Metal Dithiocarbamates and Related Species. Part 2.[1] Reaction of Zinc Thiuram Disulphides with Triphenylphosphine and Other Lewis Bases, and Anionic Dithiocarbamato-complexes of Zinc

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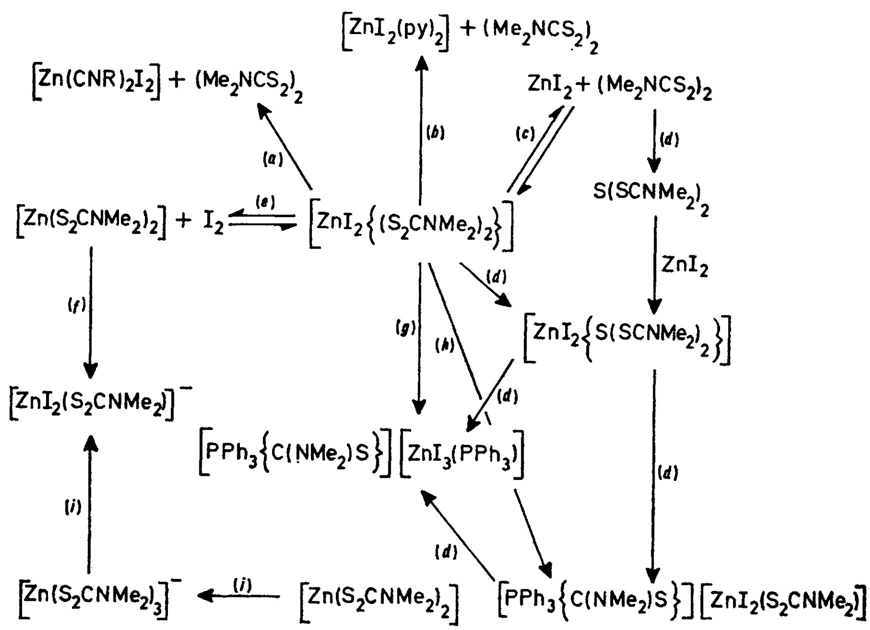
Reaction of $[ZnI_2\{(S_2CNMe_2)_2\}]$ with 1, 2, and 3 mol of PPh_3 gives $[ZnI_2\{S(SCNMe_2)_2\}]$, $[PPh_3\{C(NMe_2)S\}][ZnI_2(S_2CNMe_2)]$, and $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$, respectively, together with PPh_3S and small amounts of $[ZnI_2(PPh_3)_2]$. These reactions can be carried out in steps, and the identity of the products has been confirmed by independent synthesis and spectral methods. The species $[ZnX_2\{S(SCNMe_2)_2\}]$ (X = Cl or Br), $[NBu^n{}_4][ZnX_2(S_2CNMe_2)]$ (X = Cl, Br, or I), and $[PPh_3\{C(NMe_2)S\}]X$ (X = PF_6 or I) have been prepared. The cation $[PPh_3\{C(NMe_2)S\}]^+$ reacts with $[S_2CNMe_2]^-$ giving $S(SCNMe_2)_2$ and PPh_3. Treatment of $[Zn(S_2CNRR')_2]$ with $[S_2CNRR']^-$ affords $[Zn(S_2CNRR')_3]^-$ (R = R' = Me; R = Me, R' = Ph; isolated as $[NEt_4]^+$ or $[NBu^n{}_4]^+$ salts), while $[Zn(S_2CNR_2)_2]$ (R = Et or Bu^n) react with $[S_2CNMe_2]^-$ affording $[Zn(S_2CNEt_2)_2(S_2CNMe_2)]^-$ or $[Zn(S_2CNBu^n{}_2)(S_2CNMe_2)_2]^-$, respectively. Treatment of $[Zn(S_2CNMe_2)_2]$ with $[NBu^n{}_4][O_2CMe]$ afforded $[NBu^n{}_4][Zn(O_2CMe)(S_2CNMe_2)_2]$. Possible mechanisms for the attack of PPh_3 on metal-co-ordinated $(R_2NCS_2)_2$ and $S(SCNR_2)_2$ are discussed, and brief comments are made on the relation of species such as $[Zn(O_2CR')(S_2CNR_2)_2]^-$ to the acceleration of vulcanisation of natural rubber.

In the other papers in this series [1,2] we have described the reactions of Lewis bases, especially tertiary phosphines and isocyanides, with nickel(IV) and iron(IV) tris(dithiocarbamate) cations, $[M(S_2CNR_2)_3]^+$. Much of the chemistry we have described could be rationalised in terms of a series of internal redox reactions occasioned by Lewis-base attack on the cation, *viz.* $Ni^{IV} \longrightarrow Ni^{II}$, giving the transient $[Ni\{(S_2CNR_2)_2\}(S_2CNR_2)]^+$ followed by displacement of the thiuram disulphide by the Lewis base, or $Fe^{IV} \longrightarrow Fe^{III}$ ($\longrightarrow Fe^{II}$), with probable release of $R_2NCS_2\cdot$ which subsequently dimerised. Of particular interest in the reactions of these cations with PPh_3 was the formation of the new phosphonium ion, $[PPh_3\{C(NMe_2)S\}]^+$.

In further investigations of the reactions of PPh_3 with complexes containing at least two dithiocarbamato-ligands or co-ordinated thiuram disulphide, we have studied the behaviour of $[ZnX_2\{(S_2CNR_2)_2\}]$. In this system, the metal cannot assist in internal redox reactions which may, in part, dictate the fate of the sulphur-ligand residues. For comparison, we have also investigated reactions involving other Lewis bases. Discoveries made as a result of this work led us to the preparation of new anionic zinc dithiocarbamate complexes, and to a rational synthesis of salts of $[PPh_3\{C(NMe_2)S\}]^+$. A preliminary account of some of this work has been given.[3]



SCHEME 1 (*a*) RNC; (*b*) py; (*c*) EtOH; (*d*) PPh_3; (*e*) heat; (*f*) $[ZnI_4]^{2-}$; (*g*) 3 PPh_3; (*h*) 2 PPh_3; (*i*) I_2; (*j*) $[S_2CNMe_2]^-$

Reaction of $[ZnI_2\{(S_2CNMe_2)_2\}]$ *with* PPh_3, *and Characterisation of the Products.*—The products of the reactions of $[ZnI_2\{(S_2CNMe_2)_2\}]$ with PPh_3 depended on

[1] Part 1, J. A. McCleverty and N. J. Morrison, *J.C.S. Dalton*, 1976, 541.

[2] Part 3, J. A. McCleverty, S. A. McLuckie, N. J. Morrison, N. A. Bailey, and N. W. Walker, *J.C.S. Dalton*, in the press.

[3] J. A. McCleverty and N. J. Morrison, *J.C.S. Chem. Comm.*, 1974, 1048.

the experimental conditions, and the important observations are outlined in Scheme 1. Unless otherwise stated, all of the complexes reported have elemental analyses, ^{1}H n.m.r. and i.r. spectra, and conductivities consistent with their formulations, and these data are presented in Tables 1 and 2.

Treatment of $[ZnI_2\{(S_2CNMe_2)_2\}]$ with PPh_3 in a 1 : 1 molar ratio afforded yellow $[ZnI_2\{S(SCNMe_2)_2\}]$. With 2 mole equivalents of PPh_3 a transient orange colour appeared and then deep yellow $[PPh_3\{C(NMe_2)S\}]$-$[ZnI_2(S_2CNMe_2)]$ was formed (in a small volume of dichloromethane, $[ZnI_2\{S(SCNMe_2)_2\}]$ precipitated and then redissolved); $[ZnI_2(PPh_3)_2]$ was isolated in low yield.

(b) $[NBu^n{}_4][ZnX_2(S_2CNMe_2)]$. Treatment of ZnX_2 (X = Cl, Br, or I) with $[NBu^n{}_4][S_2CNMe_2]$ in a 1 : 1 molar ratio in acetone gave $[NBu^n{}_4][ZnX_2(S_2CNMe_2)]$ which was isolated as white crystals. The species $[NBu^n{}_4]$-$[ZnI_2(S_2CNR_2)]$ (R = Me or Et) could also be isolated from a mixture of $[NBu^n{}_4]_2[ZnI_4]$ with $[Zn(S_2CNR_2)_2]$ in acetone solution. On mixing $[NBu^n{}_4][S_2CNMe_2]$ with ZnI_2 in acetone solution (2 : 1 molar ratio) or in methanol (1 : 1 molar ratio), only $[Zn(S_2CNMe_2)_2]$ was precipitated. There was no reaction between the $[NBu^n{}_4]^+$ salt of $[ZnI_2(S_2CNMe_2)]^-$ and PPh_3 after 2 days in dichloromethane solution but, as mentioned above, the $[PPh_3$-$\{C(NMe_2)S\}]^+$ salt gave $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$.

TABLE 1

Analytical and conductivity data obtained for the new zinc complexes and their derivatives

	Analysis (%)										
	Found					Calc.					
Complex	C	H	N	S	Halogen	C	H	N	S	Halogen	Λ *
$[ZnI_2\{S(SCNMe_2)_2\}]$	13.9	2.5	5.3	18.1	48.1	13.7	2.3	5.3	18.2	48.2	
$[PPh_3\{C(NMe_2)S\}][ZnI_2(S_2CNMe_2)]$	36.6	3.7	3.4	12.1	32.3	36.5	3.4	3.6	12.2	32.2	
$[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$	44.4	3.8	1.3	3.1	34.6	44.2	3.2	1.3	3.0	36.0	82
$[ZnCl_2\{S(SCNMe_2)_2\}]$	21.0	3.7	8.3	27.9	20.6	20.9	3.5	8.1	27.9	20.6	
$[ZnBr_2\{S(SCNMe_2)_2\}]$	16.6	2.9	7.0		37.5	16.6	2.8	6.5		37.0	
$[NBu^n{}_4][ZnCl_2(S_2CNMe_2)]$	46.1	8.4	5.3	12.6	14.3	45.8	8.4	5.6	12.8	14.2	
$[NBu^n{}_4][ZnBr_2(S_2CNMe_2)]$	38.8	7.2	4.5	10.9	26.9	38.8	7.2	4.8	10.9	27.2	
$[NBu^n{}_4][ZnI_2(S_2CNMe_2)]$	33.8	6.4	4.5	9.4	37.4	33.5	6.2	4.1	9.4	37.3	
$[PPh_3\{C(NMe_2)S\}][PF_6]$	51.2	4.6	2.7			50.9	4.2	2.8			80
$[PPh_3\{C(NMe_2)S\}]I$	53.2	4.6	2.9	7.0	26.5	52.9	4.4	2.9	6.7	26.6	
$[NBu^n{}_4][ZnI_3(PPh_3)]$	43.0	5.5	1.8		39.7	42.9	5.4	1.5		40.1	
$[ZnI_2(py)_2]$	25.8	2.5	5.9			25.1	2.1	5.9			
$[Zn(CNPr^i)_2I_2]$	20.8	3.2	6.1		55.6	21.0	3.1	6.1		55.5	
$[Zn(CNBu^t)_2I_2]$	24.7	4.1	5.7		52.0	24.7	3.7	5.8		52.3	
$[Zn(en)_3]I_2$	14.3	5.0	16.5		50.3	14.4	4.8	16.8		50.9	
$[ZnI_2\{S_2CNC_5H_{10})_2\}]$	22.9	3.4	4.5	20.2	39.9	22.5	3.1	4.4	20.0	39.7	
$[NBu^n{}_4][Zn(S_2CNMe)_3]$	44.9	8.2	8.6	29.0		45.0	8.1	8.4	28.8		
$[NBu^n{}_4][Zn(S_2CNEt_2)_2(S_2CNMe_2)]$	48.2	8.7	8.0	26.4		48.1	8.6	7.7	27.1		
$[NBu^n{}_4][Zn(S_2CNBu^n{}_2)(S_2CNMe_2)_2]$	49.2	8.4	7.4	25.7		49.5	8.8	7.5	25.6		
$[NEt_4][Zn(S_2CNMe_2)_3]$	37.0	7.1	10.0	34.5		36.7	6.8	10.1	34.6		
$[NEt_4][Zn(S_2CNMePh)_3]\cdot Me_2CO\cdot H_2O$	50.7	6.6	6.9	24.8		51.4	6.4	6.7	23.5		
$[NBu^n{}_4][Zn(O_2CMe)(S_2CNMe_2)_2]$	49.3	9.0	7.0	20.8		47.6	8.4	6.9	21.1		
$[NBu^n{}_4][S_2CNMe_2]$	63.2	11.8	7.8	17.9		63.0	11.6	7.7	17.7		
$[NMe_4][S_2CNMe_2]$	42.7	9.4	14.8	33.0		43.3	9.3	14.4	33.0		

* In S cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solution in $MeNO_2$; for a 1 : 1 electrolyte, Λ = 80—100 S cm^2 mol^{-1}.

With 3 mol of PPh_3, $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$ was slowly formed as a deep yellow precipitate. The yellow products could also be obtained in a stepwise manner as indicated in Scheme 1. In all these reactions, which took place in dichloromethane, chloroform, or acetone, PPh_3S was always isolated as white needles.

The formulations of these compounds are supported by independent syntheses, by preparation of the cationic or anionic components of these species, by spectral identification and comparison, and by an *X*-ray crystallographic examination [4] of $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$.

(a) $[ZnX_2\{S(SCNMe_2)_2\}]$ (X = Cl, Br, *or* I). Treatment of ZnX_2 (X = Cl, Br, or I) with $S(SCNMe_2)_2$ afforded $[ZnX_2\{S(SCNMe_2)_2\}]$. The characteristic C=N stretching frequency of the S_2CNMe_2 group in the thiuram monosulphide increased from 1 504 to 1 516 cm^{-1} on co-ordination, and a similar increase was observed [5] in co-ordination of $S(SCNMe_2)_2$ by HgI_2.

All three complexes $[ZnX_2(S_2CNMe_2)]^-$ showed very similar i.r. spectra in the 400—4 000 cm^{-1} region, and the expected increase in ν(CN) (from 1 489 to 1 514 cm^{-1} for KBr discs) on co-ordination of $[S_2CNMe_2]^-$ was observed. In the far-i.r. region, a strong broad band shifted from 300 to 228 cm^{-1} as the halide was changed from Cl to Br. This band was replaced by two less broad bands, at 188 and 216 cm^{-1}, in the di-iodo-complex. These absorptions have been assigned to Zn–X vibrations, and for the anion $[ZnX_2(S_2CNMe_2)]^-$, of symmetry C_{2v}, two i.r.-active Zn–X bands are expected. Evidently the two bands (for X = Cl or Br) are insufficiently separated to be resolved. Coates and Ridley [6] examined the far-i.r. spectra of a large number of complexes of formula ZnX_2L_2 (L = amine or substituted phosphine) and found a wide variation in the difference between the two Zn–X frequencies. For example, the bands in $[ZnCl_2(py)_2]$ (py = pyridine)

[4] N. A. Bailey and N. W. Walker, personal communication; N. W. Walker, Ph.D. Thesis, Sheffield University, 1975.

[5] H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemse, *Rec. Trav. chim.*, 1969, **88**, 633.

[6] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

(330, 297 cm^{-1}) and $[ZnBr_2(PPh_3)_2]$ (235, 202 cm^{-1}) were separated by 33 cm^{-1} whereas only one broad unresolved band was observed for $[ZnCl_2(NEt_2H)_2]$ (296 cm^{-1}) and $[ZnBr_2(PEt_3)_2]$ (221 cm^{-1}).

(c) *Salts of the cation* $[PPh_3\{C(NMe_2)S\}]^+$. The yellow cation $[PPh_3\{C(NMe_2)S\}]^+$, as the $[PF_6]^-$ or I^- salt, could be obtained from a mixture of Me_2NCSCl, PPh_3, and either $Ag[PF_6]$ or NaI. However, quaternisation of the phosphorus was not achieved in the absence of a metal ion.

Reaction of $[PPh_3\{C(NMe_2)S\}][PF_6]$ with $[NBu^n_4]$-$[ZnI_2(S_2CNMe_2)]$ gave low yields of $[PPh_3\{C(NMe_2)S\}]$-$[ZnI_2(S_2CNMe_2)]$. The $[PF_6]^-$ salt also reacted with $[NBu^n_4][S_2CNMe_2]$ *via* an orange intermediate to afford, in high yield, PPh_3, $S(SCNMe_2)_2$, and $[NBu^n_4][PF_6]$. However, the weaker nucleophile I^- did not displace PPh_3 from $[PPh_3\{C(NMe_2)S\}]^+$ and, indeed, $[PPh_3$-$\{C(NMe_2)S\}]I$ could be conveniently recrystallised from hot methanol.

From ¹H n.m.r. spectral studies at room temperature, it was shown that the alkyl groups in $[PPh_3\{C(NR_2)S\}]^+$ (R = Me, Et,[2] or Bu^n [1]) are inequivalent. This is due to restricted rotation about the C$\cdots$N bond of the $Ph_3PC(S)\cdots NR_2$ group [ν(C$\cdots$N) at 1 512 cm^{-1}]. Coalescence of the methyl proton signals (when R = Me) occurred between 90 and 100 °C in $(CD_3)_2SO$ solution. The presence of the cation $[PPh_3\{C(NMe_2)S\}]^+$ in the salts derived by attack of PPh_3 on $[ZnI_2\{(S_2CNMe_2)_2\}]$,

TABLE 2

Infrared (cm^{-1}) and ¹H n.m.r. spectral data obtained for the new zinc complexes and their derivatives

	ν(C$\cdots$N)		¹H N.m.r. [a]		
Complex	CH_2Cl_2	KBr	δ/p.p.m.	A [b]	Assignment
$[ZnI_2\{S(SCNMe_2)_2\}]$		1 540	3.52 (s) [c]		$N(CH_3)_2$
$[PPh_3\{C(NMe_2)S\}][ZnI_2(S_2CNMe)_2]$		1 505	7.81 (m) [d]	5	$P(C_6H_5)_3$
			3.67 (s)	1	NCH_3
			3.38 (s)	2	$N(CH_3)_2$ (anion)
			3.16 (s)	1	$N(CH_3)$
$[ZnCl_2\{S(SCNMe_2)_2\}]$	1 516	1 540	3.47 (s) [c]		$N(CH_3)_2$
$[ZnBr_2\{S(SCNMe_2)_2\}]$		1 540	3.49 (s) [c]		$N(CH_3)_2$
$[NBu^n_4][ZnCl_2(S_2CNMe_2)]$	1 514	1 510	3.41 (s)	7	$N(CH_3)_2$
			3.34 (t)		$N(CH_2Pr^n)_4$
			1.56 (m)	8	$N(CH_2CH_2CH_2Me)_4$
			1.00 (t)	6	$N(CH_2CH_2CH_2CH_3)_4$
$[NBu^n_4][ZnBr_2(S_2CNMe_2)]$	1 515	1 510	3.84 (s)	7	$N(CH_3)_2$
			3.34 (t)		$N(CH_2Pr^n)_4$
			1.56 (m)	8	$N(CH_2CH_2CH_2Me)_4$
			0.98 (t)	6	$N(CH_2CH_2CH_2CH_3)_4$
$[NBu^n_4][ZnI_2(S_2CNMe_2)]$	1 515	1 510	3.41 (s)	7	$N(CH_3)_2$
			3.31 (t)		$N(CH_2Pr^n)_4$
			1.58 (m)	8	$N(CH_2CH_2CH_2Me)_4$
			1.01 (t)	6	$N(CH_2CH_2CH_2CH_3)_4$
$[NBu^n_4][ZnI_2(S_2CNEt_2)_2]$	1 498				
$[PPh_3\{C(NMe_2)S\}][PF_6]$	1 504	1 512	7.74 (m) [d]	5	$P(C_6H_5)_3$
			3.58 (s)	1	$N(CH_3)$
			3.26 (s)	1	$N(CH_3)$
$[PPh_3\{C(NMe_2)S\}]I$		1 512			
$[NBu^n_4][Zn(S_2CNMe_2)_3]$		1 482br	3.44 (s)	13	$N(CH_3)_2$
			3.35 (t)		$N(CH_2Pr^n)_4$
			1.55 (m)	8	$N(CH_2CH_2CH_2Me)_4$
			0.98 (t)	6	$N(CH_2CH_2CH_2CH_3)_4$
$[NBu^n_4][Zn(S_2CNEt_2)_2(S_2CNMe_2)]$		1 480br	3.96 (q) [c]	4	$N(CH_2Me)_2$
			3.48 (t)	7	$N(CH_2Pr^n)_4$
			3.44 (s)		$N(CH_3)_2$
			1.42 (m)	14	$N(CH_2CH_2CH_2Me)_4$
			1.23 (t)		$N(CH_2CH_3)_2$
			0.98 (t)	6	$N(CH_2CH_2CH_2CH_3)_4$
$[NBu^n_4][Zn(S_2CNBu^n_2)(S_2CNMe_2)_2]$		1 480br	3.88 (t) [c]	2	$N(CH_2Pr^n)_2$
			3.50 (t)	10	$N(CH_2Pr^n)_4$
			3.43 (s)		$N(CH_3)_2$
			1.63 (m)	12	$N(CH_2CH_2CH_2Me)_4$
			0.99 (t)	12	$N(CH_2CH_2CH_2CH_3)_4$
			0.92 (t)		$N(CH_2CH_2CH_2CH_3)_2$
$[NEt_4][Zn(S_2CNMePh)_3]$ [e]			7.46 (m)	15	$NMe(C_6H_5)$
			3.73 (s)	9	$N(CH_3)Ph$
			3.20 (q)	8	$N(CH_2Me)_4$
			2.28 (s)	2	H_2O
			2.10 (s)	6	$(CH_3)_2CO$
			1.19 (tt)	12	$N(CH_2CH_3)_4$
$[NBu^n_4][Zn(O_2CMe)(S_2CNMe_2)_2]$			3.43 (t) [c]	20	$N(CH_2Pr)_4$
			3.41 (s)		$N(CH_3)_2$
			1.89 (s)	3	O_2CCH_3
			1.58 (m)	16	$N(CH_2CH_2CH_2Me)_4$
			0.96 (t)	12	$N(CH_2CH_2CH_2CH_3)_4$

[a] In $CDCl_3$ solution at 100 MHz (30 °C). [b] Relative area. [c] In $(CD_3)_2CO$ solution. [d] In $(CD_3)_2SO$ solution. [e] The complex contained H_2O and Me_2CO of crystallisation.

and in the $[PF_6]^-$ salt, was further confirmed by ^{31}P n.m.r. spectroscopy, which revealed a singlet (δ 22.9 p.p.m. relative to H_3PO_4) in all three complexes. (An additional ^{31}P resonance, due to the other PPh_3, was observed in $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$.)

(d) $[NBu^n_4][ZnI_3(PPh_3)]$ *and* $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$. From a mixture in hot ethanol of $[NBu^n_4]I$, PPh_3, and ZnI_2, good yields of $[NBu^n_4][ZnI_3(PPh_3)]$ were obtained. However, reaction of $[PPh_3\{C(NMe_2)S\}]I$ with PPh_3 and ZnI_2 gave only a low yield of $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$.

Because of decomposition, the integrated ^1H n.m.r. spectrum of $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$ in $(CD_3)_2SO$ was not exactly consistent with our formulation. However, the ^{31}P n.m.r. spectrum clearly established the presence of the cationic component and, by comparison with $[NBu^n_4][ZnI_3(PPh_3)]$, of the anionic fragment, and full confirmation was provided by a single-crystal *X*-ray structural determination [4] of $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$.

Reaction of $[ZnI_2\{(S_2CNMe_2)_2\}]$ *with Other Lewis Bases*.—Treatment of $[ZnI_2\{(S_2CNBu^n_2)_2\}]$ with L (py, Bu^tNC, or Pr^iNC) afforded $[ZnI_2L_2]$, and with ethylenediamine $[Zn(en)_3]I_2$ was formed. Similarly, $[ZnI_2\{(S_2CNMe_2)_2\}]$ reacted with py to give $[ZnI_2(py)_2]$, and $(Me_2NCS_2)_2$ was recovered as white crystals.

Addition of ethanol to $[ZnI_2\{(S_2CNR_2)_2\}]$ caused quantitative displacement of the thiuram disulphide, and distillation of a partial solution of the zinc complexes in xylene afforded iodine, which could be recovered from the distillate, and $[Zn(S_2CNR_2)_2]$, which was isolated from the residue. It may be noted that $[ZnI_2\{(S_2CNR_2)_2\}]$ can be prepared by reaction of $[Zn(S_2CNR_2)_2]$ with iodine.

Anionic Zinc Dithiocarbamate Complexes.—Addition of $[NBu^n_4][S_2CNMe_2]$ to $[Zn(S_2CNMe_2)_2]$ in acetone afforded, after recrystallisation, crystalline $[NBu^n_4][Zn(S_2CNMe_2)_3]\cdot Me_2CO$; the $[NEt_4]^+$ salt was similarly obtained using $[NEt_4][S_2CNMe_2]$. Attempts to isolate the anion using $[NMe_2H_2]^+$, $[NMe_4]^+$, or Na^+ salts of $[S_2CNMe_2]^-$ were unsuccessful. Treatment of $[Zn(S_2CNEt_2)_2]$ with $[NBu^n_4][S_2CNMe_2]$ afforded $[NBu^n_4][Zn(S_2CNEt_2)_2(S_2CNMe_2)]$, but the product isolated (in lower yield) from the 1 : 1 mixture of $[Zn(S_2CNBu^n_2)_2]$ with the same reagent in acetone solution was $[NBu^n_4][Zn(S_2CNBu^n_2)(S_2CNMe_2)_2]$. The salt $[NEt_4][Zn(S_2CNMePh)_3]\cdot H_2O$ was obtained from the neutral bis(dithiocarbamate) and $[NEt_4][S_2CNMePh]$ in damp acetone.

Reaction of $[Zn(S_2CNMe_2)_2]$ with $[NBu^n_4][O_2CMe]$, prepared *in situ* (see Experimental section), afforded white crystals of $[NBu^n_4][Zn(O_2CMe)(S_2CNMe_2)_2]$. This adduct could not be obtained pure using $[NBu^n_4][H(O_2CMe)_2]$.

Oxidation of $[Zn(S_2CNMe_2)_3]^-$ with iodine afforded $[ZnI_2(S_2CNMe_2)]^-$ and $(Me_2NCS_2)_2$, products which would be expected from iodine oxidation of a mixture of $[Zn(S_2CNMe_2)_2]$ and $[S_2CNMe_2]^-$. Both $[S_2CNMe_2]^-$ and $[Zn(S_2CNMe_2)_3]^-$ reacted with dichloromethane, as shown by the time dependence of i.r. spectra of freshly prepared solutions in that solvent. Indeed, a 60% yield of $CH_2(S_2CNMe_2)_2$ was obtained by reaction of $[NBu^n_4][S_2CNMe_2]$ with dichloromethane after only 5 min at room temperature, in contrast to the behaviour of the Na^+ salt which only afforded the methylene compound under refluxing conditions or in the presence of PPh_3.[7] From the reaction of dichloromethane with $[Zn(S_2CNMe_2)_3]^-$, both $CH_2(S_2CNMe_2)_2$ and $[Zn(S_2CNMe_2)_2]$ were recovered.

At room temperature, the ^1H n.m.r. spectra of salts of $[Zn(S_2CNMe_2)_3]^-$ and $[Zn(S_2CNMePh)_3]^-$ in $CDCl_3$ and CD_3CN, respectively, exhibited singlets due to the methyl protons. At −40 °C the latter complex exhibited a broadened methyl proton singlet, but below this temperature the species crystallised from the solution. Thus no useful stereochemical information could be obtained by this technique; the complexes could be fluxional, like $[Fe(S_2CNRR')_3]$,[8] or undergo rapid intermolecular ligand exchange, like $[Tl(S_2CNMe_2)_3]$.[9] The ^1H n.m.r. spectral data obtained from these complexes are summarised in Table 2.

The i.r. spectrum of $[Zn(S_2CNMe_2)_3]^-$ (KBr discs) showed two bands, at 972 and 984 cm^{-1}, in the region where it has been suggested that absorptions associated with asymmetrically bonded dithiocarbamato-ligands, as in $[As(S_2CNEt_2)_3]$,[10] may occur. A single-crystal *X*-ray structural determination of $[NEt_4][Zn(S_2CNMe_2)_3]$ [11] has revealed that two of the ligands are asymmetrically bonded, and that the molecular geometry could be described in terms of a distorted tetrahedron of short Zn–S bonds with the remaining two sulphur atoms occupying positions over two faces of the idealised tetrahedron. Alternatively, the complex could be described as six-co-ordinate, the geometry being thought of as a distorted trigonal prism with each rectangular edge being bridged by an S_2CNMe_2 ligand, and each triangular face being constituted by one weakly and two strongly bonded S atoms.

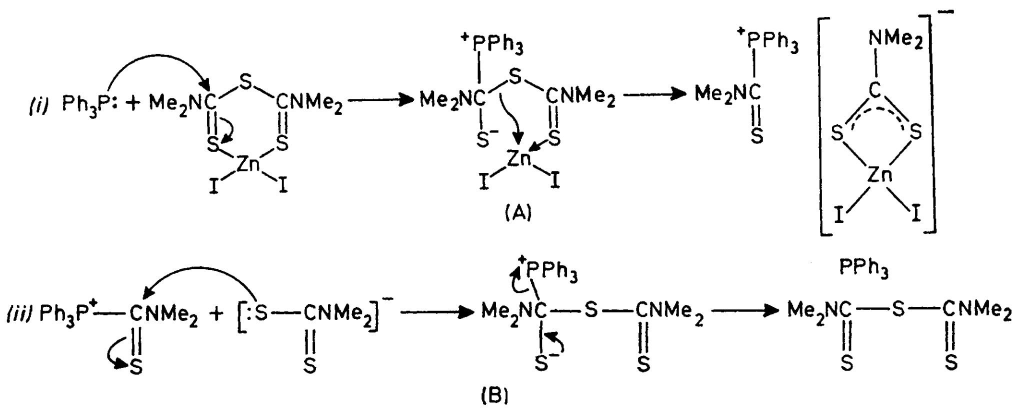
DISCUSSION

The observation that $[PPh_3\{C(NMe_2)S\}]^+$ and $[S_2CNMe_2]^-$ reacted, *via* an uncharacterised intermediate, to give PPh_3 and $S(SCNMe_2)_2$ is of significance in rationalising the reactions of $S(SCNMe_2)_2$ with PPh_3 in the presence of a metal ion. Thus, nucleophilic attack by PPh_3 at the thiocarbonyl atom, *via* intermediate (A) as shown in Scheme 2, could result in displacement of $[S_2CNMe_2]^-$. Subsequent co-ordination of this ion to another metal would reduce its nucleophilic character

[7] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.
[8] M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, jun., and L. H. Pignolet, *J. Amer. Chem. Soc.*, 1973, **95**, 4537.
[9] H. Abramson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, 1975, **14**, 2070.
[10] M. Colapietro, A. Domenicano, L. Scaramuzza, and A. Vaciago, *Chem. Comm.*, 1968, 302; C. L. Raston and A. H. White, *J.C.S. Dalton*, 1975, 2425.
[11] C. Ashworth, N. A. Bailey, M. R. Johnson, J. A. McCleverty, N. J. Morrison, and B. Tabbiner, *J.C.S. Chem. Comm.*, 1976, 743.

and thereby prevent the reverse reaction (*ii*) as shown in Scheme 2. We suggest that the orange intermediates observed transiently in the reactions between PPh_3 and $[ZnI_2\{S(SCNMe_2)_2\}]$ and between $[PPh_3\{C(NMe_2)S\}]^+$ and $[S_2CNMe_2]^-$ are the Zwitterionic species (A) and (B).

In a previous paper[1] we described how $[Ni(PPh_3)_2(S_2CNEt_2)]^+$ reacted with $(Et_2NCS_2)_2$ to give PPh_3S, $[PPh_3\{C(NEt_2)S\}]^+$, and $[Ni(S_2CNEt_2)_2]$. In view of the results reported above, a path for this reaction may be suggested. In $[Ni(PPh_3)_2(S_2CNEt_2)]^+$ one of the triphenylphosphine ligands is labile, and when dissociated in solution could attack $(Et_2NCS_2)_2$ giving PPh_3S and $S(SCNEt_2)_2$. The residual nickel species, $[Ni(PPh_3)(S_2CNEt_2)]^+$, would probably disproportionate to Ni^{2+}-(solvated), PPh_3, and $[Ni(S_2CNEt_2)_2]$. Reaction of PPh_3 with $S(SCNMe_2)_2$ in the presence of Ni^{2+} (functioning, like Zn^{2+}, as a Lewis acid) would produce more $[Ni(S_2CNEt_2)_2]$ and the other observed product, $[PPh_3\{C(NEt_2)S\}]^+$.



SCHEME 2

The isolation of a salt of $[Zn(O_2CMe)(S_2CNMe_2)_2]^-$ is of considerable significance in relation to the zinc-assisted acceleration of the vulcanisation of natural rubber. It has been proposed[12] that, in the rubber matrix, zinc dithiocarbamates form 1 : 2 adducts with naturally occurring fatty acids, *e.g.* stearic acid. We could obtain no evidence of 1 : 2 adduct formation with acetate, and, although we were unable to obtain crystalline stearate adducts, we observed that the solubility of $[Zn(S_2CNMe_2)_2]$ in organic solvents was enhanced in the presence of tetra-alkylammonium salts of carboxylic acids, and that $[Zn(O_2CMe)_2]$ dissolved easily in acetone in the presence of $[NBu^n_4][S_2CNMe_2]$ (in the absence of this anion it is barely soluble). The isolation of a 1 : 1 acetate adduct with $[Zn(S_2CNMe_2)_2]$ supports the view that fatty acids can form complexes with zinc dithiocarbamates in rubber matrices. We would add further that the enhancement of vulcanisation acceleration observed in the presence of fatty acids may be related to the increased nucleophilicity of co-ordinated dithiocarbamates in species such as $[Zn(O_2CR')(S_2CNR_2)_2]^-$ {*cf.* the reaction of $[Zn(S_2CNMe_2)_3]^-$ with dichloromethane}. This enhancement may also be partly due to the increased solubility of anionic species in the rubber polymer. Indeed, we have observed that both $[NBu^n_4][S_2CNMe_2]$ and $[NBu^n_4][Zn(S_2CNMe_2)_3]$ are substantially faster vulcanising accelerators for natural rubber than $[Zn(S_2CNMe_2)_2]$.

EXPERIMENTAL

Conductivity measurements were made at room temperature using a Philips conductivity bridge. Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrophotometers. The ^1H n.m.r. spectra were obtained at 100 MHz using a Varian HA100 spectrometer to which was fitted a variable-temperature probe. Phosphorus-31 n.m.r. spectra (quoted in p.p.m. on the δ scale relative to H_3PO_4 as internal reference) were recorded on Jeol PFT-100 and Bruker HFX-90 instruments; the sign convention, 'positive to higher frequency,' was observed. Elemental analyses were by the Microanalytical Laboratory of this Department, and yields quoted herein are relative to the zinc-containing precursor (where appropriate).

Reactions of $[ZnI_2\{(S_2CNMe_2)_2\}]$ *with* PPh_3.—The following reactions were carried out in $CHCl_3$, CH_2Cl_2, and acetone solutions, and details of reaction conditions which resulted in the easiest separation of products are presented.

(i) 1 : 1 *Molar ratio*. To a suspension of $[ZnI_2\{(S_2CNMe_2)_2\}]$ (1.12 g, 2 mmol) in CH_2Cl_2 (50 cm^3) was added a solution of PPh_3 (0.53 g) in CH_2Cl_2 (10 cm^3). The light yellow suspension was replaced by a deeper yellow precipitate. The mixture was shaken for 1 h, and then the solvent was evaporated. The residue was shaken with diethyl ether (200 cm^3) for 1 h and this mixture was filtered (A). The yellow residue, $[ZnI_2\{S(SCNMe_2)_2\}]$ was recrystallised from acetone–light petroleum (0.9 g, 86%). The filtrate (A) was evaporated, and the white residue of PPh_3S was recrystallised from boiling ethanol (0.3 g).

(ii) 1 : 2 *Molar ratio*. To a suspension of $[ZnI_2\{(S_2CNMe_2)_2\}]$ (1.12 g) in CH_2Cl_2 (50 cm^3) was added PPh_3 (1.04 g) in CH_2Cl_2 (10 cm^3). The resulting orange solution had turned yellow after 1 min. The solution was stirred for a further 10 min, then the solvent was evaporated. The solid was shaken with diethyl ether (200 cm^3) overnight and the mixture was filtered (A). The residue was extracted with acetone (50 cm^3), leaving $[ZnI_2(PPh_3)_2]$

[12] P. W. Allen, D. Barnard, and B. Saville, *Chem. in Britain*, 1970, **6**, 382.

which was recrystallised from dichloromethane–n-hexane (0.1 g). Addition of light petroleum to the acetone extract caused precipitation of more $[ZnI_2(PPh_3)_2]$, which was removed by filtration. Further addition of light petroleum caused precipitation of $[PPh_3\{C(NMe_2)S\}][ZnI_2(S_2CNMe_2)]$, which was collected and recrystallised from acetone–light petroleum (0.85 g, 54%). The complex could be obtained in a similar manner from the reaction of $[ZnI_2\{S(SCNMe_2)_2\}]$ (2.64 g, 5 mmol) with PPh_3 (1.3 g, 5 mmol). The ether extract (A) was evaporated and white crystals of PPh_3S were obtained by recrystallisation of the residue from boiling ethanol (0.3 g).

(iii) 1 : 3 *Molar ratio*. To a suspension of $[ZnI_2\{(S_2CNMe_2)_2\}]$ (2.8 g) in $CHCl_3$ (30 cm^3) was added a solution of PPh_3 (3.9 g) and the mixture was shaken. The deep orange solution had turned yellow after 1 min, and after 30 min crystals had started to form. The mixture was set aside for 36 h and then the yellow *crystals* of $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$ were filtered off (A) and recrystallised from acetone–light petroleum. This complex could be obtained similarly by mixing a suspension of $[ZnI_2\{S(SCNMe_2)_2\}]$ (2.64 g) with PPh_3 (2.6 g) in $CHCl_3$ (50 cm^3). It also crystallised from a solution containing $[PPh_3\{C(NMe_2)S\}][ZnI_2(S_2CNMe_2)]$ (4.0 g) and PPh_3 (1.3 g) in $CHCl_3$ (50 cm^3). Filtrate (A) was evaporated and the residue was shaken with diethyl ether (200 cm^3) overnight. This mixture was filtered and the filtrate was evaporated. The white solid, PPh_3S (from the evaporated filtrate), was recrystallised from boiling ethanol.

Di-iodo(NNN′N′-*tetramethylthiuram monosulphide*)*zinc*(II).—Zinc(II) iodide (3.2 g) was added to a stirred solution of $S(SCNMe_2)_2$ (2.08 g) in acetone (200 cm^3). After the ZnI_2 had dissolved, most of the acetone was evaporated. When crystals began to form, the mixture was cooled in a bath of acetone–solid CO_2. The yellow crystals were collected and washed with diethyl ether (5.2 g, quantitative). A similar procedure was used to prepare $[ZnX_2\{S(SCNMe_2)_2\}]$ (X = Cl or Br).

Tetra-n-butylammonium Di-iodo(*dimethyldithiocarbamato*)*zincate*(II).—*Method A*. A solution of $[NBu^n_4](S_2CNMe_2)]$ (3.6 g, 0.01 mol) in acetone (50 cm^3) was added to a suspension of ZnI_2 (3.2 g, 0.01 mol) in acetone (50 cm^3). The mixture was stirred to dissolve the ZnI_2, then (A) light petroleum was added. Partial evaporation of the solvent afforded white *crystals* (sometimes an oil formed first and then crystallised), which were collected, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (6.8 g, quantitative). White crystals of $[NBu^n_4][ZnX_2(S_2CNMe_2)]$ (X = Cl or Br) were obtained similarly.

Method B. A mixture of $[Zn(S_2CNMe_2)_2]$ (0.31 g, 1 mmol), ZnI_2 (0.32 g, 1 mmol), and $[NBu^n_4]I$ (0.74 g, 2 mmol) in acetone (25 cm^3) was stirred until all the reactants had dissolved. The product was obtained as from (A) above. The salt $[NBu^n_4][ZnI_2(S_2CNEt_2)]$ was obtained similarly.

Reaction of $[NBu^n_4][S_2CNMe_2]$ *with* ZnI_2.—A solution of $[NBu^n_4][S_2CNMe_2]$ (3.6 g, 0.01 mol) in methanol (100 cm^3) was mixed with a solution of ZnI_2 (3.2 g, 0.01 mol) in MeOH (100 cm^3). A white precipitate of $[Zn(S_2CNMe_2)_2]$ formed slowly. It was collected after 30 min and was washed with acetone (2.1 g, 70% based on $[S_2CNMe_2]^-$).

Reaction of $[NBu^n_4][ZnI_2(S_2CNMe_2)]$ *with* $[NBu^n_4][S_2CNMe_2]$.—A solution of $[NBu^n_4][ZnI_2(S_2CNMe_2)]$ (6.8 g, 0.01 mol) in acetone (50 cm^3) was mixed with a solution of $[NBu^n_4][S_2CNMe_2]$ in the same solvent (50 cm^3). The white precipitate of $[ZnI_2\{(S_2CNMe_2)_2\}]$ which formed slowly was collected after 30 min and washed with acetone (2.4 g, 80%).

(*Dimethylaminothioxomethyl*)*triphenylphosphonium Hexafluorophosphate*.—A solution of $Ag[PF_6]$ (2.53 g) in CH_2Cl_2 (25 cm^3) was added to a solution containing Me_2NCSCl (1.24 g) and PPh_3 (2.62 g) in CH_2Cl_2 (50 cm^3). The mixture was stirred for 6 h, the precipitate of AgCl was removed by filtration, and the solvent was evaporated. The yellow solid was dissolved in acetone and the solution filtered. Addition of ethanol to the filtrate followed by partial evaporation afforded yellow *crystals*, which were collected, washed with diethyl ether, and recrystallised from boiling ethanol (0.88 g, 25%). The yield could be increased to 50% by allowing the reaction mixture to stand for 5 d.

(*Dimethylaminothioxomethyl*)*triphenylphosphonium Iodide*.—A solution of NaI (1.5 g) in boiling acetone (25 cm^3) was added to a solution containing PPh_3 (2.62 g) and Me_2NCSCl (1.35 g) in boiling acetone (50 cm^3) and the mixture was stirred for 20 min. The yellow *precipitate* was collected, washed with water, ethanol, and diethyl ether, then recrystallised from boiling methanol (2.9 g, 63%).

Reaction of $[PPh_3\{C(NMe_2)S\}][PF_6]$ *with* $[NBu^n_4][S_2CNMe_2]$.—A solution of $[NBu^n_4][S_2CNMe_2]$ (1.8 g, 5 mmol) in acetone (50 cm^3) was mixed with a solution of $[PPh_3\{C(NMe_2)S\}][PF_6]$ (2.5 g, 5 mmol) in acetone (50 cm^3) at 0 °C. The yellow solution immediately turned orange on mixing and had returned to yellow after 5 min. The solvent was evaporated and the residue (A) was collected and washed with diethyl ether (20 cm^3). Addition of n-pentane to the ether washings afforded white needles of PPh_3, which were separated from trace amounts of $S(SCNMe_2)_2$ by two recrystallisations from diethyl ether–n-pentane and the crystals were dried *in vacuo*. Mixture (A) was dissolved in acetone (20 cm^3) and addition of diethyl ether afforded white crystals of $[NBu^n_4][PF_6]$ (1.7 g, 90%), which were filtered off (B) and recrystallised from boiling ethanol. Filtrate (B) was evaporated and the yellow solid, $S(SCNMe_2)_2$, was recrystallised from dichloromethane–n-hexane.

Tetra-n-butylammonium Tri-iodo(*triphenylphosphine*)*zincate*(II).—A mixture of $[NBu^n_4]I$ (3.7 g) and PPh_3 (2.6 g) was dissolved in hot ethanol (40 cm^3) and a solution of ZnI_2 (3.2 g) in the same solvent (10 cm^3) was added. After 2 h the white crystals were collected, washed with diethyl ether, and recrystallised from acetone–light petroleum (7.5 g, 80%).

(*Dimethylaminothioxomethyl*)*triphenylphosphonium Tri-iodo*(*triphenylphosphine*)*zincate*(II).—A solution of PPh_3 (0.65 g) in boiling methanol was added to a solution containing $[PPh_3\{C(NMe_2)S\}]I$ (1.1 g) and ZnI_2 (0.8 g) in boiling methanol (80 cm^3). The hot solution was filtered and allowed to cool overnight. The few yellow *crystals* which formed were washed with $CHCl_3$ and diethyl ether, then recrystallised from acetone–light petroleum.

Reaction of $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$ *with* Me_2SO.—The salt $[PPh_3\{C(NMe_2)S\}][ZnI_3(PPh_3)]$ (1.0 g) was dissolved in Me_2SO (15 cm^3) and the mixture was shaken overnight. The yellow crystals of $[PPh_3\{C(NMe_2)S\}]I$ which precipitated were collected and recrystallised from boiling methanol.

Reactions of $[ZnI_2\{(S_2CNBu^n_2)_2\}]$.—*With* Pr^iNC. A solution of Pr^iNC (0.14 g, 2 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of $[ZnI_2\{(S_2CNBu^n_2)_2\}]$ (0.73 g, 1 mmol) in CH_2Cl_2 (10 cm^3). The solvent was evaporated and the residue was shaken with diethyl ether. The white solid,

$[Zn(CNPr^i)_2I_2]$, was removed from the orange-yellow solution by filtration and was recrystallised from dichloromethane–n-hexane (0.40 g, 87%). White crystals of $[Zn(CNBu^t)_2I_2]$ were obtained similarly.

With pyridine. A solution of $[ZnI_2\{(S_2CNBu^n_2)_2\}]$ (0.73 g) in CH_2Cl_2 (50 cm^3) was mixed with a solution of pyridine (0.16 g, 2 mmol) in CH_2Cl_2 (5 cm^3). White needles of $[ZnI_2(py)_2]$, produced on addition of diethyl ether, were collected and washed with ether (0.38 g, 80%).

With ethylenediamine (en). A solution of $[ZnI_2\{(S_2CNBu^n_2)_2\}]$ (3.6 g, 5 mmol) in CH_2Cl_2 (200 cm^3) was mixed with a solution of ethylenediamine (0.36 g, 5 mmol) in CH_2Cl_2 (10 cm^3). The white *precipitate* of $[Zn(en)_3]I_2$ was collected, washed with diethyl ether, and recrystallised from *NN*-dimethylformamide–diethyl ether (0.3 g).

Reactions of $[ZnI_2\{(S_2CNMe_2)_2\}]$.—*With pyridine.* On adding a solution of pyridine (10 cm^3, 0.2 mol dm^{-3}) in acetone to an orange solution of $[ZnI_2\{(S_2CNMe_2)_2\}]$ (0.56 g) in acetone (50 cm^3) there was an immediate lightening of the colour to pale yellow. The solution was evaporated to *ca.* 10 cm^3 and diethyl ether (50 cm^3) was added with cooling. The white crystals of $[ZnI_2(py)_2]$ were filtered off (A), washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (0.44 g, 93%). Filtrate (A) was evaporated, and the white residue, $(Me_2NCS_2)_2$, was recrystallised from dichloromethane–n-hexane.

With $[NBu^n_4][S_2CNMe_2]$. A solution of $[NBu^n_4][S_2CNMe_2]$ (0.36 g) in acetone (10 cm^3) was added to a suspension of $[ZnI_2\{(S_2CNMe_2)_2\}]$ (0.56 g) in acetone (15 cm^3). Addition of diethyl ether (*ca.* 200 cm^3) to the yellow solution caused precipitation of $[NBu^n_4][ZnI_2(S_2CNMe_2)]$ which was filtered off (A) and recrystallised from dichloromethane–n-hexane (0.61 g, 89%). The filtrate (A) was evaporated and the white solid, $(Me_2NCS_2)_2$, was recrystallised from dichloromethane–n-hexane.

With ethanol. A suspension of $[ZnI_2\{(S_2CNMe_2)_2\}]$ (5.6 g, 0.01 mol) in EtOH (100 cm^3) was stirred for 1 h. The white solid, $(Me_2NCS_2)_2$, was collected and washed with n-pentane (2.4 g, quantitative). Similarly, $(C_5H_{10}NCS_2)_2$ was obtained quantitatively from $[ZnI_2\{(S_2CNC_5H_{10})_2\}]$.

Di-iodo[NN′-*bis(pentanediyl)thiuram disulphide*]*zinc*(II).—To a solution of $[Zn(S_2CNC_5H_{10})_2]$ (3.9 g, 0.01 mol) in CH_2Cl_2 (250 cm^3) was added to a solution of I_2 (2.5 g, 0.01 mol) in the same solvent (250 cm^3). The solvent was reduced to *ca.* 100 cm^3 by evaporation and n-hexane was added to cause further precipitation of the product. This was collected by filtration, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane. The complex $[ZnI_2\{(S_2CNMe_2)_2\}]$ was prepared similarly.

Tetra-n-butylammonium Tris(dimethyldithiocarbamato)zincate(II).—The complex $[Zn(S_2CNMe_2)_2]$ (6.1 g, 0.02 mol) was added to a solution of $[NBu^n_4][S_2CNMe_2]$ (7.2 g, 0.02 mol) in acetone (200 cm^3). The mixture was shaken until all the solid had dissolved, then light petroleum was added and the solvent was partially evaporated. The white *crystals* were collected and recrystallised from acetone–light petroleum (13.3 g, quantitative).

The salts $[NBu^n_4][Zn(S_2CNBu^n_2)(S_2CNMe_2)_2]$ (in lower yield), $[NBu^n_4][Zn(S_2CNEt_2)_2(S_2CNMe_2)]$, and $[NEt_4][Zn(S_2CNMePh)_3]$ were prepared similarly from $[Zn(S_2CNBu^n_2)_2]$, $[Zn(S_2CNEt_2)_2]$, and $[Zn(S_2CNMePh)_2]$, respectively.

Tetra-n-butylammonium Acetatobis(dimethyldithiocarbamato)zincate(II).—The salt $[NBu^n_4][OH]$ (6.7 cm^3, 40% aqueous solution) and acetic acid (0.6 g) were mixed and the solution was evaporated to dryness *in vacuo* at 60 °C. The oil which formed was dissolved in acetone (100 cm^3) and to this was added $[Zn(S_2CNMe_2)_2]$ (3.0 g). The mixture was shaken for 2 h and then filtered. To the filtrate was added light petroleum (b.p. 60—80 °C) and, after gradual evaporation, white crystals of the *product* formed. These were recrystallised from acetone–light petroleum.

Reactions of $[NBu^n_4][Zn(S_2CNMe_2)_3]$.—*With* I_2. A solution of $[NBu^n_4][Zn(S_2CNMe_2)_3]$ (0.67 g, 1 mmol) in acetone (20 cm^3) was mixed with a solution of I_2 (0.25 g, 1 mmol) in the same solvent (50 cm^3). The yellow solution was evaporated and the residue was shaken with diethyl ether (100 cm^3) overnight. The mixture was filtered (A) and the filtrate was evaporated to a small volume. The white crystals of $(Me_2NCS_2)_2$ were collected (0.23 g, 92%). Residue (A), $[NBu^n_4][ZnI_2(S_2CNMe_2)]$, was recrystallised from acetone–diethyl ether (0.50 g, 75%).

With CH_2Cl_2. A solution of $[NBu^n_4][Zn(S_2CNMe_2)_3]$ (3.3 g, 5 mmol) in dichloromethane (25 cm^3) was allowed to stand for 1 h and then evaporated to dryness. The solid residue was shaken with ethanol (15 cm^3) overnight, and the mixture was then filtered. The residue was washed with acetone (30 cm^3), dried in air, and identified as $[Zn(S_2CNMe_2)_2]$ (1.32 g, 87%). The washings and the filtrate were combined and on addition of light petroleum (b.p. 60—80 °C) afforded crystals of $CH_2(S_2CNMe_2)_2$ (0.5 g, 80%).

Tetra-n-butylammonium Dimethyldithiocarbamate.—To an aqueous solution of $[NBu^n_4][OH]$ (100 cm^3, 40%), diluted with water (250 cm^3), was added CS_2 (11.9 g) and the mixture was shaken with NMe_2H (28 cm^3, 25% aqueous solution) until it became homogeneous. The water was evaporated, keeping the temperature below 40 °C, and the pale yellow *solid* which formed was filtered off, washed with diethyl ether, and recrystallised from acetone–light petroleum (57.0 g, quantitative yield). Tetramethyl- and tetraethyl-ammonium salts of $[S_2CNMe_2]^-$, and $[NEt_4][S_2CNMePh]$, were prepared similarly.

Reaction of $[NBu^n_4][S_2CNMe_2]$ *with* CH_2Cl_2.—The salt $[NBu^n_4][S_2CNMe_2]$ (1.8 g) was dissolved in dichloromethane (25 cm^3). After 5 min the solution was rapidly evaporated to a white powder which was washed with ethanol (20 cm^3) and then pentane. The compound $CH_2(S_2CNMe_2)_2$ was recrystallised from acetone–light petroleum (b.p. 60—80 °C).

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