Synthesis and Solution Multinuclear Magnetic Resonance Studies of Homoleptic Copper(I) Complexes of Sulfur, Selenium and Tellurium Donor Ligands

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The complexes $[CuL_4][O_3SCF_3]$ (L = Me_2S, Me_2Se, Me_2Te, Ph_2S, Ph_2Se or Ph_2Te) and $[Cu(L-L)_2]PF_6$ [L-L = $RE(CH_2)_2ER$ (E = S or Se, R = Me or Ph); $RE(CH_2)_3ER$ (E = S, Se or Te; R = Me or Ph)] have been prepared and characterised by analysis, IR, and in particular multinuclear NMR spectroscopy (^1H, ^{77}Se, ^{125}Te and ^{63}Cu). Variable-temperature NMR studies have been used to probe various exchange processes occurring in solution. For a limited number of complexes ^{63}Cu NMR resonances have been observed, the first examples from Group 16 donor complexes.

We have recently reported[1] a study of various homoleptic copper(I) complexes with P-, As- or Sb-donor ligands by multinuclear NMR spectroscopy, including in many cases the observation of the copper-63 NMR resonances.† Here we report a similar study involving mono- and bi-dentate sulfur, selenium and tellurium ligands. Several copper(I) complexes of dithioethers and diphosphine disulfides or diselenides have been reported,[2–6] but homoleptic complexes with seleno- or telluroethers are unknown, and no copper-63 NMR resonances appear to have been observed with any Group 16 donor ligands.

Results

Synthesis and Properties.—The complexes $[Cu(L-L)_2]Y$ [Y = PF_6 or BF_4; L-L = $MeS(CH_2)_nSMe$, $MeSe(CH_2)_nSeMe$, $PhS(CH_2)_nSPh$ or $PhSe(CH_2)_nSePh$, n = 2 or 3; $RTe(CH_2)_3$-TeR, R = Me or Ph; $Ph_2(E)PCH_2P(E)Ph_2$, E = S or Se] were obtained in high yield from the reaction of the appropriate L–L with $[Cu(MeCN)_4]PF_6$[7] in dry methanol or CH_2Cl_2. Several of the complexes of the dithioether and phosphine sulfide and selenide ligands have been reported previously, often made by reduction of copper(II) salts with, or in the presence of, L–L.[2–6,8] The use of copper(I) precursors is a cleaner route. The ditelluroether complexes are pale orange, the others white and mostly dry-air stable in the solid state, although decomposition occurs slowly in halogenated solvents producing green or blue solutions. Analytical data are given in Table 1. The FAB mass spectra confirmed the formulations, exhibiting features due to $[Cu(L-L)_2]^+$ and $[Cu(L-L)]^+$ sometimes with lower-mass ions due to ligand fragmentation. The ^1H NMR data (Table 2) are consistent with the formulations but otherwise unexceptional. X-Ray structural data (from complexes with different anions) have confirmed the presence of a distorted-tetrahedral geometry with chelating ligands in the complexes with $MeS(CH_2)_2SMe$ and $EtS(CH_2)_2SEt$.[6,9]

The reaction of $[Cu(MeCN)_4]PF_6$ with 4 equivalents of Ph_3PE (E = S or Se)‡ gave the tris complexes $[Cu(Ph_3-PE)_3]PF_6$, previously obtained as BF_4^- or ClO_4^- salts.[2,8] The $[Cu(Ph_3PE)_3]^+$ cations are probably trigonal planar {cf.

Table 1 Analytical data

Compound	Analysis (%)[a]	
	C	H
$[Cu\{MeS(CH_2)_2SMe\}_2]PF_6$	21.3 (21.2)	4.1 (4.5)
$[Cu\{MeS(CH_2)_3SMe\}_2]PF_6$	24.9 (25.0)	4.7 (5.0)
$[Cu\{PhS(CH_2)_2SPh\}_2]BF_4$	52.2 (52.3)	4.1 (4.4)
$[Cu\{PhS(CH_2)_3SPh\}_2]BF_4\cdot0.5CH_2Cl_2$[b]	50.9 (51.3)	4.9 (4.7)
$[Cu\{MeSe(CH_2)_2SeMe\}_2]PF_6$	15.1 (15.0)	2.9 (3.2)
$[Cu\{MeSe(CH_2)_3SeMe\}_2]PF_6$	18.1 (18.0)	3.1 (3.6)
$[Cu\{PhSe(CH_2)_2SePh\}_2]PF_6$	37.9 (37.8)	3.1 (3.2)
$[Cu\{PhSe(CH_2)_3SePh\}_2]PF_6\cdot CH_2Cl_2$[b]	36.9 (37.2)	2.9 (3.4)
$[Cu\{MeTe(CH_2)_3TeMe\}_2]PF_6$	14.0 (13.9)	2.2 (2.8)
$[Cu\{PhTe(CH_2)_3TePh\}_2]PF_6$	32.4 (32.4)	2.7 (2.9)
$[Cu\{Ph_2(S)PCH_2P(S)Ph_2\}_2]PF_6$	54.0 (54.3)	3.9 (4.0)
$[Cu\{Ph_2(Se)PCH_2P(Se)Ph_2\}_2]PF_6$	46.3 (46.4)	3.1 (3.4)
$[Cu(Ph_3PS)_3]PF_6$	58.8 (59.4)	3.7 (4.2)
$[Cu(Ph_3PSe)_3]PF_6$	52.9 (52.6)	3.2 (3.7)
$[Cu(Me_2S)_4][O_3SCF_3]$	23.6 (23.4)	5.2 (5.2)
$[Cu(Me_2Se)_4][O_3SCF_3]$	16.8 (16.7)	3.9 (3.7)
$[Cu(Me_2Te)_4][O_3SCF_3]$	12.8 (12.8)	2.8 (2.9)
$[Cu(Ph_2S)_4][O_3SCF_3]$	61.6 (61.5)	4.1 (4.2)
$[Cu(Ph_2Se)_4][O_3SCF_3]$	51.2 (51.4)	3.3 (3.5)
$[Cu(Ph_2Te)_4][O_3SCF_3]$	43.4 (43.9)	2.7 (3.0)
$[Cu(Ph_2Se)_4]BF_4$	52.9 (53.2)	3.6 (3.7)
$[Cu(Ph_2Te)_4]BF_4$	44.8 (45.1)	2.8 (3.2)

[a] Calculated values in parentheses. [b] CH_2Cl_2 was present in the ^1H NMR spectra.

$[Cu(Me_3PS)_3]^{+}$[8]} and Tiethof *et al.*[2] showed by IR spectroscopy that they are extensively dissociated in solution. The ^{31}P NMR results (below) show no evidence that tetrakis complexes can be formed even with a large excess of L and are consistent with previous conclusions[2] of rapid dissociative ligand exchange.

Attempts to prepare $[CuL_4]Y$ (*e.g.* L = Me_2S, Ph_2S or Me_2Se) from $[Cu(MeCN)_4]Y$ and an excess of L in MeCN, MeOH or CH_2Cl_2 gave materials with variable composition often containing some MeCN. However the complexes $[CuL_4]BF_4$ (L = Ph_2Se or Ph_2Te) were successfully obtained by this route from anhydrous methanol solution. A more general route to the homoleptic complexes was developed involving reaction of L = Me_2E or Ph_2E (E = S, Se or Te) with $[\{Cu(O_3SCF_3)\}_2(C_6H_6)]$[10] in dry benzene under rigorously anhydrous conditions. With the exception of the pale orange Ph_2Te complex, the products were white powders which

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† ^{63}Cu, $I = \frac{3}{2}$, 69%, $\Xi = 26.528$ MHz, $D_c = 365$, quadrupole moment -0.211×10^{-28} m²; ^{65}Cu, $I = \frac{3}{2}$, 31%, $\Xi = 28.417$ MHz, $D_c = 201$, quadrupole moment -0.195×10^{-28} m².
‡ Phosphine tellurides are too unstable to be useful ligands in these systems.

decomposed in moist air and are extensively dissociated in solution (below). The $[Cu(Me_2Te)_4][O_3SCF_3]$ and $[Cu\{MeTe-(CH_2)_3TeMe\}_2]PF_6$ complexes are also light sensitive, darkening on prolonged exposure. The complexes analysed as $[CuL_4]$-$[O_3SCF_3]$ and the IR spectra are consistent with the presence of $O_3SCF_3^-$ ions.[11] These homoleptic Group 16 complexes are much less stable than the Group 15 analogues such as $[Cu(PR_3)_4]^+$.[1]

Multinuclear NMR Studies.—The ^1H NMR spectra of $[Cu\{MeE(CH_2)_nEMe\}_2]^+$ (E = S, Se or Te, n = 3; E = S or Se, n = 2) in CD_3CN showed only singlet $\delta(Me)$ resonances down to the freezing point of the solvent (228 K). Slow pyramidal inversion at the Group 16 atom would be expected to produce several closely spaced resonances due to the NMR-distinguishable invertomers. These data could either indicate that pyramidal inversion remains fast on the NMR time-scale, or that we are failing to resolve the separate resonances, since the quadrupolar copper nuclei cause broadening of the proton signals. It could also result from rapid exchange processes such as reversible intramolecular ring opening.

The $^{31}P-\{^1H\}$, $^{77}Se-\{^1H\}$, $^{125}Te-\{^1H\}$ and ^{63}Cu NMR data are collected in Tables 3–5. The behaviour shows complex variations with the ligand present and sometimes with temperature and in the presence of an excess of ligand. The spectra of the complexes will be described in turn here and rationalisations of the trends reserved for the Discussion section.

Phosphine chalcogenides. The $^{31}P-\{^1H\}$ NMR spectra of $[Cu(Ph_3PE)_3]^+$ in CH_2Cl_2 show single resonances over the temperature range 300–180 K (Table 3), little shifted from those of the free Ph_3PE. Addition of an excess of Ph_3PS to a solution of $[Cu(Ph_3PS)_3]PF_6$ in CH_2Cl_2 resulted in only a single resonance at any temperature > 175 K. Analogous results were obtained for $[Cu(Ph_3PSe)_3]PF_6$ (Tables 3 and 4). The $^{31}P-\{^1H\}$ NMR spectrum of $[Cu\{Ph_2(S)PCH_2P(S)Ph_2\}_2]PF_6$ in CH_2Cl_2 is a singlet at 300 K, and is very little affected by cooling the solution to 180 K. Addition of free L–L to this solution shows separate resonances for the free and co-ordinated L–L only at < *ca.* 233 K, above this temperature only a single sharp resonance is present consistent with fast exchange. The $^{31}P-\{^1H\}$ and $^{77}Se-\{^1H\}$ data for $[Cu\{Ph_2(Se)P-CH_2P(Se)Ph_2\}_2]PF_6$ (Tables 3 and 4) are similar, showing rapid exchange between added L–L and the complex at > *ca.* 223 K. No ^{63}Cu resonances were observed for any of the phosphine chalcogenide complexes even in the presence of an excess of L–L.

Table 2 Proton NMR data

Complex	δ (J/Hz)
$[Cu\{MeS(CH_2)_2SMe\}_2]PF_6$[a]	2.47 (s, 6 H), 3.27 (s, 4 H)
$[Cu\{MeS(CH_2)_3SMe\}_2]PF_6$[b]	2.0 (q, 2 H), 2.24 (s, 6 H), 2.75 (t, 4 H)
$[Cu\{PhS(CH_2)_2SPh\}_2]BF_4$[c]	3.30 (s, 4 H), 7.3–7.6 (m, 10 H)
$[Cu\{PhS(CH_2)_3SPh\}_2]BF_4$[a]	2.13 (q, 2 H), 3.33 (t, 4 H), 7.2–7.6 (m, 10 H)
$[Cu\{MeSe(CH_2)_2SeMe\}_2]PF_6$[c]	2.14 [s, 6 H, ^2J(Se–H) = 9], 3.10 [s, 4 H, ^2J(Se–H) = 11]
$[Cu\{MeSe(CH_2)_3SeMe\}_2]PF_6$[b]	2.0 (q, 2 H), 2.10 (s, 6 H), 2.70 (t, 4 H)
$[Cu\{PhSe(CH_2)_2SePh)_2]PF_6$[c]	3.35 [s, 4 H, ^2J(Se–H) = 11], 7.2–7.6 (m, 10 H)
$[Cu\{PhSe(CH_2)_3SePh\}_2]PF_6$[b]	1.83 (q, 2 H), 2.85 (t, 4 H), 7.2–7.6 (m, 10 H)
$[Cu\{MeTe(CH_2)_3TeMe\}_2]PF_6$[b]	1.94 (q, 2 H),[d] 2.01 (s, 6 H), 2.75 (t, 4 H)
$[Cu\{PhTe(CH_2)_3TePh\}_2]PF_6$[c]	2.00 (q, 2 H), 3.00 (t, 4 H), 7.1–7.7 (m, 10 H)
$[Cu\{Ph(S)PCH_2P(S)Ph_2\}_2]PF_6$[c]	3.90 [t, 2 H, ^2J(P–H) = 13], 7.2–7.8 (m, 20 H)
$[Cu\{Ph_2(Se)PCH_2P(Se)Ph_2\}_2]PF_6$[c]	4.10 [t, 2 H, ^2J(P–H) = 13], 7.3–7.8 (m, 20 H)
$[Cu(Me_2S)_4][O_3SCF_3]$[a]	2.69 (s)
$[Cu(Me_2Se)_4][O_3SCF_3]$[a]	2.45 (s)
$[Cu(Me_2Te)_4][O_3SCF_3]$[c]	2.06 (s)

[a] In $(CD_3)_2CO$. [b] In CD_3CN. [c] In CD_2Cl_2. [d] ^2J(Te–H) not clear due to overlap of Me and CH_2 resonances.

Table 3 $^{31}P-\{^1H\}$ NMR spectroscopic data

Complex[a]	$\delta(^{31}P)$[b]	$^1J(^{31}P-^{77}Se)$/Hz	$\delta(^{31}P)$[c]	$^1J(^{31}P-^{77}Se)$[c]/Hz
$[Cu(Ph_3PS)_3]^+$	40.3	—	43.2	—
$[Cu(Ph_3PSe)_3]^+$	29.7	640	35.8	758
$[Cu\{Ph_2(S)PCH_2P(S)Ph_2\}_2]^+$	31.3	—	35.2	—
$[Cu\{Ph_2(Se)PCH_2P(Se)Ph_2\}_2]^+$	19.7	698	25.4	754

[a] At 300 K in CH_2Cl_2. [b] Relative to external 85% H_3PO_4. [c] Free L or L–L.

Table 4 Selenium-77 and ^{125}Te NMR data

Complex[a]	$\delta(^{77}Se$ or $^{125}Te)$[b]	δ (free ligand)	Comment
$[Cu(Ph_3PSe)_3]^+$	−198	−275 (d)	Exchange at all temperatures 300–175 K
$[Cu\{Ph_2(Se)PCH_2P(Se)Ph_2\}_2]^+$	−308(d) (210 K)	−254 (d)	At 300 K very broad d at δ *ca.* −300
$[Cu\{MeSe(CH_2)_2SeMe\}_2]^{+}$[c]	+56	+127	δ +45 at 225 K, rapid exchange with L–L at > *ca.* 240 K
$[Cu\{PhSe(CH_2)_2SePh\}_2]^+$	+256	+336	δ +254 at 175 K, rapid exchange with L–L at > *ca.* 240 K
$[Cu\{MeSe(CH_2)_3SeMe\}_2]^{+}$[c]	+58	+74	δ +51.5 at 233 K
$[Cu\{PhSe(CH_2)_3SePh\}_2]^{+}$[c]	+286	+289	δ +280 at 233 K
$[Cu(Ph_2Se)_4]^{+}$[d]	+395	+416	δ +368 at 183 K
$[Cu(Me_2Se)_4]^{+}$[d]	−33 (263 K)	0	−28 at 190 K
$[Cu\{MeTe(CH_2)_3TeMe\}_2]^{+}$[c]	+49	+104	+42 at 230 K
$[Cu\{PhTe(CH_2)_3TePh\}_2]^+$	+315	+466	δ +306 at 203 K
$[Cu(Me_2Te)]^{+}$[d]	−37 (290 K)	0	δ −14 at 183 K
$[Cu(Ph_2Te)_4]^{+}$[d]	+578	+685	δ +550 at 183 K, rapid exchange with Ph_2Te at > 203 K

[a] In $CH_2Cl_2-CD_2Cl_2$ unless indicated otherwise. [b] Relative to external neat Me_2Se or Me_2Te at 300 K. [c] In $MeCN-CD_3CN$. [d] In $Me_2CO-(CD_3)_2CO$.

[CuL$_4$][O$_3$SCF$_3$](L = Me$_2$S *or* Ph$_2$S). No copper NMR resonance was observed from solutions of [Cu(Me$_2$S)$_4$]-[O$_3$SCF$_3$] in acetone over the range 300–185 K. However on adding an excess of Me$_2$S (*ca.* > 10:1 mol ratio) to the solution a copper signal was present at all temperatures (Fig. 1). This is consistent with extensive dissociation of the tetrakis complex in solution to low-symmetry species. The large excess of added L shifts the equilibrium in favour of the [CuL$_4$]$^+$ ion which is responsible for the observed signal. The resonance shifts to high frequency as the temperature is lowered (Table 5). Treatment of [Cu(MeCN)$_4$]PF$_6$ with a large excess of Me$_2$S in MeCN gave a clear solution with a similar ^{63}Cu NMR resonance, showing that the tetrakis cation is also formed under these conditions, although the pure solid complex was not isolated from such solutions. The ^{1}H NMR spectra of mixtures of [Cu(Me$_2$S)$_4$]$^+$ and Me$_2$S in (CD$_3$)$_2$CO show two resonances only at < *ca.* 235

(*a*)

(*b*)
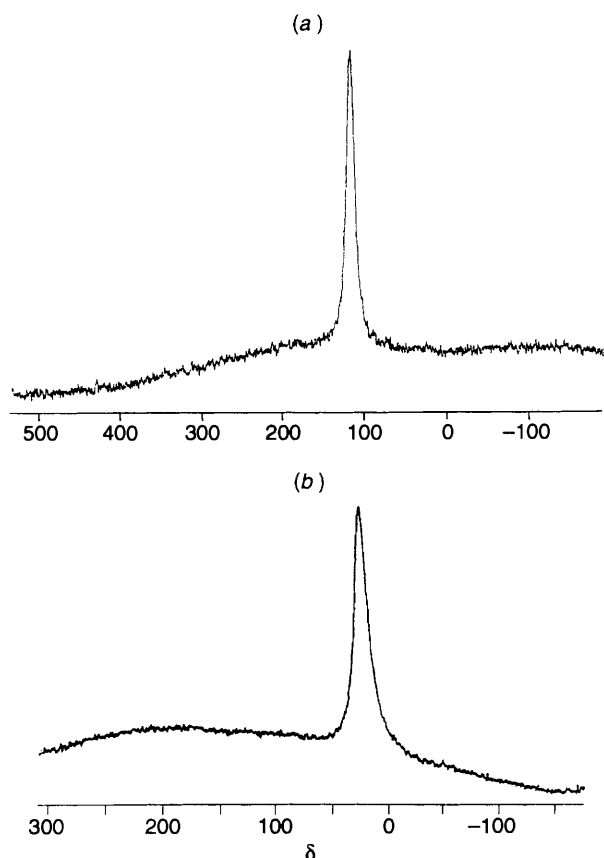
Fig. 1 Copper-63 NMR spectra of (*a*) [Cu(Me$_2$S)$_4$][O$_3$SCF$_3$] + a 10-fold excess of Me$_2$S in acetone at 183 K and (*b*) [Cu{PhSe-(CH$_2$)$_3$SePh}$_2$]PF$_6$ in MeCN at 300 K

K showing rapid exchange above this temperature. No ^{63}Cu resonance was seen for [Cu(Ph$_2$S)$_4$][O$_3$SCF$_3$] in CH$_2$Cl$_2$ even in the presence of an excess of Ph$_2$S.

[Cu(MeSCH$_2$CH$_2$SMe)$_2$]PF$_6$ *and* [Cu(PhSCH$_2$CH$_2$SPh)$_2$]-BF$_4$. No ^{63}Cu NMR resonances were found for solutions of either complex in CH$_2$Cl$_2$ over the accessible temperature range (300–175 K), even in the presence of added L–L.

[Cu(MeSCH$_2$CH$_2$CH$_2$SMe)$_2$]PF$_6$ *and* [Cu(PhSCH$_2$CH$_2$-CH$_2$SPh)$_2$]BF$_4$. The former complex exhibited δ(^{63}Cu) at +75 in MeCN solution at 300 K, which shifted to higher frequency and broadened on cooling, reaching +120 at 233 K. However no resonance was observed from solutions of [Cu(PhSCH$_2$-CH$_2$CH$_2$SPh)$_2$]BF$_4$ in Me$_2$CO at any temperature, even in the presence of an excess of L–L.

[CuL$_4$][O$_3$SCF$_3$] (L = Me$_2$Se *or* Ph$_2$Se). No ^{77}Se NMR resonance was detectable from a solution of [Cu(Me$_2$Se)$_4$]$^+$ in acetone at 300 K. On cooling a broad resonance (δ = −33) appeared at *ca.* 263 K, which sharpened quickly on cooling. Addition of varying amounts of Me$_2$Se to this solution yielded only a single resonance the chemical shift of which varied with the amount of added L, consistent with rapid exchange. Even at the lowest temperature obtainable (185 K) only a single resonance was present, showing that exchange remained fast with respect to the selenium NMR time-scale. For [Cu(Ph$_2$-Se)$_4$]$^+$ in acetone a broad resonance was present at 300 K which sharpened on cooling. The effect of adding free Ph$_2$Se to the solution mirrored that of the Me$_2$Se system. Neither complex exhibited a ^{63}Cu NMR resonance in solution at any temperature over the range 300–185 K, and no resonance was observed from solutions of [Cu(Ph$_2$Se)$_4$]$^+$ containing an excess of Ph$_2$Se over the same temperature range. In contrast, solutions of [Cu(Me$_2$Se)$_4$]$^+$ containing a large excess of Me$_2$Se (> 10:1 mol ratio) showed a broad ^{63}Cu signal at 283 K at δ *ca.* −56 ($W_{\frac{1}{2}}$ = 1500 Hz), which sharpens and drifts to higher frequency on cooling reaching −16 ($W_{\frac{1}{2}}$ = 800 Hz) at 185 K.

[Cu(MeSeCH$_2$CH$_2$SMe)$_2$]PF$_6$ *and* [Cu(PhSeCH$_2$CH$_2$Se-Ph)$_2$]PF$_6$. Both complexes exhibited single ^{77}Se NMR resonances over the range 300–225 K, but no ^{63}Cu resonances were seen. Addition of the appropriate L–L to these solutions resulted in single ^{77}Se resonances at 300 K consistent with rapid exchange. However the resonances broadened on cooling, and for both systems separate resonances for the complex and L–L were observed at < *ca.* 240 K, showing exchange slowing on lowering the temperature.

[Cu{MeSe(CH$_2$)$_3$SeMe}$_2$]PF$_6$ *and* [Cu{PhSe(CH$_2$)$_3$Se-Ph}$_2$]PF$_6$. Both complexes show relatively sharp ^{77}Se NMR resonances with small negative co-ordination shifts (Table 4). They also exhibited ^{63}Cu NMR resonances from MeCN solutions over the accessible temperature range (300–233 K) (Table 5 and Fig. 1). Whilst that of [Cu{PhSe(CH$_2$)$_3$SePh}$_2$]$^+$ shows the usual[1] high-frequency shift with decreasing

Table 5 Copper-63 NMR data

Complex	δ(^{63}Cu) ($W_{\frac{1}{2}}$/Hz)^a	Comment
[Cu(Me$_2$S)$_4$]$^{+\ b}$	+80 (2500)	At 183 K, δ +126, $W_{\frac{1}{2}}$ = 1000 Hz (only seen in presence of excess of Me$_2$S)
[Cu{MeS(CH$_2$)$_3$SMe}$_2$]$^{+\ c}$	+75 (1000)	At 233 K, δ +120, $W_{\frac{1}{2}}$ = 2000 Hz
[Cu(Me$_2$Se)$_4$]$^{+\ b}$	−56 (1500) (283 K)	At 185 K, δ −16, $W_{\frac{1}{2}}$ = 800 Hz (only seen in presence of excess of Me$_2$Se)
[Cu{MeSe(CH$_2$)$_3$SeMe}$_2$]$^{+\ c}$	+21 (1500) (293 K)	At 233 K, δ +18, $W_{\frac{1}{2}}$ = 3500 Hz
[Cu{PhSe(CH$_2$)$_3$SePh}$_2$]$^{+\ c}$	+18 (1500)	At 233 K, δ +42, $W_{\frac{1}{2}}$ = 2500 Hz
[Cu(Me$_2$Te)$_4$]$^{+\ b}$	−56 (600) (290 K)	At 193 K, δ −39, $W_{\frac{1}{2}}$ = 750 Hz (resonances quoted in presence of a large excess of Me$_2$Te, see text)
[Cu(Ph$_2$Te)$_4$]$^{+\ b}$	−153 (3400)	At 233 K, δ −116, $W_{\frac{1}{2}}$ = 4500 Hz, signal disappears at < 220 K (only seen in the presence of an excess of Ph$_2$Te)
[Cu{MeTe(CH$_2$)$_3$TeMe}$_2$]$^{+\ c}$	+21 (1500)	At 230 K, δ +13, $W_{\frac{1}{2}}$ = 3000 Hz
[Cu{PhTe(CH$_2$)$_3$TePh}$_2$]$^{+\ d}$	−36 (6000) (at 273 K)	No resonance at 300 or < *ca.* 220 K

^{a} At 300 K relative to [Cu(MeCN)$_4$]$^+$ in MeCN–CD$_3$CN. ^{b} In Me$_2$CO–(CD$_3$)$_2$CO. ^{c} In MeCN–CD$_3$CN. ^{d} In CH$_2$Cl$_2$–CD$_2$Cl$_2$.

temperature, curiously the resonance position of [Cu{MeSe(CH$_2$)$_3$SeMe}$_2$]$^+$ was essentially unchanged with temperature.

[CuL$_4$][O$_3$SCF$_3$] (L = Me$_2$Te or Ph$_2$Te). The ^{125}Te NMR spectrum of [Cu(Me$_2$Te)$_4$]$^+$ in acetone at 300 K was a sharp singlet, which broadened and shifted to high frequency on cooling. Rapid exchange occurred with added Me$_2$Te down to the freezing point of the solvent. In contrast to other [CuL$_4$]$^+$ complexes, a solution of [Cu(Me$_2$Te)$_4$]$^+$ in acetone exhibited a very broad ^{63}Cu resonance at δ −126 ($W_{\frac{1}{2}}$ = 3500 Hz), which broadened rapidly on cooling and was not observed at < ca. 250 K. However, in the presence of a large excess (> 10-fold) of Me$_2$Te, a sharp ^{63}Cu resonance is present at δ − 56 ($W_{\frac{1}{2}}$ = 600 Hz) at 290 K, which shifts on cooling to higher frequency but is still sharp at 193 K (δ −39, $W_{\frac{1}{2}}$ = 750 Hz) (Fig. 2). Solutions containing smaller excesses of Me$_2$Te gave broader ^{63}Cu resonances at intermediate chemical shifts. The sharp ^{63}Cu resonance observed in the presence of a large excess of Me$_2$Te must correspond to that of the tetrakis complex for which slow quadrupolar relaxation of the copper would be expected. In the absence of added Me$_2$Te, or with only small

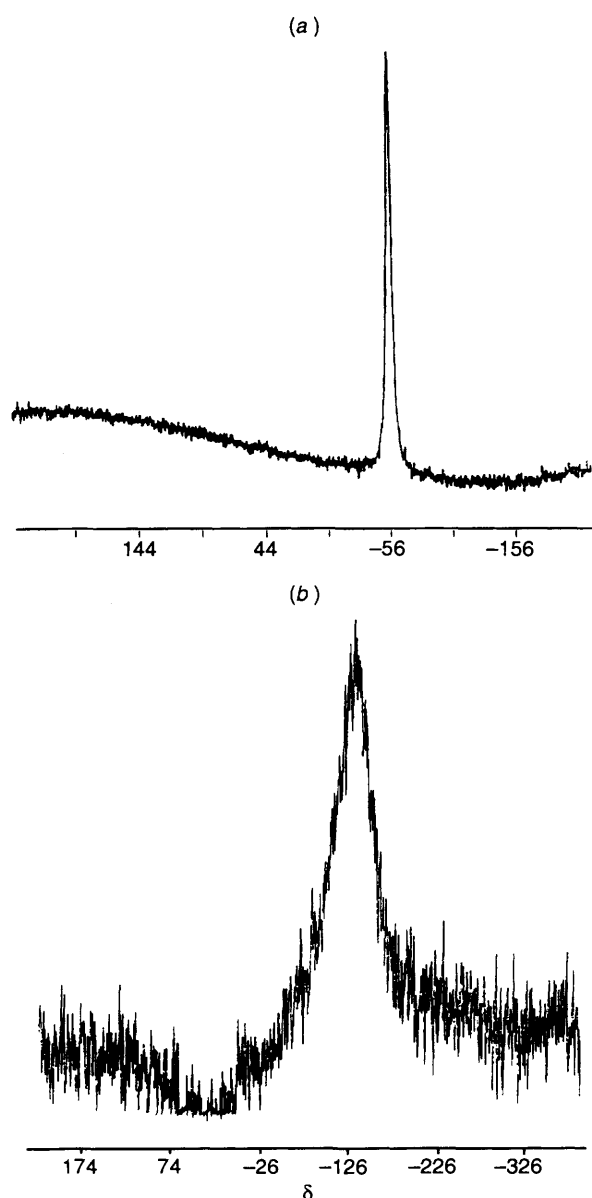quantities of it, dissociative equilibria [Cu(Me$_2$Te)$_4$]$^+$ ⇌ [Cu(Me$_2$Te)$_3$]$^+$ + Me$_2$Te {⇌ [Cu(Me$_2$Te)$_2$]$^+$ + Me$_2$Te?} are probably present and exchange with the (unobserved) lower-symmetry complexes would account for these effects.[12]

In the case of [Cu(Ph$_2$Te)$_4$]$^+$ in acetone a single ^{125}Te resonance was present at room temperature, and this remained over the accessible temperature range, showing a small low-frequency shift with decreasing temperature. Addition of an excess of Ph$_2$Te to the solution gave only a singlet at ambient temperatures, but this broadened on cooling below ca. 220 K, and below ca. 210 K separate resonances for free Ph$_2$Te and [Cu(Ph$_2$Te)$_4$]$^+$ were resolved (Fig. 3). No ^{63}Cu resonance was observed from solutions of [Cu(Ph$_2$Te)$_4$]$^+$ in acetone, but with added Ph$_2$Te a broad resonance at δ −153 ($W_{\frac{1}{2}}$ = 3400 Hz) was present at 300 K. On cooling this broadened and disappeared altogether at < 220 K.

[Cu{MeTe(CH$_2$)$_3$TeMe}$_2$]PF$_6$ and [Cu{PhTe(CH$_2$)$_3$Te-Ph}$_2$]PF$_6$. The former complex exhibited a sharp singlet ^{125}Te NMR resonance in MeCN solution which varied little with temperature. A relatively broad ^{63}Cu resonance was present at 300 K, δ +21 ($W_{\frac{1}{2}}$ = 1500 Hz) which broadened on cooling, but the chemical shift of which was insensitive to temperature. In contrast, although the [Cu{PhTe(CH$_2$)$_3$TePh}$_2$]PF$_6$ complex in CH$_2$Cl$_2$ exhibited a relatively sharp ^{125}Te resonance over the range 300–185 K, no ^{63}Cu signal was evident at room temperature. On cooling to 273 K a broad resonance at δ −36 ($W_{\frac{1}{2}}$ = 6000 Hz) appeared, but on further cooling this broadened rapidly and merged into the baseline at < ca. 220 K.

Discussion

The homoleptic copper(I) complexes formed with monodentate Group 16 ligands R$_2$E, which have not been reported previously,[13,14] are tetrakis(ligand) species on the basis of the analytical data. However they are highly unstable, decomposing readily in air, and extensively dissociated in solution on the basis of the NMR studies described above. The rapid exchange in solution with added ligand observed for all the complexes over a wide temperature range demonstrates the extreme substitution lability of these systems. The observation of ^{63}Cu NMR resonances from solutions of [CuL$_4$]$^+$ (L = Me$_2$S, Me$_2$Se, Me$_2$Te or Ph$_2$Te) in the presence of a large excess of the appropriate L shows that the equilibria can be shifted in favour of the tetrakis complexes, since the copper resonance will be seen only in an environment approaching cubic symmetry. The

(a)

144   44   −56   −156

(b)

174   74   −26   −126   −226   −326

δ

Fig. 2 Copper-63 NMR spectra of (a) [Cu(Me$_2$Te)$_4$][O$_3$SCF$_3$] + a 10-fold excess of Me$_2$Te in acetone at 300 K and (b) [Cu-(Me$_2$Te)$_4$][O$_3$SCF$_3$] in acetone at 300 K

680   640   600   560

δ
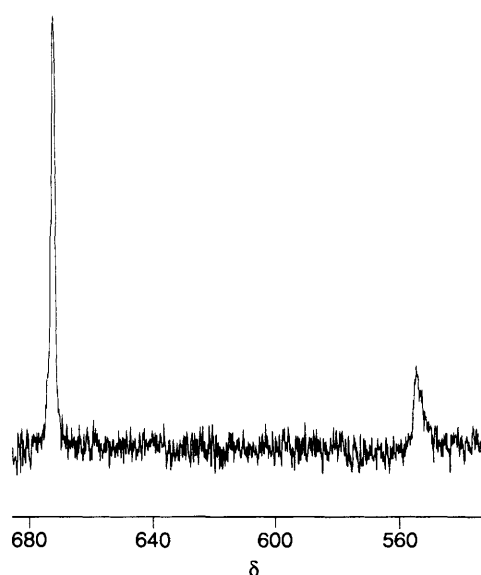
Fig. 3 The ^{125}Te-{^{1}H} NMR spectrum of a mixture of [Cu(Ph$_2$-Te)$_4$][O$_3$SCF$_3$] + Ph$_2$Te in acetone at 210 K

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corresponding failure to observe ^{63}Cu resonances from solutions of Ph$_2$S or Ph$_2$Se complexes, even in the presence of an excess of L, is taken as evidence for extensive dissociation under these conditions. Comparison with previous studies of copper(I)–Group 15 ligand complexes[1,15] shows that the present Group 16 complexes are much more substitution labile and more extensively dissociated. Even the complexes of the chelating bidentate ligands are remarkably labile in solution, with exchange with added L–L rapid on the NMR time-scale down to quite low temperatures. This must largely reflect electronic differences between the donor types, since steric effects are relatively unimportant in Group 16 ligand chemistry.[14] Neutral Group 16 donor ligands are weaker σ donors than are their Group 15 analogues,[16,17] and when bound to the electron-rich d^{10} copper(I) centre the second lone pair on the donor atom may produce significant π repulsion. Although studies of Group 16–transition metal bonds have attracted much less discussion than M–P bonding, it has been suggested that in bonds to electron-rich metal centres (which would include Cu^{I}) the lability decreases and the bond strength increases as Group 16 is descended.[17] Our data are consistent with this.

Multinuclear NMR Studies.—Apart from the evidence for extensive dissociation and rapid exchange in solution discussed above, the main features of interest in the ^{77}Se and ^{125}Te NMR spectra are the co-ordination shifts. In most transition-metal systems, co-ordination of mono- or bi-dentate seleno- or telluro-ethers results in high-frequency shifts in the selenium or tellurium resonance.[13] Particularly large high-frequency shifts are observed with five-membered chelate rings, with smaller shifts in six-membered chelate rings and with monodentate ligands. These effects parallel those familiar in ^{31}P NMR studies of the corresponding phosphine systems.[18] Rare exceptions to these generalisations have been reported in some [PtMe$_3$X-(L–L)] systems (L–L = diseleno- or ditelluro-ether).[19] In all the copper(I) systems co-ordination of the ligand results in a shift of the selenium or tellurium NMR resonance to low frequency of the free L–L resonance (Table 4). Moreover for the selenium ligands where data are available for comparable five- and six-membered rings, the largest low-frequency shifts are present for the smaller-ring complexes. The origin of the 'chelate ring effect' is disputed even in the much studied diphosphine systems.[18] The low-frequency co-ordination shifts in the Group 16 systems presumably result from the effect of the electron-rich d^{10} metal centre.

The co-ordinated bidentate ligands are chiral and the presence of invertomers is usually evident in the ^{1}H, ^{77}Se or ^{125}Te NMR spectra.[20] In these copper systems we have no evidence for such invertomers; either pyramidal inversion remains fast on the NMR time-scale over the temperature range studied, or the relatively broad lines preclude observation of the small differences in chemical shifts expected between the invertomers.

A major interest in the present work was to study the ^{63}Cu NMR spectra, since no examples from Group 16 donor complexes have been reported previously.[15] ^{63}Cu resonances were observed only from a limited range of complexes (Table 5) and disappointingly no examples of ^1J couplings to ^{77}Se or ^{125}Te were resolved. The factors which affect the observation of ^{63}Cu NMR resonances are the rate of quadrupolar relaxation of the ^{63}Cu nuclei and the nature and rate of dynamic processes occurring in solution. These will in turn be influenced by the temperature, distortions from regular symmetry and the electronic properties of the ligands. It is also clear that there is considerable interrelation between these various factors and hence the observed behaviour is complex. In fact, ^{63}Cu resonances were observed only with some monodentate ligands and in some six-membered chelate-ring complexes, presumably because these ligands are better able to approach the tetrahedral geometry required at the copper centre, whereas the five-

membered rings deviate further from T_d geometry. The fact that [Cu{PhS(CH$_2$)$_3$SPh}$_2$]$^+$ fails to exhibit a ^{63}Cu resonance and that [Cu{PhTe(CH$_2$)$_3$TePh}$_2$]$^+$ does so only over a limited range of conditions shows how sensitive the relaxation rates are to small changes in metal environment.

Comparison of the ^{63}Cu chemical shifts reported show that as in Group 15[1] the chemical shifts move to low frequency as the donor atom becomes heavier, and that the typical shifts with donor lie in the order (for a limited range of examples) P > S > Se $\approx$ Te $\approx$ As > Sb > halide.

Experimental

The ^{1}H NMR spectra were recorded from solutions in CD$_2$Cl$_2$, CD$_3$CN or (CD$_3$)$_2$CO on JEOL FX90Q or Bruker AC300 or AM360 spectrometers, ^{31}P-{^{1}H} spectra from 5% CD$_2$Cl$_2$–CH$_2$Cl$_2$ solutions on a Bruker AM360 at 145.8 MHz, ^{77}Se-{^{1}H} spectra at 68.68 MHz, ^{125}Te-{^{1}H} spectra at 113.6 MHz, and ^{63}Cu spectra similarly at 95.5 MHz. Phosphorus chemical shifts are reported relative to external 85% H$_3$PO$_4$, selenium shifts relative to neat external Me$_2$Se, tellurium shifts relative to neat external Me$_2$Te, and copper shifts relative to a solution of [Cu(MeCN)$_4$]BF$_4$ in MeCN at 300 K. The FAB mass spectra were recorded on a VG Analytical 70–250-SE normal-geometry double-focusing spectrometer using 3-nitrobenzyl alcohol as the matrix.

The complexes [Cu(MeCN)$_4$]Y (Y = PF$_6$ or BF$_4$)[7] and [{Cu(O$_3$SCF$_3$)}$_2$(C$_6$H$_6$)][10] were made by literature methods. Complexes were made in dried solvents under a dry nitrogen atmosphere. The [CuL$_4$][O$_3$SCF$_3$] complexes were stored and handled in a dry-box.

[CuL$_4$][O$_3$SCF$_3$] (L = Me$_2$S, Me$_2$Se, Me$_2$Te, Ph$_2$S or Ph$_2$Se).—The compound L (3.4 mmol) was added to [{Cu-(O$_3$SCF$_3$)}$_2$(C$_6$H$_6$)] (0.4 mmol) in freshly distilled benzene (10 cm^3). The solvent was removed *in vacuo*, and dry diethyl ether (10 cm^3) was added to the resulting oil, while cooling the flask in an ice-bath. The white solid was filtered off using a Schlenk stick, washed with anhydrous diethyl ether (2 $\times$ 10 cm^3), and dried *in vacuo*. The complex [Cu(Ph$_2$Te)$_4$][O$_3$SCF$_3$] was made similarly, except that the oil was triturated with pentane, and the pale orange solid washed with pentane (2 $\times$ 10 cm^3) and dried *in vacuo*. Yields typically 50%.

[Cu(Ph$_3$PE)$_3$]PF$_6$.—A solution of Ph$_3$PE (4 mmol) and [Cu(MeCN)$_4$]PF$_6$ (0.37 g, 1.0 mmol) were refluxed in dry CH$_2$Cl$_2$ (15 cm^3) under nitrogen for 30 min. The solution was cooled, dry diethyl ether added producing a white precipitate, and the mixture refrigerated. The product was filtered off, washed with diethyl ether (2 $\times$ 10 cm^3), and dried *in vacuo*. Complexes of the diphosphine disulfide and diselenide ligands were made similarly using a 2:1 ligand:Cu ratio. Yields 60–75%.

The complexes of the bidentate ligands were made by similar routes, typical examples being described.

[Cu{MeS(CH$_2$)$_2$SMe}$_2$]PF$_6$.—A solution of MeS(CH$_2$)$_2$-SMe (0.3 g, 3.5 mmol) and [Cu(MeCN)$_4$]PF$_6$ (0.56 g, 1.5 mmol) in anhydrous methanol (20 cm^3) was refluxed for 20 min. On cooling a white crystalline solid separated, which was filtered off, washed with diethyl ether (2 $\times$ 10 cm^3) and dried *in vacuo*. Yield 0.46 g, 68%.

[Cu{PhS(CH$_2$)$_3$SPh}$_2$]BF$_4$.—A solution of PhS(CH$_2$)$_3$SPh (0.49 g, 1.88 mmol) and [Cu(MeCN)$_4$]BF$_4$ (0.28 g, 0.89 mmol) in CH$_2$Cl$_2$ (10 cm^3) was warmed and stirred for 20 min. The reaction mixture was evaporated to an oil which was triturated with pentane (10 cm^3) and then ethanol (2 $\times$ 10 cm^3). The white product was washed with diethyl ether (10 cm^3) and dried *in vacuo*. Yield 0.30 g, 50%.

[Cu{MeSe(CH$_2$)$_3$SeMe}$_2$]PF$_6$.—A solution of MeSe-(CH$_2$)$_3$SeMe (0.55 g, 2.4 mmol) and [Cu(MeCN)$_4$]PF$_6$ (0.41 g, 1.1 mmol) in CH$_2$Cl$_2$ (15 cm^3) was refluxed for 30 min and filtered on cooling. Addition of pentane (20 cm^3) to the filtrate yielded a white solid, which was filtered off, washed with pentane (3 × 10 cm^3), and dried *in vacuo*. Yield 0.52 g, 70%.

[Cu{PhSe(CH$_2$)$_2$SePh}$_2$]PF$_6$.—A solution of PhSe(CH$_2$)$_2$-SePh (1.38 g, 4.05 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to a suspension of [Cu(MeCN)$_4$]PF$_6$ (0.75 g, 2.0 mmol) in CH$_2$Cl$_2$ (10 cm^3). The mixture was refluxed for 1 h, cooled and filtered, and the filtrate concentrated to yield an oily material. This was redissolved in CH$_2$Cl$_2$ (10 cm^3) and pentane added until the solution became cloudy. Removal of the solvent *in vacuo* left a white solid which was washed with pentane (3 × 10 cm^3) and dried *in vacuo*. Yield 1.24 g, 69%.

[Cu{MeTe(CH$_2$)$_3$TeMe}$_2$]PF$_6$.—A solution of MeTe-(CH$_2$)$_3$TeMe (1.04 g, 3.2 mmol) and [Cu(MeCN)$_4$]PF$_6$ (0.57 g, 1.53 mmol) in dry CH$_2$Cl$_2$ (15 cm^3) was refluxed for 30 min and filtered on cooling. Anhydrous diethyl ether (25 cm^3) was added to the filtrate, which became cloudy and an oily solid separated. The solvent was removed *in vacuo*, and the pale yellow solid washed with dry diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield 0.98 g, 74%.

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