to acquire the data. The potential of the ferrocene–ferrocenium couple (0.100 V, Ag–Ag$^+$) was measured in methanol solution under the same conditions to enable correction for junction potential.

Crystallography

The preliminary cell dimensions and space group of $[Cu(dppt)_2(H_2O)_2][ClO_4]_2$ were determined and refined on a Siemens R3m/V diffractometer. The intensities were collected at 296 K with graphite-monochromatised Mo-Kα radiation (λ 0.710 73 Å). An ω scan was employed with a variable scan speed. Details of the data collection and processing are in Table 1. The background was measured using a stationary crystal and counter at the beginning and end of the scan, each for 50.0% of the total scan time. The number of reflections collected was 6892 of which 2678 had $F > 3.0\sigma(F)$. The structure was solved by direct methods and refined on F^2 by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. No absorption correction was applied. The positions of the H atoms were calculated geometrically using a riding model, except for water molecules, with a fixed isotropic U. The weighting scheme used was $w^{-1} = \sigma^2(F) + 0.0005F^2$. All calculations were carried out with SHELXTL PLUS.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/19.

Results and Discussion

Crystal structure of $[Cu(dppt)_2(H_2O)_2][ClO_4]_2$

Fig. 1 shows an ORTEP[7] diagram of the discrete $[Cu(dppt)_2(H_2O)_2]^{2+}$ cation with the atom and plane numbering scheme; selected bond lengths and angles are given in Table 2. The centrosymmetric copper(II) ion is in an elongated octahedral environment. The equatorial plane is formed by two pyridine and two triazine N(2) nitrogens and the axial sites are occupied by two water molecules at longer distances (2.448 Å), as a consequence of the Jahn–Teller effect. The two dppt ring systems are strictly coplanar and are bound to Cu^{II} in *trans* configuration. The co-ordination plane is not a perfect square as shown by the bite angles which are not equal to 90°. There is no significant difference between Cu–N (pyridine) and Cu–N (triazine) bond lengths, revealing that the two nitrogens are equal in donor strength. The mean Cu–N bond distance (2.034 Å) is slightly longer than those (1.98–1.99 Å) in square-based bipyridyl complexes,[8–11] demonstrating that the bonds in the present complexes are comparatively weaker.

The two phenyl rings at C(7) and C(8) of the triazine ring are not coplanar with the co-ordination plane 1, as is evident from the dihedral angles (**1**–**4** 35.19, **1**–**5** 127.97°) formed by the least-squares planes. The phenyl–phenyl repulsion is evidenced by their high dihedral angle of 120.1°. The perchlorate ions lie

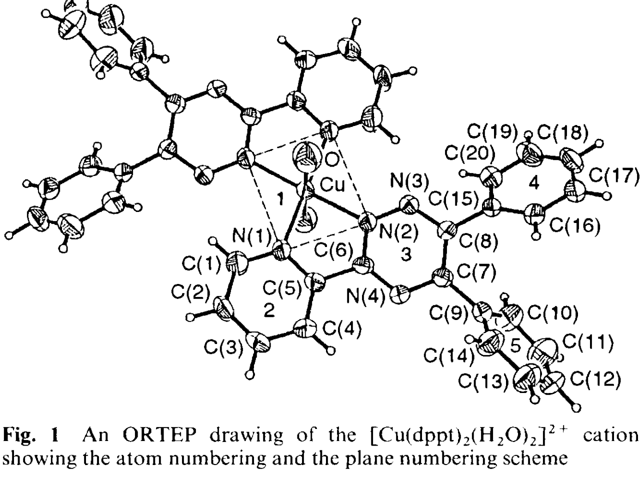


Fig. 1 An ORTEP drawing of the $[Cu(dppt)_2(H_2O)_2]^{2+}$ cation showing the atom numbering and the plane numbering scheme

Table 1 Crystallographic and data-collection parameters for [Cu(dppt)$_2$(H$_2$O)$_2$][ClO$_4$]$_2$

Formula	$C_{40}H_{32}Cl_2CuN_8O_{10}$
M	919.2
Crystal symmetry	Monoclinic
Space group	$C2/c$
a/Å	12.111(3)
b/Å	11.367(2)
c/Å	29.919(5)
β/°	92.95(2)
U/Å^3	4113.3(14)
Z	4
μ(Mo-Kα)/mm^{-1}	0.754
Crystal dimensions/mm	0.27 × 0.31 × 0.15
D_c/g cm^{-3}	1.484
θ range/°	2–30
F(000)	1868
No. reflections collected	6892
No. independent reflections	6036 (R_{int} = 0.0126)
No. observed reflections	2678 [$F > 3.0\sigma(F)$]
R	0.0963
R'	0.0876

Table 2 Selected bond lengths (Å) and angles (°) for [Cu(dppt)$_2$(H$_2$O)$_2$][ClO$_4$]$_2$

Cu–N(1)	2.036(5)	Cu–O	2.448(5)
Cu–N(2)	2.033(5)	N(1)–C(1)	1.336(10)
N(1)–C(5)	1.350(8)	C(1)–C(2)	1.384(12)
C(2)–C(3)	1.360(11)	C(3)–C(4)	1.378(10)
C(4)–C(5)	1.374(9)	N(2)–C(6)	1.329(8)
N(4)–N(3)	1.330(7)	N(3)–C(8)	1.332(8)
N(4)–C(6)	1.341(8)	N(4)–C(7)	1.325(8)
C(5)–C(6)	1.458(9)	C(7)–C(8)	1.430(9)
N(1)–Cu–N(2)	79.7(2)	N(2)–Cu–N(1A)	100.3(2)
N(2)–Cu–N(2A)	180.0(1)	Cu–N(1)–C(1)	128.6(5)
Cu–N(1)–C(5)	114.9(4)	C(1)–N(1)–C(5)	116.4(6)
Cu–N(2)–N(3)	126.2(4)	Cu–N(2)–C(6)	114.4(4)
N(3)–N(2)–C(6)	119.4(5)	N(2)–N(3)–C(8)	120.0(5)
N(1)–C(5)–C(6)	114.1(5)	N(2)–C(6)–N(4)	124.4(6)
N(2)–C(6)–C(5)	116.7(5)	N(4)–C(7)–C(8)	120.0(6)
N(4)–C(7)–C(9)	115.0(6)	C(8)–C(7)–C(9)	125.1(6)
N(3)–C(8)–C(7)	119.1(5)	N(3)–C(8)–C(15)	114.5(5)

Table 3 Electronic absorption spectral data;[a] $\tilde{\nu}_{max}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1} in parentheses); L = dppt

Compound	Medium	Ligand field	c.t.[b]
CuL$_2$(ClO$_4$)$_2$	Solid	15 600, 11 100	21 700
	MeNO$_2$	15 100 (140)	25 400 (4145)
	MeCN	14 600 (95)	
		12 300 (sh) (70)	
	dmf	16 600 (203)	20 600 (533)
		12 100 (sh) (40)	
CuL$_2$(BF$_4$)$_2$	Solid	15 200, 11 200 (sh)	21 800
	MeOH	14 900 (25)	—
	MeCN	14 700 (40)	—
	dmf	16 100 (89)	20 900 (268)
CuL$_2$(NO$_3$)$_2$	Solid	14 800, 11 100 (sh)	21 200
	MeOH	14 900 (25)	—
	MeCN	14 200 (55)	—
		10 800 (27)	—
CuL$_2$Cl$_2$	Solid	13 400, 11 200	21 300
	MeOH	13 200 (274)	21 800 (184)
		10 900 (247)	
	dmf	10 900 (212)	—
		8 400 (200)	
CuL$_2$Br$_2$	Solid	13 500	24 500
	dmf	12 600 (224)	—

[a] Concentration 0.001 mol dm^{-3}. [b] $N_{hat}\rightarrow Cu^{II}$.

> 3.6 Å away from the co-ordination site and are heavily distorted.

In contrast to the present complex, the analogous diimine complexes [Cu(bipy)$_2$(H$_2$O)][S$_3$O$_6$],[12] [Cu(phen)$_2$(H$_2$O)][NO$_3$]$_2$[13] and [Cu(phen)$_2$(H$_2$O)][BF$_4$]$_2$[14] possess distorted trigonal-bipyramidal geometry. The steric repulsion between the two hydrogen atoms at the 2 and 9 positions in phen and 6 and 6′ positions in bipy complexes prevent coplanar disposition of the ligands. Similarly the repulsion between the CH$_3$ groups at the 2 and 9 positions in [Cu(dmphen)$_2$(H$_2$O)][BF$_4$]$_2$·H$_2$O leads to a distorted trigonal-bipyramidal[15] geometry with water occupying one of the equatorial positions. In contrast, in the present complex cation there is no such steric repulsion between the adjacent ligand molecules, resulting in a square-planar geometry for copper(II).

IR Spectra

The IR spectrum of the perchlorate salt displays two well split bands at 1100 and 1050 cm^{-1}. Such splitting normally arises due to co-ordination or hydrogen bonding[16] of ClO$_4^-$; however, none of these is present in the crystal structure. The fluoroborate exhibited a broad unsplit peak around 1070 cm^{-1}, suggesting that the anion is not co-ordinated.[11] The presence of a band at 1380 cm^{-1} for the nitrate suggests the presence of unco-ordinated nitrate ion.[17,18]

Electronic and EPR spectra

The essentially axial EPR spectrum and the position and separation between the two ligand-field bands (Table 3) in the reflectance spectrum of the perchlorate complex are consistent with the elongated-octahedral geometry[12,19] revealed in its crystal structure. As similar spectral features are exhibited by the BF$_4^-$ and NO$_3^-$ complexes they are suggested to possess comparable stereochemistries. On dissolution of all these salts in different solvents the ligand-field spectral features undergo changes indicating a change in structure in solution. The position and separation of the bands are suggestive of solvent/anion participation in the co-ordination sphere; this is similar to the observation made for the copper(II) complexes of diimine ligands like bipy.[13] Thus the average of the band positions decreases in the order ClO$_4^-$ $\approx$ BF$_4^-$ > NO$_3^-$ > Br$^-$ > Cl$^-$; dmf > MeOH > MeCN. The $\tilde{\nu}_{max}$ and $g_{\parallel}$ values (Table 4) of both ClO$_4^-$ and BF$_4^-$ complexes are respectively lower and higher than those expected for a CuN$_4$ chromophore,[14,20,21] suggesting axial interaction[22] by MeCN and dmf. The $g_{\parallel}/A_{\parallel}$ quotients (110–134 cm) are suggestive[23] of negligible distortion from the CuN$_4$ co-ordination plane.

In contrast to the ClO$_4^-$ complex, the halide complexes are not dihydrates suggesting that an elongated-octahedral geometry similar to the latter is not feasible for them. These complexes could involve a six-co-ordinate CuN$_4$(H$_2$O)Cl or CuN$_4$X$_2$ (X = Cl or Br) chromophore or alternatively a five-co-ordinate CuN$_4$X chromophore with a near trigonal-bipyramidal geometry. Conductometric studies were consistent with the absence of co-ordination of or the presence of less than one co-ordinated complex anion; however, they revealed the co-ordination of only one halide ion in solution. Thus the significantly lower energies of the ligand-field bands of the halide complexes, compared to those of the three hydrates, suggest that a near trigonal-bipyramidal geometry could not be ruled out. For the chloride the rhombic cryogenic solution EPR spectrum (Fig. 2) with the lowest g value < 2.04 suggests a predominantly d_{z^2} ground state in this geometry.[24–27] On the other hand, the frozen-solution EPR spectrum of the bromide complex is poorly defined and lends no support to the suggested geometry.

Redox chemistry

All the complexes exhibit clean electrochemistry as signified by linear plot,[28] of i_{pc} *vs.* $v^{\frac{1}{2}}$ from the cyclic voltammograms obtained at scan rates 0.01–1.0 V s^{-1}. The diffusion coefficients

Table 4 Electron paramagnetic resonance spectral data[a]; L = dppt

Compound	Medium	g_a/g_0	A_a/A_0	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$[b]	$g_{\parallel}/A_{\parallel}$
$CuL_2(ClO_4)_2$	Powder	—	—	2.229	161	2.060	138
	MeCN–MeOH	2.122	75	2.235	188	2.062	119
	dmf–Me_2CO	2.135	71	2.275	181	2.062	126
$CuL_2(BF_4)_2$	Powder[c]	—	—	2.220	—	2.062	—
	MeCN–MeOH	2.119	66	2.231	162	2.060	124
	MeOH–Me_2CO	2.137	67	2.239	187	2.076	119
	dmf–Me_2CO	2.137	85	2.277	170	2.070	134
$CuL_2(NO_3)_2$	Powder[c]	2.070	21	—	—	—	—
	MeCN–MeOH	2.127	82	2.239	201	2.065	111
CuL_2Cl_2	Powder[c]	2.099	63	—	—	—	—
	MeCN–MeOH[d]	2.121	67	2.232	177	2.060	126
CuL_2Br_2	Powder[c]	2.053	23	—	—	—	—
	dmf–MeOH[e]	2.125	91	—	—	—	—
$[Cu(pbspt)_2]^{2-}$	Water–MeOH[f] (4:1 v/v)	2.130	—	2.231	182	2.072	123

[a] All hyperfine coupling constants in units of 10^{-4} cm^{-1}. [b] Values for frozen solution; agree with those calculated using the equation $g_{\perp} = \frac{1}{2}(3g_0 - g_{\parallel})$. [c] A_0 = One third of the linewidth between the first-derivative spectrum's maximum and minimum. [d] $g_1 = 2.038$. [e] Parallel component not resolved. [f] Tetrafluoroborate salt used.

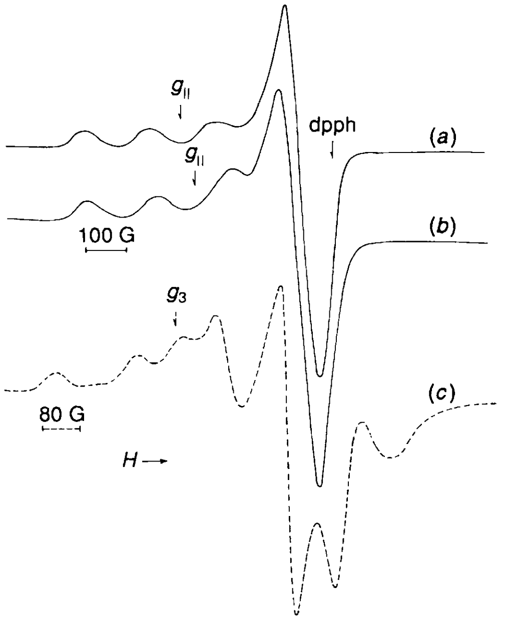


Fig. 2 EPR spectra of (*a*) $[Cu(dppt)_2][ClO_4]_2$ in dmf–Me_2CO, (*b*) $[Cu(dppt)_2][NO_3]_2$ in MeOH–MeCN and (*c*) $[Cu(dppt)_2Cl]Cl$ in MeOH–MeCN at 77 K

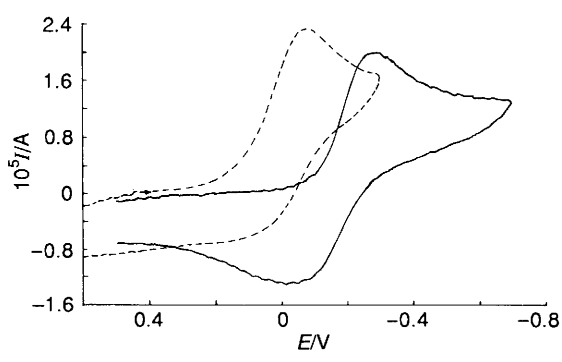


Fig. 3 Cyclic voltammograms of a ≈0.001 mol dm^{-3} solution of $[Cu(dppt)_2(H_2O)_2][ClO_4]_2$ in MeCN (——) and in dmf (- - -) at 25 °C; scan rate 0.05 V s^{-1}

(*D*) calculated by substituting the slope from this plot into the Randles–Sevciks equation[29] are typical of the Cu^{II}–Cu^{I} couple. The limiting peak-to-peak separation ΔE_p° (ΔE_p at zero i_{pc}) for the nitrate and fluoroborate are 59 and 67 mV respectively, suggesting an almost reversible Cu^{II}–Cu^{I} redox process (ΔE_p = 60 mV for a Nernstian one-electron redox system). The ΔE_p decreases in the order Cl^- > ClO_4^- (dmf) > ClO_4^- (MeCN) > Br^- > BF_4^- ≈ NO_3^- (Fig. 3) while $E_{\frac{1}{2}}$ decreases, irrespective of the anions, in the order MeCN > MeOH > dmf supporting the ligand-field spectral results. The K_{2+}/K_{+} ratio calculated[30] from the net shift in $E_{\frac{1}{2}}$ (Table 5) clearly shows that MeCN and dmf stabilise Cu^{I} in $[Cu(dppt)_2]^+$ more than methanol does. The $E_{\frac{1}{2}}$ values exhibited by the present complexes are comparable to those of analogous bipy and dmphen complexes.[15] The weak σ bonding caused by the highly electron-withdrawing phenyl groups as well as strong π back bonding[7] involving the phenyl and pyridine rings, rather than the bulkiness of the ligand molecule, is responsible for the positive $E_{\frac{1}{2}}$ values. The lowest unoccupied molecular orbital (LUMO) (π*) of phenyl-substituted pyridyl triazine[7] is lower in energy than those of bipyridyl and bipyrazine ligands.

Ligand field and redox chemistry of $[Cu(pbspt)_2(H_2O)_2]^{2-}$ at various pH

To ascertain the composition of the copper(II) complex of pbspt spectral measurements were carried out with mixtures of copper(II) perchlorate (1 × 10^{-3} mol dm^{-3}) and pbspt (1 × 10^{-3} mol dm^{-3}). A plot of the absorbance of the complex at 680 nm for a continuous variation of the Cu:pbspt ratio revealed the formation of a 1:2 complex. Zhang and Anson[31] have arrived at the same conclusion during the course of this investigation and have shown that the copper(I) complex of pbspt also possesses 1:2 stoichiometry. These observations suggest that the reduction of the 1:2 copper(II) complex will not be accompanied by ligand dissociation.

The effect of pH on the spectra of solutions containing copper(II) perchlorate (1 × 10^{-3} mol dm^{-3}) and pbspt (1 × 10^{-3} mol dm^{-3}) in 1:2.1 molar ratio has been studied; the conditions employed are sufficient to ensure complete formation of the bis(chelate). With increase in pH from 3.3 to 7.6 the $\tilde{\nu}_{max}$ value decreases with concomitant decrease in absorbance. At low pH the more basic pyridyl nitrogen would be protonated and the triazine N(2) atom co-ordinated. This is consistent with the observation that the probable site of reduction of pbspt is one of the nitrogens of the N=N bond.[32] Between pH 4.6 and 7.6 two species are in equilibrium (Scheme 1) as evident from the occurrence of only one isosbestic point in the spectra.

The cryogenic EPR spectrum obtained at pH 7.1 is axial, with the parameters (Table 4) being typical of a CuN_4 chromophore. Above pH 7.6 but below 9.6 the deprotonation of co-ordinated

Table 5 Electrochemical data[a] for complexes at 50 mV s^{-1} scan rate; L = dppt

Compound	Solvent	Electrolyte	$E_{p,c}$/V	$E_{p,a}$/V	ΔE_p/mV	$\Delta E_p^{\circ b}$/mV	$E_{\frac{1}{2}}$/V	$E_{\frac{1}{2}}^{c}$/V	i_{pa}/i_{pc}	10^{-6} D cm^2 s^{-1}	K_{2+}/K_{+} ^{d}
$CuL_2(ClO_4)_2$	MeCN	$N(C_6H_{13})_4ClO_4$	−0.079	0.134	262	232	+0.026	−0.021	0.7	4.1	3.35×10^4
	dmf	NEt_4ClO_4	−0.290	−0.016	274	186	−0.153	−0.198	1.0	3.9	5.35×10^4
$CuL_2(BF_4)_2$	MeOH	NEt_4BF_4	−0.076	0.004	80	67	−0.036	−0.049	1.0	5.1	9.25×10^4
$CuL_2(NO_3)_2$	MeOH	$N(C_6H_{13})_4ClO_4$	−0.108	−0.014	94	59	−0.061	−0.071	1.0	1.7	3.49×10^4
CuL_2Cl_2	dmf	$N(C_6H_{13})_4ClO_4$	−0.304	−0.106	410	386	−0.099	−0.186	1.1	2.7	2.76×10^7
CuL_2Br_2	dmf	$NBu^n{}_4ClO_4$	−0.279	−0.127	152	144	−0.203	−0.215	1.2	3.5	2.26×10^2

[a] $E_{\frac{1}{2}}$ in V *vs.* Ag–Ag$^+$, 0.1 mol dm^{-3} $N(C_6H_{13})_4ClO_4$ in MeCN, add 0.544 V to convert into values *vs.* NHE. [b] From the plot of ΔE_p *vs*, I_{pc}. [c] From DPV at scan rate 0.001 V s^{-1}, pulse height 0.05 V. [d] E° of free Cu^{II}–Cu^{I} *vs.* NHE: dmf, 0.006;[25] MeCN, 0.173;[5] MeOH, 0.215;[5] water, 0.155 V.[5]

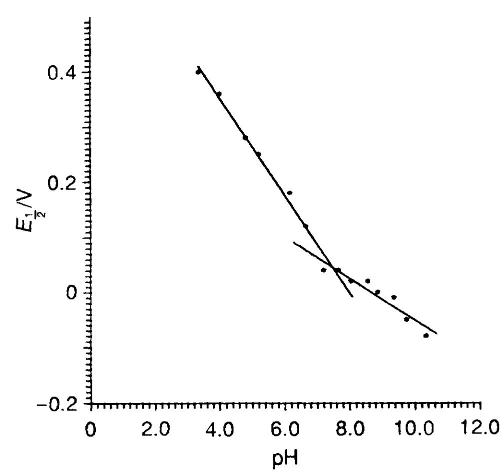
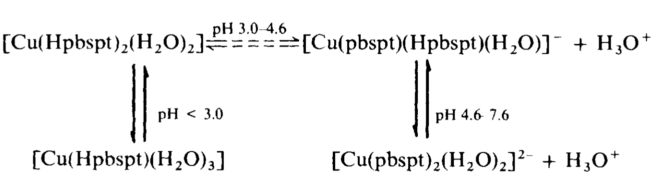


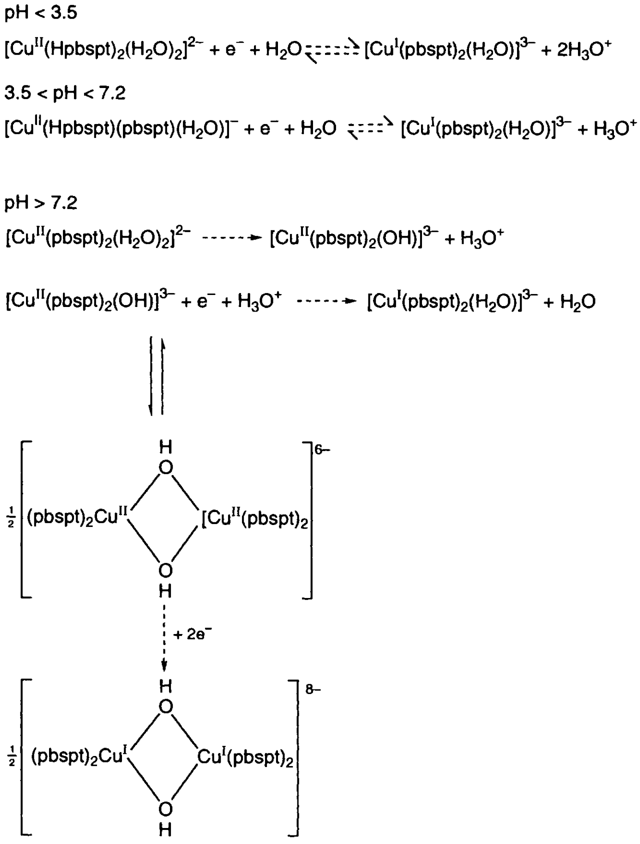
Fig. 4 Dependence of the differential pulse voltammetric half-wave potentials upon pH of a Cu^{II}-pbspt aqueous solution at 25 °C, supporting electrolyte NaClO$_4$, scan rate 0.005 V s^{-1}, pulse height 0.05 V



Scheme 1

water molecules (Scheme 2) may occur; this is consistent with the increase in absorbance. Beyond pH 9.6 a brown solid is formed and the absorbance decreases.

Electrochemical investigation at various pH was performed on the 1 : 2 complex generated in solution by mixing copper(II) perchlorate (2×10^{-4} mol dm^{-3}) and pbspt (4.2×10^{-4} mol dm^{-3}). In the range pH 3.3–7.2 the Cu^{II}–Cu^{I} redox process is irreversible as seen from the absence of an anodic wave; however, at pH 7.5 both the waves are discernible. With increase in pH the $E_{\frac{1}{2}}$ from DPV (see SUP 57132) is shifted to more negative values, with an inflection around pH 7.5 (Fig. 4). The estimated pK_a value of 7.5 is close to that (7.6) previously reported.[31] The negative shift in $E_{\frac{1}{2}}$ in the range pH 3.3–7.2 is consistent with the stabilisation of Cu^{II} by the CuN$_4$ chromophore generated, as inferred from the increase in $\tilde{\nu}_{max}$. The shift in $E_{\frac{1}{2}}$ per unit increase in pH is around 85 mV, which affords[33] the number of protons (q) involved in the present n = 1 electrode reaction, ≈1.4; this is consistent with the proposed mechanism (Scheme 2) which involves two copper(II) species in the range pH 3.5–7.2, as revealed by spectral studies and an average of ≈1.5 protons. However, no significant pH dependence of $E_{\frac{1}{2}}$ below pH 7.2 has been observed previously.[31] The shift in $E_{\frac{1}{2}}$ per unit increase in pH, which is around 38 mV in the range pH 7.2–10.0, corresponds to $q \approx 0.6$ for the Cu^{II}–Cu^{I} couple (Scheme 2); however, a value of $q \approx 1$ has been obtained previously.[31] It appears that the deprotonated species form di-μ-hydroxo dimeric copper(II) species the two-electron reduction of which would involve no protons, thus corresponding to a q value of ≈0.5. Such dimeric species have been characterised[34] crystallographically.



Scheme 2

Thus the present spectral and electrochemical results are consistent with a change in geometry on reduction to Cu^{I} with the concomitant deprotonation of the co-ordinated ligand or water, the latter at pH > 7.2. McMillin and co-workers[2] have provided structural evidence for such a change in co-ordination using similar sterically constrained bipyridyl ligands. Lappin and co-workers[35] have made similar observations for [Cu^{II}(dmsphen)$_2$(H$_2$O)]$^{2-}$ but no significant pH dependence of $E_{\frac{1}{2}}$ below pH 8.0 was noted.

Conclusion

The copper(II) complexes of dppt have a square-based geometry which is in contrast to those of analogous bipy or phen type diimine complexes; this is because of the lack of H and H or R and H/R interligand steric repulsions. They possess relatively high $E_{\frac{1}{2}}$ values due to effective withdrawal of electron density from copper through the extended π system involving the phenyl and pyridyl rings. They exhibit interesting anion- and solvent-dependent electrochemistry. In aqueous solution the 1:2 Cu^{II}–pbspt system is less effective as a redox reagent than $[Cu(dmsphen)_2]^{2-}$[2a] for which the sterically hindered ligands favour a compressed tetrahedral geometry suitable for Cu^{I}.

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