Syntheses, Spectroscopic, and Electrochemical Properties of Dinuclear Copper(II) Complexes bridged by a Single Thiolate Sulphur Atom; *X*-Ray Crystal Structures of $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ and $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)][ClO_4]$†

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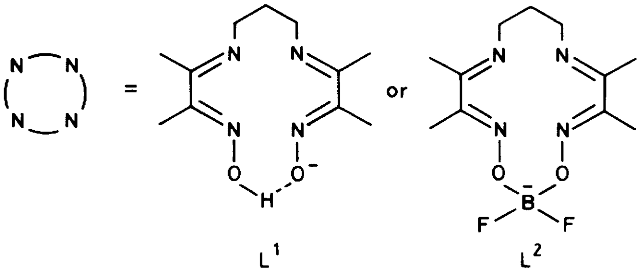
Dinuclear copper(II) complexes $[Cu_2(L^1)_2(SR)][PF_6]$ {L^1 = 3,3′-(trimethylenedinitrilo)bis[butan-2-one oximato(1−)]; R = C_6H_4Cl-4(**1**), C_6H_4Br-4 (**2**), or $C_6H_4CH_3$-4 (**3**)} and $[Cu_2(L^2)_2(SR)][ClO_4]$ [L^2 = difluoro{3,3′-(trimethylenedinitrilo)bis[butan-2-one oximato(2−)]} borate(1−); R = $C_6H_4CH_3$-4 (**4**), $C_6H_4CH_3$-2 (**5**), or C_6H_4Cl-4 (**6**)] have been prepared. Single-crystal *X*-ray structure analyses of (**1**) and (**4**) reveal that two copper atoms are bridged by a single thiolate-sulphur atom. Complex (**1**) crystallizes in space group $P\bar{1}$, with a = 11.230(3), b = 14.079(3), c = 12.540(3) Å, α = 97.04(2), β = 101.59(2), γ = 72.95(2)°, and Z = 2. Complex (**4**) crystallizes in space group $P\bar{1}$, with a = 12.329(6), b = 15.447(6), c = 11.018(7) Å, α = 94.45(5), β = 92.22(5), γ = 96.13(4)°, and Z = 2. The structures of (**1**) and (**4**) were refined by least-squares methods to R = 0.064 and 0.089 for 4 416 and 2 167 reflections respectively. In dichloromethane complexes (**1**)—(**6**) exhibit absorption bands in the region 320—420 nm due to the thiolate sulphur-to-copper(II) charge-transfer transitions. E.s.r. spectra of these complexes showed a half-band signal due to the Cu–Cu interaction around 1 500 G in dichloromethane–toluene (1 : 1 v/v) at 77 K. The dinuclear structure of the complexes is retained not only in very dilute (*ca.* 10^{-5} mol dm^{-3}) dichloromethane solutions but also in the two successive reduced forms, as confirmed by the absorption spectra and cyclic voltammetry, respectively.

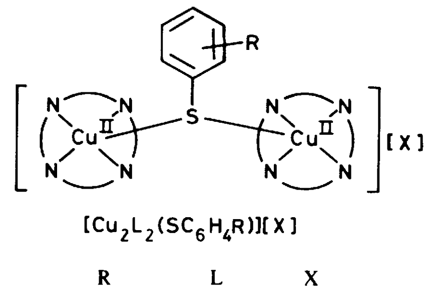
Copper(II)–thiolate complexes are of much interest in relation to the active site of blue copper proteins containing copper(II)–thiolate bonds.[1] To date, however, only a limited number of copper(II)–thiolate complexes have been isolated and structurally characterized,[2–7] since such complexes are thermodynamically unstable and readily undergo redox reactions to give Cu^I complexes and disulphides. Thus, the isolation of copper(II)–thiolate complexes is a challenging problem.

Recently, we have isolated relatively stable alkane- and arene-thiolato copper(II) complexes containing 3,3′-(trimethylenedinitrilo)bis[butan-2-one oximate(1−)] (L^1) and difluoro{3,3′-(tetramethylenedinitrilo)bis[butan-2-one oximato(2−)]}borate(1−) (L^2) ligands.[8]

This paper reports the isolation and properties of stable dinuclear copper(II) complexes $[Cu_2L_2(SC_6H_4R)][X]$ (**1**)—(**6**), bridged by a single thiolate-sulphur atom, and the *X*-ray molecular structures of $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) and $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)][ClO_4]$ (**4**) [L^2 = difluoro{3,3′-trimethylenedinitrilo)bis[butan-2-one oximato(2−)]}borate(1−)]. A preliminary report on the molecular structure and properties of (**4**) has appeared.[9]



L^1 L^2



$[Cu_2L_2(SC_6H_4R)][X]$

	R	L	X
(1)	4-Cl	L^1	PF_6
(2)	4-Br	L^1	PF_6
(3)	4-CH_3	L^1	PF_6
(4)	4-CH_3	L^2	ClO_4
(5)	2-CH_3	L^2	ClO_4
(6)	4-Cl	L^2	PF_6

Experimental

Materials.—Mononuclear copper(II) complexes $[Cu(L^1)][PF_6]\cdot H_2O$,[4] $[Cu(L^2)][ClO_4]\cdot H_2O$,[10] $[Cu(L^2)][PF_6]$,[4] and $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$[4] were prepared according to literature methods.

Commercially available 4-methylbenzenethiol, 2-methylbenzenethiol, 4-chlorobenzenethiol, and 4-bromobenzenethiol were used without further purification.

All solvents used were purified by the usual methods.[11]

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† μ-*p*-Chlorophenylthio-bis[{3,3′-(trimethylenedinitrilo)bis[butan-2-one oximato(1−)]-*NN′N″N‴*}copper(II)] hexafluorophosphate and μ-*p*-methylphenylthio-bis[{[difluoro{3,3′-(trimethylenedinitrilo)bis[butan-2-one oximato(2−)]}borato(1−)]-*NN′N″N‴*}copper(II)] perchlorate respectively.

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

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

Preparation of the Thiolate-bridged Dinuclear Copper(II) *Complexes.*—To a cold (ice-bath) methanol (20 cm^3) solution of [Cu(L^1)][PF$_6$]·H$_2$O (115 mg, 0.25 mmol) was added dropwise an equimolar mixture of 4-ClC$_6$H$_4$SH (17 mg, 0.12 mmol) and NaOCH$_3$ in methanol (10 cm^3) under a nitrogen atmosphere. The resulting solution was refrigerated at −15 °C for *ca.* 24 h to give dark green crystals of [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$] (**1**), which were collected by filtration, washed with a small amount of diethyl ether, and dried *in vacuo* (26% yield). Complexes [Cu$_2$(L^1)$_2$(SR)][PF$_6$] [R = C$_6$H$_4$Br-4 (**2**) or C$_6$H$_4$CH$_3$-4 (**3**)] were prepared similarly by using 4-BrC$_6$H$_4$SH and 4-CH$_3$C$_6$H$_4$SH, respectively, instead of 4-ClC$_6$H$_4$SH (59 and 31% yields, respectively). The L^2 analogues [Cu$_2$(L^2)$_2$(SR)][ClO$_4$] [R = C$_6$H$_4$CH$_3$-4 (**4**), C$_6$H$_4$CH$_3$-2 (**5**), or C$_6$H$_4$Cl-4 (**6**)] were similarly prepared by reaction of [Cu(L^2)][ClO$_4$]·H$_2$O or [Cu(L^2)][PF$_6$] with the corresponding monosubstituted benzenethiol in the presence of NaOCH$_3$ (47, 54, and 57% yields, respectively). Analytical data of the complexes are summarized in Table 1.

Physical Measurements.—Electronic absorption spectra were measured with a Union SM-401 spectrophotometer. E.s.r. spectra were recorded on a JEOL ME-2X spectrometer and calibrated with diphenylpicrylhydrazyl (*g* = 2.0037). Cyclic voltammetry was performed in dichloromethane with a Yanagimoto P-1000 voltammetric analyzer in a conventional cell equipped with a glassy carbon (working electrode), a platinum wire (counter electrode), and an Ag–AgCl reference electrode, using [NBu$^n{}_4$][BF$_4$] (0.1 mol dm^{-3}) as a supporting electrode.

Table 1. Elemental analyses* of the copper(II) complexes

Complex	Analysis (%) C	H	N
(**1**) [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$]	37.9	5.0	12.85
	(37.6)	(4.75)	(12.55)
(**2**) [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Br-4)][PF$_6$]	36.05	4.85	11.8
	(35.85)	(4.5)	(11.95)
(**3**) [Cu$_2$(L^1)$_2$(SC$_6$H$_4$CH$_3$-4)][PF$_6$]	39.9	5.35	13.1
	(39.85)	(5.2)	(12.8)
(**4**) [Cu$_2$(L^2)$_2$(SC$_6$H$_4$CH$_3$-4)][ClO$_4$]	37.8	4.9	11.65
	(37.7)	(4.7)	(12.15)
(**5**) [Cu$_2$(L^2)$_2$(SC$_6$H$_4$CH$_3$-2)][ClO$_4$]	37.65	5.0	11.85
	(37.7)	(4.7)	(12.15)
(**6**) [Cu$_2$(L^2)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$]	33.95	3.9	11.1
	(34.0)	(4.05)	(11.3)

* Calculated values in parentheses.

X-*Ray Crystal-structure Determinations of* [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$] (**1**) *and* [Cu$_2$(L^2)$_2$(SC$_6$H$_4$CH$_3$-4)][ClO$_4$] (**4**).—Cell constants (Table 2) were determined from the least-squares fit of the angular co-ordinates of 25 reflections with 2θ values in the ranges 12—20° for (**1**) and 9—24° for (**4**), which were measured on a computer-controlled Rigaku four-circle diffractometer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Intensity data were collected on the same diffractometer. No significant intensity decay was observed during the data collections. Data were corrected for background attenuators, and Lorentz and polarization effects in the usual fashion. No absorption correction was made. Experimental details are listed in Table 2. The structures were solved by conventional Patterson and Fourier techniques. By assuming space group $P\bar{1}$ for (**1**), the block-diagonal least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms and with isotropic thermal parameters for four phenyl hydrogen atoms and two oxime hydrogen atoms led to the residual indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.064$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.077$. The weighting scheme, $w^{-1} = \sigma^2(F_o) + 0.001(F_o)^2$, was used. By assuming space group $P\bar{1}$ also for (**4**), the refinement with anisotropic thermal parameters for all the non-hydrogen atoms led to the residual indices $R = 0.089$ and $R' = 0.10$. The weighting scheme, $w^{-1} = \sigma^2(F_o) + 0.0025(F_o)^2$, was used. No attempt was made to refine hydrogen atoms at any stage of the analysis. Atomic scattering factors were taken from ref. 12. The final atomic co-ordinates for (**1**) and (**4**) are listed in Tables 3 and 4, respectively. Crystallographic calculations were performed on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figures for the molecular structures were drawn by the local version of the ORTEP-II program.[13]

Table 2. Summary of crystal data and experimental details for the structure determination of complexes [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$] (**1**) and [Cu$_2$(L^2)$_2$(SC$_6$H$_4$CH$_3$-4)][ClO$_4$] (**4**)

Complex	(**1**)	(**4**)
Formula	$C_{28}H_{42}ClCu_2F_6N_8O_4PS$	$C_{29}H_{43}B_2ClCu_2F_4N_8O_8S$
M	894.2	923.9
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.230(3)	12.329(6)
b/Å	14.079(3)	15.447(6)
c/Å	12.540(3)	11.018(7)
α/°	97.04(2)	94.45(5)
β/°	101.59(2)	92.22(5)
γ/°	72.95(2)	96.13(4)
U/Å^3	1 852.6(8)	2 078(2)
Z	2	2
D_c/g cm^{-3}	1.604(1)	1.447(2)
Crystal dimensions/mm	0.80 × 0.55 × 0.50	0.34 × 0.25 × 0.22
Radiation (λ/Å)	Mo-K_α (0.710 69)	Mo-K_α (0.710 69)
Monochromator	Graphite	Graphite
μ/cm^{-1}	14.4	12.3
F(000)	916	948
Scan range/°	1 + 0.35tanθ	1 + 0.35tanθ
2θ limits/°	3—50	3—45
Reflections, total	6 586	5 494
Reflections, $|F_o| > 3\sigma(F)$	4 416	2 167

Table 3. Atomic co-ordinates (× 10^4; H, × 10^3) for $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	217.8(8)	6 756.7(6)	3 994.4(7)	C(7)	−1 498(7)	5 739(6)	4 147(6)
Cu(2)	120.0(8)	7 854.5(6)	785.9(7)	C(8)	4 074(8)	5 971(7)	3 675(8)
Cl	−5 937(2)	10 117(2)	3 222(2)	C(9)	3 212(9)	8 125(7)	4 593(7)
S	−790(2)	7 279(2)	2 128(2)	C(10)	−3 087(8)	6 962(8)	5 258(9)
P	5 657(2)	2 959(2)	2 316(2)	C(11)	−2 252(10)	4 992(8)	3 890(8)
F(1)	6 588(9)	3 361(8)	1 898(7)	C(12)	2 567(7)	6 636(5)	685(6)
F(2)	5 740(8)	3 616(5)	3 432(6)	C(13)	1 689(7)	6 132(5)	−73(6)
F(3)	4 742(6)	2 529(6)	2 761(6)	C(14)	−533(8)	6 227(6)	−808(7)
F(4)	5 571(6)	2 279(5)	1 259(5)	C(15)	−1 518(9)	7 054(7)	−1 458(7)
F(5)	4 518(8)	3 748(6)	1 758(7)	C(16)	−2 343(8)	7 891(7)	−801(7)
F(6)	6 801(6)	2 110(5)	2 889(5)	C(17)	−1 955(7)	9 442(6)	147(6)
O(1)	2 092(5)	5 081(4)	3 137(5)	C(18)	−1 041(6)	9 913(6)	858(6)
O(2)	59(5)	4 746(4)	3 258(4)	C(19)	3 995(7)	6 234(7)	820(7)
O(3)	2 628(4)	7 987(4)	1 873(4)	C(20)	2 238(9)	5 164(6)	−670(8)
O(4)	929(5)	9 585(4)	1 910(5)	C(21)	−3 290(8)	10 092(8)	−222(9)
N(1)	1 855(5)	6 018(4)	3 602(5)	C(22)	−1 277(8)	11 010(6)	1 123(7)
N(2)	1 196(5)	7 711(4)	4 580(5)	C(23)	−2 265(6)	8 123(5)	2 344(6)
N(3)	−1 155(5)	7 273(4)	4 827(5)	C(24)	−3 313(7)	7 762(5)	2 261(7)
N(4)	−457(6)	5 605(4)	3 824(5)	C(25)	−4 445(7)	8 381(6)	2 512(7)
N(5)	1 977(5)	7 439(4)	1 189(5)	C(26)	−4 523(7)	9 358(6)	2 845(6)
N(6)	502(6)	6 599(4)	−137(5)	C(27)	−3 535(7)	9 756(5)	2 902(7)
N(7)	−1 539(5)	8 497(5)	−90(5)	C(28)	−2 376(7)	9 125(5)	2 667(6)
N(8)	5(5)	9 261(4)	1 239(5)	H[O(1)]	108(7)	481(6)	312(7)
C(1)	2 745(7)	6 454(6)	3 849(6)	H[O(3)]	181(9)	862(7)	189(8)
C(2)	2 312(7)	7 471(6)	4 361(6)	H[C(24)]	−308(9)	697(7)	219(8)
C(3)	603(8)	8 689(6)	5 108(8)	H[C(25)]	−526(7)	800(6)	257(7)
C(4)	−163(8)	8 522(6)	5 922(7)	H[C(27)]	−365(8)	1 047(6)	309(7)
C(5)	−1 399(8)	8 271(6)	5 447(7)	H[C(28)]	−168(8)	939(6)	265(7)
C(6)	−1 886(7)	6 719(6)	4 751(6)				

Table 4. Atomic co-ordinates (× 10^4) for $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)][ClO_4]$ (**4**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	777(2)	3 013(2)	353(3)	C(5)	−668(21)	1 353(15)	706(25)
Cu(2)	3 874(2)	1 798(2)	767(3)	C(6)	−46(18)	1 621(14)	−1 313(21)
Cl	2 523(6)	7 620(5)	3 975(7)	C(7)	574(17)	2 241(14)	−2 074(22)
S	2 222(5)	2 348(4)	1 514(6)	C(8)	1 048(20)	5 687(12)	1 752(23)
F(1)	2 563(13)	4 921(9)	−1 992(13)	C(9)	−118(23)	4 436(19)	3 513(26)
F(2)	3 082(10)	4 003(8)	−635(12)	C(10)	−552(24)	770(14)	−1 951(27)
F(3)	1 716(10)	849(9)	−620(13)	C(11)	704(21)	2 081(17)	−3 346(23)
F(4)	2 126(11)	46(9)	−2 322(13)	C(12)	3 945(19)	45(17)	1 296(20)
O(1)	1 591(12)	4 791(9)	−347(13)	C(13)	4 509(20)	620(16)	2 336(22)
O(2)	1 591(12)	3 579(9)	−1 982(13)	C(14)	5 094(21)	2 135(16)	3 206(21)
O(3)	3 212(11)	48(9)	−603(14)	C(15)	6 020(20)	2 608(16)	2 589(23)
O(4)	3 118(13)	1 334(9)	−1 846(14)	C(16)	5 716(20)	3 271(17)	1 716(25)
O(5)	2 038(19)	7 723(15)	2 898(21)	C(17)	4 975(18)	3 081(15)	−497(24)
O(6)	3 411(24)	7 243(25)	3 964(29)	C(18)	4 231(16)	2 547(13)	−1 446(20)
O(7)	2 941(44)	8 379(18)	4 480(33)	C(19)	3 806(21)	−920(13)	1 206(26)
O(8)	1 876(23)	7 180(24)	4 716(27)	C(20)	5 031(30)	179(19)	3 403(25)
N(1)	1 112(13)	4 275(10)	495(15)	C(21)	5 724(26)	3 919(16)	−782(30)
N(2)	−34(14)	3 285(12)	1 841(17)	C(22)	4 202(21)	2 730(16)	−2 784(21)
N(3)	−131(13)	1 896(11)	−208(18)	C(23)	2 617(16)	3 199(13)	2 626(20)
N(4)	1 013(13)	2 924(11)	−1 369(16)	C(24)	3 147(18)	3 993(12)	2 373(19)
N(5)	3 622(14)	511(11)	413(16)	C(25)	3 420(18)	4 659(13)	3 252(20)
N(6)	4 538(13)	1 454(12)	2 268(16)	C(26)	3 233(18)	4 562(14)	4 509(21)
N(7)	5 017(13)	2 814(11)	652(17)	C(27)	2 689(19)	3 785(13)	4 757(21)
N(8)	3 685(13)	1 907(10)	−956(16)	C(28)	2 368(18)	3 086(14)	3 850(21)
C(1)	833(16)	4 699(15)	1 460(21)	C(29)	3 561(23)	5 317(17)	5 484(24)
C(2)	216(18)	4 070(17)	2 284(18)	B(1)	2 219(22)	4 294(15)	−1 240(22)
C(3)	−582(23)	2 558(18)	2 534(26)	B(2)	2 537(21)	600(19)	−1 284(25)
C(4)	−1 270(22)	1 936(20)	1 594(29)				

Results and Discussion

Crystal Structures of $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) and $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)][ClO_4]$ (**4**).—Both crystals of (**1**) and (**4**) consist of discrete complex cations $\{[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)]^+$ and $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)]^+$ respectively$\}$ and isolated hexafluorophosphate and perchlorate anions, respectively. Molecular geometries of these cations, together with the atom-labelling scheme, are depicted in Figures 1 and 2. In both complex cations, two copper(II) ions which are each co-ordinated by an N_4-macrocyclic ligand are bridged by a thiolate-sulphur atom located in an apical position to form essentially square-pyramidal configurations. Related distances and angles for these cations are summarized in Tables 5 and 6.

In complex (**1**), there is no significant difference between the two Cu–N(oxime) bond distances, unlike the Cu–N(imine) bonds. Although the average Cu(1)–N distance (1.955 Å) is somewhat shorter than the average Cu(2)–N distance (1.973 Å), four nearly equal Cu–N distances have been observed for each of [Cu(L^1)(SC$_6$H$_5$)] (1.984 Å),[4] [Cu(L^1)(SC$_6$H$_4$Cl-4)] (1.976 Å),[4] [Cu(L^1)(H$_2$O)][ClO$_4$]·H$_2$O (1.957 Å),[14] and [Cu(L^1)(ClO$_4$)]·0.5CH$_3$OH (1.948 Å),[15] respectively. The observed changes in the average Cu–N(macrocycle) bond lengths are accompanied by parallel changes in the apical displacement of the copper(II) ion from the basal plane of the macrocyclic N$_4$ atoms. The apical displacements in (**1**) [0.31 Å for Cu(1) and 0.40 Å for Cu(2)] are somewhat smaller than that in [Cu(L^1)(SC$_6$H$_5$)] (0.430 Å),[4] although both displacements are appreciably larger than that of [Cu(L^1)(H$_2$O)][ClO$_4$]·H$_2$O (0.10 Å)[14] and [Cu(L^1)(ClO$_4$)]·0.5CH$_3$OH (0.13 Å).[15] Since the apical displacement reflects the strength of the copper(II)–apical ligand bonding, the bridging thiolate-sulphur atom of (**1**) is somewhat weakly bound to the copper(II) ions compared with the sulphur atoms of the above mentioned mononuclear thiolato-complexes. It should be noted that in (**1**) the central atom of the trimethylene linkage of each L^1 ligand lies on the opposite side to the N$_4$-reference plane with respect to the copper(II) ion. This is in contrast to [Cu(L^1)X] (X = SC$_6$H$_5$,[4] SC$_6$H$_4$Cl-4,[4] H$_2$O,[14] or ClO$_4$[15]) in which the central atom of the trimethylene linkage lies on the same side as the N$_4$-reference plane with respect to

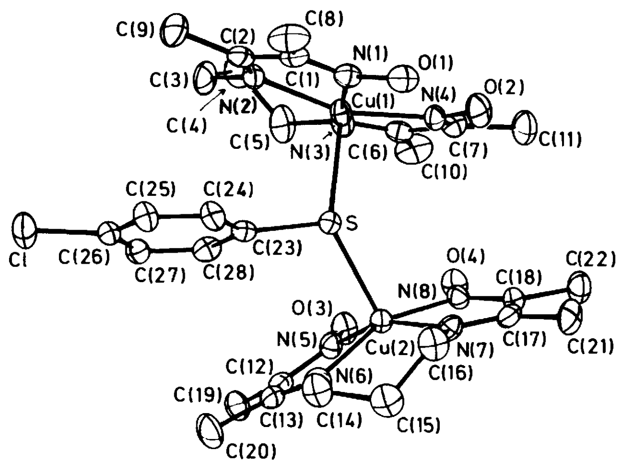

Figure 1. Molecular structure of the cation of [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$] (**1**) showing the atom-labelling scheme

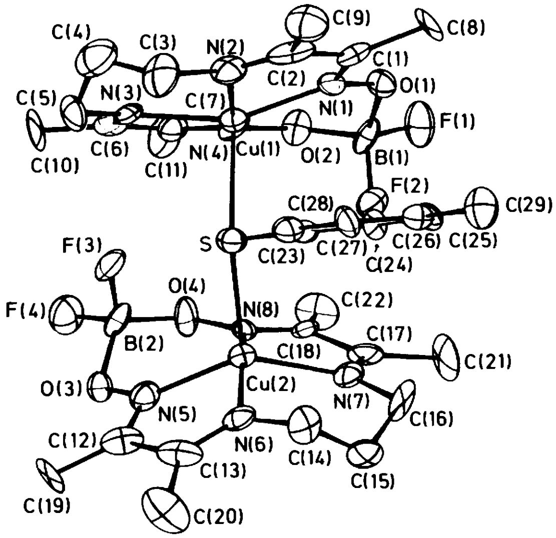

Figure 2. Molecular structure of the cation of [Cu$_2$(L^2)$_2$(SC$_6$H$_4$CH$_3$-4)][ClO$_4$] (**4**) showing the atom-labelling scheme

Table 5. Selected bond lengths (Å) and angles (°) for [Cu$_2$(L^1)$_2$(SC$_6$H$_4$Cl-4)][PF$_6$] (**1**) with estimated standard deviations in parentheses

Cu(1)–S	2.484(2)	O(1)–N(1)	1.349(7)	N(6)–C(13)	1.292(9)	C(6)–C(10)	1.536(13)
Cu(1)–N(1)	1.955(6)	O(2)–N(4)	1.359(7)	N(6)–C(14)	1.479(11)	C(7)–C(11)	1.501(15)
Cu(1)–N(2)	1.962(6)	O(3)–N(5)	1.335(8)	N(7)–C(16)	1.509(11)	C(12)–C(13)	1.500(11)
Cu(1)–N(3)	1.949(6)	O(4)–N(8)	1.351(8)	N(7)–C(17)	1.293(9)	C(12)–C(19)	1.519(10)
Cu(1)–N(4)	1.955(7)	N(1)–C(1)	1.288(11)	N(8)–C(18)	1.305(8)	C(13)–C(20)	1.497(11)
Cu(2)–S	2.459(3)	N(2)–C(2)	1.276(10)	C(1)–C(2)	1.480(10)	C(14)–C(15)	1.536(12)
Cu(2)–N(5)	1.969(5)	N(2)–C(3)	1.481(10)	C(1)–C(8)	1.496(11)	C(15)–C(16)	1.534(12)
Cu(2)–N(6)	1.975(6)	N(3)–C(5)	1.498(10)	C(2)–C(9)	1.522(14)	C(17)–C(18)	1.474(11)
Cu(2)–N(7)	1.982(5)	N(3)–C(6)	1.271(12)	C(3)–C(4)	1.539(15)	C(17)–C(21)	1.523(10)
Cu(2)–N(8)	1.966(6)	N(4)–C(7)	1.268(11)	C(4)–C(5)	1.521(13)	C(18)–C(22)	1.494(11)
S–C(23)	1.782(7)	N(5)–C(12)	1.292(8)	C(6)–C(7)	1.481(11)		
S–Cu(1)–N(1)	95.4(2)	N(5)–Cu(2)–N(8)	93.2(2)	C(5)–N(3)–C(6)	121.9(7)	N(1)–C(1)–C(2)	112.3(6)
S–Cu(1)–N(2)	104.0(2)	N(6)–Cu(2)–N(7)	97.3(2)	Cu(1)–N(4)–O(2)	122.1(5)	N(2)–C(2)–C(1)	115.3(7)
S–Cu(1)–N(3)	103.3(2)	N(6)–Cu(2)–N(8)	156.9(3)	Cu(1)–N(4)–C(7)	116.5(5)	N(2)–C(3)–C(4)	108.5(7)
S–Cu(1)–N(4)	93.7(2)	N(7)–Cu(2)–N(8)	80.0(2)	O(2)–N(4)–C(7)	120.8(7)	C(3)–C(4)–C(5)	117.0(7)
N(1)–Cu(1)–N(2)	80.0(2)	Cu(1)–S–Cu(2)	128.6(1)	Cu(2)–N(5)–O(3)	123.1(4)	N(3)–C(5)–C(4)	110.7(6)
N(1)–Cu(1)–N(3)	161.1(2)	Cu(1)–S–C(23)	102.6(2)	Cu(2)–N(5)–C(12)	116.7(5)	N(3)–C(6)–C(7)	115.8(7)
N(1)–Cu(1)–N(4)	95.5(3)	Cu(2)–S–C(23)	111.7(3)	O(3)–N(5)–C(12)	120.0(6)	N(4)–C(7)–C(6)	112.1(8)
N(2)–Cu(1)–N(3)	98.5(3)	Cu(1)–N(1)–O(1)	123.2(5)	Cu(2)–N(6)–C(13)	115.4(5)	N(5)–C(12)–C(13)	112.9(6)
N(2)–Cu(1)–N(4)	162.1(2)	Cu(1)–N(1)–C(1)	116.8(5)	Cu(2)–N(6)–C(14)	120.4(4)	N(6)–C(13)–C(12)	114.7(6)
N(3)–Cu(1)–N(4)	80.1(3)	O(1)–N(1)–C(1)	120.0(6)	C(13)–N(6)–C(14)	124.1(6)	N(6)–C(14)–C(15)	111.3(7)
S–Cu(2)–N(5)	108.8(2)	Cu(1)–N(2)–C(2)	115.0(5)	Cu(2)–N(7)–C(6)	121.6(5)	C(14)–C(15)–C(16)	116.7(8)
S–Cu(2)–N(6)	97.8(2)	Cu(1)–N(2)–C(3)	121.1(5)	Cu(2)–N(7)–C(17)	114.2(5)	N(7)–C(16)–C(15)	109.8(7)
S–Cu(2)–N(7)	94.6(2)	C(2)–N(2)–C(3)	123.4(7)	Cu(16)–N(7)–C(17)	123.1(6)	N(7)–C(17)–C(18)	115.8(6)
S–Cu(2)–N(8)	105.3(2)	Cu(1)–N(3)–C(5)	123.5(6)	Cu(2)–N(8)–O(4)	124.4(4)	N(8)–C(18)–C(17)	112.2(6)
N(5)–Cu(2)–N(6)	80.3(2)	Cu(1)–N(3)–C(6)	121.9(7)	Cu(2)–N(8)–C(18)	116.8(5)		
N(5)–Cu(2)–N(7)	156.6(3)			O(4)–N(8)–C(18)	118.8(6)		

Table 6. Selected bond lengths (Å) and angles (°) for $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)][ClO_4]$ (4) with estimated standard deviations in parentheses

Cu(1)–S	2.506(7)	O(2)–N(4)	1.406(22)	N(6)–C(13)	1.294(31)	C(4)–C(5)	1.543(40)
Cu(2)–S	2.436(7)	O(2)–B(1)	1.455(26)	N(6)–C(14)	1.505(28)	C(6)–C(7)	1.491(32)
Cu(1)–N(1)	1.943(15)	O(3)–N(5)	1.333(22)	N(7)–C(16)	1.510(30)	C(6)–C(10)	1.503(31)
Cu(1)–N(2)	1.993(15)	O(3)–B(2)	1.478(33)	N(7)–C(17)	1.362(33)	C(7)–C(11)	1.422(35)
Cu(1)–N(3)	1.995(16)	O(4)–N(8)	1.376(20)	N(8)–C(18)	1.295(26)	C(12)–C(13)	1.495(31)
Cu(1)–N(4)	1.927(17)	O(4)–B(2)	1.466(31)	F(1)–B(1)	1.367(28)	C(12)–C(19)	1.477(33)
Cu(2)–N(5)	1.985(17)	N(1)–C(1)	1.282(28)	F(2)–B(1)	1.368(30)	C(13)–C(20)	1.556(40)
Cu(2)–N(6)	1.953(18)	N(2)–C(2)	1.273(30)	F(3)–B(2)	1.343(31)	C(14)–C(15)	1.503(35)
Cu(2)–N(7)	2.009(17)	N(2)–C(3)	1.520(34)	F(4)–B(2)	1.417(29)	C(15)–C(16)	1.524(38)
Cu(2)–N(8)	1.937(18)	N(3)–C(5)	1.490(32)	C(1)–C(2)	1.542(32)	C(17)–C(18)	1.499(30)
S–C(23)	1.743(20)	N(3)–C(6)	1.271(30)	C(1)–C(8)	1.528(29)	C(17)–C(21)	1.567(35)
O(1)–N(1)	1.380(22)	N(4)–C(7)	1.315(26)	C(2)–C(9)	1.516(36)	C(18)–C(22)	1.522(33)
O(1)–B(1)	1.492(29)	N(5)–C(12)	1.328(31)	C(3)–C(4)	1.523(38)		

S–Cu(1)–N(1)	109.3(5)	Cu(1)–S–Cu(2)	128.6(3)	O(1)–N(1)–C(1)	114.6(16)	N(6)–C(13)–C(12)	116.9(22)
S–Cu(1)–N(2)	93.2(6)	Cu(1)–S–C(23)	99.8(8)	C(2)–N(3)–C(2)	124.6(20)	N(6)–C(14)–C(15)	106.3(18)
S–Cu(1)–N(3)	96.7(5)	Cu(2)–S–C(23)	107.7(7)	C(5)–N(3)–C(6)	123.4(18)	C(14)–C(15)–C(16)	116.4(21)
S–Cu(1)–N(4)	111.0(5)	Cu(1)–N(1)–O(1)	127.7(12)	O(2)–N(4)–C(7)	114.8(17)	N(7)–C(16)–C(15)	110.0(19)
N(1)–Cu(1)–N(2)	81.4(7)	Cu(1)–N(1)–C(1)	117.7(15)	O(3)–N(5)–C(12)	115.3(17)	N(7)–C(17)–C(18)	118.4(19)
N(1)–Cu(1)–N(3)	154.0(7)	Cu(1)–N(2)–C(2)	111.9(15)	C(13)–N(6)–C(14)	124.7(19)	N(8)–C(18)–C(17)	110.1(19)
N(1)–Cu(1)–N(4)	92.8(7)	Cu(1)–N(2)–C(3)	120.9(15)	C(16)–N(7)–C(17)	125.5(18)	O(1)–B(1)–O(2)	115.8(19)
N(2)–Cu(1)–N(3)	96.7(7)	Cu(1)–N(3)–C(5)	119.6(14)	O(4)–N(8)–C(18)	111.3(17)	O(1)–B(1)–F(1)	101.8(17)
N(2)–Cu(1)–N(4)	155.6(7)	Cu(1)–N(3)–C(6)	115.8(14)	N(1)–O(1)–B(1)	112.7(15)	O(1)–B(1)–F(2)	109.0(17)
N(3)–Cu(1)–N(4)	78.2(7)	Cu(1)–N(4)–O(2)	124.4(11)	N(4)–O(2)–B(1)	117.3(15)	O(2)–B(1)–F(1)	107.9(18)
S–Cu(2)–N(5)	109.9(5)	Cu(1)–N(4)–C(7)	120.7(15)	N(5)–O(3)–B(2)	108.2(16)	O(2)–B(1)–F(2)	110.7(18)
S–Cu(2)–N(6)	101.2(6)	Cu(2)–N(5)–O(3)	129.1(13)	N(8)–O(4)–B(2)	110.3(16)	F(1)–B(1)–F(2)	111.4(20)
S–Cu(2)–N(7)	108.8(8)	Cu(2)–N(5)–C(12)	115.6(14)	N(1)–C(1)–C(2)	110.3(19)	O(3)–B(2)–O(4)	116.8(19)
S–Cu(2)–N(8)	101.3(5)	Cu(2)–N(6)–C(13)	114.8(15)	N(2)–C(2)–C(1)	116.9(19)	O(3)–B(2)–F(3)	111.1(21)
N(5)–Cu(2)–N(6)	81.3(7)	Cu(2)–N(6)–C(14)	120.4(14)	N(2)–C(3)–C(4)	106.4(22)	O(3)–B(2)–F(4)	103.6(20)
N(5)–Cu(2)–N(7)	141.2(7)	Cu(2)–N(7)–C(16)	124.7(15)	C(3)–C(4)–C(5)	117.8(22)	O(4)–B(2)–F(3)	112.1(22)
N(5)–Cu(2)–N(8)	88.2(7)	Cu(2)–N(7)–C(17)	109.4(13)	N(3)–C(5)–C(4)	109.4(20)	O(4)–B(2)–F(4)	101.6(19)
N(6)–Cu(2)–N(7)	93.5(7)	Cu(2)–N(8)–O(4)	129.0(12)	N(3)–C(6)–C(7)	115.7(19)	F(3)–B(2)–F(4)	110.7(19)
N(6)–Cu(2)–N(8)	157.3(7)	Cu(2)–N(8)–C(18)	119.4(14)	N(4)–C(7)–C(6)	109.0(20)		
N(7)–Cu(2)–N(8)	82.2(7)			N(5)–C(12)–C(13)	111.3(21)		

the copper(II) ion. This may arise from steric repulsions between the bridging thiolate ligand and the central methylene groups of the trimethylene linkages in (**1**).

In complex (**4**), an appreciable difference between Cu(1)–N(oxime) [1.927(17) and 1.943(15) Å] and Cu(1)–N(imine) [1.993(15) and 1.995(16) Å] distances is detected, although no distinct tendency is observed among the Cu(2)–N distances because the copper(II) ion is located in a distorted environment. Small differences of this type were reported for several metal complexes with dioxime–diimine ligands: copper(II)[15,16] and cobalt(III) complexes[17] with L^1 and analogous ligands, and copper(I)[18] and rhodium(III) complexes[19,20] with L^2 and analogous ligands. However, the variation in Cu–N bond lengths in (**4**) is in contrast to $[Cu(L^2)X]$ (X = NCO,[21] CN,[22] or I[23]) and $[Cu(L^2)L]^+$ [L = H_2O[14] or pyridine(py)[24]], which show no appreciable differences among the four Cu–N distances. The apical displacements of the copper(II) ions from the basal planes of the four macrocyclic nitrogen atoms in complex (**4**) [0.43 Å for Cu(1) and 0.52 Å for Cu(2)] are somewhat larger than those of $[Cu(L^2)(H_2O)]^+$ (0.32 Å),[14] $[Cu(L^2)I]$ (0.38 Å),[23] and $[Cu(L^2)(py)]^+$ (py = pyridine) (0.40 Å),[24] but smaller than those of $[Cu(L^2)(CN)]$ (0.56 Å)[22] and $[Cu(L^2)(NCO)]$ (0.58 Å).[20]

Although the Cu(1)–S distance is significantly different from Cu(2)–S both in (**1**) [2.484(2) and 2.459(3) Å] and (**4**) [2.506(7) and 2.436(7) Å], these Cu–S distances are somewhat larger than those of $[Cu(L^1)(SC_6H_5)]$ and $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$ [2.424(2) Å].[4] This is consistent with the fact that (**1**) and (**4**) are electrochemically less stabilized than the mononuclear copper(II)–thiolate complexes.

Electronic Absorption and E.S.R. Spectra, and Redox Behaviour.—Figure 3(*a*) and (*b*) show the electronic absorption

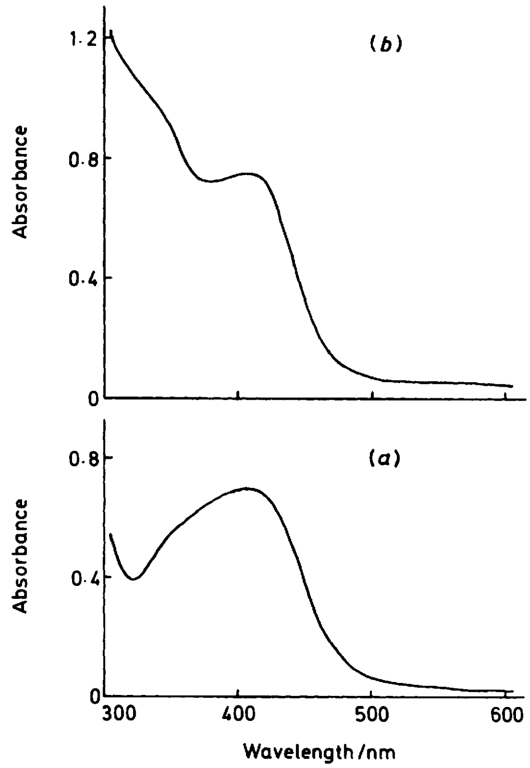

Figure 3. Electronic absorption spectra of (*a*) $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) and (*b*) $[Cu_2(L^2)_2(SC_6H_4CH_3\text{-}4)][ClO_4]$ (**4**); 1.0×10^{-4} mol dm^{-3}, in dichloromethane at 25 °C

spectra of (**1**) and (**4**) in dichloromethane, respectively. A strong band and a shoulder which appear in the 320—420 nm region in each complex may be assigned to the thiolate sulphur-to-copper(II) charge-transfer (c.t.) transition, since neither the corresponding CuN_4-type complex without thiolate ligands nor the thiolate anions exhibit an absorption band in this region. Both the high-energy bands which appear as shoulders around 320 nm for (**1**) and around 360 nm for (**4**) may be assigned to $S(\sigma) \longrightarrow Cu^{II}$ c.t. transitions, and both low-energy bands at 408 nm for (**1**) and 415 nm for (**4**) to $S(\pi) \longrightarrow Cu^{II}$ c.t. transitions. Similarly, two bands were reported to appear in the same region for $[Cu(L^1)(SC_6H_5)]$ (354 and 428 nm in dichloromethane),[4] $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$ (355 and 428 nm in dichloromethane),[4] and $[Cu(L^3)(o\text{-}SC_6H_4CO_2)]$ (L^3 = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)-(360 and 425 nm in methanol).[2] It is noted that the c.t. transition of (**1**) occurs at a somewhat higher energy compared with $[Cu(L^1)(SC_6H_5)]$ and $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$.[4] This is consistent with the fact that the Cu–S bond lengths in (**1**) are significantly longer than those in $[Cu(L^1)(SC_6H_5)]$ and $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$,[4] as confirmed by the *X*-ray structure analysis. The absorption maxima and apparent absorption coefficients of complexes (**1**)—(**6**) are summarized in Table 7.

The absorption intensities of (**1**) in dichloromethane follow the Beer–Lambert law in the concentration range 1×10^{-2} – 1×10^{-5} mol dm^{-3}. Moreover, as shown in Figure 4, the e.s.r. spectrum of (**1**) in dichloromethane–toluene (1:1 v/v) at 77 K exhibits a weak signal around 1 500 G, which is assignable to the $\Delta M = \pm 2$ transition caused by the Cu^{II}–Cu^{II} interaction, and no signal due to any monomer species. Thus, the dinuclear structure of the complex is retained without fission of the Cu^{II}–S–Cu^{II} linkage in dichloromethane. These solution behaviours were also observed for complexes (**2**)—(**6**). Complexes (**1**)—(**3**), (**5**), and (**6**) are significantly stable in dichloromethane at room temperature, whereas (**4**) is relatively unstable. The extreme stability of these dinuclear copper(II) complexes in less polar solvents is in contrast to the appreciable instability of mononuclear copper(II)-thiolate complexes such as $[Cu(L^1)(SC_6H_5)]$.[4] On the other hand, in *N*,*N*-dimethylformamide (dmf), complexes (**1**)—(**6**) gradually decompose, probably due to reduction of the copper(II) centres by the thiolate ligand. The absorption spectrum of (**1**) immediately after dissolution in dmf at 25 °C is depicted in Figure 5; the positions of the absorption maxima are almost identical with those of the spectrum of $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$ in the same solvent. Thus, the dinuclear copper(II) complex is suggested to undergo dissociation to $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$ and $[Cu(L^1)]^+$ to a considerable extent in dmf.

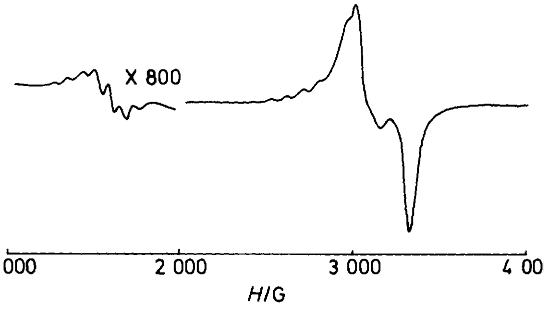

Figure 4. *X*-Band e.s.r. spectrum of $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) in dichloromethane–toluene (1:1 v/v) at 77 K

Table 7. Electronic absorption bands for the copper(II) complexes in dichloromethane at 25 °C*

Complex	$\lambda_{max.}$/nm	
(**1**)	321 (10 900)	408 (7 620)
(**2**)	328 (9 970)	407 (7 050)
(**3**)	323 (8 470)	416 (6 040)
(**4**)	360 (5 670)	415 (6 480)
(**5**)	360 (4 900)	408 (6 150)
(**6**)	354 (5 570)	403 (6 860)

* Molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses.

The cyclic voltammogram of complex (**1**) in dichloromethane containing $[NBu^n_4][BF_4]$ (0.1 mol dm^{-3}) as a supporting electrolyte gives two quasi-reversible redox waves at $E_{\frac{1}{2}} = -0.53$ and -0.78 V *vs.* Ag–AgCl with the peak separations 160 and 200 mV, respectively, as shown in Figure 6. This electrochemical process seems to consist of two successive one-electron redox reactions, expressed by equation (1) (R =

$$[Cu^{II}_2(L^1)_2(SR)] \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} [Cu^{II}Cu^{I}(L^1)_2(SR)] \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} [Cu^{I}_2(L^1)_2(SR)] \quad (1)$$

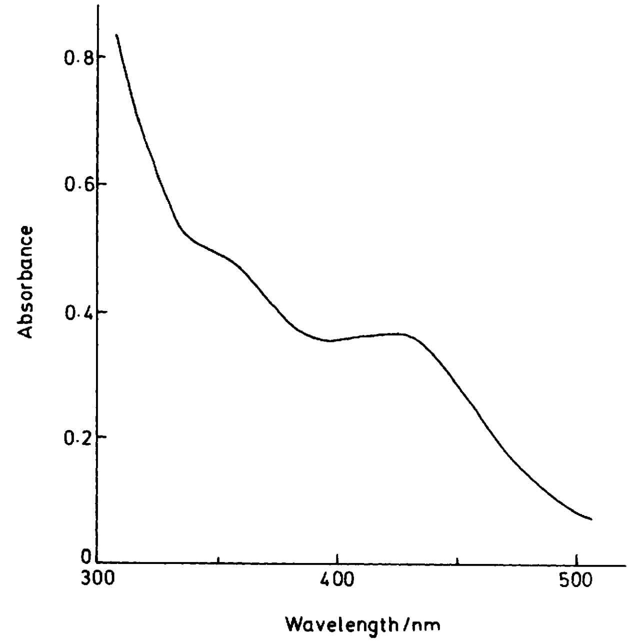

Figure 5. Electronic absorption spectrum of $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) (1.0×10^{-4} mol dm^{-3}) measured immediately after dissolution in dmf at 25 °C

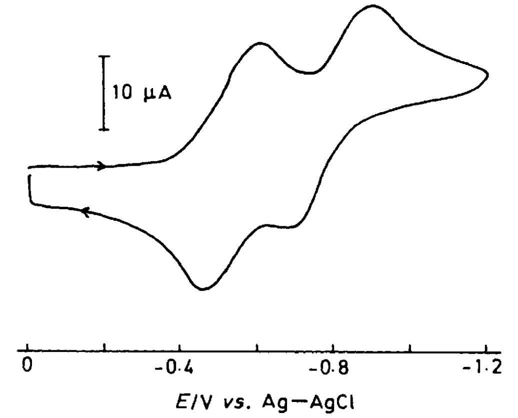

Figure 6. Cyclic voltammogram of $[Cu_2(L^1)_2(SC_6H_4Cl\text{-}4)][PF_6]$ (**1**) in dichloromethane containing $[NBu^n_4][BF_4]$ (0.1 mol dm^{-3}), at 25 °C; scan rate 0.1 V s^{-1}

Table 8. Electrochemical parameters for the copper(II) complexes

Complex	$E_{\frac{1}{2}}$*/V	
(**1**)	−0.53 (160)	−0.78 (200)
(**2**)	−0.53 (100)	−0.77 (160)
(**3**)	−0.57 (120)	−0.79 (260)
(**4**)	−0.31 (110)	−0.57 (90)
(**5**)	−0.31 (110)	−0.56 (80)
(**6**)	−0.34 (130)	−0.56 (110)

* $(E_{pc} + E_{pa})/2$ *vs.* Ag—AgCl; sweep rate 0.1 V s^{-1} in dichloromethane containing 0.1 mol dm^{-3} $[NBu^n_4][BF_4]$. $|E_{pc} - E_{pa}|$/mV in parentheses.

C_6H_4Cl-4), which is confirmed from the fact that the e.s.r. signal of (**1**) in dichloromethane was appreciably weakened under the controlled-potential electrolysis at −0.7 V *vs.* Ag–AgCl at room temperature and the successive electrolysis at −1.20 V *vs.* Ag–AgCl led to the disappearance of the signal. Similar redox behaviours have been observed for complexes (**2**)—(**6**). Thus, the Cu–S–Cu linkages of (**1**)—(**6**) are still retained in the two reduced forms. The electrochemical parameters for (**1**)—(**6**) are listed in Table 8. The first $E_{\frac{1}{2}}$ values of (**1**)—(**3**) and (**4**)—(**6**) are negatively shifted compared with those of $[Cu(L^1)][ClO_4]\cdot 2H_2O$ (−0.48 V *vs.* Ag–AgCl) and $[Cu(L^2)][ClO_4]\cdot H_2O$ (−0.21 V *vs.* Ag–AgCl) in dichloromethane, respectively. This indicates that the co-ordination of the thiolate ligand may stabilize the Cu^{II} state of the dinuclear copper(II) complexes. However, the first and second $E_{\frac{1}{2}}$ values of complexes (**1**)—(**3**) are more positive than those of $[Cu(L^1)(SC_6H_4Cl\text{-}4)]$ ($E_{\frac{1}{2}} = -0.85$ V *vs.* Ag–AgCl)[4] and $[Cu(L^1)(SC_6H_5)]$ ($E_{\frac{1}{2}} = -0.84$ V *vs.* Ag–AgCl),[4] although there are no data available for analogous $Cu^{II}L^2$ thiolate complexes with which to compare the $E_{\frac{1}{2}}$ values of (**4**)—(**6**). Thus, the thiolato-bridged dinuclear copper geometry electrochemically stabilizes less effectively the copper(II) state than the mononuclear copper(II) thiolate complex.

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