Reactions of Copper(II) with $[S_2P(OR)_2]^-$ (R = Et or Pr^i) and Single-crystal *X*-Ray Studies of $Cu[S_2P(OEt)_2]{\cdot}bipy$ and $Cu[S_2P(OEt)_2]{\cdot}2PPh_3$*

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The position of the equilibrium (i) (R = Et or Pr^i) has been shown to be solvent dependent. The

$$2Cu[S_2P(OR)_2]_2 \rightleftharpoons 2Cu[S_2P(OR)_2] + [(RO)_2P(S)S\text{–}]_2 \qquad (i)$$

addition of nitrogen bases or triphenylphosphine affects the position of the equilibrium; for instance aromatic bases and PPh_3 favour the formation of copper(I) adducts. The structures of two such adducts, $Cu[S_2P(OEt)_2]{\cdot}bipy$ (**1**) (bipy = 2,2′-bipyridyl) and $Cu[S_2P(OEt)_2]{\cdot}2PPh_3$ (**2**), have been determined by *X*-ray methods. Complex (**1**) is triclinic, space group $P\bar{1}$, with a = 9.388(6), b = 10.208(7), c = 10.704(7) Å, α = 95.88(5), β = 68.44(5), γ = 115.94(6)°, and Z = 2. 2 190 Independent reflections above background were measured and the structure refined to R 0.080. Complex (**2**) is monoclinic, space group $P2_1/n$, with a = 11.88(1), b = 14.70(1), c = 22.09(1) Å, β = 91.0(1)°, and Z = 4. 4 087 Independent reflections above background were measured and the structure refined to R = 0.056. Complex (**1**) exists as a centrosymmetric dimer with a $\overline{\text{Cu–S–P–S–Cu–S–P–S}}$ chair-shaped ring in which two $S_2P(OEt)_2$ groups bridge two four-co-ordinate metal atoms. The co-ordination spheres of the metal atoms consist of two sulphur atoms [Cu–S(1) 2.347(3), Cu–S(2) 2.323(4) Å] and two nitrogen atoms from chelating bipy groups [Cu–N(1) 2.059(10), Cu–N(2) 2.132(8) Å], making up a distorted tetrahedral environment. Complex (**2**) is monomeric, with the metal atom bound to two PPh_3 molecules [Cu–P(1) 2.282(2), Cu–P(2) 2.264(2) Å] and a $[S_2P(OEt)_2]^-$ ion [Cu–S(1) 2.453(2), Cu–S(2) 2.440(2) Å] to give an approximately tetrahedral co-ordination sphere.

The reactions between copper(II) and $[S_2P(OR)_2]^-$ are of interest for two reasons. First, zinc dialkyl dithiophosphates are used as anti-wear and anti-oxidant additives in engine oils.[1] In the course of engine bearing wear copper(II) is likely to be generated and may react with free $[S_2P(OR)_2]^-$ thus causing a modification of the engine oil. Secondly, in the degradation of certain organophosphorus pesticides, free $[S_2P(OR)_2]^-$ ions are produced and these possibly interact with trace elements such as copper and make them unavailable to plants and animals.[2]

We decided to investigate the copper–dialkyl dithiophosphate interaction and the effect of nitrogen bases upon the system because amine mixtures are added to engine oil together with zinc dialkyl dithiophosphates. Previous work in this area has led to conflicting reports. Some groups have reported the isolation of copper(II) compounds[3–5] {*i.e.* $Cu[S_2P(OR)_2]_2$} while others suggest that $[S_2P(OR)_2]^-$ reduces copper(II) according to the equilibrium reaction (1).[2,6–8]

$$2Cu^{2+} + 4[S_2P(OR)_2]^- \rightleftharpoons 2Cu[S_2P(OR)_2] + [(RO)_2P(S)S\text{–}]_2 \qquad (1)$$

Experimental

Solvents were used as supplied and constant boiling ethanol was used throughout. Ammonium dialkyl dithiophosphate was prepared as described previously.[1] Analytical data for all the compounds are given in Table 1.

Preparations.—(*i*) *Light brown solids with analyses approximating to those required for* $Cu[S_2P(OR)_2]_2$. A solution of $CuSO_4{\cdot}5H_2O$ (0.049 mol, 100 cm^3 H_2O) was added to a solution of $NH_4[S_2P(OR)_2]$ (0.098 mol, 200 cm^3 H_2O) (R = Et or Pr^i). Brown precipitates formed whose analyses were close to those expected for $Cu[S_2P(OR)_2]_2$.

(*ii*) $Cu[S_2P(OEt)_2]$. The mixture formed in (*i*) (R = Et) was extracted with CH_2Cl_2 (300 cm^3). The black organic layer was separated from the aqueous layer and the solvent removed. The resulting sticky, black solid was stirred with methanol (200 cm^3) from which white $Cu[S_2P(OEt)_2]$ precipitated. This was recrystallised from CH_2Cl_2–$C_6H_5CH_3$ (1:1, v/v). Yield: 82%.

The analogous compound with R = Pr^i was obtained by the method of Dickert and Rowe.[9]

(*iii*) $Cu[S_2P(OR)_2]{\cdot}L$ [R = Et, L = 2,2′-*bipyridyl* (bipy) *or* 1,10-*phenanthroline* (phen); R = Et *or* Pr^i, L = 2,9-*dimethyl*-1,10-*phenanthroline* (dmphen) *or* $2PPh_3$]. A solution of $CuCl_2{\cdot}2H_2O$ (0.0059 mol, 20 cm^3 EtOH) was added with stirring to a warm, filtered solution of $NH_4[S_2P(OR)_2]$ (0.0188 mol) and L (0.0559 mol or 0.0118 mol PPh_3) in ethanol (40 cm^3). The crystalline solid (white for $2PPh_3$, red for all other L) which precipitated was filtered off by suction, washed with water followed by light petroleum (b.p. 40—60 °C), and dried *in vacuo* over BaO. Yields: 75—85%.

The filtrates from the dmphen and PPh_3 reactions yielded a further portion of the appropriate copper(I) compound, $Cu[S_2P(OR)_2]{\cdot}L$, and $[(RO)_2P(S)S\text{–}]_2$. By contrast the green filtrates from the other reactions gave $Cu(OH)_2{\cdot}L$ and $[(RO)_2P(S)S\text{–}]_2$.

(*iv*) $Cu[S_2P(OEt)_2]{\cdot}L$ (L = bipy *or* $2PPh_3$) *prepared from* $Cu[S_2P(OEt)_2]$. A solution of bipy (0.006 mol) or PPh_3 (0.012

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* Di-μ-(diethyl dithiophosphato)-bis[2,2′-bipyridylcopper(I)] and (diethyl dithiophosphato-*S,S*′)bis(triphenylphosphine)copper(I) respectively.

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

Table 1. Analytical data (%)

Complex	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
Cu[S$_2$P(OEt)$_2$]	19.4	4.0		19.3	4.05	
Cu[S$_2$P(OEt)$_2$]·bipy	41.5	4.4	6.9	41.5	4.5	6.9
Cu[S$_2$P(OEt)$_2$]·phen	45.3	4.4	6.6	44.8	4.25	6.55
Cu[S$_2$P(OEt)$_2$]·dmphen	47.35	4.9	6.05	47.3	4.85	6.15
Cu[S$_2$P(OEt)$_2$]·2PPh$_3$	61.9	5.3		62.1	5.2	
Cu[S$_2$P(OPr^i)$_2$]·bipy	43.6	4.8	6.6	44.4	5.1	6.45
Cu[S$_2$P(OPr^i)$_2$]·phen·C$_6$H$_5$CH$_3$	53.3	5.55	5.2	54.7	5.5	5.1
Cu[S$_2$P(OPr^i)$_2$]·phen·Pr^{i}OH	48.35	5.8	5.25	48.8	5.85	5.4
Cu[S$_2$P(OPr^i)$_2$]·dmphen	49.6	5.45	5.7	49.5	5.4	5.75
Cu[S$_2$P(OPr^i)$_2$]·2PPh$_3$	63.05	5.65		62.95	5.55	
Cu[S$_2$P(OPr^i)$_2$]$_2$·bipy	40.4	5.6	4.15	40.9	5.6	4.3
Cu[S$_2$P(OPr^i)$_2$]·phen·PPh$_3$	60.2	5.15	3.8	60.1	5.2	3.9
Cu[S$_2$P(OPr^i)$_2$]·dmphen·PPh$_3$	61.2	5.55	3.65	61.05	5.55	3.75
Cu[S$_2$P(OEt)$_2$]·phen·PPh$_3$	59.25	4.8	3.95	59.1	4.8	4.05
[Cu(en)$_2$][S$_2$P(OEt)$_2$]$_2$	26.3	6.5	10.1	26.0	6.55	10.1
[Cu(dmen)$_2$][S$_2$P(OEt)$_2$]$_2$	30.9	7.25	9.45	31.5	7.25	9.2
[Cu(en)$_2$][S$_2$P(OPr^i)$_2$]$_2$	31.3	7.35	9.2	31.5	7.25	9.2

Table 2. Crystal data for complexes Cu[S$_2$P(OEt)$_2$]·bipy (**1**) and Cu[S$_2$P(OEt)$_2$]·2PPh$_3$ (**2**)

Compound	(**1**)	(**2**)
Formula	C$_{14}$H$_{15}$CuN$_2$O$_2$PS$_2$	C$_{40}$H$_{40}$CuO$_4$P$_3$S$_2$
M	404.8	773.3
F(000)	832	1 608
Z	2	4
Space group	$P\bar{1}$	$P2_1/n$
a/Å	9.388(6)	11.88(1)
b/Å	10.208(7)	14.70(1)
c/Å	10.704(7)	22.09(1)
α/°	95.88(5)	
β/°	68.44(5)	91.0(1)
γ/°	115.94(6)	
U/Å^3	855.84	3 857.12
D_m/g cm^{-3} (flotation)	1.56	1.33
D_c/g cm^{-3}	1.55	1.33
μ/cm^{-1}	16.6	8.22
Number of unique reflections	3 155	5 712
Criteria for inclusion	$I > 5\sigma(I)$	$I > 2\sigma(I)$
Reflections used in refinement	2 190	4 087
Final *R*	0.080	0.056
Final *R′*	0.084	0.057

mol) in ethanol (50 cm^3) was added to a solution of Cu[S$_2$P(OEt)$_2$] (0.006 mol) in CH$_2$Cl$_2$ (100 cm^3). Crystals of the products separated as the solvents evaporated. Yields: 80—85%.

(*v*) Cu[S$_2$P(OPr^i)$_2$]$_2$·bipy. This complex is very soluble in ethanol. Thus it was prepared by a method similar to (*iii*) except that the CuCl$_2$·2H$_2$O was dissolved in ethanol–water (20 cm^3, 1:1). The dark green precipitate was isolated immediately, washed with water, and dried *in vacuo* over BaO. Yield: 70%.

(*vi*) Cu[S$_2$P(OPr^i)$_2$]·bipy. Aqueous solutions of NH$_4$[S$_2$P(OPr^i)$_2$] (0.0118 mol, 40 cm^3) and CuSO$_4$·5H$_2$O (0.0058 mol, 20 cm^3) were mixed and the resulting brown solid extracted into CH$_2$Cl$_2$ (100 cm^3) to give a black solution. To the dried extract (Na$_2$SO$_4$) was added bipy (0.0058 mol) dissolved in CH$_2$Cl$_2$ (5 cm^3). A reddish brown solution formed to which was added light petroleum (40 cm^3, b.p. 80—100 °C). The CH$_2$Cl$_2$ was allowed to evaporate whence sticky red crystals of Cu[S$_2$P(OPr^i)$_2$]·bipy separated. These were recrystallised from light petroleum (b.p. 100—120 °C). Yield: 55%.

(*vii*) Cu[S$_2$P(OPr^i)$_2$]·phen. The conditions of reaction (*v*) were used but with phen in place of bipy. A sticky brown solid was obtained which was separated from the reaction mixture, dissolved in boiling toluene (25 cm^3) and the solution filtered into hot light petroleum (50 cm^3, b.p. 100—120 °C). As the solution cooled, red crystals of Cu[S$_2$P(OPr^i)$_2$]·phen with solvent toluene (1:1) were obtained. Recrystallisation from propan-2-ol gave crystals of the propan-2-ol solvate.

(*viii*) Cu[S$_2$P(OR)$_2$]·L·PPh$_3$ (L = phen, R = Et *or* Pr^i; L = dmphen, R = Pr^i). A hot solution of L (0.0038 mol) in toluene (10 cm^3) was added to a hot solution of Cu[S$_2$P(OR)$_2$]·2PPh$_3$ (0.0038 mol) in toluene (20 cm^3). A yellow or orange (dependent on L and R) crystalline precipitate of Cu[S$_2$P(OR)$_2$]·L·PPh$_3$ separated almost immediately. This was isolated from the cooled solution, washed with light petroleum (b.p. 100—120 °C), and dried *in vacuo*. Yields: 85—90%.

(*ix*) [CuL$_2$][S$_2$P(OR)$_2$]$_2$ [R = Et *or* Pr^i, L = H$_2$NCH$_2$CH$_2$NH$_2$ (en); R = Et, L = MeHNCH$_2$CH$_2$NHMe (dmen)]. L (0.0118 mol) was added to the black CH$_2$Cl$_2$ solution obtained as in (*vi*). A deep blue solution formed immediately. This was diluted with light petroleum (50 cm^3, b.p. 100—120 °C) and as the CH$_2$Cl$_2$ evaporated purple crystals of [CuL$_2$][S$_2$P(OR)$_2$]$_2$ were obtained. Yields: 65—75%.

The compound [Cu(en)$_2$][S$_2$P(OEt)$_2$]$_2$ may also be prepared by method (*iii*). The other ionic compounds are very soluble in ethanol and difficult to isolate using this method.

(*x*) *Reaction of* O$_2$ *with* Cu[S$_2$P(OEt)$_2$]·L (L = bipy *or* dmen). L = bipy. A CH$_2$Cl$_2$ solution of Cu[S$_2$P(OEt)$_2$] (0.006 mol, 150 cm^3) was placed in a three-necked flask fitted with N$_2$ and O$_2$ inlets. The solution was flushed with N$_2$ saturated with CH$_2$Cl$_2$ after which a CH$_2$Cl$_2$ solution of bipy (0.006 mol) was added and the mixture turned red rapidly. After several hours the N$_2$ flow was replaced by one of O$_2$. A slow reaction took place and a blue solid, Cu(OH)$_2$·bipy·2H$_2$O, was deposited over a period of several days. [(EtO)$_2$P(S)S–]$_2$ was subsequently obtained from the solution.

L = dmen. The method was essentially that adopted for L = bipy. The addition of dmen produced no colour change but the passage of O$_2$ immediately gave an emerald green solution. After 30 min the solvent was removed using a rotary evaporator and dark green oil was obtained from which only [(EtO)$_2$P(S)S–]$_2$ and a blue non-stoicheiometric Cu–OH–dmen species were obtained.

Physical Measurements.—I.r. spectra of Nujol mulls were obtained using Perkin-Elmer 683 or 983 spectrometers. ^{1}H N.m.r. spectra of solutions in $CDCl_3$ were recorded with either a Varian T-60 or HA-100 apparatus.

Single-crystal X*-Ray Determinations of* $Cu[S_2P(OEt)_2]\cdot bipy$ (**1**) *and* $Cu[S_2P(OEt)_2]\cdot 2PPh_3$ (**2**).—Crystal data for (**1**) and (**2**) are given in Table 2. Intensity data were obtained with a Stoe Stadi-2 diffractometer using Zr-filtered Mo-K_α radiation and ω scans of width (1.5 + 0.5 sin μ/tan θ). The scan speed was 0.033° s^{-1} and the background was measured at the ends of the ω scans for 20 s. Measurements of standard reflections showed no deterioration throughout the periods of data collection. The structures were determined by the heavy-atom method. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions at 0.95 Å from the carbon atom to which they were bonded. In (**1**) they were given one of three overall isotropic thermal parameters [CH_3, CH_2, or CH(aromatic)] all of which were refined. In (**2**) hydrogen atoms in each phenyl ring were given a common thermal parameter while hydrogen atoms in methylene or methyl groups bonded to the same carbon atom were given a common thermal parameter.

The weighting schemes used were $w = 1/[\sigma^2(F) + 0.000\,06F^2]$ for (**1**) and $w = 1/[\sigma^2(F) + 0.003F^2]$ for (**2**) where $\sigma(F)$ was taken from counting statistics. Scattering factors and dispersion corrections were taken from ref. 10. Calculations were carried out using SHELX 76[11] on the Amadahl V7 computer of the University of Reading. Final R values were 0.080 (R' 0.084) for (**1**) and 0.056 (R' 0.057) for (**2**).

Atomic co-ordinates for (**1**) and (**2**) are given in Tables 3 and 4 and the geometries of the metal co-ordination spheres in Tables 5 and 6.

Table 3. Atomic co-ordinates (× 10^4) for $Cu[S_2P(OEt)_2]\cdot bipy$ (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	670(2)	1 845(1)	592(1)
S(1)	2 528(3)	2 346(3)	−1 663(3)
S(2)	1 066(3)	425(3)	1 880(3)
P	1 315(3)	1 028(3)	−2 784(3)
N(1)	−1 593(10)	1 987(9)	1 093(8)
N(2)	1 301(10)	4 005(8)	1 244(9)
O(1)	2 513(9)	315(7)	−3 671(7)
O(2)	1 240(9)	1 986(7)	−3 859(7)
C(11)	1 973(21)	−728(18)	−4 604(18)
C(12)	2 892(26)	−1 634(18)	−4 952(16)
C(21)	2 816(18)	3 118(16)	−4 757(14)
C(22)	2 467(22)	4 015(20)	−5 474(19)
C(601)	−3 078(12)	904(10)	1 102(10)
C(501)	−4 519(12)	1 102(10)	1 445(11)
C(401)	−4 469(14)	2 467(12)	1 740(12)
C(301)	−2 976(13)	3 569(11)	1 765(10)
C(201)	−1 577(12)	3 276(10)	1 443(10)
C(202)	56(12)	4 434(9)	1 503(9)
C(302)	298(14)	5 840(10)	1 828(11)
C(402)	1 809(14)	6 830(11)	1 899(11)
C(502)	3 070(14)	6 401(11)	1 651(11)
C(602)	2 773(12)	4 974(10)	1 329(11)

Results and Discussion

The reactions of copper(II) with $[S_2P(OR)_2]^-$ (R = Et or Pr^i) are summarised in the Scheme. The interaction of copper(II) and $NH_4[S_2P(OR)_2]$ (R = Et or Pr^i) in aqueous solution gives light brown solids that have analyses close to those required for $Cu[S_2P(OR)_2]_2$ [see Scheme, reaction (*i*)]. However a comparison of their i.r. spectra with those of pure $Cu[S_2P(OR)_2]$, $Zn[S_2P(OR)_2]_2$, and $[(RO)_2P(S)S-]_2$ demonstrates that the light brown solids contain significant amounts of the disulphides $[(RO)_2P(S)S-]_2$, with bands at 463 and 502 cm^{-1} (R = Et) and 455 and 500 cm^{-1} (R = Pr^i) not present in the spectra of the pure metal complexes. Solutions of the light brown solids in CH_2Cl_2 give strong e.s.r. signals of a type that are characteristic of copper(II) and identical to those

Table 4. Atomic co-ordinates (× 10^4) for $Cu[S_2P(OEt)_2]\cdot 2PPh_3$ (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	10 417.3(5)	2 231.7(4)	2 170.3(3)
P(1)	9 383(1)	2 321(1)	1 292(1)
C(21)	8 671(4)	3 397(3)	1 128(2)
C(31)	10 211(4)	2 134(4)	611(2)
C(41)	8 223(4)	1 502(3)	1 218(3)
C(22)	8 142(4)	3 820(4)	1 611(3)
C(23)	7 555(5)	4 622(4)	1 521(3)
C(24)	7 483(5)	5 008(4)	960(3)
C(25)	8 008(6)	4 595(4)	477(3)
C(26)	8 607(5)	3 796(4)	562(3)
C(32)	10 048(5)	1 406(4)	229(3)
C(33)	10 764(6)	1 269(5)	−261(3)
C(34)	11 613(6)	1 866(6)	−368(3)
C(35)	11 760(6)	2 604(5)	−3(3)
C(36)	11 085(5)	2 741(4)	494(3)
C(42)	8 301(6)	692(4)	1 526(3)
C(43)	7 412(8)	77(5)	1 504(4)
C(44)	6 452(6)	268(5)	1 172(3)
C(45)	6 375(5)	1 062(5)	849(4)
C(46)	7 261(5)	1 673(4)	871(3)
P(2)	12 233(1)	1 803(1)	2 060(1)
C(51)	13 157(4)	2 682(3)	1 764(3)
C(61)	12 324(4)	829(4)	1 553(3)
C(71)	13 018(4)	1 411(3)	2 730(3)
C(52)	12 751(5)	3 553(4)	1 729(3)
C(53)	13 409(6)	4 259(4)	1 516(3)
C(54)	14 489(6)	4 094(5)	1 352(3)
C(55)	14 928(5)	3 238(5)	1 407(3)
C(56)	14 274(5)	2 531(4)	1 613(3)
C(62)	12 842(5)	830(4)	995(3)
C(63)	12 813(7)	65(5)	634(3)
C(64)	12 265(8)	−703(5)	814(4)
C(65)	11 735(6)	−709(5)	1 365(4)
C(66)	11 757(6)	43(4)	1 729(4)
C(72)	13 826(4)	710(4)	2 723(3)
C(73)	14 399(5)	483(4)	3 250(3)
C(74)	14 220(6)	951(5)	3 784(3)
C(75)	13 431(6)	1 620(5)	3 790(3)
C(76)	12 837(4)	1 853(4)	3 270(3)
S(1)	10 220(1)	3 460(1)	2 913(1)
P(3)	9 217(1)	2 517(1)	3 239(1)
S(2)	9 602(1)	1 287(1)	2 958(1)
O(11)	7 961(3)	2 805(3)	3 076(2)
O(14)	9 154(4)	2 550(3)	3 957(2)
C(12)	7 018(5)	2 186(5)	3 049(4)
C(13)	5 970(6)	2 760(7)	2 958(4)
C(15)	10 178(9)	2 465(10)	4 327(4)
C(16)	10 180(11)	1 752(12)	4 724(7)

previously reported.[3,7,12,13] An identical spectrum was also obtained from the brown solution produced when pure samples of the white compounds $Cu[S_2P(OEt)_2]$ and $[(EtO)_2P(S)S-]_2$ (2:1 molar ratio) were dissolved in CH_2Cl_2. The evidence thus suggests that the equilibrium depicted in equation (1) occurs.

The position of equilibrium (1) can be altered by use of suitable solvents or solvent mixtures. Thus if methanol is added to the CH_2Cl_2 extract of the brown solid, formed by mixing copper(II) and $[S_2P(OEt)_2]^-$, a white precipitate of the copper(I) compound $Cu[S_2P(OEt)_2]$ is formed [see Scheme, reaction (*ii*)].

The above leads us to believe that reports of the isolation of copper(II) compounds of the type $Cu[S_2P(OR)_2]_2$ must be treated with some scepticism unless, as in the case of $Cu[S_2P(OC_6H_4Me\text{-}o)_2]_2$,[14] there is evidence provided by a single-crystal study.

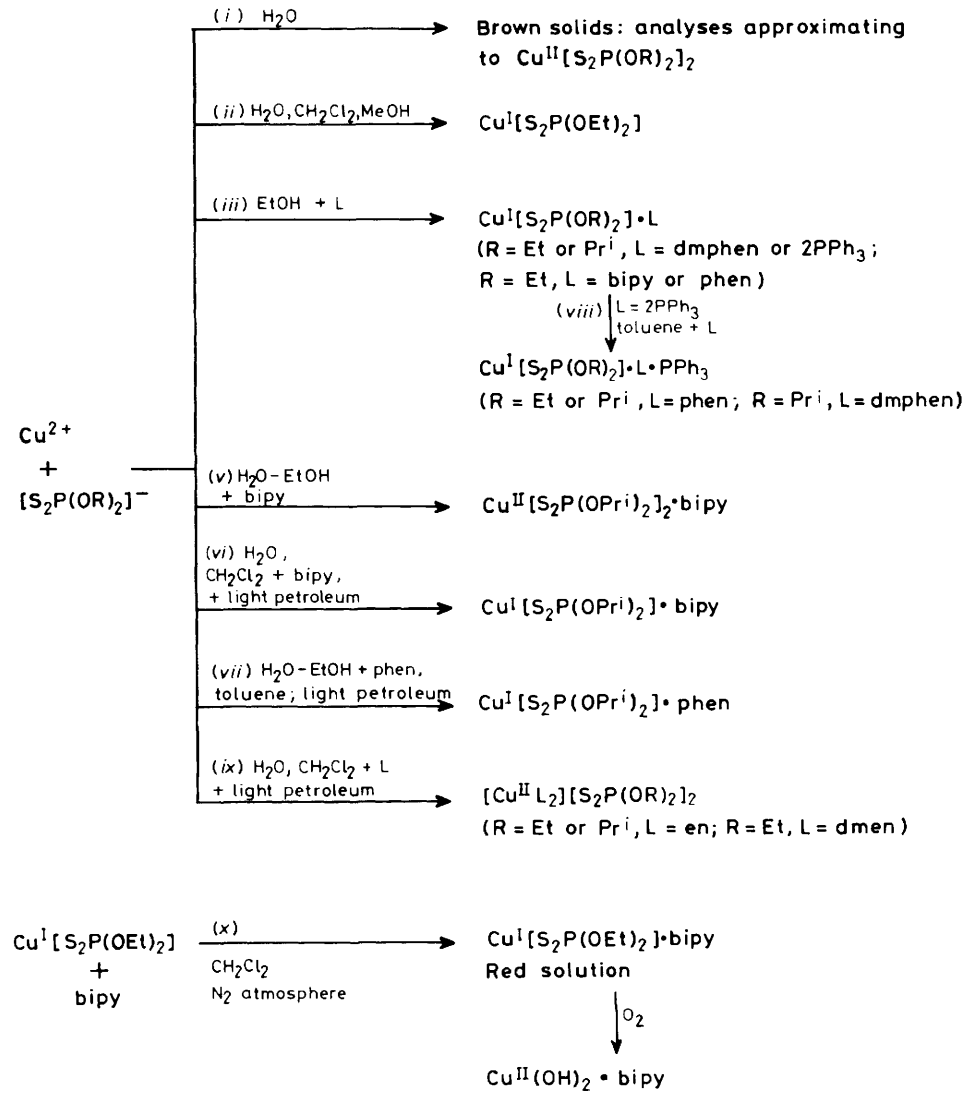
Table 5. Important bond lengths (Å) and angles (°) in $Cu[S_2P(OEt)_2]\cdot$bipy (**1**)*

S(1)–Cu	2.347(3)	N(2)–Cu	2.132(8)
S(2)–Cu	2.323(4)	P–S(1)	1.969(4)
N(1)–Cu	2.059(10)	P–S(2′)	1.984(3)
S(2)–Cu–S(1)	114.68(13)	N(2)–Cu–N(1)	78.33(34)
N(1)–Cu–S(1)	118.73(28)	P–S(1)–Cu	108.60(12)
N(2)–Cu–S(1)	100.43(21)	P′–S(2)–Cu	100.40(18)
N(1)–Cu–S(2)	122.59(25)	S(2′)–P–S(1)	118.36(17)
N(2)–Cu–S(2)	111.43(32)		

* Primed atoms indicate symmetry operation $-x, -y, -z$.

Table 6. Selected bond lengths (Å) and angles (°) in $Cu[S_2P(OEt)_2]\cdot 2PPh_3$ (**2**)

Cu–P(1)	2.282(2)	Cu–S(2)	2.440(2)
Cu–P(2)	2.264(2)	S(1)–P(3)	1.973(2)
Cu–S(1)	2.453(2)	P(3)–S(2)	1.967(2)
P(1)–Cu–P(2)	115.07(6)	S(1)–Cu–S(2)	84.17(5)
P(1)–Cu–S(1)	118.03(5)	Cu–S(2)–P(3)	78.43(7)
P(2)–Cu–S(1)	112.29(5)	Cu–S(1)–P(3)	78.00(7)
P(1)–Cu–S(2)	115.11(6)	S(1)–P(3)–S(2)	112.69(9)
P(2)–Cu–S(2)	108.03(6)		



Scheme. (*i*)—(*x*) Refer to the preparations given in the Experimental section

Reactions with Nitrogen Bases (L).—The nature of the product isolated when nitrogen ligands are added to copper(II) and $\mathrm{[S_2P(OR)_2]^-}$ [equation (2)] varies with the ligand, the

$$2\mathrm{Cu[S_2P(OR)_2]_2{\cdot}L} \rightleftharpoons 2\mathrm{Cu[S_2P(OR)_2]{\cdot}L} + \mathrm{[(RO)_2P(S)S-]_2} \quad (2)$$

solvent, and the R group. The effects of these factors on the position of the equilibrium is illustrated by a consideration of the conditions which lead to the isolation of $\mathrm{Cu[S_2P(OR)_2]{\cdot}L}$, $\mathrm{Cu[S_2P(OPr^i)_2]_2{\cdot}bipy}$, and $\mathrm{[CuL_2][S_2P(OR)_2]_2}$.

Formation of $\mathrm{Cu[S_2P(OR)_2]{\cdot}L}$. These copper(I) compounds (R = Et, L = bipy, phen, dmphen, or $\mathrm{2PPh_3}$, R = $\mathrm{Pr^i}$, L = dmphen or $\mathrm{2PPh_3}$) were readily formed when ethanolic solutions of copper(II) salts were mixed with solutions of $\mathrm{NH_4[S_2P(OR)_2]}$ and L [see Scheme, reaction (*iii*)]. However the complexes with R = $\mathrm{Pr^i}$ and L = bipy or phen cannot be obtained by this simple method. To isolate $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}bipy}$ it was necessary to mix $\mathrm{Cu^{II}}$ and $\mathrm{[S_2P(OPr^i)_2]^-}$ in water, change the solvent by extracting the product into $\mathrm{CH_2Cl_2}$ and then add bipy followed by light petroleum. {See Scheme reaction (*vi*) and for route to $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}phen}$ see (*vii*)}.

Formation of $\mathrm{Cu[S_2P(OPr^i)_2]_2{\cdot}bipy}$. Whilst the copper(I) compound $\mathrm{Cu[S_2P(OEt)_2]{\cdot}bipy}$ is readily obtained from ethanolic solution as described above, similar reactions with R = $\mathrm{Pr^i}$ lead to the isolation of the green copper(II) compound $\mathrm{Cu[S_2P(OPr^i)_2]_2{\cdot}bipy}$ [see Scheme, reaction (*v*)] which has a room-temperature magnetic moment of 1.8 B.M. and a strong e.s.r. signal. All attempts to isolate an equivalent compound with R = Et led to the formation of copper(I) compounds. Indeed, we were unable to obtain any other $\mathrm{Cu^{II}}$ complex containing an aromatic nitrogen base.

Formation of $\mathrm{[CuL_2][S_2P(OR)_2]_2}$. These ionic copper(II) compounds (R = Et or $\mathrm{Pr^i}$, L = en; R = Et, L = dmen) are obtained from $\mathrm{Cu^{II}}$ starting materials irrespective of solvent. They have a high solubility in many solvents and are best prepared by the addition of L to the $\mathrm{CH_2Cl_2}$ extract of an aqueous mixture of $\mathrm{Cu^{II}}$ and $\mathrm{[S_2P(OR)_2]^-}$ [see Scheme, reaction (*ix*)].

The ability of nitrogen ligands to stabilise copper(II) relative to copper(I) has been shown to decrease in the order en > bipy > phen > dmphen [15] and the results reported here are in accord with this series. No data are available for $\mathrm{PPh_3}$ but being a 'soft' ligand it is expected to stabilise copper(I). This is illustrated by its effect on the reaction of $\mathrm{CuCl_2}$–$\mathrm{[S_2P(OPr^i)_2]^-}$–phen mixtures in 96% ethanol. Without added $\mathrm{PPh_3}$ no $\mathrm{[S_2P(OPr^i)_2]^-}$ complex is obtained, the solution remains dark green and ammonia is slowly evolved (due to the production of $\mathrm{OH^-}$ in the presence of $\mathrm{NH_4^+}$, see below). When $\mathrm{PPh_3}$ ($\mathrm{Cu:PPh_3}$ 1:1 molar ratio) is incorporated in the reaction mixture $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}phen}$ is precipitated together with some $\mathrm{SPPh_3}$ which is formed by sulphur abstraction either from $\mathrm{[S_2P(OPr^i)_2]^-}$ or $\mathrm{[(RO)_2P(S)S-]_2}$. If the $\mathrm{Cu:PPh_3}$ ratio is increased to 1:3 only yellow solutions are obtained, but treating $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}2PPh_3}$ with L (L = phen or dmphen) in toluene gave the mixed-ligand complexes $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}L{\cdot}PPh_3}$ [see Scheme, reaction (*viii*)]. Mixed-ligand complexes were not obtained with bipy, the starting materials being recovered from the reaction mixture.

Formation of $\mathrm{Cu(OH)_2{\cdot}L}$ (L = bipy *or* phen) via *Reaction* (3).—The compounds $\mathrm{Cu[S_2P(OR)_2]{\cdot}L}$ (L = bipy or phen)

$$2\mathrm{Cu[S_2P(OR)_2]{\cdot}L} + \mathrm{O_2} + 2\mathrm{H_2O} \longrightarrow 2\mathrm{Cu(OH)_2{\cdot}L} + \mathrm{[(RO)_2P(S)S-]_2} \quad (3)$$

can be isolated by a variety of reactions in which it is not necessary to exclude air or moisture (see Scheme and discussion above). However if saturated ethanolic solutions of these complexes are left exposed to the atmosphere for a few days (R = $\mathrm{Pr^i}$) or several weeks (R = Et), both $\mathrm{Cu(OH)_2{\cdot}bipy}$ and $\mathrm{[(RO)_2P(S)S-]_2}$ crystallise from solution. The influence of the nitrogen base on this process was investigated by passing oxygen into solutions containing $\mathrm{Cu[S_2P(OEt)_2]}$ and bipy or dmen [see Scheme, reaction (*x*)]. With bipy a slow reaction ensued and blue crystalline $\mathrm{Cu(OH)_2{\cdot}bipy}$ was deposited over a period of several days, whereas reactions in which bipy was replaced by dmen were very rapid and yielded a blue non-stoicheiometric Cu–OH–dmen species.

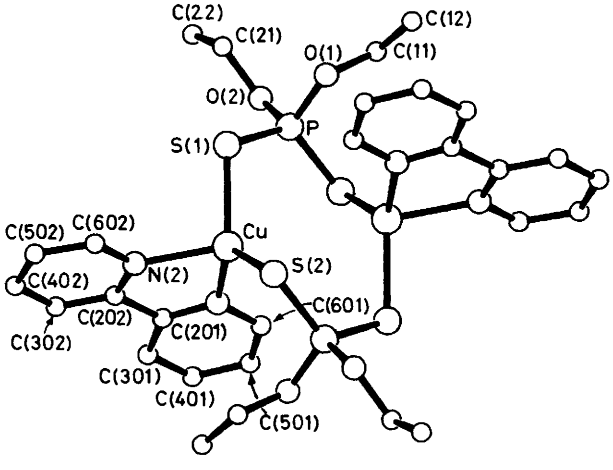


Figure 1. Molecular structure of $\mathrm{Cu[S_2P(OEt)_2]{\cdot}bipy}$ (**1**)

The sensitivity of reaction (3) to the nature of L (L = $\mathrm{2PPh_3}$, bipy, phen, or dmphen) is also demonstrated by ^{1}H n.m.r. measurements on $\mathrm{CDCl_3}$ solutions of $\mathrm{Cu[S_2P(OR)_2]{\cdot}L}$ (R = Et or $\mathrm{Pr^i}$). With L = bipy or phen noisy spectra are obtained and $\mathrm{Cu(OH)_2{\cdot}L}$ ultimately separates from solution, whereas compounds with L = $\mathrm{2PPh_3}$ or dmphen give sharp, well defined spectra. The ^{1}H n.m.r. spectra of $\mathrm{CDCl_3}$ solutions of $\mathrm{Cu[S_2P(OR)_2]{\cdot}phen{\cdot}PPh_3}$ show the influence of R on reaction (3). The complex with R = Et gives sharp resonances whereas by contrast that with R = $\mathrm{Pr^i}$ produces broad resonances and ultimately $\mathrm{Cu(OH)_2{\cdot}phen}$ precipitates.

The effect of solvent on reaction (3) can be considerable. If the reaction between $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}2PPh_3}$ and phen is carried out in toluene the mixed compound $\mathrm{Cu[S_2P(OPr^i)_2]{\cdot}phen{\cdot}PPh_3}$ is obtained as discussed above [see Scheme, reaction (*viii*)]. However by mixing the reactants in $\mathrm{CCl_4}$, blue $\mathrm{Cu(OH)_2{\cdot}phen}$ and $\mathrm{[(Pr^iO)_2P(S)S-]_2}$ are immediately formed.

The Crystal Structures of $\mathrm{Cu[S_2P(OEt)_2]{\cdot}bipy}$ (**1**) *and* $\mathrm{Cu[S_2P(OEt)_2]{\cdot}2PPh_3}$ (**2**).—Only two copper dialkyl dithiophosphate structures have been reported. The copper(I) compound $\mathrm{Cu[S_2P(OPr^i)_2]}$ contains tetrameric units [14,16] which are formed *via* both Cu–Cu bonds and bridging $\mathrm{S_2P(OPr^i)_2}$ moieties, whilst the copper(II) compound $\mathrm{Cu[S_2P(OC_6H_4Me\text{-}\mathit{o})_2]_2}$ [14] is monomeric with two chelating $\mathrm{S_2P}$ fragments that form an approximate square plane around the metal atom.

Complex (**1**) exists as a centrosymmetric dimer, shown in Figure 1 together with atomic numbering scheme, with an eight-membered Cu–S–P–S–Cu–S–P–S ring as the central feature. The torsion angles of the ring show that atoms Cu, S(1), P(1), and S(2′) form an approximate plane that is parallel to the Cu′, S(1′), P(1′), S(2) plane. These two planes both form an angle of 72.3° with the Cu, S(2), Cu′, S(2′) plane giving rise to a 'chair like' eight-membered ring.

The important bond lengths and angles are given in Table 5. The copper atom is bonded to two nitrogen atoms [Cu–N(1)

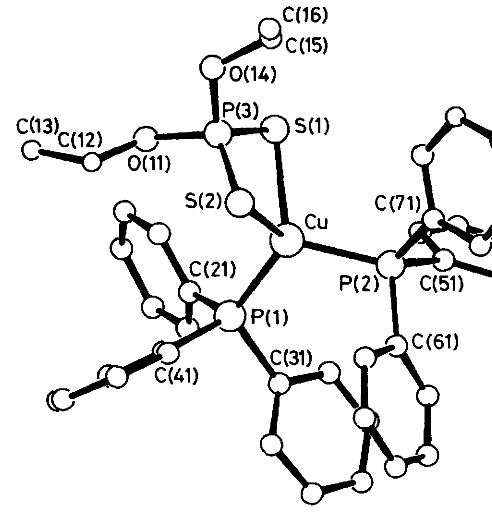


Figure 2. Molecular structure of Cu[$S_2P(OEt)_2$]·2PPh$_3$

2.059(10), Cu–N(2) 2.132(8) Å] and two sulphur atoms [Cu–S(1) 2.347(3), Cu–S(2) 2.323(4) Å]. Often in zinc dialkyl dithiophosphates and dialkyl dithiophosphinates eight-membered rings are observed in which there are additional weak Zn$\cdots$S interactions (3.35—3.48 Å) across the ring.[17–19] This is not the case in (**1**) as the intramolecular distances are 3.984(3) [Cu$\cdots$S(1′)] and 3.692(3) Å [Cu$\cdots$S(2′)].

The separation of the two copper atoms [3.664(4) Å] is greater than that in either Cu[$S_2C(OEt)$]·phen[20] [3.10(1) Å], a compound of similar structure, or Cu[$S_2P(OPr^i)_2$][16] [four Cu–Cu contacts at a mean of 2.74 Å and two at a mean of 2.95 Å]. Such distances represent significant Cu–Cu interactions.

The Cu–S distances are comparable with those shown by a number of copper(I) compounds {2.247—2.289 Å in Cu[$S_2P(OPr^i)_2$],[16] 2.246—2.290 Å in Cu(S_2CNEt_2),[21] and 2.27 and 2.28 Å in Cu[$S_2C(OEt)$]·phen[20]}. The difference between Cu–S(1) [2.347(3) Å] and Cu–S(2) [2.323(4) Å] is probably significant and is reflected in the P–S distances [P–S(1) 1.969(4), P–S(2′) 1.984(3) Å]. This asymmetric bonding is a feature often exhibited by dialkyl dithiophosphate and dialkyl dithiophosphinate complexes.[17–19,22]

There is a significant difference between the two Cu–N distances [Cu–N(1) 2.059(10), Cu–N(2) 2.132(8) Å]. Similar bond lengths and disparities have been reported for both copper(I) and copper(II) complexes of bipy[23] and methyl substituted bipy.[24] It has been suggested[24,25] that the difference in the Cu–N bond lengths in these complexes is correlated to the dihedral angle between the C_5N planes of the bipy rings. We have examined a range of the published copper(I) and copper(II) complexes[26] but could find no such correlation. Indeed we found similar disparities[26] in the Cu–N bond lengths of a range of phen complexes where the two C_5N rings must be essentially planar. Within all these compounds the differences between the Cu–N bond lengths were generally greater in the Cu^{II} than in the Cu^{I} complexes.

The angles subtended at the copper atom deviate markedly from the idealised tetrahedral value (Table 5), although the overall distortion is less than that in Cu[$S_2C(OEt)$]·phen.[20] The smallest angle is, as expected, that associated with the 'bite' of the bipy molecule [78.3(3)°] and this in part accounts for the variation of the angles from the tetrahedral value. The largest angles are formed by N(1) the atom forming the shortest Cu–N bond [N(1)–Cu–S(1) 118.7(3), N(1)–Cu–S(2) 122.6(3)°]. We were unable to identify any steric interactions that could account for this feature.

The structure of complex (**2**) is depicted in Figure 2 together with the atom numbering scheme. The metal atom is four-co-ordinate, being bonded to a chelating [$S_2P(OEt)_2$]$^-$ group [Cu–S(1) 2.453(2), Cu–S(2) 2.440(2) Å] and two PPh$_3$ molecules [Cu–P(1) 2.282(2), Cu–P(2) 2.264(2) Å]. The Cu–P bond lengths are comparable to those found in other copper(I)–PPh$_3$ complexes [2.233, 2.240 Å in Cu(O_2CCH_3)·PPh$_3$,[27] and 2.28, 2.26 Å in Cu(η^2-B_5H_8)·2PPh$_3$[28]]. The Cu–S distances are longer than those in (**1**) and in Cu[$S_2P(OPr^i)_2$][16] [2.247(9)—2.289(9) Å]. The longer distances in (**2**) are either caused by the steric effects of the bulky PPh$_3$ groups or the constraints imposed by a chelating [$S_2P(OEt)_2$]$^-$ group, as in the other two copper(I) dialkyl dithiophosphate structures that have been studied only bridging $S_2P(OR)_2$ fragments are present.

The geometry around the metal atom (Table 6) is close to that expected for a tetrahedral co-ordination sphere; the only major deviation being caused by the 'bite' of the [$S_2P(OEt)_2$]$^-$ group [S(1)–Cu–S(2) 84.17(5)°]. The angle between the Cu, P(1), P(2) and Cu, S(1), S(2) planes is 89.6°, close to the expected 90°.

The most interesting difference between the two structures is the formation of a dimeric species in (**1**) and a monomeric fragment in (**2**). This difference we attribute to steric considerations. If we assume, by analogy with the zinc complexes, that the dimeric form is the most stable, then the presence of the very bulky PPh$_3$ groups in (**2**) will preclude this dimer from being formed. In (**1**) the steric constraints of the bipy group are less because the ligand is perpendicular to the CuS$_2$ plane and so the usual dimeric ring can be formed. In both compounds though there will be considerable steric strain induced by the bulky [$S_2P(OEt)_2$]$^-$ groups.

Conclusions

The results reported here show that the equilibrium positions of reactions (1), (2), and (3) are markedly influenced by the nature of R and the solvent. The effect of nitrogen ligands on the Cu^{II}–Cu^{I} redox couple is well documented,[15] but although we see a marked influence of L on the type of compounds isolated *via* reaction (2) which follow the expected trends, we are unable to say if the products obtained are the kinetically or thermodynamically favoured species. However we are able to assert that as the result of engine bearing wear in the presence of [$S_2P(OR)_2$]$^-$ and aliphatic amines products derived from Cu(OH)$_2$ will result.

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