A Structural Comparison of Bis(quinoxaline-2,3-dithiolato)cuprate Complexes†

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The crystal structures, u.v.-visible spectra, and electrochemical properties of $[Cu(qdt)_2]^{2-}$ and $[Cu(qdt)_2]^-$ (qdt = quinoxaline-2,3-dithiolate) are reported. The compound $[PPh_4]_2[Cu(qdt)_2]$ crystallizes in space group $P2_1/c$ with $a = 9.9320(4)$, $b = 23.8217(10)$, $c = 11.9178(5)$ Å, $\beta = 95.075(5)°$, and $Z = 2$; $[PPh_4][Cu(qdt)_2]$ crystallizes in space group $P2/n$ with $a = 23.709(2)$, $b = 7.192(1)$, $c = 24.188(2)$ Å, $\beta = 119.170(6)°$, and $Z = 4$. In both anions the CuS_4 moiety is essentially planar, with the mean Cu–S bond length in $[Cu(qdt)_2]^-$ [2.187(1) Å] being significantly shorter than that in $[Cu(qdt)_2]^{2-}$ [2.260(1) Å], consistent with the unpaired electron of the latter complex occupying an orbital which is antibonding with respect to the Cu–S σ bonds. The $[Cu(qdt)_2]^-$–$[Cu(qdt)_2]^{2-}$ couple is electrochemically reversible with $E_{\frac{1}{2}} = -0.18$ V *vs.* saturated calomel electrode in dimethylformamide; a quasi-reversible process with $E_{\frac{1}{2}} = -1.28$ V observed in this solvent is attributed to the $[Cu(qdt)_2]^{2-}$–$[Cu(qdt)_2]^{3-}$ couple.

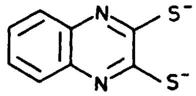
Metal complexes of quinoxaline-2,3-dithiolate (qdt) are analogous to metal dithiolenes[1,2] and are expected to be capable of reversible one-electron redox reactions at the MS_2C_2 ring. The ligand also involves a pyrazine ring and several organic molecules incorporating this group can be reversibly reduced to form radical anions which are stable in aprotic media.[3] Thus, qdt complexes can, in principle, undergo redox reactions at two distinct sites in the molecule and could act as multi-electron reservoirs.

Complexes of qdt with Mo[2] and with some of the later transition metals[4,5] have been reported previously, including both members of the redox couple $[Cu(qdt)_2]^-$–$[Cu(qdt)_2]^{2-}$. We have carried out structural studies on $[Cu(qdt)_2]^-$ and $[Cu(qdt)_2]^{2-}$ to determine whether significant changes in the geometry of the complex accompany the redox process and whether such changes permit the distinction between a process centred on the MS_2C_2 or the pyrazine rings.

Herein we report the crystal structures of $[PPh_4]_2[Cu(qdt)_2]$ and $[PPh_4][Cu(qdt)_2]$. Also, we report the u.v.-visible spectra of these complexes, not previously defined, and details of the electrochemistry of $[Cu(qdt)_2]^{n-}$ (n = 1, 2, or 3) in dimethylformamide (dmf) solution.

Experimental

Materials and Methods.—The compound H_2qdt was prepared by the method of Morrison and Furst,[6] and the procedure of Theriot *et al.*,[4] for the synthesis of the corresponding $[NBu_4]^+$ salts, was used for the preparation of $[PPh_4]_2[Cu(qdt)_2]$ (**1**), obtained in 71% yield, and $[PPh_4][Cu(qdt)_2]$ (**2**), obtained in 85% yield. The compounds were crystallized from $MeCN$–Et_2O, (**1**), and CH_2Cl_2–hexane, (**2**). All manipulations except the aerial oxidation of $[Cu(qdt)_2]^{2-}$ were performed under an atmosphere of dinitrogen using Schlenk-type apparatus [Found: C, 68.0; H, 4.3; Cu, 5.3; N, 4.9; P, 5.5; S, 11.6. Calc. for $C_{64}H_{48}CuN_4P_2S_4$, (**1**): C, 68.2; H, 4.3; Cu, 5.6; N, 5.0; P, 5.5; S, 11.4. Found: C, 60.5; H, 3.6; Cu, 7.9; N, 7.0; P, 3.8; S, 15.5. Calc. for $C_{40}H_{28}CuN_4PS_4$, (**2**): C, 60.1; H, 3.6; Cu, 8.0; N, 7.1; P, 3.9; S, 16.3%].



qdt

Instrumentation.—U.v.-visible spectra were recorded on a Shimadzu UV-260 spectrophotometer. Cyclic voltammograms were obtained using a PAR model 175 waveform generator and model 173 potentiostat. Potentials were determined relative to the saturated calomel electrode (s.c.e.); the potential for the ferrocenium–ferrocene couple is +480 mV *vs.* s.c.e. under the conditions employed.

X-*Ray Crystallography.*—*Crystal data.* (**1**), $C_{64}H_{48}CuN_4P_2S_4$, $M_r = 1\,126.8$, monoclinic, space group $P2_1/c$, $a = 9.9320(4)$, $b = 23.8217(10)$, $c = 11.9178(5)$ Å, $\beta = 95.075(5)°$, $U = 2\,808.7$ Å^3, $Z = 2$, $D_c = 1.332$ g cm^{-3}, $F(000) = 1\,166$, $\mu = 0.63$ mm^{-1} for Mo-K_α radiation, $\lambda = 0.710\,73$ Å.

(**2**), $C_{40}H_{28}CuN_4PS_4$ (ignoring partially occupied water site, see below), $M_r = 787.5$, monoclinic, space group $P2/n$, $a = 23.709(2)$, $b = 7.192(1)$, $c = 24.188(2)$ Å, $\beta = 119.170(6)°$, $U = 3\,601.4$ Å^3, $Z = 4$, $D_c = 1.452$ g cm^{-3}, $F(000) = 1\,616$, $\mu = 0.91$ mm^{-1}.

Data collection and reduction. For complex (**1**) [for (**2**) in square brackets where different]: crystal size 0.45 × 0.38 × 0.27 mm [0.50 × 0.42 × 0.31 mm]; Siemens AED2 diffractometer, Mo-K_α radiation; $T = 293$ K; $2\theta_{max.}$ 50°; index ranges h −11 to 2, k 0 to 28, l −14 to 14 [h 0 to 28, k −8 to 8, l −28 to 28]; no significant intensity variation for three standard reflections, 6 427 [12 240] reflections measured, 4 943 [6 343] unique, 3 880 [4 801] with $F > 4\sigma(F)$ for structure refinement. Semi-empirical absorption correction, transmission 0.735—0.750 [0.732—0.803], merging R_{int} for equivalent reflections = 0.017 [0.024].

Structure solution and refinement.[7] Automatic multisolution direct methods [Cu atoms at unit-cell corners and face centres, deduced from intensity statistics and Patterson, other atoms by Fourier recycling], anisotropic thermal parameters for all non-H atoms, H atoms constrained to give C–H 0.96 Å on external bisectors of ring angles, blocked-cascade refinement to minimize $\Sigma w\Delta^2$, $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) + gF^2$, $g = 0.000\,07$ [0]. No extinction correction. [Residual electron density after all

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates ($\times 10^4$) for compound (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	5 000	5 000	5 000	C(16)	471(3)	4 297(1)	7 303(2)
S(1)	5 294(1)	5 787(1)	6 076(1)	C(21)	862(3)	3 630(1)	9 760(2)
S(2)	3 776(1)	4 607(1)	6 287(1)	C(22)	1 971(3)	3 500(1)	10 498(2)
C(1)	4 560(2)	5 616(1)	7 305(2)	C(23)	2 139(3)	3 755(1)	11 541(2)
C(2)	3 891(2)	5 075(1)	7 408(2)	C(24)	1 210(3)	4 140(1)	11 844(2)
N(1)	4 622(2)	5 986(1)	8 128(2)	C(25)	111(3)	4 277(1)	11 111(2)
N(2)	3 371(2)	4 930(1)	8 336(2)	C(26)	−64(3)	4 026(1)	10 069(2)
C(3)	4 132(3)	5 824(1)	9 120(2)	C(31)	−613(3)	2 715(1)	8 535(2)
C(4)	3 534(2)	5 292(1)	9 229(2)	C(32)	−1 525(3)	2 725(1)	9 350(2)
C(5)	3 115(3)	5 126(1)	10 284(2)	C(33)	−2 468(3)	2 301(1)	9 380(3)
C(6)	3 303(3)	5 477(1)	11 192(2)	C(34)	−2 515(3)	1 875(1)	8 623(3)
C(7)	3 878(3)	6 006(1)	11 083(2)	C(35)	−1 623(3)	1 863(1)	7 815(3)
C(8)	4 278(3)	6 180(1)	10 074(2)	C(36)	−661(3)	2 281(1)	7 763(3)
P	550(1)	3 287(1)	8 416(1)	C(41)	2 088(3)	3 005(1)	7 947(2)
C(11)	−194(3)	3 789(1)	7 427(2)	C(42)	2 671(3)	2 529(1)	8 473(3)
C(12)	−1 418(3)	3 681(1)	6 807(2)	C(43)	3 845(3)	2 315(1)	8 120(3)
C(13)	−1 973(3)	4 081(1)	6 076(2)	C(44)	4 443(3)	2 563(1)	7 250(3)
C(14)	−1 317(4)	4 581(1)	5 943(3)	C(45)	3 880(3)	3 028(1)	6 724(3)
C(15)	−96(3)	4 688(1)	6 544(2)	C(46)	2 693(3)	3 252(1)	7 070(3)

Table 2. Atomic co-ordinates ($\times 10^4$) for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0	0	0	C(311)	2 103(1)	1 659(3)	2 797(1)
S(11)	−115(1)	2 218(1)	553(1)	C(312)	1 637(1)	2 895(4)	2 382(1)
S(12)	−908(1)	−1 310(1)	−188(1)	C(313)	1 336(2)	4 082(4)	2 607(2)
C(11)	−934(1)	2 076(4)	334(1)	C(314)	1 495(1)	4 050(4)	3 233(2)
C(12)	−1 289(1)	438(4)	10(1)	C(315)	1 952(1)	2 843(4)	3 639(1)
N(11)	−1 199(1)	3 454(3)	468(1)	C(316)	2 260(1)	1 639(4)	3 430(1)
N(12)	−1 899(1)	207(3)	−146(1)	C(321)	1 933(1)	−1 327(3)	1 893(1)
C(13)	−1 850(1)	3 307(5)	271(1)	C(322)	2 168(1)	−2 618(4)	1 628(1)
C(14)	−2 194(1)	1 664(4)	−26(1)	C(323)	1 748(1)	−3 882(4)	1 186(1)
C(15)	−2 861(1)	1 580(5)	−227(1)	C(324)	1 107(1)	−3 867(4)	1 017(1)
C(16)	−3 170(2)	3 080(6)	−150(1)	C(325)	877(1)	−2 617(4)	1 279(1)
C(17)	−2 832(2)	4 688(6)	135(2)	C(326)	1 283(1)	−1 339(4)	1 720(1)
C(18)	−2 180(2)	4 819(5)	347(1)	P(4)	7 500	4 646(1)	2 500
Cu(2)	0	5 000	5 000	C(411)	7 782(1)	6 129(3)	2 090(1)
S(21)	642(1)	2 805(1)	5 012(1)	C(412)	7 354(1)	7 402(4)	1 657(1)
S(22)	−188(1)	5 944(1)	4 063(1)	C(413)	7 561(2)	8 601(4)	1 349(1)
C(21)	428(1)	2 591(4)	4 212(1)	C(414)	8 195(2)	8 542(4)	1 471(1)
C(22)	51(1)	4 041(3)	3 779(1)	C(415)	8 618(1)	7 298(4)	1 905(1)
N(21)	609(1)	1 106(3)	4 031(1)	C(416)	8 419(1)	6 073(4)	2 217(1)
N(22)	−124(1)	3 970(3)	3 177(1)	C(421)	8 129(1)	3 133(3)	3 042(1)
C(23)	400(1)	949(4)	3 395(1)	C(422)	8 349(1)	3 151(3)	3 686(1)
C(24)	38(1)	2 384(4)	2 969(1)	C(423)	8 816(1)	1 884(4)	4 071(1)
C(25)	−173(1)	2 134(5)	2 319(1)	C(424)	9 061(1)	637(3)	3 816(1)
C(26)	−40(1)	527(5)	2 104(1)	C(425)	8 840(1)	581(4)	3 176(1)
C(27)	314(1)	−885(5)	2 528(1)	C(426)	8 369(1)	1 827(3)	2 785(1)
C(28)	532(1)	−676(4)	3 161(1)	O	−538(4)	6 549(12)	1 169(4)
P(3)	2 500	179(1)	2 500				

other atoms found was assigned to H_2O with partial site occupancy 0.333(6), weakly hydrogen bonded to one nitrogen atom; analytical and i.r. spectroscopic evidence for the presence of this water was inconclusive.] No significant features in the final difference synthesis. Final $R = 0.038$ [0.042], $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.041$ [0.031].

Atomic co-ordinates are given in Tables 1 and 2.

Results and Discussion

Theriot *et al.*[4] reported difficulty in obtaining the u.v.–visible spectrum of $[Cu(qdt)_2]^{2-}$ due to the presence of $[Cu(qdt)_2]^-$ as an impurity. We have recorded spectra for $[PPh_4]_2[Cu(qdt)_2]$ and $[PPh_4][Cu(qdt)_2]$, and the absorption maxima and absorption coefficients are listed in Table 3. Unlike the earlier workers, we find no absorptions at $\lambda_{max.} > 500$ nm in the spectrum of $[Cu(qdt)_2]^{2-}$ and, therefore, we conclude that this solution was free of $[Cu(qdt)_2]^-$.

The electron-transfer reactivity of $[Cu(qdt)_2]^{n-}$ complexes in dmf solution has been investigated by cyclic voltammetry (Figure 1). Two redox processes are observed, at $E_{\frac{1}{2}} = -0.18$ and -1.28 V *vs.* s.c.e. The first process corresponds to the $[Cu(qdt)_2]^-$–$[Cu(qdt)_2]^{2-}$ couple and is fully reversible ($i_{pa}/i_{pc} = 1.0 \pm 0.05$); $\Delta E_p = 60$ mV, independent of scan rate). The second process, which is attributed to the $[Cu(qdt)_2]^{2-}$–$[Cu(qdt)_2]^{3-}$ couple, is quasi-reversible, ΔE_p increases and $i_p/v^{\frac{1}{2}}$ decreases with increasing scan rate (Table 4).

The structures of $[Cu(qdt)_2]^{2-}$ and $[Cu(qdt)_2]^-$ are illustrated in Figures 2 and 3, respectively. The structure of compound (**2**) contains two crystallographically independent

Table 3. U.v. visible spectroscopic data for $[Cu(qdt)_2]^{n-}$ (n = 1 or 2)[a]

$\lambda_{max.}$/nm (ε/l mol^{-1} cm^{-1})	
$[Cu(qdt)_2]^{2-}$ [b]	$[Cu(qdt)_2]^{-}$ [c]
480 (sh) (4 020)	879 (250)
425 (52 600)	580 (480)
404 (50 400)	408 (61 000)
	392 (43 000)

[a] Absorptions at $\lambda < 270$ nm are obscured by bands due to $[PPh_4]^+$. [b] In MeCN solution. [c] In CH_2Cl_2 solution.

Table 4. Scan-rate dependence of the $[Cu(qdt)_2]^{2-}$–$[Cu(qdt)_2]^{3-}$ couple*

v/mV s^{-1}	ΔE_p/mV	$i_{pc}v^{-\frac{1}{2}}$/μA dm^3 s$^{\frac{1}{2}}$ mV$^{-\frac{1}{2}}$ mmol^{-1}
50	70	9.2
100	76	9.0
200	83	8.9
500	90	8.8

* Measurements were made for 1 mmol dm^{-3} $[PPh_4]_2[Cu(qdt)_2]$ in dmf containing 0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a vitreous carbon working electrode.

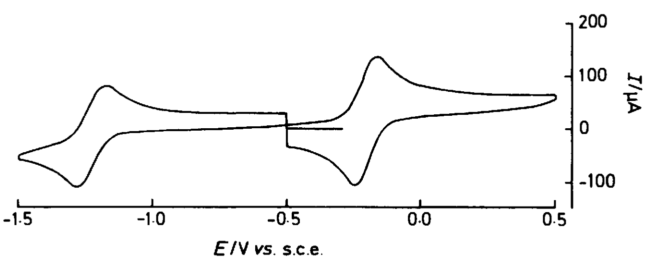

Figure 1. Cyclic voltammogram of $[Cu(qdt)_2]^{2-}$ in dmf and 0.2 mol dm^{-3} $[NBu_4][BF_4]$. Scan rate = 200 mV s^{-1}

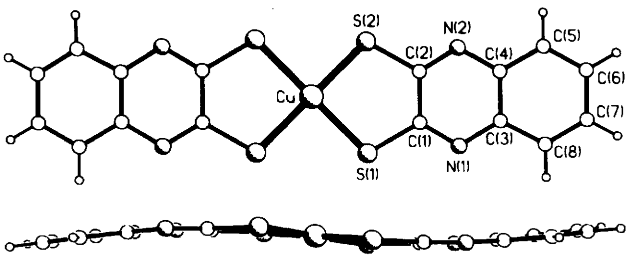

Figure 2. The structure of the anion in $[PPh_4]_2[Cu(qdt)_2]$

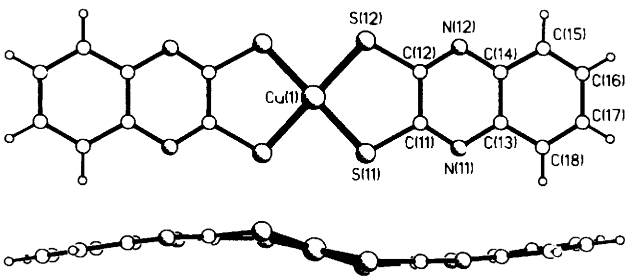

Figure 3. The structure of anion 1 in $[PPh_4][Cu(qdt)_2]$

anions: Figure 3 depicts anion 1; the dimensions of anion 2 are not significantly different. In the $[Cu(qdt)_2]^{n-}$ (n = 1 or 2) anions the CuS_4 groups and the ligand $C_8N_2S_2$ groups are essentially planar; the angles between the CuS_4 and $C_8N_2S_2$ planes are 10.0° for $[Cu(qdt)_2]^{2-}$ and 21.4 and 24.0° for anions 1 and 2, respectively, of $[Cu(qdt)_2]^-$.

Bond lengths and bond angles in the anions are detailed in Tables 5 and 6 and compared with the relevant data for the analogous copper complexes of dithio-oxalate (dto)[8] and maleonitriledithiolate (mnt);[9,10] the results presented for the latter complex are for the planar as opposed to the non-planar[11,12] form of $[Cu(mnt)_2]^{2-}$.

The greatest structural difference between $[Cu(qdt)_2]^{2-}$ and $[Cu(qdt)_2]^-$ is in the length of the Cu–S bonds. The values for the $[Cu(qdt)_2]^-$ anions [mean 2.184(1) and 2.189(1) Å] are significantly less than for both the Cu–S bonds in $[Cu(qdt)_2]^{2-}$ [2.275(1) and 2.244(1) Å; we see no obvious reason for the difference of *ca.* 0.03 Å between them]. A similar decrease in Cu–S bonds lengths upon oxidation occurs for the corresponding dto[8] and mnt[9,10] complexes. The structure of $[Cu(tdt)_2]^-$ (tdt = toluene-3,4-dithiolate) has recently been reported;[13] the mean Cu–S bond length in this complex [2.164(2) Å] is close to those of the other monoanionic complexes $[CuL_2]^-$ (L = qdt, mnt, or dto). These structural differences are in agreement with the molecular orbital schemes which have been proposed[14–16] for square-planar metal complexes of unsaturated 1,2-dithiolates (metal dithiolenes).[1] Thus, the unpaired electron in $[Cu(qdt)_2]^{2-}$ is predicted to occupy an orbital of b_{1g} symmetry, based on the metal d_{xy} orbital, which is antibonding with respect to the Cu–S σ bonds.

The dimensions of the ligands in $[Cu(qdt)_2]^{2-}$ and $[Cu(qdt)_2]^-$ are similar to those which have been reported for $[Ni(qdt)_2]^{2-}$ [17] and for $[Mo(qdt)_3]^{2-}$,[2] and the intraligand bond lengths are significantly less affected than the Cu–S bonds by the redox change. However, it is apparent that in the copper qdt complexes the oxidized complex has significantly shorter C(1)–C(2) bonds and slightly longer C–S bonds than the corresponding reduced complex. This pattern in bond lengths is also apparent for the dto and mnt analogues (Table 5). The variations are contrary to the suggestion[1] that oxidation of metal dithiolenes should reduce the electron density on the ligands and cause them to adopt a more dithione-like structure, *i.e.* decrease the C–S and increase the C(1)–C(2) bond length. It is possible that the tendency for the ligands to adopt a dithione-like structure, in $[Cu(qdt)_2]^-$ as compared to $[Cu(qdt)_2]^{2-}$, is outweighed by the distortions of the CuS_2C_2 ring induced by the shortening of the Cu–S bonds upon oxidation which forces the ligands to have a smaller bite.

Structural studies for the nickel dithiolene redox pairs $[Ni(mnt)_2]^-$–$[Ni(mnt)_2]^{2-}$ [18,19] and $[Ni(dtpt)_2]^-$–$[Ni(dtpt)_2]^{2-}$ [20,21] (dtpt = 2-thioxo-1,3-dithiacyclopent-4-ene-4,5-dithiolate) have identified significant but smaller contractions of the Ni–S bond lengths upon oxidation; for $[Ni(mnt)_2]^{n-}$ Ni–S is reduced from 2.165(5)[19] for n = 2 to 2.146(1) Å,[18] and for $[Ni(dtpt)_2]^{n-}$ the corresponding change is 2.216(4)[21] to 2.156(3) Å.[20] These changes have been interpreted[16] as implying that oxidation of these dianions involves loss of an electron from a weakly Ni–S antibonding orbital of b_{3g} symmetry, based on the metal d_{xy} orbital. Changes in the length of the C–S and C(1)–C(2) bonds upon oxidation of these nickel(II) complexes are marginally significant and no clear picture of an alteration in the electronic structure of the ligand is manifest.

The electrochemical reduction of $[Cu(qdt)_2]^{2-}$ is less reversible than the oxidation of this anion, implying slower electron-transfer kinetics for the reduction.[22] The electrochemical behaviour of $[Cu(tdt)_2]^{n-}$ (n = 1—3) has recently been inves-

Table 5. Bond lengths (Å) for $[Cu(qdt)_2]^{n-}$ (n = 1 or 2) and related copper complexes

	$[Cu(qdt)_2]^{2-}$[a]	$[Cu(qdt)_2]^{-}$[a] Anion 1	Anion 2	$[Cu(dto)_2]^{2-}$[b]	$[Cu(dto)_2]^{-}$[b]	$[Cu(mnt)_2]^{2-}$[c]	$[Cu(mnt)_2]^{-}$[d]
Cu–S(1)	2.275(1)	2.183(1)	2.183(1)	2.268(2)	2.164(1)	2.286(1)	
Cu–S(2)	2.244(1)	2.185(1)	2.194(1)	2.253(2)	2.178(1)	2.265(1)	
Mean Cu–S[e]	2.260(1)	2.184(1)	2.189(1)	2.261(2)	2.171(1)	2.276(1)	2.170(4)
S(1)–C(1)	1.741(3)	1.749(3)	1.751(3)	1.704(5)	1.737(5)	1.727(3)	
S(2)–C(2)	1.737(3)	1.747(3)	1.745(3)	1.702(5)	1.723(5)	1.729(3)	
Mean S–C[e]	1.739(3)	1.748(3)	1.748(3)	1.703(5)	1.730(5)	1.728(3)	1.73(1)
C(1)–C(2)	1.459(3)	1.437(4)	1.440(3)	1.545(7)	1.524(7)	1.359(4)	1.32(2)
S(1) ··· S(2)(bite)	3.209(4)	3.147(4)	3.137(4)	3.165(2)	3.137(2)[f]	3.238[g]	3.13[g]
C(1)–N(1)	1.315(3)	1.297(4)	1.304(4)				
C(2)–N(2)	1.307(3)	1.314(4)	1.306(4)				
Mean C–N[e]	1.311(3)	1.306(4)	1.305(4)				
N(1)–C(3)	1.374(3)	1.379(4)	1.374(4)				
N(2)–C(4)	1.368(3)	1.368(4)	1.374(4)				
Mean N–C[e]	1.371(3)	1.374(4)	1.374(4)				
C(3)–C(4)	1.409(4)	1.415(4)	1.414(4)				
C(3)–C(8)	1.416(4)	1.405(4)	1.398(5)				
C(4)–C(5)	1.416(4)	1.411(5)	1.411(5)				
C(5)–C(6)	1.368(4)	1.367(6)	1.366(5)				
C(6)–C(7)	1.395(4)	1.385(5)	1.395(4)				
C(7)–C(8)	1.364(4)	1.373(5)	1.366(5)				

[a] This work. [b] Data from ref. 8. [c] Data from ref. 9. [d] Data from ref. 10. This is the only one of these complexes in which the ligands are not related by a crystallographically imposed symmetry element; mean values are tabulated. [e] The estimated standard deviations in parentheses indicate the precision of individual values, not their agreement. [f] This value, taken from ref. 8, is inconsistent with the Cu–S bond lengths and S(1)–Cu–S(2) angle, given in the same source, which imply a value of 3.002(2) Å for this intraligand S(1) ··· S(2) separation. [g] Calculated from published Cu–S and S–Cu–S dimensions.

Table 6. Bond angles (°) for $[Cu(qdt)_2]^{n-}$ (n = 1 or 2) and related copper complexes*

	$[Cu(qdt)_2]^{2-}$	$[Cu(qdt)_2]^{-}$ Anion 1	Anion 2	$[Cu(dto)_2]^{2-}$	$[Cu(dto)_2]^{-}$	$[Cu(mnt)_2]^{2-}$	$[Cu(mnt)_2]^{-}$
S(1)–Cu–S(2)	90.5(1)	92.2(1)	91.5(1)	88.85(7)	87.48(5)	90.7(1)	92.4(2)
Cu–S(1)–C(1)	103.9(1)	102.9(1)	102.9(1)	104.5(2)	105.7(1)	101.5(1)	101.9(5)
Cu–S(2)–C(2)	104.8(1)	102.8(1)	102.8(1)	105.0(2)	105.5(2)	101.7(1)	
S(1)–C(1)–C(2)	102.3(2)	118.8(2)	118.9(2)	119.7(3)	117.5(2)	122.7(2)	
S(1)–C(1)–N(1)	118.4(2)	118.8(2)	118.5(2)				
C(2)–C(1)–N(1)	121.3(2)	122.4(3)	122.6(3)				
S(2)–C(2)–C(1)	120.1(2)	119.7(2)	119.1(2)	119.6(3)	117.6(2)	123.1(2)	121.8(11)
S(2)–C(2)–N(2)	118.5(2)	118.3(2)	118.8(2)				
C(1)–C(2)–N(2)	121.4(2)	122.1(3)	122.0(3)				
C(1)–N(1)–C(3)	117.2(2)	116.8(3)	116.5(2)				
C(2)–N(2)–C(4)	117.6(2)	116.5(2)	116.5(2)				
N(1)–C(3)–C(4)	121.1(2)	120.7(3)	121.0(3)				
N(1)–C(3)–C(8)	120.2(2)	119.8(3)	119.5(2)				
C(4)–C(3)–C(8)	118.6(2)	119.5(3)	119.5(3)				
N(2)–C(4)–C(3)	121.1(2)	121.3(3)	121.2(3)				
N(2)–C(4)–C(5)	119.4(2)	119.8(3)	120.2(2)				
C(3)–C(4)–C(5)	119.5(2)	118.8(3)	118.6(3)				
C(4)–C(5)–C(6)	120.0(3)	120.3(3)	120.6(3)				
C(5)–C(6)–C(7)	120.5(3)	120.6(3)	120.3(3)				
C(6)–C(7)–C(8)	120.7(3)	121.1(4)	120.5(3)				
C(3)–C(8)–C(7)	120.5(3)	119.7(3)	120.5(3)				

* See Table 5 for explanatory footnotes.

tigated by Sawyer *et al.*[13] Although these workers describe the $[Cu(tdt)_2]^{2-}$–$[Cu(tdt)_2]^{3-}$ couple as reversible, the published cyclic voltammogram appears to indicate that, for $[Cu(tdt)_2]^{2-}$ as for $[Cu(qdt)_2]^{2-}$, reduction to the corresponding trianion is a less reversible process than oxidation to the monoanion. This could indicate that the reduction involves a greater change in the geometry about the copper atom than the oxidation. The reduced complex, $[Cu(qdt)_2]^{3-}$, could have a distorted tetrahedral geometry similar to that of the valence-isoelectronic complex $[Cd(tdt)_2]^{2-}$.[23] Such a structural change, from square planar to tetrahedral geometry, on reduction has been observed for the structurally characterized redox pair $[Mn(tdt)_2]^{-}$–$[Mn(tdt)_2]^{2-}$;[24] this couple has been variously reported as a reversible process in MeCN ($E_{\frac{1}{2}}$ = − 0.67 V)[13] and an electrochemically irreversible process in dmf ($E_{\frac{1}{2}}$ = −1.09 V, ΔE_p = 0.61 V) and in CH_2Cl_2 ($E_{\frac{1}{2}}$ = −0.82 V, ΔE_p = 0.27 V).[24] Further investigation appears necessary to resolve this situation.

This study has shown that the oxidation of $[Cu(qdt)_2]^{2-}$ involves a change in the electron population of molecular orbitals localized on the CuS_2C_2 groups, without significant changes in electron density in the pyrazine rings. We note, however, that electrochemical reduction of pyrazines in protic solvents becomes a reversible two-electron process accompanied by protonation, forming the 1,4-dihydropyrazines,[25] a reduction analogous to the redox reactions of flavin[26] and pterin[27] cofactors in biological systems. Therefore, we are currently investigating the electrochemistry of qdt complexes in protic media to determine whether ligand-based redox processes can be observed under these more favourable conditions.

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References

1 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.
2 S. Boyde, C. D. Garner, J. H. Enemark, and R. C. Ortega, *Polyhedron*, 1986, **5**, 377; *J. Chem. Soc., Dalton Trans.*, 1987, 297.
3 J. C. M. Henning, *J. Chem. Phys.*, 1966, **44**, 2139.
4 L. J. Theriot, K. K. Ganguli, S. Kavarnos, and I. Bernal, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3133.
5 K. K. Ganguli, G. O. Carlisle, H. J. Hu, L. J. Theriot, and I. Bernal, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3579.
6 D. C. Morrison and A. Furst, *J. Org. Chem.*, 1956, **21**, 470.
7 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining and displaying crystal structures from diffraction data, Revision 5, University of Göttingen, 1985.
8 M. G. Kanatzidis, N. C. Baenziger, and D. Coucouvanis, *Inorg. Chem.*, 1985, **24**, 2680.
9 K. W. Plumlee, B. M. Hoffman, J. A. Ibers, and Z. G. Soos, *J. Chem. Phys.*, 1975, **63**, 1926.
10 J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1964, **3**, 1507.
11 D. Snaathorst, H. M. Doesburg, J. A. A. J. Perenboom, and C. P. Keijzers, *Inorg. Chem.*, 1981, **20**, 2526.
12 P. Kuppusamy and P. T. Manohoran, *Inorg. Chem.*, 1985, **24**, 3053.
13 D. T. Sawyer, G. S. Srivatsa, M. E. Bodini, W. P. Schaefer, and R. M. Wing, *J. Am. Chem. Soc.*, 1986, **108**, 936.
14 S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 4594.
15 S. Zalis and A. A. Vlcek, *Inorg. Chim. Acta*, 1982, **58**, 89.
16 S. Alvarez, R. Vicente, and R. Hoffman, *J. Am. Chem. Soc.*, 1985, **107**, 6253.
17 A. Pignedoli, G. Peyronel, and L. Antolini, *Acta Crystallogr., Sect. B*, 1974, **30**, 2181.
18 C. J. Fritchie, jun., *Acta Crystallogr.*, 1966, **20**, 107.
19 R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 113; R. Eisenberg, and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 605.
20 O. Lindqvist, L. Andersen, J. Sieler, G. Steimecke, and E. Hoyer, *Acta Chem. Scand., Ser. A*, 1982, **36**, 855.
21 O. Lindqvist, L. Sjölin, J. Sieler, G. Steimecke, and E. Hoyer, *Acta Chem. Scand., Ser. A*, 1979, **33**, 445.
22 W. E. Geiger, *Prog. Inorg. Chem.*, 1985, **33**, 275.
23 L. Bustos, M. A. Khan, and D. G. Tuck, *Can. J. Chem.*, 1983, **61**, 1146.
24 G. Henkel, K. Griewe, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 117.
25 J. E. O'Reilly and T. J. Elving, *J. Am. Chem. Soc.*, 1972, **94**, 7941.
26 H. J. Bright and D. T. J. Porter, in 'The Enzymes,' ed. P. D. Boyer, 3rd edn., Academic Press, New York, 1975, vol. 12, p. 421.
27 G. Dryhurst, R. Raghavan, D. Ege-Serpkenci, and L. G. Karber, 'Electrochemical and Spectroelectrochemical Studies of Biological Redox Components,' ed. K. M. Kadish, American Chemical Society, Washington, D.C., 1982, p. 457.

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