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 = Me₂S, Me₂Se, Me₂Te, Ph₂S, Ph₂Se or Ph₂Te) and $[Cu(L-L)_2]PF_6$ [L-L = RE(CH₂)₂ER (E = S or Se, R = Me or Ph); RE(CH₂)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, ⁷⁷Se, ¹²⁵Te and ⁶³Cu). Variable-temperature NMR studies have been used to probe various exchange processes occurring in solution. For a limited number of complexes ⁶³Cu NMR resonances have been observed, the first examples from Group 16 donor complexes.

We have recently reported¹ 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 telluro-ethers 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 $[Y = PF_6 \text{ or } BF_4; L-L = MeS(CH_2)_nSMe, MeSe(CH_2)_nSeMe,$ $PhS(CH_2)_nSPh$ or $PhSe(CH_2)_nSePh$, n = 2 or 3; $RTe(CH_2)_3$ -TeR, R = Me or Ph; Ph₂(E)PCH₂P(E)Ph₂, 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(CH₂)₂SMe and EtS(CH₂)₂SEt.^{6,9}

The reaction of $[Cu(MeCN)_4]PF_6$ with 4 equivalents of Ph₃PE (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

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Compound	С	Н
$[Cu{MeS(CH_2)_2SMe}_2]PF_6$	21.3 (21.2)	4.1 (4.5)
Cu{MeS(CH ₂) ₃ SMe} 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)
$[Cu{PhS(CH_2)_3SPh}_2]BF_4 \cdot 0.5CH_2Cl_2^b$	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	₂ Cl ₂ was presen	t in the ¹ H

Analysis (%)^a

NMR spectra. CH_2Cl_2 was present in the "H

 $[Cu(Me_3PS)_3]^{+8}$ and Tiethof *et al.*² showed by IR spectroscopy that they are extensively dissociated in solution. The ³¹P NMR results (below) show no evidence that tetrakis complexes can be formed even with a large excess of L and are consistent with previous conclusions² 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

^{† &}lt;sup>63</sup>Cu, $I = \frac{3}{2}$, 69%, Ξ = 26.528 MHz, $D_c = 365$, quadrupole moment -0.211 × 10⁻²⁸ m²; ⁶⁵Cu, $I = \frac{3}{2}$, 31%, Ξ = 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.

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 CD₃CN showed only singlet δ (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 NMRdistinguishable 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 $^{31}P-\{^{1}H\},~^{77}Se-\{^{1}H\},~^{125}Te-\{^{1}H\}$ and ^{63}Cu NMR data are collected in Tables 3-5. The behaviour shows complex

J. CHEM. SOC. DALTON TRANS. 1994

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 ${}^{31}P{}^{1}H$ 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 Ph₃PE. Addition of an excess of Ph₃PS to a solution of [Cu(Ph₃PS)₃]PF₆ in CH₂Cl₂ resulted in only a single resonance at any temperature > 175 K. Analogous results were obtained for [Cu(Ph₃PSe)₃]PF₆ (Tables 3 and 4). The ³¹P-{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 $^{31}P\{H}$ and $^{77}Se\{H}$ data for $[Cu\{Ph_2(Se)P\{Cu}\}$ $CH_2P(Se)Ph_2_2$ PF₆ (Tables 3 and 4) are similar, showing rapid exchange between added L-L and the complex at > ca. 223 K. No ⁶³Cu 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

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$ \begin{bmatrix} Cu\{MeS(CH_2)_3SMe\}_2 \end{bmatrix} PF_6^{b} & 2.0 (q, 2 H), 2.24 (s, 6 H), 2.75 (t, 4) \\ \begin{bmatrix} Cu\{PhS(CH_2)_2SPh\}_2 \end{bmatrix} BF_4^{c} & 3.30 (s, 4 H), 7.3-7.6 (m, 10 H) \\ \begin{bmatrix} Cu\{PhS(CH_2)_3SPh\}_2 \end{bmatrix} BF_4^{a} & 2.13 (q, 2 H), 3.33 (t, 4 H), 7.2-7.6 (m, 10 H) \\ \end{bmatrix} $	
$[Cu{PhS(CH_2)_2SPh}_2]BF_4 = 3.30 (s, 4 H), 7.3-7.6 (m, 10 H) [Cu{PhS(CH_2)_3SPh}_2]BF_4 = 2.13 (q, 2 H), 3.33 (t, 4 H), 7.2-7.6 (m, 10 H) $	H)
$[Cu{PhS(CH_2)}_{3}SPh]_{2}]BF_{4}^{a}$ 2.13 (a, 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, ² J(Se-H) = 9], 3.10 [s,	$4 \text{ H}, {}^{2}J(\text{Se-H}) = 11$]
$[Cu{MeSe(CH_2)_3SeMe}_2]PF_6^b \qquad 2.0 (q, 2 H), 2.10 (s, 6 H), 2.70 (t, 4)$	H)
$[Cu{PhSe(CH_2)_2SePh)_2}]PF_6^{c} \qquad 3.35 [s, 4 H, {}^2J(Se-H) = 11], 7.2-7$.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), ⁴ 2.01 (s, 6 H), 2.75 (t, 4)	4 H)
$[Cu{PhTe(CH2)3TePh}2]PF6c 2.00 (q, 2 H), 3.00 (t, 4 H), 7.1-7.7 (t, 4 H)$	m, 10 H)
$[Cu{Ph(S)PCH_2P(S)Ph_2}_2]PF_6^c \qquad 3.90 [t, 2 H, ^2J(P-H) = 13], 7.2-7.8$	3 (m, 20 H)
$[Cu{Ph_2(Se)PCH_2P(Se)Ph_2}_2]PF_6^c \qquad 4.10 [t, 2 H, ^2J(P-H) = 13], 7.3-7.8$	3 (m, 20 H)
$[Cu(Me_2S)_4][O_3SCF_3]^4$ 2.69 (s)	
$[Cu(Me_2Se)_4][O_3SCF_3]^{a}$ 2.45 (s)	
$[Cu(Me_2 Ie)_4][O_3SCF_3]^2 \qquad 2.06 (s)$	

^a In (CD₃)₂CO. ^b In CD₃CN. ^c In CD₂Cl₂. ^{d 2}J(Te-H) not clear due to overlap of Me and CH₂ resonances.

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

Complex ^a	$\delta(^{31}P)^b$	$^{1}J(^{31}P-^{77}Se)/Hz$	δ(³¹ P) ^c	$^{1}J(^{31}P-^{77}Se)^{c}/Hz$
$[Cu(Ph_3PS)_3]^+$	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 ₂ Cl ₂ . ^b Relative to external 85% H ₃ PO ₄ .	^c Free L or I	L-L.		

Table 4 Selenium-77 and ¹²⁵Te 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 $\delta ca300$
$[Cu{MeSe(CH_2)_2SeMe}_2]^{+c}$	+ 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	$\delta + 51.5$ at 233 K
$[Cu{PhSe(CH_2)_3SePh}_2]^+$	+286	+ 289	δ + 280 at 233 K
$[Cu(Ph_2Se)_4]^{+d}$	+ 395	+416	$\delta + 368 \text{ at } 183 \text{ K}$
$[Cu(Me_2Se)_4]^{+d}$	- 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	$\delta - 14$ at 183 K
$[Cu(Ph_2Te)_4]^{+d}$	+ 578	+ 685	δ + 550 at 183 K, rapid exchange with Ph ₂ Te at > 203 K
^{<i>a</i>} In CH_2Cl_2 - CD_2Cl_2 unless indicated of	therwise. ^b Relative to e	xternal neat Me ₂ Se of	r Me ₂ Te at 300 K. ^c In MeCN–CD ₃ CN. ^d In Me ₂ CO–(CD ₃) ₂ CO

 $[CuL_4][O_3SCF_3](L = Me_2S \text{ or } Ph_2S)$. No copper NMR resonance was observed from solutions of [Cu(Me₂S)₄]-[O₃SCF₃] in acetone over the range 300–185 K. However on adding an excess of Me_2S (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 Me₂S in MeCN gave a clear solution with a similar ⁶³Cu 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 ¹H NMR spectra of mixtures of [Cu(Me₂S)₄]⁺ and Me₂S in (CD₃)₂CO show two resonances only at < ca. 235



Fig. 1 Copper-63 NMR spectra of (a) $[Cu(Me_2S)_4][O_3SCF_3] + a$ 10-fold excess of Me₂S in acetone at 183 K and (b) $[Cu{PhSe-(CH_2)_3SePh}_2]PF_6$ in MeCN at 300 K

K showing rapid exchange above this temperature. No 63 Cu resonance was seen for [Cu(Ph₂S)₄][O₃SCF₃] in CH₂Cl₂ even in the presence of an excess of Ph₂S.

[Cu(MeSCH₂CH₂SMe)₂]PF₆ and [Cu(PhSCH₂CH₂SPh)₂]-BF₄. No ⁶³Cu NMR resonances were found for solutions of either complex in CH₂Cl₂ over the accessible temperature range (300–175 K), even in the presence of added L–L.

[Cu(MeSCH₂CH₂CH₂SMe)₂]PF₆ and [Cu(PhSCH₂CH₂-CH₂SPh)₂]BF₄. The former complex exhibited δ ⁽⁶³Cu) 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(PhSCH₂-CH₂CH₂SPh)₂]BF₄ in Me₂CO at any temperature, even in the presence of an excess of L–L.

 $[CuL_4][O_3SCF_3]$ (L = Me₂Se or Ph₂Se). No ⁷⁷Se NMR resonance was detectable from a solution of $[Cu(Me_2Se)_4]^+$ in acetone at 300 K. On cooling a broad resonance ($\delta = -33$) appeared at ca. 263 K, which sharpened quickly on cooling. Addition of varying amounts of Me₂Se 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(Ph2-Se)₄]⁺ in acetone a broad resonance was present at 300 K which sharpened on cooling. The effect of adding free Ph₂Se to the solution mirrored that of the Me₂Se system. Neither complex exhibited a ⁶³Cu NMR resonance in solution at any temperature over the range 300-185 K, and no resonance was observed from solutions of [Cu(Ph₂Se)₄]⁺ containing an excess of Ph₂Se over the same temperature range. In contrast, solutions of $[Cu(Me_2Se)_4]^+$ containing a large excess of Me_2Se (>10:1 mol ratio) showed a broad ⁶³Cu signal at 283 K at δ ca. -56 ($W_{\frac{1}{2}}$ = 1500 Hz), which sharpens and drifts to higher frequency on cooling reaching $-16 (W_{1} =$ 800 Hz) at 185 K.

 $[Cu(MeSeCH_2CH_2SMe)_2]PF_6$ and $[Cu(PhSeCH_2CH_2Se-Ph)_2]PF_6$. Both complexes exhibited single ⁷⁷Se NMR resonances over the range 300–225 K, but no ⁶³Cu resonances were seen. Addition of the appropriate L–L to these solutions resulted in single ⁷⁷Se 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.

 $[Cu\{MeSe(CH_2)_3SeMe\}_2]PF_6$ and $[Cu\{PhSe(CH_2)_3SePh\}_2]PF_6$. Both complexes show relatively sharp ⁷⁷Se NMR resonances with small negative co-ordination shifts (Table 4). They also exhibited ⁶³Cu NMR resonances from MeCN solutions over the accessible temperature range (300–233 K) (Table 5 and Fig. 1). Whilst that of $[Cu\{PhSe(CH_2)_3SePh\}_2]^+$ shows the usual ¹ high-frequency shift with decreasing

Table 5 Copper-63 NMR data

Complex	$\delta(^{63}Cu) (W_{\frac{1}{2}}/Hz)^a$	Comment
$[Cu(Me_2S)_4]^{+b}$	+80(2500)	At 183 K, δ + 126, W_{\star} = 1000 Hz (only seen in presence of excess of Me ₂ S)
$[Cu{MeS(CH_2)_3SMe}_2]^+$	+ 75 (1000)	At 233 K, $\delta + 120$, $W_{\pm} = 2000$ Hz
$[Cu(Me_2Se)_4]^+ b$	- 56 (1500) (283 K)	At 185 K, $\delta - 16$, $W_{+} = 800$ Hz (only seen in presence of excess of Me ₂ Se)
$[Cu{MeSe(CH_2)_3SeMe}_2]^+$	+21 (1500) (293 K)	At 233 K, $\delta + 18$, $W_{\star} = 3500$ Hz
$[Cu{PhSe(CH_2)_3SePh}_2]^+$	+ 18 (1500)	At 233 K, $\delta + 42$, $W_{\star} = 2500$ Hz
$[Cu(Me_2Te)_4]^{+b}$	- 56 (600) (290 K)	At 193 K, $\delta - 39$, $\dot{W}_{*} = 750$ Hz (resonances quoted in presence of a large excess of
		Me_2Te , see text)
$[Cu(Ph_2Te)_4]^{+b}$	-153 (3400)	At 233 K, $\delta - 116$, $W_{\pm} = 4500$ Hz, signal disappears at <220 K (only seen in the
		presence of an excess of Ph_2Te)
$[Cu{MeTe(CH_2)_3TeMe}_2]^+$	+21 (1500)	At 230 K, δ + 13, W_{\pm} = 3000 Hz
$[Cu{PhTe(CH_2)_3TePh}_2]^{+d}$	- 36 (6000) (at 273 K)	No resonance at 300 or $< ca. 220$ K
^a At 300 K relative to [Cu(MeC	CN) ₄] ⁺ in MeCN–CD ₃ Cl	N. ^b In Me ₂ CO–(CD ₃) ₂ CO. ^c In MeCN–CD ₃ CN. ^d In CH_2Cl_2 –CD ₂ Cl ₂ .

temperature, curiously the resonance position of $[Cu{MeSe(CH_2)_3SeMe}_2]^+$ was essentially unchanged with temperature.

 $[CuL_4][O_3SCF_3] (L = Me_2Te \text{ or } Ph_2Te)$. The ¹²⁵Te NMR spectrum of [Cu(Me₂Te)₄]⁺ in acetone at 300 K was a sharp singlet, which broadened and shifted to high frequency on cooling. Rapid exchange occurred with added Me₂Te down to the freezing point of the solvent. In contrast to other $[CuL_4]^{\dagger}$ complexes, a solution of $[Cu(Me_2Te)_4]^+$ in acetone exhibited a very broad ⁶³Cu 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 Me₂Te, a sharp ⁶³Cu resonance is present at $\delta - 56 (W_{\star} = 600 \text{ Hz})$ 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_2Te gave broader ⁶³Cu resonances at intermediate chemical shifts. The sharp ⁶³Cu resonance observed in the presence of a large excess of Me₂Te must correspond to that of the tetrakis complex for which slow quadrupolar relaxation of the copper would be expected. In the absence of added Me₂Te, or with only small



Fig. 2 Copper-63 NMR spectra of (a) $[Cu(Me_2Te)_4][O_3SCF_3] + a$ 10-fold excess of Me₂Te in acetone at 300 K and (b) $[Cu-(Me_2Te)_4][O_3SCF_3]$ in acetone at 300 K

quantities of it, dissociative equilibria $[Cu(Me_2Te)_4]^+ \rightleftharpoons [Cu(Me_2Te)_3]^+ + Me_2Te \{ \rightleftharpoons [Cu(Me_2Te)_2]^+ + Me_2Te ? \}$ are probably present and exchange with the (unobserved) lower-symmetry complexes would account for these effects.¹² In the case of $[Cu(Ph_2Te)_4]^+$ in acetone a single ¹²⁵Te

In the case of $[Cu(Ph_2Te)_4]^+$ in acetone a single ¹²⁵Te 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 Ph₂Te 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 Ph₂Te and $[Cu(Ph_2Te)_4]^+$ were resolved (Fig. 3). No ⁶³Cu resonance was observed from solutions of $[Cu(Ph_2Te)_4]^+$ in acetone, but with added Ph₂Te a broad resonance at $\delta - 153$ ($W_{\frac{1}{2}} = 3400$ Hz) was present at 300 K. On cooling this broadened and disappeared altogether at < 220 K.

 $[\hat{Cu}{MeTe(CH_2)_3TeMe}_2]PF_6$ and $[Cu{PhTe(CH_2)_3Te-Ph}_2]PF_6$. The former complex exhibited a sharp singlet ¹²⁵Te NMR resonance in MeCN solution which varied little with temperature. A relatively broad ⁶³Cu resonance was present at 300 K, $\delta + 21$ ($W_{\pm} = 1500$ Hz) which broadened on cooling, but the chemical shift of which was insensitive to temperature. In contrast, although the $[Cu{PhTe(CH_2)_3TePh}_2]PF_6$ complex in CH₂Cl₂ exhibited a relatively sharp ¹²⁵Te resonance over the range 300–185 K, no ⁶³Cu signal was evident at room temperature. On cooling to 273 K a broad resonance at $\delta - 36$ ($W_{\pm} = 6000$ Hz) appeared, but on further cooling this broadened rapidly and merged into the baseline at < *ca.* 220 K.

Discussion

The homoleptic copper(1) complexes formed with monodentate Group 16 ligands R_2E , 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 ⁶³Cu NMR resonances from solutions of $[CuL_4]^+$ (L = Me₂S, Me₂Se, Me₂Te or Ph₂Te) 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



Fig. 3 The $^{125}\text{Te}{}^{1}\text{H}$ NMR spectrum of a mixture of [Cu(Ph₂-Te)₄][O₃SCF₃] + Ph₂Te in acetone at 210 K

corresponding failure to observe ⁶³Cu resonances from solutions of Ph₂S or Ph₂Se 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(1)-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 o donors than are their Group 15 analogues, 16,17 and when bound to the electron-rich d¹⁰ copper(1) 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 ⁷⁷Se and ¹²⁵Te 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 ³¹P NMR studies of the corresponding phosphine systems.¹⁸ Rare exceptions to these generalisations have been reported in some [PtMe₃X-(L-L)] systems (L-L = diseleno- or ditelluro-ether).¹⁹ In all the copper(1) 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 fiveand 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 ¹H, ⁷⁷Se or ¹²⁵Te 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 ⁶³Cu NMR spectra, since no examples from Group 16 donor complexes have been reported previously.¹⁵ ⁶³Cu resonances were observed only from a limited range of complexes (Table 5) and disappointingly no examples of ${}^{1}J$ couplings to 77 Se or 125 Te were resolved. The factors which affect the observation of ⁶³Cu NMR resonances are the rate of quadrupolar relaxation of the ⁶³Cu 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, ⁶³Cu 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 fivemembered rings deviate further from T_d geometry. The fact that $[Cu{PhS(CH_2)_3SPh}_2]^+$ fails to exhibit a ⁶³Cu resonance and that $[Cu{PhTe(CH_2)_3TePh}_2]^+$ 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 ⁶³Cu chemical shifts reported show that as in Group 15¹ 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

Physical measurements were made as described previously.²¹ The ¹H NMR spectra were recorded from solutions in CD₂Cl₂, CD₃CN or (CD₃)₂CO on JEOL FX90Q or Bruker AC300 or AM360 spectrometers, ³¹P-{¹H} spectra from 5% CD₂Cl₂-CH₂Cl₂ solutions on a Bruker AM360 at 145.8 MHz, ⁷⁷Se-{¹H} spectra at 68.68 MHz, ¹²⁵Te-{¹H} spectra at 113.6 MHz, and ⁶³Cu spectra similarly at 95.5 MHz. Phosphorus chemical shifts are reported relative to external 85% H₃PO₄, selenium shifts relative to neat external Me₂Se, tellurium shifts relative to neat external Me₂Te, and copper shifts relative to a solution of [Cu(MeCN)₄]BF₄ 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 = PF₆ or BF₄)⁷ and $[{Cu(O_3SCF_3)}_2(C_6H_6)]^{10}$ were made by literature methods. Complexes were made in dried solvents under a dry nitrogen atmosphere. The $[CuL_4][O_3SCF_3]$ complexes were stored and handled in a dry-box.

 $[CuL_4][O_3SCF_3]$ (L = Me₂S, Me₂Se, Me₂Te, Ph₂S or Ph₂Se).—The compound L (3.4 mmol) was added to [{Cu-(O_3SCF_3)}₂(C₆H₆)] (0.4 mmol) in freshly distilled benzene (10 cm³). The solvent was removed *in vacuo*, and dry diethyl ether (10 cm³) 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 × 10 cm³), and dried *in vacuo*. The complex [Cu(Ph₂Te)₄][O₃SCF₃] was made similarly, except that the oil was triturated with pentane, and the pale orange solid washed with pentane (2 × 10 cm³) and dried *in vacuo*. Yields typically 50%.

 $[Cu(Ph_3PE)_3]PF_6$.—A solution of Ph_3PE (4 mmol) and $[Cu(MeCN)_4]PF_6$ (0.37 g, 1.0 mmol) were refluxed in dry CH_2Cl_2 (15 cm³) 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 × 10 cm³), 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.

 $[Cu{MeS(CH_2)_2SMe}_2]PF_6$.—A solution of MeS(CH₂)₂-SMe (0.3 g, 3.5 mmol) and $[Cu(MeCN)_4]PF_6$ (0.56 g, 1.5 mmol) in anhydrous methanol (20 cm³) was refluxed for 20 min. On cooling a white crystalline solid separated, which was filtered off, washed with diethyl ether (2 × 10 cm³) and dried *in vacuo*. Yield 0.46 g, 68%.

 $[Cu{PhS(CH_2)_3SPh}_2]BF_4$.—A solution of PhS(CH₂)₃SPh (0.49 g, 1.88 mmol) and $[Cu(MeCN)_4]BF_4$ (0.28 g, 0.89 mmol) in CH₂Cl₂ (10 cm³) was warmed and stirred for 20 min. The reaction mixture was evaporated to an oil which was triturated with pentane (10 cm³) and then ethanol (2 × 10 cm³). The white product was washed with diethyl ether (10 cm³) and dried *in vacuo*. Yield 0.30 g, 50%.

 $[Cu{MeSe(CH_2)_3SeMe}_2]PF_6$.—A solution of MeSe-(CH₂)₃SeMe (0.55 g, 2.4 mmol) and [Cu(MeCN)₄]PF₆ (0.41 g, 1.1 mmol) in CH_2Cl_2 (15 cm³) was refluxed for 30 min and filtered on cooling. Addition of pentane (20 cm³) to the filtrate yielded a white solid, which was filtered off, washed with pentane (3 \times 10 cm³), and dried in vacuo. Yield 0.52 g, 70%.

 $[Cu{PhSe(CH_2)_2SePh}_2]PF_6$.—A solution of PhSe(CH₂)₂-SePh (1.38 g, 4.05 mmol) in CH₂Cl₂ (10 cm³) was added to a suspension of $[Cu(MeCN)_4]PF_6$ (0.75 g, 2.0 mmol) in CH₂Cl₂ (10 cm³). The mixture was refluxed for 1 h, cooled and filtered, and the filtrate concentrated to yield an oily material. This was redissolved in CH₂Cl₂ (10 cm³) and pentane added until the solution became cloudy. Removal of the solvent in vacuo left a white solid which was washed with pentane $(3 \times 10 \text{ cm}^3)$ and dried in vacuo. Yield 1.24 g, 69%.

(0.57 g, 1.53 mmol) in dry CH₂Cl₂ (15 cm³) 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 $(2 \times 10 \text{ cm}^3)$ and dried in vacuo. Yield 0.98 g, 74%.

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J. CHEM. SOC. DALTON TRANS. 1994

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