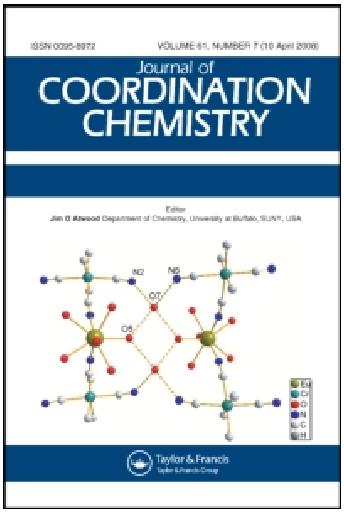

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TRANSITION METAL COMPLEXES OF OLIGOTHIOETHER QUINOLYLOXY TERMINATED PODANDS: PART 2. CRYSTAL AND MOLECULAR STRUCTURE OF (1,8-BIS(QUINOLYLOXY)-3,6-DITHIAOCTANE)-COPPER(II) DIPERCHLORATE TRIHYDRATE

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TRANSITION METAL COMPLEXES OF OLIGOTHIOETHER QUINOLYLOXY TERMINATED PODANDS: PART 2.† CRYSTAL AND MOLECULAR STRUCTURE OF (1,8-BIS(QUINOLYLOXY)-3,6-DITHIAOCTANE)-COPPER(II) DIPERCHLORATE TRIHYDRATE

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We wish to dedicate this paper to Professor Harry M.N.H. Irving on the occasion of his 87th birthday on the 19th November 1992.

The synthesis of the new ligand 1,8-*bis*(quinolyloxy)-3,6-dithiaoctane (**1**) and the corresponding Cu(II), Cu(I) and Co(II) complexes is reported. The crystal and molecular structure of the copper(II) complex, $[Cu(\mathbf{1})](ClO_4)_2 . 3H_2O$, has been determined by X-ray diffraction methods. The complex crystallizes in the orthorhombic space group *Fddd*, with cell data $Z = 16$, $a = 20.326(2)$, $b = 20.879(3)$ and $c = 28.308(4)$Å. The structure consists of discrete $[Cu(\mathbf{1})]^{2+}$ cations separated by (structurally disordered) perchlorate anions and three lattice water molecules per cation. The coordination geometry about the copper atom is *pseudo*-octahedral with the quinoline nitrogen and thioether sulfur atoms at the equatorial positions and the ether oxygen atoms at the axial positions. ^1H NMR line-broadening experiments indicate that electron-transfer self-exchange reactions between the copper(I) and copper(II) complexes of (**1**) is immeasurably slow on the NMR time-scale. The coordination chemistry of (**1**) is compared with its oxygen analogue, 1,8-*bis*(quinolyloxy)-3,6-dioxaoctane.

KEY WORDS: Podands, 1,8-*bis*(quinolyloxy)-3,6-dithiaoctane, copper(II/I), cobalt(II), X-ray structure, electron-transfer self-exchange.

INTRODUCTION

A variety of metalloproteins characterized by X-ray diffraction are known to contain sulfur donor atoms as part of the coordination environment of metal ions.[2] The role played by sulfur donor atoms is therefore of fundamental chemical importance in contributing to the understanding of the specific properties of the metal centres in

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†For Part 1 see reference 1.

sulfur coordinated transition metal ions in biological systems, particularly copper containing proteins.[3-4]

In recent years, numerous sulfur containing ligands intended to emulate the coordination sphere of the metal atom in metalloproteins have been prepared and their complexes studied.[5] Not surprisingly, a number of macrocyclic thia-crown ether type ligands have also received considerable attention. Several studies have since shown that thioether coordination in coronands can confer interesting and unusual electronic, redox and magnetic properties to metal complexes.[6] One striking aspect of thioether macrocycles is a marked preference for adopting an exodentate conformation, in which the sulfur atom lone pair of electrons are directed outward of the ring in contrast to the oxa-crown ether macrocycles.[6]

An analysis of the crystal structures of several thioether macrocycles has revealed that the exodentate orientation of the sulfur atoms arises from the preference of C-S linkages to adopt a *gauche* conformation, which contrasts with the *trans* preference of C-O bonds of crown ethers. This difference is thought to arise from the difference in the C-E bond lengths (E = O, S) and the different 1,4-interactions in *gauche* C-C-E-C and E-C-C-E units, which combine in polyether macrocycles to give *trans* C-O and *gauche* C-C bonds, but in thioether macrocycles to give *gauche* C-S and *trans* C-C bonds.[6] A recent study has shown that the strong tendency for C-S-C-C units to adopt *gauche* conformations is also observed in homologous acyclic polythioethers, suggesting that the *gauche* preference does not simply result from a macrocyclic ring constraint.[7]

We have synthesized the acyclic thioether podand, 1,8-*bis*(quinolyloxy)-3,6-dithiaoctane (**1**), with the specific purpose of comparing the coordination chemistry of this molecule with the well known oligoether quinolyloxy terminated podands, pioneered by Vögtle and coworkers.[8] In this regard we have found that the podand 1,8-*bis*(quinolyloxy)-3,6-dioxaoctane (**2**) readily forms stable helical complexes with potassium ions,[1] as has been observed for several other similar cases.[8] The incorporation of sulfur donor atoms into the oligoether backbone of (**2**) is thus expected to profoundly influence the coordination chemistry of these podands.

EXPERIMENTAL

Materials and instrumentation

The starting materials 3,6-dithiaoctane-1,8-diol and 1,8-dichloro-3,6-dithiaoctane were prepared according to literature methods.[9,10] **CAUTION: 1,8-dichloro-3,6-dithiaoctane is a severe vesicant and must be handled with extreme care.** $Cu(CH_3CN)_4PF_6$ was prepared according to the method described in the literature.[11] All reagents and solvents were of analytical reagent grade and were used as received.

Infrared spectra were measured in nujol mulls between KBr disks on a Perkin Elmer 983 infrared spectrophotometer. Electronic spectra were recorded on a Varian Superscan 3 spectrophotometer in the absorbance mode using 1.00 cm matching quartz cells. Elemental analyses for C, H and N were carried out on a Heraeus Universal Combustion Analyzer. Proton NMR spectra at 25°C were obtained on a Varian VXR-200 Fourier transform spectrometer operating at 200.02 MHz. Melting points were determined using a Reichert Thermovar hot-stage microscope and are uncorrected.

Synthesis of 1,8-bis(quinolyloxy)3,6-dithiaoctane (1)

1,8-Dichloro-3,6-dithiaoctane (1.09 g, 5 mmol) dissolved in 10 cm^3 dichloromethane was added dropwise to a refluxing solution containing 1.46 g (10 mmol) 8-hydroxyquinoline (Merck) and 0.58 g (10 mmol) KOH in 50 cm^3 absolute ethanol. The reaction mixture was heated under reflux for 4 hours, allowed to cool to room temperature, filtered to remove KCl and the filtrate evaporated using a rotary evaporator. The resultant red oil was taken up in chloroform and washed with dilute NaOH several times followed by water to remove any unreacted 8-hydroxyquinoline. The organic layer was dried with anhydrous Na_2SO_4 and concentrated to a volume of about 10 cm^3. Chromatography on alumina (Merck, basic, activity 1) with chloroform gave the pure compound as a white solid which was recrystallized from ethanol yielding a white crystalline compound: Yield 26%. mp 134-137°C. IR (KBr): 1615(m), 1595(m), 1568(m), 1500(s), 1425(s), 1319(s), 1260(s), 1197(m), 1184(s), 1131(m), 1106(vs), 1072(s), 1031(m), 1015(m), 992(s), 861(m), 817(s), 803(m), 790(s), 765(m), 750(s), 718(m), 682(m)cm^{-1}. ^{1}H NMR ($CDCl_3$) 8.95-8.92 (m, 2H, quinoline), 8.14-8.09 (m, 2H, quinoline), 7.44-7.37 (m, 6H, quinoline), 7.08-7.04 (m, 2H, quinoline), 4.41 (m, 4H, $-OCH_2-$), 3.17 (m, 4H, $-CH_2S-$), 2.99 (s, 4H, $-SCH_2-$) ppm. *Anal.*; Calcd. for $C_{24}H_{24}N_2O_2S_2$; C, 66.2; H, 5.5; N, 6.4%. Found; C, 66.2; H, 5.7; N, 6.0%.

Preparation of Copper(II) and Cobalt(II) complexes of (1)

$[Cu(1)](ClO_4)_2.3H_2O$

A solution of $Cu(ClO_4)_2.6H_2O$ (50 mg, 0.14 mmol, Alfa Chemical Co.) in 2 cm^3 acetone was added to a solution of (**1**) (47 mg, 0.11 mmol) in 10 cm^3 chloroform giving rise to a bright, emerald green solution. On standing at room temperature (<2 hrs), the complex, $[Cu(\mathbf{1})](ClO_4)_2.3H_2O$, deposited as beautiful green octahedral crystals, which were collected by filtration, washed with chloroform and dried under vacuum over silica gel, (yield: 51%). Recrystallization from a chloroform/acetone mixture (1:1, v/v) afforded crystals suitable for X-ray diffraction analysis: mp 177-178°C. IR (KBr): 3582(br), 3349(br), 1617(s), 1584(s), 1552(m), 1503(s), 1422(s), 1399(s), 1316(vs), 1262(s), 1240(m), 1226(m), 1210(m), 1179(s), 1084(vs), 1002(s), 972(s), 930(m), 828(s), 805(m), 786(m), 752(s), 735(s), 677(m), 623(s), 577(m), 480(m), 434(m) cm^{-1}.

$[Co(1)](BF_4)_2.3H_2O$

The cobalt(II) tetrafluoroborate complex of (**1**) was prepared as that described above, using the corresponding salt, $Co(BF_4)_2.6H_2O$ (Aldrich). Recrystallization from acetone/chloroform mixtures (1:1, v/v) gave red, needle-like crystals: Yield: 60%. mp >230°C. IR (KBr): 3611(br), 3378(br), 1623(m), 1585(s), 1504(s), 1414(s), 1317(vs), 1260(s), 1213(m), 1175(s), 1101(vs), 1062(s), 967(s), 830(s), 818(m), 754(s), 737(s), 625(s), 524(m), 484(m) cm^{-1}.

Preparation of Copper(I) complex of (1)

A solution of $Cu(CH_3CN)_4PF_6$ (40 mg, 0.11 mmol) in 5 cm^3 acetonitrile was added, under nitrogen, to a degassed solution of (**1**) (49 mg, 0.11 mmol) in 2.5 cm^3 dichloromethane to give a bright yellow solution. The volume of the solution was reduced by passing N_2 gas through and then treated with degassed anhydrous diethyl ether at O°C to a yield a yellow oil. The oil, when dried under vacuum, solidified to yield the air-stable [Cu(1)PF_6] complex as a bright yellow, flaky material: Yield 60%. mp 87-89°C. IR (KBr): 3376(w, br), 1615(m), 1574(m), 1501(s), 1314(s), 1261(s), 1179(n), 1108(s), 841(vs), 784(s), 755(m), 721(m), 625(m), 557(m)cm^{-1}. ^1H NMR ($CDCl_3$) 8.78 (m, 2H, quinoline), 8.23 (m, 2H, quinoline), 7.58-7.55 (m, 4H, quinoline), 7.46-7.41 (m, 2H, quinoline), 4.47 (m, 4H, -OCH_2-), 3.18 (m, 4H, -CH_2S-), 3.00 (s, 4H, -SCH_2-) ppm.

X-ray Structure Determination

Preliminary cell dimensions and space group symmetry were determined from Weissenberg and precession photographs (CuK_α radiation, $\lambda = 1.5418$Å). Accurate cell parameters were obtained from a least-squares analysis of the setting angles of 24 reflections in the range of $16° < \theta < 17°$ automatically located and centred on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.7107$Å). The intensities were collected at room temperature with an ω-2θ scan, with variable scan width and a maximum recording time of 40s. During data collection, the intensities of three reference reflections were monitored every hour, while re-centring was checked after every 200 measured reflections. Lorentz-polarization and empirical absorption (program EAC, Enraf-Nonius package) corrections were applied.

The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares (SHELX76).[12] Atomic scattering factors and dispersion corrections were taken from International Tables for X-ray Crystallography.[13] With Z = 16, the cation is required to possess C_2 symmetry. The Cu atom was placed at Wyckoff position (f) with the y coordinate determined from a Patterson synthesis. Remaining atoms of the cation and anions were located from subsequent difference Fourier syntheses. Refinement by least-squares employing anisotropic thermal parameters gave $R = 0.11$ and a difference Fourier synthesis revealed two peaks (one lying on a two-fold axis) interpreted as oxygen atoms of water of crystallization. Their inclusion in the refinement led to $R = 0.087$. Normal site-occupancy factors were assigned to these oxygen atoms to be consistent with the microanalytical data (Table 4) which indicated three H_2O molecules per formula unit. Refined temperature factors for these atoms were rather high, however, indicating possible disorder. At this stage clear evidence for disorder in the ClO_4^- anion was detected and a second, alternative orientation of the anion was included with a site-occupancy factor of 0.3 for the O atoms and the latter was refined so that the sum of the site-occupancy factors for the two orientations was unity. Final refinement gave a ratio of 0.369:0.631 for the two orientations. All hydrogen atoms (except for those of the waters of crystallization) were included in idealised positions (C-H = 1.08Å) in a riding model with common isotropic temperature factors for chemically similar groups.

Full details of the data collection, structure solution and refinement are summarized in Table 1. The fractional atomic coordinates for the non-hydrogen atoms are listed in Table 2.

RESULTS AND DISCUSSION

Description of the Molecular Structure of [Cu(1)](ClO_4)$_2$.3H_2O

The molecular structure of the cation with the atom-labelling scheme is shown in Figure 1. Relevant interatomic bond lengths, bond angles and torsion angles are

Table 1 Summary of crystal data, experimental and final refinement parameters for $[Cu(1)](ClO_4)_2 . 3H_2O$.

Crystal data	
Molecular formula	$C_{24}H_{30}N_2O_{13}S_2CuCl_8$
Molecular weight/g mol^{-1}	753.1
Crystal system	orthorhombic
Space group	*Fddd*
a/Å	20.326(2)
b/Å	20.879(3)
c/Å	28.308(4)
V/Å^3	12013(3)
Z	16
D_c/g cm^{-3}	1.666
$\mu(MoK_\alpha)$/cm^{-1}	11.1
$F(000)$	6192
Data collection	
Crystal dimensions (mm)	0.31 × 0.31 × 0.22
Scan mode	$\omega - 2\theta$ scan
Scan width (°)	$(0.90 + 0.35 \tan \theta)$
Aperture width (mm)	$(1.12 + 1.05 \tan \theta)$
θ Range scanned (°)	1 – 25
range of h, k, l	$0 \leqslant h \leqslant 24; 0 \leqslant k \leqslant 24; 0 \leqslant l \leqslant 33$
Intensity decay (%)	3.0
Empirical absorption correction, max/min	1.00/0.97
Number of unique reflections collected	2109
Number of observed reflections, N, with $I_{rel} > 2\sigma(I_{rel})$	1449
Final refinement	
Average parameter shift/e.s.d.	0.05
Residual electron density/eÅ^{-3} (max/min)	0.37/−0.33
Number of parameters, N_P	238
$R = \sum \Vert F_0\vert - \vert F_c\Vert / \sum \vert F_0\vert$	0.051
$R_w = \sum w^{1/2} \Vert F_0\vert - \vert F_c\Vert / \sum w^{1/2} \vert F_0\vert$	0.052
Weighting scheme, w	$1/[\sigma^2(F_0) + 4.39 \times 10^{-4}(F_0)^2]$

listed in Table 3. The structure consists of discrete $[Cu(1)]^{2+}$ cations which are separated by (structurally disordered) perchlorate anions and lattice water molecules (three H_2O molecules per cation). The $[Cu(1)]^{2+}$ cations possess crystallographically imposed C_2 symmetry, the two-fold rotation axis passing through the metal and the midpoint of the C(1)-C(1B) bond (Figure 1). The coordinate bonds from equivalent S, O and N atoms in the two halves of the podand therefore have identical lengths: Cu-Su(1) 2.357(2)Å, Cu-N(1) 2.005(5)Å and Cu-O(1) 2.257(3)Å.

In the $[Cu(1)]^{2+}$ cation, the copper ion is bonded to all six heteroatoms of the podand, which is wrapped around the metal ion in such a way that the nitrogen and sulfur atoms are *cis* relative to each other in the equatorial plane, whilst the oxygen atoms assume axial positions *trans* to each other. The complex cation can therefore exist as two enantiomers, both of which are present in the crystal lattice since the crystal structure is centrosymmetric.

The Cu-S(1) bond distance is slightly longer than the sum of the covalent radii, 2.34Å,[14] but is well within the range (2.30 – 2.45Å) reported for equatorial Cu-S

Table 2 Fractional atomic coordinates (× 10^4) of the non-hydrogen atoms with estimated standard deviations in parentheses for $[Cu(\mathbf{1})](ClO_4)_2 . 3H_2O$.

Atom	*x/a*	*y/b*	*z/c*
Cu	1250	3159(1)	1250
S	2002(1)	3696(1)	1039(1)
C(1)	1551(5)	4682(4)	1129(5)
C(2)	2573(4)	3910(4)	1521(3)
C(3)	2289(4)	3704(4)	2000(2)
O(1)	1881(2)	3166(2)	1906(1)
C(4)	1598(3)	2824(3)	2263(2)
C(5)	1804(4)	2817(4)	2717(3)
C(6)	1501(5)	2425(5)	3047(3)
C(7)	1004(5)	2036(4)	2919(3)
C(8)	766(4)	2023(3)	2445(3)
C(9)	1059(3)	2445(3)	2118(2)
N(1)	828(3)	2497(2)	1664(2)
C(10)	335(4)	2131(3)	1533(3)
C(11)	42(4)	1687(3)	1843(3)
C(12)	250(4)	1635(3)	2285(3)
O(6)	29(7)	6250	1250
O(7)	705(6)	6500(6)	1947(4)
Cl	3722(1)	219(1)	456(1)
O(2A)*	4332(8)	64(8)	279(6)
O(3A)	3249(11)	354(12)	137(8)
O(4A)	3775(8)	740(7)	808(6)
O(5A)	3535(7)	−272(9)	756(6)
O(2B)*	3735(16)	−428(13)	264(12)
O(3B)	4349(18)	408(19)	523(14)
O(4B)	3588(17)	683(20)	104(16)
O(5B)	3326(17)	215(15)	778(10)

* A and B refer to alternative orientations of ClO_4^-.

bond distances.[5,15–19] The Cu-N(1) bond distance, which is shorter than the sum of the covalent radii, 2.05Å,[14] is comparable to the Cu-N bond distances observed for numerous copper(II) complexes with a variety of acyclic and cyclic ligands containing N, S and N, S, O donor atoms.[5,15–19] The Cu-O(1) bond distance is 0.23Å longer than the sum of the covalent radii, 2.03Å,[14] confirming the expected distortion for six-coordinate copper(II) complexes, as a consequence of the Jahn-Teller effect. The Cu-O(1) bond distance for $[Cu(\mathbf{1})]^{2+}$ compares favourably with the axial Cu-O distances observed with oxygen donor ligands such as H_2O, for example, 2.296(7)Å in the copper(II).3,6,10,13-tetrathiapentadecane complex, $Cu(Et_2\text{-}2,3,2\text{-}S_4)ClO_4 . H_2O$,[16] as well as the Cu-O(ether) distance, 2.29(1)Å, in the copper(II) complex of 1-oxa-4,3-dithia-7,10-diazacyclopentadecane.[17]

In the present case, owing to the limited "bite" of the 5-membered rings, the N(1)-Cu-O(1), O(1)-Cu-S(1), S(1)-Cu-S(1B) and S(1)-Cu-N(1) bond angles deviate from regular octahedral coordination. The conformations about the ethylene fragments, O(1)-C(3)-C(2)-S(1) and S(1)-C(1)-C(1B)-S(1B), are *gauche* and *eclipsed*, respectively (Table 3). The torsion angle of 174(1)° for the C(2)-C(3)-O(1)-C(4) fragment reflects *trans* conformation and for C(1)-S(1)-C(2)-C(3) and C(2)-S(1)-C(1)-C(1B) the torsion angles 76(1)° and −93(1)°, respectively, indicate a *gauche* conformation. These results

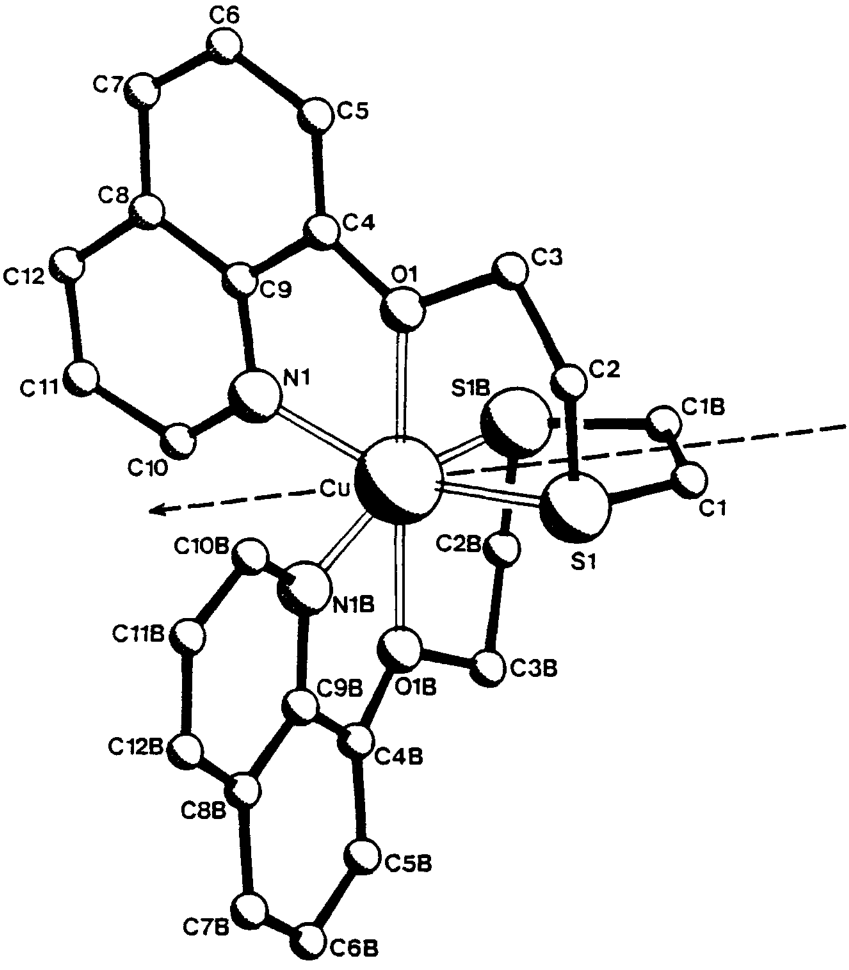

Figure 1 Perspective view of the molecular structure of $[Cu(1)]^{2+}$ showing the atom numbering scheme for all non-hydrogen atoms. The arrow indicates the two-fold rotation axis passing through the metal ion and the midpoint between the C(1)-C(1B) bond. The H atoms are omitted for clarity.

are in accordance with the conformational preferences observed for C-O and C-S bonds.[6] All the interatomic bond distances and bond angles within the ligand are unexceptional and will therefore not be discussed further here.

Inspection of the structure of $[Cu(1)]^{2+}$ clearly demonstrates that the copper(II) ion is completely engulfed by (**1**) to yield a *pseudo*-octahedral complex, in which the ligand can adopt a relatively strain-stree conformation.

Cobalt(II) and Copper(II/I) Complexes of (1)

The podand, 1,8-*bis*(quinolyloxy)-3,6-dithiaoctane (**1**) readily forms complexes with transition metal cations yielding well-defined, stable cobalt(II), copper(II) and

Table 3 Relevant bond lengths (Å), bond angles (°) and torsion angles (°) with estimated standard deviations in parentheses for $[\mathrm{Cu}(\mathbf{1})](\mathrm{ClO_4})_2 . 3\mathrm{H_2O}$.

Bond lengths		**Bond angles**	
Cu-S(1)	2.357(2)	N(1)-Cu-O(1)	76.5(2)
Cu-N(1)	2.005(5)	O(1)-Cu-S(1)	80.5(1)
Cu-O(1)	2.257(3)	S(1)-Cu-N(1)	157.0(2)
C(1B)-C(1)	1.402(9)	S(1)-Cu-S(1B)	98.1(2)
C(1)-S(1)	1.767(9)	C(1)-S(1)-C(2)	106.5(5)
S(1)-C(2)	1.796(9)	Cu-S(1)-C(2)	100.2(3)
C(2)-C(3)	1.535(11)	Cu-S(1)-C(1)	103.4(4)
C(3)-O(1)	1.421(9)	C(3)-O(1)-C(4)	121.4(4)
O(1)-C(4)	1.365(7)	Cu-O(1)-C(3)	119.4(3)
C(4)-C(9)	1.412(9)	Cu-O(1)-C(4)	111.5(3)
C(9)-N(1)	1.373(8)	C(9)-N(1)-C(10)	118.6(6)
C(10)-N(1)	1.314(9)	Cu-N(1)-C(9)	117.1(4)
		Cu-N(1)-C(10)	124.2(5)

Torsion angles	
C(2)-C(3)-O(1)-C(4)	174(1)
S(1)-C(2)-C(3)-O(1)	47(1)
C(1)-S(1)-C(2)-C(3)	76(1)
C(2)-S(1)-C(1)-C(1B)	−93(1)
S(1)-C(1)-C(1B)-S(1B)	−17(1)

Table 4 Analytical data and electronic properties* for the cobalt(II), copper(II) and copper(I) complexes of (**1**).

Complex	Analytical data (%C; H; N)	λ (nm)	ε ($\mathrm{M^{-1}\,cm^{-1}}$)
$[\mathrm{Cu}(\mathbf{1})](\mathrm{ClO_4})_2 . 3\mathrm{H_2O}$	*Calc*: 38.3; 4.0; 3.7	747	680
	Found: 38.2; 4.1; 3.65	375	5500(shoulder)
		328	10 900
$[\mathrm{Co}(\mathbf{1})](\mathrm{BF_4})_2 . 3\mathrm{H_2O}$	*Calc*: 39.9; 4.2; 3.9	530	140
	Found: 40.1; 4.15; 3.8	430	300
		360	3700(shoulder)
		327	9000
$[\mathrm{Cu}(\mathbf{1})]\mathrm{PF_6} . \mathrm{H_2O}$	*Calc*: 43.5; 3.95; 4.2	330	4800
	Found: 43.5; 4.0; 4.0		

*In acetone solution at 25°C.

copper(I) crystalline complexes, whereas a potassium complex of (**1**) analogous to that of 1,8-*bis*(quinolyloxy)-3,6-dioxaoctane could not be isolated. The analytical data and electronic properties of the cobalt and copper complexes are given in Table 4.

The cobalt(II) and copper(II) complexes have similar IR spectra (see Experimental section), indicating that these complexes are isostructural. This is consistent with the electronic spectral features observed for these complexes in acetone solution (Table 4), as the d-d bands are in the expected regions for six-coordinate complexes.[20] The intense absorption bands at about 330 nm are assigned to S(σ)-M(II) ligand to metal charge-transfer (LMCT) transitions confirming the coordination of the thioether donor atoms to the metal cations.

An interesting feature of the electronic spectrum of the copper complex of (**1**) is that the d-d absorption band at 747 nm has a higher intensity than that observed for Cu(N_xO_y) chromophores ($\varepsilon < 300\,M^{-1}\,cm^{-1}$).[20] The relatively high molar extinction coefficient for the d-d band of the copper(II)-(**1**) complex is reminiscent of a characteristic feature observed for copper-sulfur complexes,[20] as well as for copper complexes of macrocyclic polythioethers which exhibit an intense band in the 600 nm region ($\varepsilon = 800 - 2000\,M^{-1}\,cm^{-1}$).[21] The origin of this enhancement has evoked considerable discussion especially as it is one of the unique spectral features of the blue copper proteins, which have an extremely intense band in this region ($\varepsilon = 3000 - 5000\,M^{-1}\,cm^{-1}$).[4] This intense band of the blue copper proteins is now unequivocally assigned to a charge-transfer (S(σ)-Cu(II)) transition.[20] On the other hand, for the low molecular copper(II) thioether complexes, the reasons for the relatively intense band in the ligand field region is not fully understood and has been variously assigned. Nevertheless, Lever concludes that this band may be attributed to a d-d transition of enhanced intensity due to the close proximity of the strong (S(σ)-Cu(II)) LMCT band.[20]

It is noteworthy that cobalt(II) is generally thought to form only weak bonds to thioether sulfur,[15] as is clearly demonstrated in the case of 1,8-*bis*(salicylideneamino)-3,6-dithiaoctane where it was found that only under anaerobic conditions was it possible to isolate an orange-red cobalt(II) complex, which is readily oxidized in air or by mild oxidizing agents to a dark green cobaltic compound.[22] Interestingly, we find that with the *bis*(quinoline) podand, (**1**), which has a similar donor atom set, the complex $[Co(\mathbf{1})](BF_4)_2 . 3H_2O$ is quite stable to air. The enhanced stability of this complex could possibly be ascribed to the coordination of the heteroaromatic quinoline moieties, as it has been suggested that the π-delocalization arising from an aromatic ring significantly enhances the stability of complexes with S(R)N chelates.[23]

A further notable feature of the thioether podand (**1**) is its ability to form stable complexes with both copper(II) and copper(I) metal cations. The copper(I) complex can be conveniently prepared by the reaction of (**1**) in dichloromethane and $Cu(CH_3CN)_4PF_6$ in acetonitrile under an inert atmosphere and is air-stable in the dry state. In acetone and chloroform solutions, however, the copper(I) is very slowly oxidized to copper(II). The copper(I) complex can also be obtained by reducing the copper(II) complex in solution by the addition of ascorbic acid.

According to the ^1H NMR spectrum of the copper(I) complex, the podand is symmetrically coordinated to the Cu(I) ion, at least on the NMR time-scale, as only one set of resonances for magnetically equivalent protons in the molecule are observed. Scale (Drieding) molecular models suggest that if the copper(I) is coordinated to two nitrogen and two sulfur atoms, the podand can adopt a tetrahedral arrangement around the Cu(I) ion, without engendering severe strain in the molecular framework.

Electron-transfer self-exchange kinetic studies

The prevalence of the Cu(II)/Cu(I) redox couple in enzymes involved in biological oxidation-reduction processes[24,25] has stimulated much interest in the mechanistic details associated with electron transfer at the copper centre.[3,25-27] Attention has been focused on the kinetics of the blue electron carriers (azurin, plastocyanin, rusticyanin and stellacyanin), which contain a single copper atom and appear to exhibit relatively large self-exchange rate constant, equation (*1*) of the order $k_{ex} = 10^4 - 10^6\ M^{-1}\ s^{-1}$.[25]

$$^{*}Cu^{II} + Cu^{I} \xrightarrow{k_{ex}} {}^{*}Cu^{I} + Cu^{II} \tag{1}$$

Crystal structures of oxidized azurin and plastocyanin have revealed that the copper in these proteins is constrained by the protein matrix to adopt a distorted tetrahedral coordination geometry, which is presumed to undergo little change upon reduction of the copper centre.[3] In conjunction with the hydrophobic environment of the copper (which minimizes or eliminates the solvent reorganizational contribution), this relatively rigid geometry should result in a small Franck-Condon barrier for the self-exchange (*1*), thereby accounting for the large self-exchange electron-transfer rate constants observed for this class of metalloproteins.[27]

Several electron-transfer kinetic studies have been carried out with low molecular weight copper complexes.[26-29] In these cases larger rearrangements of the inner-coordination sphere may be anticipated, since Cu(II) tends to prefer distorted octahedral (tetragonal) or square pyramidal geometries whereas Cu(I) shows a strong preference for a tetrahedral environment. The self-exchange rate constants observed for these low molecular weight copper complexes range from 10 to $10^{-5}\ M^{-1}\ s^{-1}$.[26-29]

Although the copper ion in low molecular weight complexes with tetra- or pentadentate ligands may be regarded as being easily accessible, the observed electron-transfer self-exchange rate constants, k_{ex}, are much lower than those observed for the blue copper proteins, where the copper ion is buried within the hydrophobic shell of the protein. According to Canters *et al.*,[26] the difference between the k_{ex} values for the low molecular weight copper complexes and the blue copper proteins may be explained in terms of the four contributions to the free energy of activation $\Delta G\ddagger$ for the electron exchange reaction. For the low molecular weight copper complexes the energy required to bring the two reactants together, the increased repulsion between the reactants of like charge and the relatively high reorganizational energies result in a decrease in the rate of electron transfer in these complexes. On the other hand, for the blue copper proteins, it has been argued that the redox partners associate along the so-called hydrophobic patch on their protein surface, which provides for a large favourable entropy term in the energy required to bring the two reactants together. In proteins, the reorganizational energies are thought to be significantly reduced. These factors favour electron transfer and lead to enhanced self-exchange rate constants in the blue copper proteins.

It was therefore of interest to compare the rate of electron transfer of the $[Cu(\mathbf{1})]^{n+}$ (n = 1, 2) system reported here since the copper(II) ion is evidently completely engulfed by the ligand (**1**).

It has been shown that the self-exchange rate constant, k_{ex}, can be determined directly using an NMR line-broadening technique,[26,27,29] in which this constant can be estimated from the paramagnetic line broadening ($\Delta\nu_{1/2}$) induced when small quantities of copper(II) complex are added to a solution containing the copper(I) species. The self-exchange rate constant, k_{ex}, can then be estimated from (*2*), where $1/T_{2n}$ represents the natural transverse relaxation time and $1/T_e$ represents the exchange contribution to the relaxation time.

$$\pi\Delta\nu_{1/2} = 1/T_2 = 1/T_{2n} + 1/T_e = k_{ex}[Cu^{II}(\mathbf{1})^{2+}] + 1/T_{2n} \tag{2}$$

This equation is valid in the slow-exchange regime and for dilute solutions of the paramagnetic species (fraction, f_p, of paramagnetic species: $f_p < 0.1$).[26,29]

Upon addition of [Cu^{II}(**1**)$^{2+}$] ($f_p = 0.02 - 0.15$) to the copper(I) complex in CD_3CN or CD_3COCD_3, the line-widths of the proton resonances of the Cu(I) species hardly changed (< 0.5 Hz), indicating that the self-exchange rate for the [Cu(**1**)$^{n+}$] (n = 1, 2) electron transfer reaction is immeasurably slow.

These results could be explained by the fact that in addition to the structural and stereochemical changes for the two reactants, [Cu(**1**)]$^{2+}$ and [Cu(**1**)]$^{+}$, which result in an appreciable activation energy barrier to electron transfer, the Cu(II) ion in the complex is completely enclosed by the podand in a stable *pseudo*-octahedral configuration, thereby reducing access to the copper centre and prohibiting electron transfer. The other contributions to the free energy of activation $\Delta G\ddagger$ of the electron exchange reaction will also, as in the case of the other low molecular weight copper complexes, result in a decrease in the self-exchange rate constant. Since relatively higher self-exchange rate constants have been observed for low molecular weight copper complexes with tetra- and pentadentate ligands where a possible inner-sphere electron transfer mechanism may be invoked, the complete enclosure of the copper(II) ion in the present case presumably excludes such a mechanism.

In conclusion, by altering the donor atom set of the quinoline terminated podands from NOOOON to NOSSON, a marked difference in the coordination chemistry of these ligands results. The oligoether podand, (**2**), readily forms stable 1:1 crystalline complexes with potassium salts,[1] but not with transition metal cations such as cobalt(II) and copper(II). The complexation reaction between cobalt(II) and (**2**) yields the diprotonated salt of the podand[30] and with copper(II) a bright green crystalline complex can be isolated but the stoichiometry of this complex could not be unambiguously established.[31] By contrast, the thioether analogue readily forms stable 1:1 complexes with copper(II) and cobalt(II) but not with potassium salts.

Moreover, the structures of the resultant complexes differ markedly. In the potassium-oligoether *bis*(quinolyloxy) podand complexes, electrostatic considerations and the length of the oligoether chain determine to a large extent the structure of the complexes. The podand (**2**) wraps around the "spherical" potassium ion in a helical conformation thereby optimizing the podand-cation interactions as well as cation-anion interactions.[1] On the other hand, for (**1**), the stereoelectronic demands of the transition metal ion dictate the geometry of the resulting complex. The ability of (**1**) to adopt a *pseudo*-octahedral arrangement is undoubtedly facilitated by the strong preference for *gauche* conformation at the C-S bonds.

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SUPPLEMENTARY MATERIAL

Full lists of bond lengths and angles, hydrogen atom positions, temperature factors, and observed and calculated structure factors are available from KRK. Arrangements to deposit this material in the Cambridge Crystallographic Data Centre will be made.

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