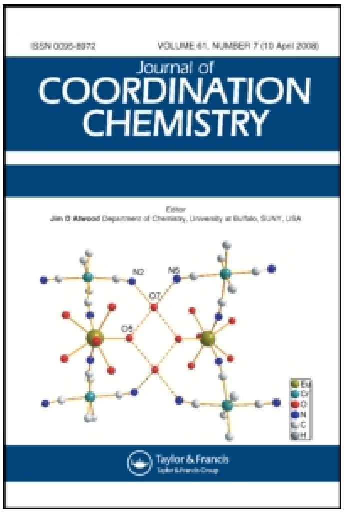

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SELENOETHER COMPLEXES OF COPPER(II) - SYNTHESIS, SPECTROSCOPY AND STRUCTURES

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SELENOETHER COMPLEXES OF COPPER(II) – SYNTHESIS, SPECTROSCOPY AND STRUCTURES

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The red-brown copper(II) diselenoether complexes, [Cu (L-L)$_2$][BF$_4$]$_2$ (L-L = MeSeCH$_2$CH$_2$SeMe, MeSeCH$_2$CH$_2$CH$_2$SeMe or PhSeCH$_2$CH$_2$SePh) have been prepared from copper(II) fluoroborate and the ligands in anhydrous dichloromethane. Some new dithioether analogues are also described. The reaction of MeSeCH$_2$CH$_2$SeMe and copper(II) fluoroborate in ethanol led to an unstable dark green substance which appeared to contain both copper(I) and copper(II) and was formulated [Cu(MeSeCH$_2$CH$_2$SeMe)$_2$] [BF$_4$]$_x$. The complexes were characterised by analysis, UV-visible and e.p.r. spectroscopy, and magnetic measurements, and cyclic voltammetry has been used to probe the Cu (II)/ Cu(I) redox couples. The complexes are too unstable in solution to obtain crystals for an X-ray study, but structural data has been obtained for both the Cu(II) and Cu(I) complexes by copper K-edge EXAFS studies. Ditelluroethers reduce copper(II) salts to copper(I) complexes.

KEYWORDS: copper(II), selenoether complexes, EXAFS

INTRODUCTION

Copper(II) complexes of thioether ligands have been studied in great detail, and examples with mono-, bi-, and poly-dentate ligands and thiamacrocycles are well known.[1,2] Studies of blue copper proteins have prompted many studies of copper (II) complexes with a variety of polythioethers and polydentate N/S donors.[3] In contrast only one copper(II) complex of a selenoether ligand has been thoroughly characterised, the red-black [Cu{[16]-aneSe$_4$}][SO$_3$CF$_3$]$_2$([16]aneSe$_4$ = 1,5,9,13-tetraselenacyclohexadecane),[4] and even this decomposes quite rapidly in solution in organic solvents, forming a polymeric copper(I) complex and the organoselenium cation [16-aneSe$_4$] [SO$_3$CF$_3$]$_2$. We have recently reported[5] a detailed multinuclear NMR study of various homoleptic copper(I) complexes of sulphur, selenium and tellurium donor ligands, and recount here our studies of some copper(II) analogues.

EXPERIMENTAL

EPR spectra were measured from powdered samples at 295 K or from frozen solutions (180 K) in nitromethane on a Bruker ECS106 and referenced to DPPH. Other physical measurements were made as described previously.[6] EXAFS data at the Cu and Se K-edges were collected in transmission mode on station 7.1 at the Daresbury

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Synchrotron Radiation Source from samples diluted with BN. Details of the data collection and treatment are described elsewhere.[7] The copper(II) samples used for EXAFS studies were freshly prepared (<48 h) and were stored at 0°C until required. The copper(I) complexes[5] and the ligands[8] were made as described elsewhere.

The syntheses were all carried out under a dry N_2 atmosphere. All products were stored under N_2 in a freezer.

$[Cu\{MeS(CH_2)_2SMe\}_2](BF_4)_2$

2,5-Dithiahexane, MeS $(CH_2)_2SMe$ (0.519 g, 4.25 mmol) was added dropwise to a solution of $Cu(BF_4)_2 \cdot 4H_2O$ (0.567 g, 1.83 mmol) in 10 cm^3 ethanol. A dark red-brown precipitate was formed immediately which was filtered off, washed with ethanol (2×10 cm^3) and dried *in vacuo.* Yield: 0.68 g (77%).

$[Cu\{PhS(CH_2)_2SPh\}_2](BF_4)_2$

A solution of Cu $(BF_4)_2 \cdot 4H_2O$ (0.627 g, 2.03 mmol) in 2,2-dimethoxypropane (5 cm^3) and CH_2Cl_2 (10 cm^3) was heated to reflux (colour change blue to green) then cooled in an ice bath. $PhS(CH_2)_2SPh$ (1.00 g, 4.06 mmol) in 10 cm^3 CH_2Cl_2 was added dropwise. The solution was evaporated to a dark brown oily residue which was triturated with pentane (4×15 cm^3) giving the solid which was filtered off and dried *in vacuo.* Yield: 1.14 g (77%).

$[Cu\{MeSe(CH_2)_2SeMe\}_2](BF_4)_2$

A solution of $Cu(BF_4)_2 \cdot 4H_2O$ (0.193 g, 0.62 mmol) in 2, 2-dimethoxypropane (5 cm^3) and anhydrous CH_2Cl_2 (10 cm^3) was heated to reflux, giving a colour change from blue to green. The solution was cooled in a CCl_4 slush-bath (−24°C), stirred vigorously, and $MeSeCH_2CH_2SeMe$ (0.277 g, 1.28 mmol) added dropwise, when a dark-brown precipitate formed immediately. The solvent was decanted off, and the solid dried under vacuum, while cooled in the slush bath.

"$[Cu\{MeSe(CH_2)_2SeMe\}_2](BF_4)_x$"

$Cu(BF_4)_2 \cdot 4H_2O$ (0.362 g, 1.17 mmol) in 2, 2-dimethoxypropane (5 cm^3) was heated to reflux. Anhydrous ethanol (10 cm^3) was added, the mixture was cooled in ice, and MeSe $(CH_2)_2SeMe$ (0.563 g, 2.61 mmol) was added dropwise. A dark green precipitate formed immediately, which was filtered off, washed with anhydrous ethanol (5 cm^3), and then with anhydrous diethyl ether (10 cm^3), and dried *in vacuo.* Yield: 0.35 g.

$[Cu\{PhSe(CH_2)_2SePh\}_2](BF_4)_2$

A solution of $Cu(BF_4)_2 \cdot 4H_2O$ (0.145 g, 0.4 mmol) in 2, 2-dimethoxypropane (5 cm^3) and anhydrous CH_2Cl_2 (15 cm^3) was heated to reflux (colour change blue to green) then cooled in an ice bath. A solution of $PhSe(CH_2)_2SePh$ (0.331 g, 0.97 mmol) in anhydrous CH_2Cl_2 (5 cm^3) was added. The solution was evaporated to an oily residue which was triturated with anhydrous ether (2×10 cm^3). The dark brown solid was dried under vacuum. Yield: 0.28 g (65%).

[Cu{MeS(CH$_2$)$_3$SMe}$_2$] (BF$_4$)$_2$

A solution of $Cu(BF_4)_2 \cdot 4H_2O$ (0.345 g, 1.12 mmol) in 2, 2-dimethoxypropane (5 cm^3) and anhydrous CH_2Cl_2 (10 cm^3) was heated to reflux (colour change blue to green) then cooled in an ice bath. 2, 6-Dithiaheptane, MeS $(CH_2)_3$SMe (0.350 g, 2.57 mmol) was added dropwise and the solvent removed *in vacuo.* The residue was repeatedly triturated with ice cold anhydrous diethyl ether. The resulting dark brown solid was dried under vacuum. Yield: 0.38 g (67%).

[Cu{MeSe(CH$_2$)$_3$SeMe}$_2$] (BF$_4$)$_2$

A solution of $Cu(BF_4)_2 \cdot 4H_2O$ (0.158 g, 0.51 mmol) in 2,2-dimethoxypropane (5 cm^3) and anhydrous CH_2Cl_2 (15 cm^3) was heated to reflux (colour change blue to green) then cooled in an ice bath. 2,6-Diselenaheptane, MeSe$(CH_2)_3$SeMe (0.263 g, 1.14 mmol) was added dropwise. The resulting dark brown solution was evaporated to an oily residue and 15 cm^3 anhydrous diethyl ether was added. The mixture was stored under N_2 in a freezer for 24h then the ether decanted and the dark brown solid dried *in vacuo.*

[Cu{MeS(CH$_2$)$_2$SMe} Cl$_2$]

MeS $(CH_2)_2$SMe (0.495 g, 4.05 mmol) was added dropwise to a solution of $CuCl_2$ (0.229 g, 1.70 mmol) in methanol (15 cm^3) while cooling the reaction vessel in ice. The resulting dark green precipitate was filtered, washed with cold methanol (5 cm^3) and dried *in vacuo* Yield: 0.20 g (46%).

RESULTS AND DISCUSSION

Dithioethers

The homoleptic dithioether complexes $[Cu(MeSCH_2CH_2SMe)_2Y_2]$ ($Y = ClO_4$, BF_4) which have *trans* tetragonal octahedral geometry with weak anion coordination in the solid state, have been studied in considerable detail.[9-11] Since the perchlorate is explosive,[9] we used the tetrafluoroborate complex as a model for the present study, and our data (Tables 1–3) are in good agreement with the literature. It has been suggested[11] that the differences in uv-visible and e.p.r. spectra between the solid and solutions in organic solvents, are due to thioether ligand dissociation. An alternative explanation of the differences, is due to the change in geometry from tetragonal octahedral in the solid to four-coordinate in polar solvents. In contrast both the uv-visible and e.p.r. spectra of $[Cu(PhSCH_2CH_2SPh)_2]$ $[BF_4]_2$ are effectively the same in both the solid and in polar solvents, and suggest that four-coordinate copper is present in the solid also (see Figure 1).

The reaction of $Cu[BF_4]_2 \cdot 4H_2O$ with MeS$(CH_2)_3$SMe in dry CH_2Cl_2 gave an unstable brown solid, [Cu(MeS $(CH_2)_3SMe)_2$] $[BF_4]_2$ which decomposed rapidly to Cu(I) in polar solvents. Repeated attempts to isolate homoleptic copper(II) complexes of PhS$(CH_2)_3$SPh or Me_2S produced intractable brown oils. The uv-visible spectra of these oils were very similar to those of the isolated complexes, as was the e.p.r. spectrum of the Me_2S product (the oil from PhS$(CH_2)_3$SPh was

Table 1 Selected physical data

Complex	Colour	C%[a]	H%	μ/B.M.	$E_e{}^b$/V
$[Cu(MeSCH_2CH_2SMe)_2]\ [BF_4]_2$	red-brown	19.7(19.9)	4.1(4.2)	2.0^c 1.7^d	1.07 (1.07)
$[Cu(PhSCH_2CH_2SPh)_2]\ [BF_4]_2$	dark brown	46.4(46.1)	4.1(3.9)	-	1.13 (0.97)
$[Cu(MeSCH_2CH_2CH_2SMe)_2]\ [BF_4]_2$	dark brown	23.9(23.6)	4.6(4.7)	-	1.09 (1.09)
$[Cu(MeSeCH_2CH_2SeMe)_2]\ [BF_4]_2$	dark brown	14.6(14.4)	3.2(3.0)	1.95^d	- (1.02)
"$[Cu(MeSeCH_2CH_2SeMe)_2]\ [BF_4]_x$"	dark green	$15.6(14.4)^e$	3.3(3.0)	$0.73^{d,f}$	-
$[Cu(MeSeCH_2CH_2CH_2SeMe)_2]\ [BF_4]_2$	dark brown	17.7(17.2)	3.7(3.5)	1.6^c	0.81 (0.80)
$[Cu(PhSeCH_2CH_2SePh)_2]\ [BF_4]_2$	dark brown	36.8(36.7)	3.0(3.1)	1.8^c	1.05 (1.02)
$[Cu(MeSCH_2CH_2SMe)Cl_2]$	dark green	19.0(18.7)	4.0(3.9)	1.7^d	0.65

[a]Calculated values in parenthesis. [b]cyclic voltammetric data. Nitromethane solutions containing $[NBu_4]\ [BF_4]$, scan rate 100 mV sec^{-1}, potentials vs the Fc/Fc^+ couple at +0.40 V. Potentials in parenthesis measured starting from the copper(I) analogue also in nitromethane. [c]±0.05 B.M. in $MeNO_2$ by the Evans method. [d]Solid Gouy method. [e] calculated figures are for the Cu(II) formulation; for Cu(I) C, 16.5, H 3.5%. [f]Magnetic moment calculated on M. Wt. of Cu(II) complex (669.2).

Table 2 UV-visible data

Compound		$E_{max}{}^a/10^3\ cm^{-1}$ ($\varepsilon_{mol}/\ dm^3cm^{-1}mol^{-1}$)	$E_{max}{}^b/10^3\ cm^{-1}$
$[Cu(MeSCH_2CH_2SMe)_2]\ [BF_4]_2$	MeCN	37.5(sh), 25.1(2290), 16.3(190)	*ca* 41.0(sh), 22.5, 18.2(sh)
	Me_2CO	27.2(580), 23.5(770), 18.0(sh)(105)	
	$MeNO_2$	23.1(4850), 17.9(650)	
$[Cu(PhSCH_2CH_2SPh)_2]\ [BF_4]_2$	MeCN	39.2(13240), 29.9(1200), 25.3(750), 20.7(480)	38.3, 25.0, 20.8, 37.5
	CH_2Cl_2	29.3(1145), 25.1(720), 21.1(490)	30.6, 25.0, 20.7(sh)[d]
$[Cu(MeSCH_2CH_2CH_2SMe)_2]\ [BF_4]_2$	$MeCN^c$	24.4(370), 21.0(sh), 17.4(sh)	40.5, 33.3, 20.9
	$CH_2Cl_2{}^c$	32.9, 24.3, 20.6, 17.3(sh)	
	$MeNO_2$	24.2(435), 21.0(sh), 17.4(sh)	
$[Cu(MeSeCH_2CH_2SeMe)_2]\ [BF_4]_2$	$MeNO_2{}^c$	21.3, 18.5	39.7, 21.9, 18.5(sh), ca 15.4(sh)
"$[Cu(MeSeCH_2CH_2SeMe)_2]\ [BF_4]_x$"	$CH_2Cl_2{}^c$	21.7, 18.5(sh)	39.7, 24.0(sh), 21.0, ca 16.7(sh)
$[Cu(MeSeCH_2CH_2CH_2SeMe)_2]\ [BF_4]_2$	MeCN	24.7(415), 20.5(sh), 17.4(sh)	38.3, 27.8, 20.6(sh)
	CH_2Cl_2	33.3(sh), 24.3(460), 21.1(sh), 17.5(sh)	
$[Cu(PhSeCH_2CH_2CH_2SePh)_2]\ [BF_4]_2$	MeCN	36.3(12100), 25.0(1500), 21.0(885)	37.8, 20.7
	$MeNO_2$	24.7(1560), 20.6(1040), 17.6(sh)	
	CH_2Cl_2	24.7(1440), 20.4(970), 17.3(sh)	

[a]In solvent specified. [b]Diffuse reflectance diluted with MgO. [c]Complex decomposes rapidly, hence meaningful ε_{mol} values were not obtained. [d]Diffuse reflectance diluted with $BaSO_4$.

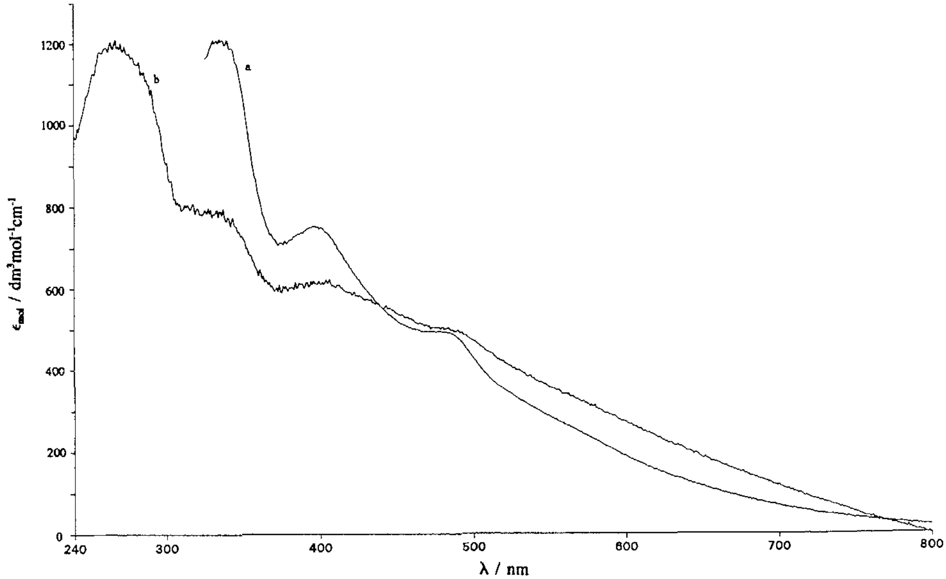

Figure 1 UV-Visible spectrum of (a) a freshly prepared solution of $[Cu(PhSCH_2CH_2SPh)_2]\ [BF_4]_2$ in MeCN, (b) diffuse reflectance spectrum of the same complex diluted with $BaSO_4$.

e.p.r. silent) strongly suggesting that CuS_4 moieties may be present, but in the absence of analytically pure solids, the studies were not pursued.

Diselenoethers

A variety of potential routes to copper(II) selenoethers were explored, including oxidation of the copper(I) analogues[5] suspended in HBF_4 with HNO_3, or with $NOBF_4$ in MeCN, but without success. The red-brown $[Cu(MeSe(CH_2)_nSeMe)_2]\ [BF_4]_2$ (n = 2 or 3) and $[Cu(PhSeCH_2CH_2SePh)_2]\ [BF_4]_2$ were obtained from

Table 3 E.P.R. data

Compound	Conditions	g value[a]
$[Cu(MeSCH_2CH_2SMe)_2]\ [BF_4]_2$	solid 295K	g_1 2.18, g_2 2.12, g_3 2.11
	$MeNO_2$ glass 180K	g_1 2.10, g_2 2.02, g_3 1.96
$[Cu(PhSCH_2CH_2SPh)_2]\ [BF_4]_2$	solid 295K	g_{av} 2.20
	$MeNO_2$ glass 183K	g_{av} 2.07
$[Cu(MeSCH_2CH_2CH_2SMe)_2]\ [BF_4]_2$	solid 295K	no spectrum[b]
$[Cu(MeSeCH_2CH_2SeMe)_2]\ [BF_4]_2$	solid 295K	g_1 2.11, g_2 2.04
"$[Cu(MeSeCH_2CH_2SeMe)_2]\ [BF_4]_x$"	solid 295K	g_{av} 2.06
$[Cu(MeSeCH_2CH_2CH_2SeMe)_2]\ [BF_4]_2$	solid 295K	g_{av} 2.15
$[Cu(PhSeCH_2CH_2SePh)_2]\ [BF_4]_2$	solid 295K	g_{av} 2.00
$[Cu(MeSCH_2CH_2SMe)Cl_2]$	solid 295K	g_{av} 2.08
	$MeNO_2$ glass 180K	g_{av} 2.10

[a] X-band spectra calibrated with DPPH. [b] No resonance observed, presumably due to unfavourable relaxation.

$Cu[BF_4]_2 \cdot 4H_2O$ and the appropriate ligand in dry CH_2Cl_2 with 2,2-dimethoxypropane as the dehydrating agent. Copper(II) trifluoromethanesulphonate and $[Cu(MeCN)_4][BF_4]_2$ were also used, but were less successful than the fluoroborate. If the reaction of $Cu(BF_4)_2$ and $MeSeCH_2CH_2SeMe$ was conducted in ethanol, a green product was obtained which is described in more detail below.

These complexes are markedly less stable than the thioether analogues and decompose to copper(I) fairly rapidly in solution, and more slowly in the solid state, although samples can be kept for some time in a freezer. The uv-visible spectra are similar in solution and in the solid state (Table 2), although the poor stability in many solvents limits the data obtainable. The e.p.r spectrum of solid $[Cu(MeSeCH_2CH_2SeMe)_2][BF_4]_2$ (see Figure 2) showed two g values (Table 3), but for the others only single isotropic signals were observed. By comparison with the dithioethers, these data suggest that $[Cu(MeSeCH_2CH_2SeMe)_2][BF_4]_2$ may be distorted octahedral in the solid, but the other diselenoether complexes contain four-coordinate copper both in solution and in the solid state. Brown oils were obtained from similar reactions of $Cu(BF_4)_2 \cdot 4H_2O$ and $PhSeCH_2CH_2CH_2SePh$ or Me_2Se; again the spectroscopic data are consistent with $CuSe_4$ species, but full characterisation was not obtained.

$[Cu(MeSeCH_2CH_2SeMe)_2][BF_4]_x$

In contrast to the reaction in CH_2Cl_2 described above, addition of $MeSeCH_2CH_2SeMe$ to $Cu(BF_4)_2 \cdot 4H_2O$/2, 2-dimethoxypropane in ethanol gave an initial dark brown precipitate, which rapidly turned dark green. Analytical data on several green samples indicated an approximate 2:1 ligand:Cu ratio. This solid decomposed rapidly to copper(I) when dissolved in MeCN or $MeNO_2$, but in CH_2Cl_2 solution it was stable enough for a uv-visible spectrum, which was very similar in profile to that obtained from the brown Cu(II) analogue. The diffuse reflectance spectra of the brown and green forms are similar but not identical (Table 2). The e.p.r. spectrum of the green solid shows an isotropic spectrum consistent with the presence of a four-coordinated Cu(II) Se_4 chromophore. However the magnetic moment of the green complex was *ca* 0.73 B.M, well below the 1.96 B.M. found for the brown $[Cu(MeSeCH_2CH_2SeMe)_2][BF_4]_2$ (Table 1). At this point the

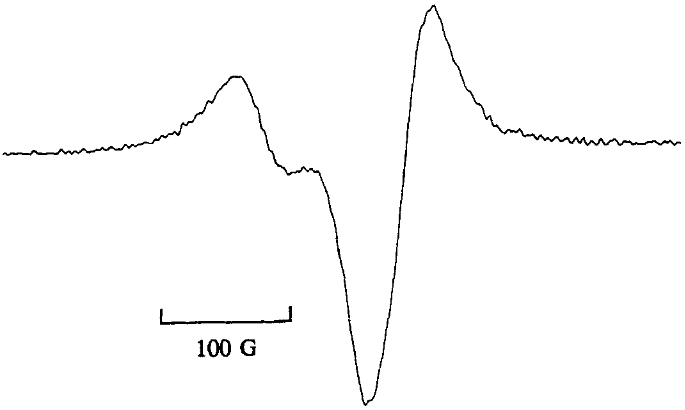

Figure 2 E.P.R. spectrum of solid $[Cu(MeSeCH_2CH_2SeMe)_2][BF_4]_2$ at room temperature.

analogy with the Cu-$MeSCH_2CH_2SMe$ system studied in great detail by Olmstead *et al.*,[14] was clear. In this system, in addition to the red-brown Cu(II) complex $[Cu(MeSCH_2CH_2SMe)_2]$ $[ClO_4]_2$ and the white Cu(I) $[Cu(MeSCH_2CH_2SMe)_2]$ $[ClO_4]$, a dark-green mixed-valence material $[Cu(MeSCH_2CH_2SMe)_2]$ $[ClO_4]_{4/3}$ was isolated and structurally characterised. The spectroscopic signatures of the copper (II) centres in the pure copper(II) complex and in the mixed-valence material were characteristic but not greatly different.[14] The considerably reduced stability of the copper(II)-diselenoether complexes, makes a full characterisation of the dark-green product difficult, but the presence of a mixed valence Cu(I)–Cu(II) species which we formulate $[Cu(MeSeCH_2CH_2SeMe)_2]$ $[BF_4]_x$ is consistent with the data. The material is too unstable to permit recrystallisation, and it is likely that x may vary from sample to sample. The brown solid $[Cu(MeSeCH_2CH_2SeMe)_2]$ $[BF_4]_2$ decomposes on standing to the white copper(I) complex, and the green mixed-valence material is formed only in the presence of solvents, which would be consistent with co-crystallisation of four-coordinate Cu(I) and Cu(II) diselenahexane cations to form this material (*cf* ref. 14).

Ditelluroethers

The reaction of either $MeTe(CH_2)_3TeMe$ or $PhTe(CH_2)_3TePh$ with Cu $[BF_4]_2 \cdot 4H_2O$ in dry ethanol or CH_2Cl_2 and with 2,2-dimethoxypropane as dehydrating agent, produced orange solutions, from which the known copper(I) complexes[5] $[Cu(L\text{-}L)_2]BF_4$ were isolated, usually in impure form contaminated with intractable oxidation products of the ligands. The products were e.p.r. silent consistent with the presence of only copper(I). Insoluble orange materials of approximate 1:1 stoichiometry ([Cu(L-L)Cl]) were formed from reaction of the ditelluroethers with copper(II) chloride in acetone or CH_2Cl_2. These substances gave only low mass ions in the FAB mass-spectrum, and in view of their insolubility in common organic solvents were not further studied. Despite many attempts we have no evidence that copper(II)-telluroether complexes form.

Halide Systems

Copper(II) chloride forms 1:1 complexes with dithioethers including $[CuCl_2(L\text{-}L)]$ where L-L = $MeSCH_2CH_2SMe$,[12] $BuSCH_2CH_2SBu$,[13] and $EtSCH_2CH_2SEt$.[14] The $[Cu(MeSCH_2CH_2SMe)Cl_2]$ complex was prepared in the present work. Although a green solid was produced from $CuCl_2$ and $MeSeCH_2CH_2SeMe$, it was not obtained in a pure state.

Electrochemistry

Cyclic voltammograms were run for both the copper(II) complexes and the copper(I) analogues in various solvents and at scan rates of 200, 100 and 50 mV sec^{-1}. Nitromethane was found most suitable for the copper(II) complexes and was subsequently used for the copper(I) complexes. Starting with the copper(II) complexes, *quasi*-reversible Cu(II)-Cu(I) couples were observed in nitromethane solutions containing $[NBu_4]$ $[BF_4]$ (see Figure 3) (Table 1) essentially independent of scan rate, typically with the peak heights on the reduction somewhat smaller than those on the (reverse) oxidation sweep. We attribute this to some spontaneous

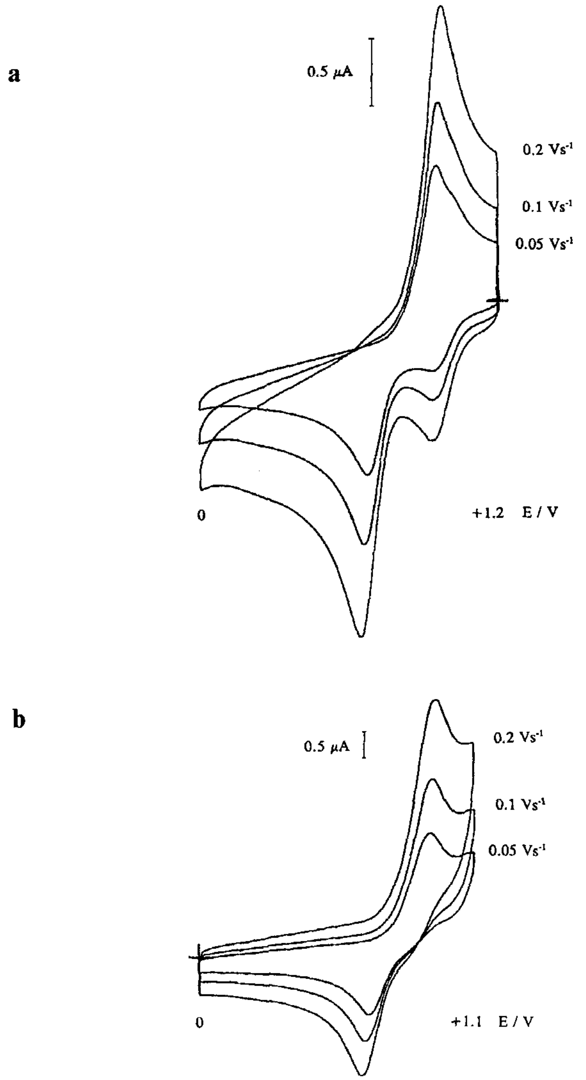

Figure 3 Cyclic Voltammograms obtained from (a) $[Cu(MeSeCH_2CH_2CH_2SeMe)_2]$ $[BF_4]_2$ in $MeNO_2$, and (b) $[Cu(MeSeCH_2CH_2CH_2SeMe)_2]$ $[PF_6]$ also in $MeNO_2$.

decomposition of the copper(II) complexes in solution prior to the measurements. This behaviour was more marked in the diselenoether complexes than the dithioethers, and $[Cu(MeSeCH_2CH_2SeMe)_2]$ $[BF_4]_2$, in particular, proved so prone to decomposition that useful data were not obtained. For $[Cu\ (MeSCH_2CH_2SMe)_2]^{2+/+}$ the couple was confirmed as a one-electron process by coulometry, but coulometric studies of the diselenoether systems were not successful due to the instability of the copper(II) complexes in solution. Cyclic voltammetry on the copper(I) ditelluroether complexes showed complex irreversible oxidations.

EXAFS Studies

Due to solution instablility of the selenoether complexes, crystals suitable for an X-ray study could not be grown. However structural data have been obtained for both copper(I) and copper(II) selenoethers using Cu K-edge EXAFS (Extended X-ray Absorption Fine Structure). The results are summarised in Table 4 and Figure 4 shows a representative example. Similar EXAFS data were also obtained for one copper(I) telluroether, and for the new copper(II) thioether complexes, with $[Cu(MeSCH_2CH_2SMe)_2]$ $[BF_4]_2$ which has been the subject of a single-crystal X-ray study,[10] serving as a 'model' complex, used to check the data collection and treatment. For $[Cu(MeSCH_2CH_2SMe)_2]$ $[BF_4]_2$ the Cu K-edge EXAFS data refined to place *d*(Cu-S) at 2.32 Å which can be compared with the crystallographic value[10] of 2.317 Å(av). The X-ray structure also revealed long $Cu\cdot\cdot FBF_3$ contacts at *ca* 2.58 Å completing a very distorted octahedron, but these were not evident in the EXAFS data; two weak back-scattering fluorines at relatively long distances would not be expected to contribute significantly to the EXAFS amplitude. The *d*(Cu-S) at 2.29 Å in $[Cu(PhSCH_2CH_2SPh)_2]$ $[BF_4]_2$ was 0.03 Å shorter than the value in the dithiahexane complex, consistent with the deduction from the spectroscopic data that $[Cu(PhSCH_2CH_2SPh)_2]$ $[BF_4]_2$ contains four-coordinate copper.

In the two copper(I) and two copper(II) diselenoether complexes examined, the *d*(Cu-Se) distances were not significantly different at *ca* 2.39 Å (Table 4). This is tentatively interpreted in terms of four-coordinate geometries for all four complexes. Although by analogy with the dithioethers, any $Cu\cdot\cdot FBF_3$ contacts in a tetragonal octahedral geometry might not be evident in the EXAFS, the increase in coordination number of the copper would be expected to lead to longer Cu-Se bonds. Whilst one must be careful extrapolating from macrocyclic complexes to acyclic analogues, it is notable that in the [Cu $([16]\text{-ane}Se_4)]$ $[BF_4]_2$ which contains six-coordinate copper, *d*(Cu-Se) is 2.46Å (av).[4] The EXAFS data on

Table 4 Cu K-edge EXAFS and relevant crystallographic data.

Compound	d(Cu-E)/Å[a]	$2\sigma^2$/Å^{2b}	F.I.[c]	R.[d]	Ref.
$[Cu(MeSCH_2CH_2SMe)_2]$ $[BF_4]_2$	2.322(2)	0.0092(3)	3.4	24.5	e
$[Cu(PhSCH_2CH_2SPh)_2]$ $[BF_4]_2$	2.290(2)	0.0175(3)	2.1	19.5	e
"$[Cu(MeSeCH_2CH_2SeMe)_2]$ $[BF_4]_x$"[f]	2.382(1)	0.0124(1)	0.7	12.4	e
$[Cu(MeSeCH_2CH_2CH_2SeMe)_2]$ $[BF_4]_2$	2.401(1)	0.0141(1)	1.2	17.1	e
$[Cu(PhSeCH_2CH_2SePh)_2]$ $[BF_4]_2$	2.389(1)	0.0130(1)	0.4	8.9	e
$[Cu(MeSeCH_2CH_2SeMe)_2]$ $[PF_6]$	2.385(1)	0.0137(1)	0.8	14.1	e
$[Cu(MeSeCH_2CH_2CH_2SeMe)_2]$ $[PF_6]$	2.391(2)	0.0153(1)	2.2	23.0	e
$[Cu(PhTeCH_2CH_2CH_2TePh)_2]$ $[PF_6]$	2.550(1)	0.0181(2)	3.5	23.9	e
$[Cu(MeSCH_2CH_2SMe)Cl_2]$[g]	2.335(3)	0.0052(5)	2.2	22.2	e
$[Cu(MeSCH_2CH_2SMe)_2]$ $[BF_4]_2$	2.317(2)av	$[Cu...FBF_3 = 2.579(5)]$			10
$[Cu(MeSCH_2CH_2SMe)_2]$ $[ClO_4]_2$	2.337(5)av	$[Cu...OClO_3 = 2.549(3)]$			11
$[Cu(MeSCH_2CH_2SMe)_2]$ $[ClO_4]_{4/3}$	2.27(2)				11
$[Cu(EtSCH_2CH_2SEt)_2]$ $[BF_4]$	2.303(5)av				10
$[Cu(MeSCH_2CH_2SMe)_2]$ ClO_4	2.263(6)				11
$[Cu([16]aneSe_4)]$ $[SO_3CF_3]_2$	2.457(2)av	$[Cu...OSO_2CF_3 = 2.464(5)]$			4

[a] Standard deviations in parenthesis. Note that systematic errors in bond distances arising from data collection and analysis procedures are *ca* ± 0.02Å for well defined shells. [b] Debye-Waller factor. [c] Fit index defined as $\Sigma_i[(\chi^T - \chi^E)k^3{}_i]^2$. [d] R factors defined as $[\int (\chi^T - \chi^E)k^3dk / \int \chi^E k^3 dk] \times 100\%$. [e] This work. [f] Se K-edge data d(Se-C) = 1.951(4)Å, $2\sigma^2$ 0.0026(7), d(Se-Cu) 2.381(4)Å $2\sigma^2$ 0.0085(5), F.I. = 8.1, R = 30.0. [g] Cu-Cl 2.218(2)Å $2\sigma^2$ = 0.0053(4).

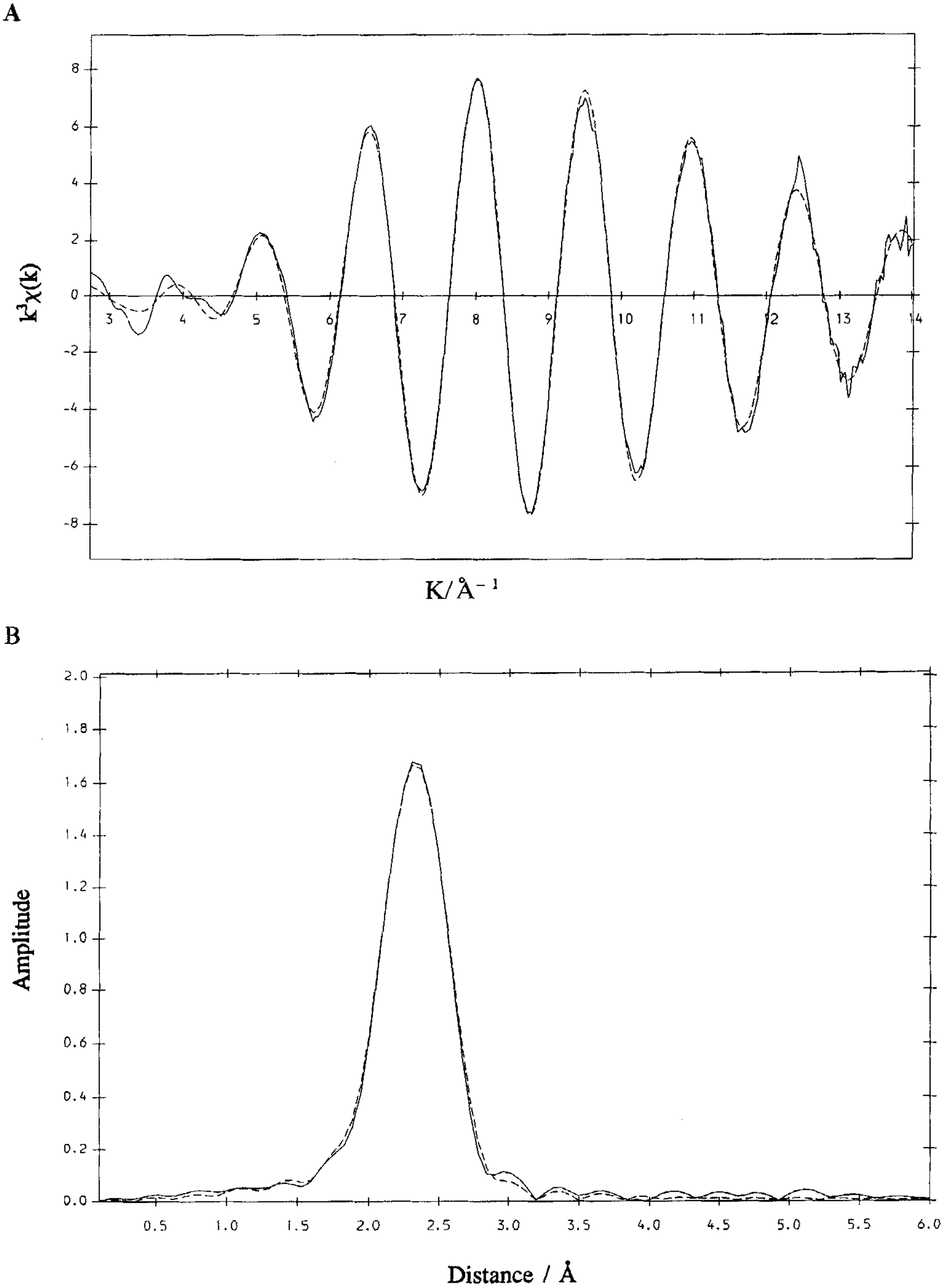

Figure 4 Background subtracted Copper K-edge EXAFS spectrum of $[Cu(PhSeCH_2CH_2SePh)_2][BF_4]_2$, and the corresponding Fourier transform. (Full line – experimental data, broken line – theoretical fit).

"[Cu(MeSeCH$_2$CH$_2$SeMe)$_2$] [BF$_4$]$_x$" placed *d* (Cu-Se) at 2.38Å. We note that the X-ray structure of [Cu(MeSCH$_2$CH$_2$SMe)$_2$] [ClO$_4$]$_{4/3}$ did not distinguish Cu(II) and Cu(I) sites.[14] Selenium K-edge EXAFS data were also recorded for [Cu(MeSeCH$_2$CH$_2$SeMe)$_2$] [BF$_4$]$_x$ and showed Se-C (1.95Å) and Cu-Se (2.38Å) as the only statistically significant features, although we note that the latter distance is in excellent agreement with the value determined from the Cu K-edge data.

The *d*(Cu-Te) bond length of 2.55Å found in [Cu(PhTeCH$_2$CH$_2$CH$_2$TePh)$_2$] [BF$_4$] is reasonable when compared with the average value[14] of 2.58Å in [Cu (Et$_2$Te)Cl] which is a chain polymer with asymmetric tellurium bridges.

SUMMARY

This study has shown that homoleptic copper(II) complexes with acyclic selenoethers can be prepared, and has provided spectroscopic and structural characterisation on three examples. In comparison with the dithioether analogues, these diselenoether complexes are surprisingly unstable, reducing very readily to copper(I). The trend continues down group 16, in that all attempts to isolate copper(II) ditelluroethers have been unsuccessful. Evidence for a mixed-valence diselenoether species has also been obtained.

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