Sulphur-ligand–Metal Complexes. Part 7.[1] The Interaction of some Diphosphine Dichalcogenides and Tetra-alkylthiuram Disulphides with Halogens and some First-row Transition-metal Salts

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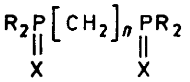
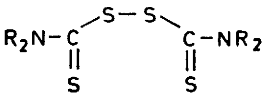
Iodine interacts with $R_2P(X)\cdot[CH_2]_n\cdot(X)PR_2$ [R = Ph, X = S, n = 1 (L′); R = Ph, X = S, n = 2 (L²); or R = Me, X = S, n = 0 (L⁴)] to give charge-transfer adducts of the type $L\cdot 2I_2$ or $L\cdot I_2$, whereas corresponding reactions with $R_2N\cdot CS\cdot S_2\cdot CS\cdot NR_2$ [R = Me (L⁵) or Et (L⁶)] give products of the type $L'\cdot I_6$ in which L′ is oxidised probably to give a dication with the cyclised structure $[\overline{C(:NR_2)\cdot S\cdot S\cdot C(:NR_2)\cdot S\cdot S}]^{2+}$ (A) (L⁸, R = Et; L⁹, R = Me) with two $[I_3]^-$ as counter ions. The interactions of L′ with $FeCl_3$, $Co[BF_4]_2\cdot 6H_2O$, and $CoCl_2\cdot 6H_2O$ (all in excess) in diethyl ether or acetone–chloroform also give products containing the species (A) in the following complexes; $[L^9][FeCl_4]_2$, $[L^8][FeCl_4]_2$, $[L^9][BF_4]_2$, and $[L^9][CoCl_4]$ as well as dithiocarbamato-complexes. Dimethylcarbamoyl dimethylthiocarbamoyl disulphide and bis(diethyldithiocarbamylthio)methane with $FeCl_3$ are each thought to produce cyclised dications similar to (A). With the appropriate copper(II) salts (in excess) and L′ in acetone, the copper(III) derivatives $[CuCl_2(S_2CNR_2)]$ and $[Cu(S_2CNR_2)_2][BF_4]$ (R = Me or Et) have been isolated. In the first two cases when the solvent is changed to chloroform–ethanol the copper(II) derivatives $[CuCl(S_2CNR_2)]$ are found. With $Ni[BF_4]_2\cdot 6H_2O$ and $NiCl_2\cdot 6H_2O$ in excess and acetone as solvent, L′ gives $[Ni(S_2CNMe_2)_3]X$ ($X = BF_4^-$ or Cl^-), the oxidation state of nickel probably being IV, while excess of $Fe[ClO_4]_2\cdot 6H_2O$ gives the known iron(IV) derivative $[Fe(S_2CNMe_2)_3][ClO_4]$.

RECENTLY[2] we reported that copper(II) salts reacted with some 'diphosphine disulphides' and 'diphosphine diselenides' (L¹—L⁴) to produce copper(I) derivatives but we were not able to determine the nature of the oxidised products. We now report the nature of the products formed when iodine and bromine are allowed to react with the above system, as well as of the products of the corresponding reactions with some dithiones, *e.g.* tetra-alkylthiuram disulphides (L⁵ and L⁶). The interaction of the above thiuram disulphides with Cu^{II}, Ni^{II}, Co^{II}, and Fe^{II} has not been as extensively studied as with the dialkyldithiocarbamates, and these reactions have been re-examined and the products identified, and hence alternative ways for the preparation of some previously reported compounds are described and some new compounds characterised.



$$R_2\underset{\underset{X}{\|}}{P}[CH_2]_n\underset{\underset{X}{\|}}{P}R_2$$

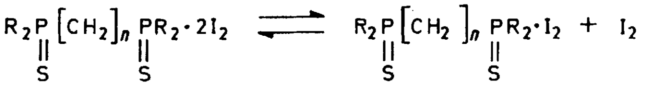
	R	X	n
L¹	Ph	S	1
L²	Ph	S	2
L³	Ph	Se	2
L⁴	Me	S	0



	R
L⁵	Me
L⁶	Et

RESULTS AND DISCUSSION

Interaction of the Diphosphine Disulphides and Diphosphine Diselenides with Halogens.—Iodine reacted with compounds L²—L⁴ in a 2 : 1 mol ratio in chloroform to give $L\cdot 2I_2$ as solid products (see Table), whereas $L^1\cdot 2I_2$ could not be isolated in the solid state; L⁴ also reacted with iodine in a 1 : 1 mol ratio to give $L^4\cdot I_2$. The i.r. spectra of all these compounds were similar to the parent species; in particular $L^4\cdot 2I_2$ and $L^4\cdot I_2$ were similar to L⁴ which has a *trans* configuration in the solid state;[3] also ν(P=S) decreased by *ca.* 18 cm^{-1} showing that an interaction between sulphur donating to I_2 had occurred.[2] The other adducts showed smaller lowerings of ν(P=S) (see Table 4) but a $S \longrightarrow I_2$ interaction is suggested; an *X*-ray crystallographic study[4] on a related compound $PPh_3S\cdot 1.5I_2$ has demonstrated this. In chloroform a 'blue shift' occurred in the free-iodine absorption[5] from 511 to *ca.* 304—322 nm in the adducts (see Table) and the free-iodine band also appeared. On addition of more ligand the free-iodine band decreased in intensity while the 'blue-shift' band increased suggesting equilibrium (1). Similar shifts occurred in acetone. The conductivity values in acetone for the adducts lie between a non-electrolyte and a 1 : 1 electrolyte, with $L^4\cdot 2I_2$ having twice the conductance of $L^4\cdot I_2$ (see Table). Equation (2) may explain these values, with the equilibrium being to the left. These compounds are



$$R_2\underset{\underset{S}{\|}}{P}[CH_2]_n\underset{\underset{S}{\|}}{P}R_2\cdot 2I_2 \rightleftharpoons R_2\underset{\underset{S}{\|}}{P}[CH_2]_n\underset{\underset{S}{\|}}{P}R_2\cdot I_2 + I_2 \qquad (1)$$

$$L^4\cdot I_2 \rightleftharpoons L^4\cdot I^+ + I^- \qquad (2)$$

then probably best considered as charge-transfer adducts as are the similar unidentate phosphine chalcogen compounds.[5] Bromine interacted with L⁴ to give $PBrMe_2S$ [6] but no oxidation of L² occurred.

Interactions of Tetra-alkylthiuram Disulphides.—With

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[1] Part 6, E. W. Ainscough, A. M. Brodie, and K. C. Palmer, *J.C.S. Dalton*, 1976, 2375.

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halogens. Wase and Christensen[7] first reported that tetraethylthiuram disulphide (antabuse, L^6) reacted with iodine but the nature of the products was not determined. A violet-brown adduct of stoicheiometry $L^6{\cdot}I_6$ was isolated from chloroform solution when L^6 and iodine were added in a 1 : 3 mol ratio. In chloroform this compound showed three bands at 294, 362, and 511 nm (see Table). The last band is due to iodine whereas the first two bands correspond to those of the $[I_3]^-$ species whose spectral details are known.[8] In acetone a weak shoulder due to free iodine was found at 540 nm while an $[I_3]^-$ band occurred at 366 nm.

Analytical data, conductivities, and i.r. and electronic spectra for the compounds

Compound	Analysis (%) [a] C	H	I	N	Λ [b] S cm^2 mol^{-1}	I.r. (cm^{-1}) ν(P=S)	Electronic spectra (nm) [c]
$L^2{\cdot}2I_2$	32.1	2.6	52.6		113 [d]	615,	304 (3 425), 511 (1 710); [f] 366 (20 400),
	(32.2)	(2.5)	(52.4)			597 [e]	540w (sh) [d]
$L^3{\cdot}2I_2$	29.5	2.4	47.8		*g*	527 [h]	322, 511 [d]
	(29.3)	(2.3)	(47.7)				
$L^4{\cdot}2I_2$	7.6	2.2	70.1		130 [d]	551 [i]	315 (1 250), 511 (1 900); [f] 365 (18 000),
	(6.9)	(1.7)	(73.2)				540w (sh) [d]
$L^4{\cdot}I_2$	11.1	2.9	56.7		59 [d]	550	315 (450), 511 (823); [f] 365 (9 500),
	(10.9)	(2.7)	(57.7)				540w (sh) [d]
$[L^8][I_3]_2$	11.6	2.1	72.2	2.65	188 [d]	1 560 [j,k]	294 (13 800), 362 (9 000), 511 (2 200); [f,l]
	(11.5)	(1.9)	(72.0)	(2.65)	220 [m]		366 (15 000), 540w (sh) [d,l]
$[L^9][I_3]_2$	6.8	1.4	77.9		194 [d]	1 572 [j,n]	366 (21 700), 540w (sh) [d,l]
	(7.2)	(1.2)	(76.0)		216 [m]		
$[L^9][Br_5]$ [o]	11.6	1.9	58.0	4.4	*g*	1 578 [j]	*g*
	(11.3)	(1.9)	(62.5) [p]	(4.4)			
$[L^8][FeCl_4]_2$	17.6	2.9	18.2	4.3	203 [m]	1 565 [j]	240 (12 150), 273 (18 600) 314 (7 200),
	(17.4)	(2.9)	(18.5) [q]	(4.05)			362 (6 750) [l,m]
$[L^9][FeCl_4]_2$	10.2	2.5	44.6	3.8	220 [m]	1 580 [j]	240 (12 150), 273 (17 100), 314 (6 800),
	(11.3)	(1.9)	(44.6) [r]	(4.4)			362 (6 600) [l,m]
$[L^{12}][FeCl_4]_2{\cdot}0.5H_2O$	11.1	2.7	46.3	4.15	227 [m]	1 580 [j,s]	240 (12 150), 274 (18 000), 314 (6 800),
	(11.4)	(2.1)	(45.1) [r]	(4.45)			362 (6 500) [l,m]
$[L^{13}][FeCl_4]_2{\cdot}3H_2O$	17.15	3.65	37.0	3.5	219 [m]	1 555 [j,t]	240 (12 150), 272 (20 000), 314 (6 800),
	(17.4)	(3.7)	(37.35)	(3.7)			362 (6 900) [l,m]
$[CuCl_2(S_2CNEt_2)]$	21.4	3.7	25.0	5.0	35 [u]	1 593 [j]	470br, 520br, 735; [v] 425 (7 600), 520
	(21.2)	(3.5)	(25.1) [r]	(4.95)			(sh), 645 (140) [u]
$[CuCl_2(S_2CNMe_2)]$	14.3	2.7	28.2	5.2	*x*	1 615 [j]	460br, 510br, 745; [v] 420, 510 (sh),
	(14.1)	(2.4)	(27.8) [r]	(5.5)			650 [u]
$[CuCl(S_2CNMe_2)]$	17.3	2.7	16.2	6.1	*x*	1 557 [j]	406, 465 (sh), 612; [v] 420, 640 [u]
	(16.4)	(2.7)	(16.7) [r]	(6.4)			
$[CuCl(S_2CNEt_2)]$	24.6	4.1	15.5	5.8	*y*	1 515 [j]	407, 475 (sh), 620; [v] 422, 650 [u]
	(24.3)	(4.0)	(14.4) [r]	(5.7)			
$[Cu(S_2CNEt_2)_2][BF_4]$	26.7	4.7		6.3	54 [u]	1 586 [j]	420 (24 300), 635 (510); [u] 380, 465,
	(26.8)	(4.5)		(6.3)			660 [v]
$[Cu(S_2CNMe_2)_2][BF_4]$	18.8	3.1		7.0	68 [u]	1 581 [j]	423 (22 800); 645 (700) [u]
	(18.4)	(3.1)		(7.2)			
$[Ni(S_2CNMe_2)_3][BF_4]$	22.1	3.7	36.2	8.0	112 [m]	1 577 [j]	440 (4 700), 490 (sh) (3 400), 550 (sh),
	(21.35)	(3.55)	(37.9) [q]	(8.3)			(2 300) [m]
$[Ni(S_2CNMe_2)_3]Cl$ [z]	21.0	4.25			*	1 577 [j]	440, 490 (sh), 550 (sh) [m]
	(23.8)	(4.0)					
$[Fe(S_2CNMe_2)_3][ClO_4]$	21.6	4.5		7.9	41 †	1 563 [j]	395 (4 400), 515 (1 250), 595 (1 000) †
	(21.0)	(3.5)		(8.15)			
$[L^9][CoCl_4]$	16.8	3.2	33.9	6.5	50 †	1 587 [j]	610 (sh) (330), 678 (535) †, ‡
	(16.3)	(2.7)	(32.2) [r]	(6.35)			
$[L^8][CoCl_4]$	25.8	4.2	28.6	5.7	51 †	1 558 [j]	610 (sh) (309), 678 (510) †, ‡
	(24.1)	(4.0)	(27.5) [r]	(5.6)			

[a] Calculated values are given in parentheses. [b] 10^{-3} mol dm^{-3} solution in solvent indicated. [c] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses where measured. [d] In acetone. [e] L^2 has ν(P=S) at 614 and 610 cm^{-1}. [f] In chloroform. [g] Insoluble. [h] L^3 has ν(P=Se) at 530 cm^{-1}. [i] L^4 has ν(P=S) at 568 cm^{-1}. [j] The ' thioureide ' band, ν(C$\overset{\cdots}{-}$N). [k] L^6 has ν(C$\overset{\cdots}{-}$N) at 1 495 cm^{-1}. [l] The absorption coefficients were calculated per mol of anion. [m] In acetonitrile. [n] L^5 has ν(C$\overset{\cdots}{-}$N) at 1 500 cm^{-1}. [o] Fumes in air. [p] Br. [q] S. [r] Cl. [s] L^{12} has ν(C$\overset{\cdots}{-}$N) at 1 502 cm^{-1}. [t] L^{13} has ν(C$\overset{\cdots}{-}$N) at 1 480 cm^{-1}. [u] In nitromethane. [v] Reflectance spectra. [x] Insufficiently soluble. [y] Not determined. [z] Partly decomposes to $[Ni(S_2CNMe_2)_2]$ after 1 week.

* Partly decomposes to $Ni(S_2CNMe_2)_2$ in acetonitrile. † In dimethylformamide. ‡ The band at 678 nm is assigned to the $^4A_2 \longrightarrow {}^4T_1(P)$ absorption of a tetrahedral species.

In acetone and acetonitrile the compound behaved as a 2 : 1 electrolyte (see Table).[9] Finally the ' thioureide band ' ν(C$\overset{\cdots}{-}$N) in L^6 moved from 1 495 to 1 560 cm^{-1} in $L^6{\cdot}I_6$, suggestive of a higher C$\overset{\cdots}{-}$N bond order, and the band at 1 002 cm^{-1} in L^6 which has a contribution from ν(C=S) was missing.[10] These data (see Table) indicate that either the monomeric ion L^7 or the dipositive ion L^8 with a tetrathian ring is present. Molecular models suggest L^7 would be unstable due to considerable ring strain so L^8 is favoured. This same cation has been suggested to exist in the product obtained from reaction of $[Fe(S_2CNEt_2)_3]$ with chlorine.[11] The adduct $L^5{\cdot}I_6$ was prepared similarly to $L^6{\cdot}I_6$ and u.v.–visible

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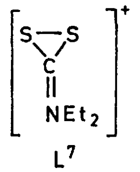
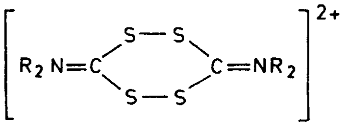
studies detected the presence of $[I_3]^-$, conductivity studies indicated a 2 : 1 electrolyte, and i.r. studies showed a shift in $\nu(\mathrm{C{\cdots}N})$ to higher energies and the virtual disappearance of the $\nu(\mathrm{C{=}S})$ band[12] at 973 cm^{-1} (see Table). Structure L^9 is suggested for the cation. Hence oxidation of thiuram disulphides occurs with I_2, so antabuse (L^6), which is used in the treatment for alcoholism, is an antithyroid reagent. The compound L^5 reacted with excess of bromine to produce $L^9\cdot Br_5$ which also can be formulated to contain the cation L^9 from i.r. studies, it being too insoluble for other studies.



L^7

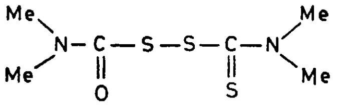


R

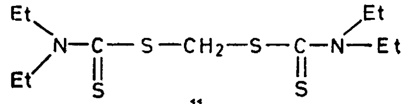
L^8 Et

L^9 Me

With iron salts.—Tamminen and Hjelt[13] first reported the reaction of L^6 with excess of $FeCl_3$ in diethyl ether and obtained a complex of composition $FeCl_4(S_2CNEt_2)$. Subsequently Willemse and Steggerda[11] reinvestigated this complex and suggested that it contained the cation L^8. We have repeated this reaction and obtained a more extensive series of complexes $[L''][FeCl_4]_2$ [L'' = the dication of L^5, L^6, dimethylcarbamoyl dimethylthiocarbamoyl disulphide (L^{10}), and bis(diethylthiocarbamoylthio)methane (L^{11})]. The complexes $[L''][FeCl_4]_2$ were 2 : 1 electrolytes in acetonitrile and all had bands at 240, 314, and 362 nm which are consistent with the presence[14] of $[FeCl_4]^-$ (see Table). The i.r. spectra showed bands at 375 cm^{-1} which is the antisymmetric ν(Fe–Cl) for $[FeCl_4]^-$,[15] and for the first two L'' complexes the i.r. spectra were similar to $[L^9][I_3]_2$ and $[L^8][I_3]_2$ respectively. Cations L^9, L^8, L^{12}, and L^{13} are present in the above complexes respectively.

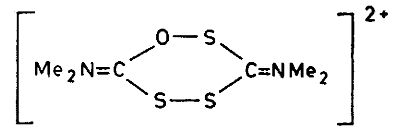


L^{10}

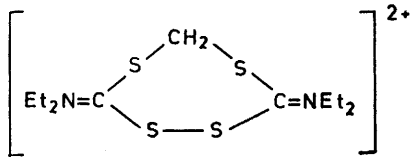


L^{11}

Other iron products containing $[S_2CNEt_2]^-$ and $[S_2CNMe_2]^-$ are present in the mother liquors for the thiuram disulphides.[13,16] The oxidation of the thiuram disulphides to 3,6-bis(dialkyliminio)-1,2,4,5-tetrathiolan cations (L^8 and L^9) is similar to the behaviour of pentane-2,4-dithione which can be oxidised to a 3,5-dimethyl-1,2-dithiolylium cation,[17] to tetramethylthiuram monosulphide which can be oxidised to the 3,5-bis(diethyliminio)-1,2,4-trithiolen cation,[18,19] and to dithiobiuret which can be oxidised to the 3,5-diamino-1,2,4-dithiazolium cation.[20] Finally, and in contrast to the above reactions, when L^5 was added to $Fe[ClO_4]_2\cdot 6H_2O$ in acetone (1 : 4 mol ratio) blackish crystals of $[Fe(S_2CNMe_2)_3][ClO_4]$ were isolated. This cation was first isolated as a $[BF_4]^-$ salt by Pasek and Straub[21] by the aerial oxidation of $[Fe(S_2CNMe_2)_3]$ with gaseous BF_3. The single-crystal *X*-ray structure of the related dipyrrolidinyldithiocarbamate complex $[Fe\{S_2CN(C_4H_8N)_2\}_3][ClO_4]$ shows the iron to be six-co-ordinate and is consistent with it being in oxidation state IV.[22]



L^{12}



L^{13}

With copper(II) *salts.* Tamminen and Hjelt[13] found that L^6 reacted with $Cu[SO_4]\cdot 5H_2O$ in a 1 : 1 mol ratio to produce the known $[\{Cu(S_2CNEt_2)_2\}_2]$.[23] We treated L^6 with copper(II) chloride dihydrate (in a 1 : 6 or 1 : 3 mol ratio) in acetone and isolated red-brown crystals of the diamagnetic copper(III) derivative $[CuCl_2(S_2CNEt_2)]$. Similarly with L^5, $[CuCl_2(S_2CNMe_2)]$ was prepared. The u.v.–visible absorption spectra (see Table) of these complexes were similar to those of $[CuBr_2(S_2CNBu_2)]$ obtained from oxidation of $Cu[S_2CNBu_2]$ with Br_2 and which contains a square-planar arrangement of ligands about Cu^{III} as shown by a single-crystal *X*-ray

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study.[24] Consistent with $[CuCl_2(S_2CNEt_2)]$ and $[CuCl_2(S_2CNMe_2)]$ being copper(III) compounds are the high $\nu(C\overset{\cdots}{-}N)$ frequencies at 1 593 and 1 615 cm^{-1} compared with 1 490 and 1 520 cm^{-1} for $[\{Cu(S_2CNEt_2)_2\}_2]$ and $[\{Cu(S_2CNMe_2)_2\}_2]$ respectively. When these reactions were performed in $CHCl_3$–EtOH mixtures the copper(II) derivatives $[CuCl(S_2CNEt_2)]$ and $[CuCl(S_2CNMe_2)]$ were obtained, the $\nu(C\overset{\cdots}{-}N)$ frequencies decreasing to 1 510 and 1 557 cm^{-1} respectively. From a single-crystal *X*-ray analysis,[25] the complex $[CuCl(S_2CNEt_2)]$ is a chloro-bridged dimer with the fifth position being occupied by a bridging sulphur. The complexes $[CuCl(S_2CNEt_2)]$[25] and $[CuCl(S_2CNMe_2)]$ have sub-normal magnetic moments (1.52 and 1.54 B.M. respectively) * at 30 °C.

When $Cu[BF_4]_2 \cdot 6H_2O$ and L^5 or L^6 were mixed in a 3 : 1 mol ratio in acetone $[Cu(S_2CNMe_2)_2][BF_4]$ and $[Cu(S_2CNEt_2)_2][BF_4]$ were isolated. The latter copper(III) complex has been prepared previously[16] as the $[FeCl_4]^{2-}$ and $[ClO_4]^-$ salts by oxidation of $[\{Cu(S_2CNEt_2)_2\}_2]$ with $FeCl_3$ and $Cu[ClO_4]_2 \cdot 6H_2O$ respectively, while the former complex is new. Both are diamagnetic and showed $\nu(C\overset{\cdots}{-}N)$ bands at high wavenumbers consistent with their high oxidation states (*e.g.* 1 586 and 1 581 cm^{-1} respectively). The u.v.–visible absorption spectra (see Table) had bands at *ca.* 640 and 425 nm in $MeNO_2$ and are similar to the isoelectronic $[Ni(S_2CNEt_2)_2]$; also they are 1 : 1 electrolytes in this solvent. A single-crystal *X*-ray analysis[26] on a related complex, bis(tetramethylenedithiocarbamato)copper(III) perchlorate, has shown this to contain a square-planar arrangement of the sulphur atoms about Cu^{III} and we suggest a similar structure for each of these complexes.

The complex $[Cu(S_2CNEt_2)_2][BF_4]$ interacted with L^6 in acetone to produce the copper(II) derivative $[\{Cu(S_2CNEt_2)_2\}_2]$. The first stage then is reduction of L^6 by Cu^{2+} to produce $[S_2CNEt_2]^-$ and Cu^{3+}, the latter being stabilised by $[S_2CNEt_2]^-$. The second stage is reduction of $[Cu(S_2CNEt_2)_2]^+$ by L^6 to produce $[\{Cu(S_2CNEt_2)_2\}_2]$ and presumably the dication L^8. The ability of L^6 to be reduced and then later oxidised is an interesting feature of this ligand. As expected $[Cu(S_2CNEt_2)_2][BF_4]$ was obtained when $Cu[BF_4]_2 \cdot 6H_2O$ and $Na[S_2CNEt_2] \cdot 3H_2O$ were mixed in a 3 : 1 mol ratio in acetone and similarly for $[Cu(S_2CNMe_2)_2][BF_4]$. For the latter complex reduction by L^5 did not readily occur.

With nickel(II) *salts*. When $Ni[BF_4]_2 \cdot 6H_2O$ and L^5 were mixed in a 3 : 1 mol ratio in acetone–chloroform reduction of the ligand occurred and brown-red crystals of $[Ni(S_2CNMe_2)_3][BF_4]$ (with nickel tentatively in oxidation state IV) were isolated. Similarly, with $NiCl_2 \cdot 6H_2O$, $[Ni(S_2CNMe_2)_3]Cl$ was obtained although it decomposed to give $[Ni(S_2CNMe_2)_2]$ in solution and in the solid state. It was sensitive to heat and light.[27] The former complex is a 1 : 1 electrolyte in acetonitrile, and the electronic spectra of the two complexes are nearly identical to $[Ni(S_2CNBu_2)_3]Br$[28] and similar to $[Co(S_2CNEt_2)_3]$. Also, $\nu(C\overset{\cdots}{-}N)$ at *ca.* 1 577 cm^{-1} for both complexes is consistent with nickel being in a high oxidation state. A single-crystal *X*-ray structural analysis[27] on $[Ni(S_2CNBu_2)_3]Br$ has shown this to have a distorted octahedral structure about nickel. Finally, Contreras and Cortés[29] have prepared complexes of Ni^{II} with L^5 and L^6 intact. The intact ligands have also been found in complexes of Cr^{III}[12] and Hg^{II}.[30,31]

With cobalt(II) *salts*. The compounds L^5 and L^6 reacted with $CoCl_2$ in a 1 : 1 mol ratio to give $CoCl_2L_2$ which are distorted octahedral.[29] However, repeating these reactions in a 1 : 3 mol ratio gave new products; *e.g.* L^5 reacted with $Co[BF_4]_2 \cdot 6H_2O$ to give a small amount of white precipitate from a green solution $\{$containing $[Co(S_2CNMe_2)_3]\}$. The i.r. spectrum of the white compound showed the presence of ionic $[BF_4]^-$, $\nu(C\overset{\cdots}{-}N)$ increased to 1 595 cm^{-1}, $\nu(C{=}S)$ was missing, and the spectrum was generally similar to $L^5 \cdot I_6$. Unfortunately the compound decomposed after a couple of days but we suggest that $[L^9][BF_4]_2 \cdot xH_2O$ may have formed, the smaller anion not stabilising the cation. When L^5 or L^6 was treated with $CoCl_2 \cdot 6H_2O$ (1 : 3 mol ratio) in acetone a small amount of a light green complex, $[L^9][CoCl_4]$ or $[L^8][CoCl_4]$, was isolated. The *d–d* spectra of each complex were consistent with a tetrahedral cobalt(II) ion (see Table) and the i.r. spectra showed the 'thioureide' band at 1 587 and 1 558 cm^{-1} respectively; also for each complex, $\nu(C{=}S)$ was absent and an i.r. band at *ca.* 284 cm^{-1} was consistent with $\nu(Co{-}Cl)$ for $[CoCl_4]^{2-}$. On a similar basis to the above, we suggest that the oxidised forms of the ligands are present in these complexes (see structures of the cations L^8 and L^9); hence they are formulated as given. The filtrates from these reactions yielded the known cobalt(III) derivatives $[Co(S_2CNMe_2)_3]$ and $[Co(S_2CNEt_2)_3]$[13] and these were characterised by m.p., i.r., and electronic spectra.

EXPERIMENTAL

Infrared spectra were recorded on Beckman IR20 (250—4 000 cm^{-1}) and Perkin-Elmer 720 (600—4 000 cm^{-1}) spectrophotometers. Magnetic moments were measured using a Cahn electrobalance and electronic spectra on a Shimadzu MPS 5000 spectrophotometer. Conductivity measurements were made at 20 °C using a Phillips PR 9500 conductivity meter and cell. Microanalyses were by

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

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Professor A. D. Campbell, University of Otago. Analytical data are summarised in the Table.

Laboratory grade solvents were used as purchased while L^5 (tetramethylthiuram disulphide) and L^6 (tetraethylthiuram disulphide) were obtained from B.D.H. and Sigma Chemical Company respectively; L^{10} (dimethylcarbamoyl dimethylthiocarbamoyl disulphide) was obtained from a published procedure[32] and L^{11} [bis(diethyldithiocarbamylthio)methane] was prepared by refluxing $Na[S_2CNEt_2]\cdot 3H_2O$ (9.0 g, 0.04 mol) with CH_2I_2 (5.46 g, 0.02 mol) in methanol (35 cm^3) for 3 h. On cooling (overnight) white crystals of the product appeared and these were filtered off and recrystallised from chloroform (30 cm^3) placed in an ice-bath, yield 4.2 g, m.p. 73 °C. Compounds L^1—L^4 were obtained as previously described.[2]

Preparations.—The adducts $L\cdot 2I_2$ ($L = L^2$, L^3, *or* L^4). These were obtained by similar methods of which the following is typical. To L^2 (0.23 g, 0.5 mmol) dissolved in $CHCl_3$ (12 cm^3) was slowly added iodine (0.254 g, 1 mmol) dissolved in $CHCl_3$ (*ca.* 70 cm^3). On removal of over half the solvent on a rotatory evaporator a dark red-brown precipitate appeared, and this was filtered off and washed with hexane and diethyl ether. Yields were *ca.* 50—60%. M.p.s: $L^2\cdot 2I_2$, 183; $L^3\cdot 2I_2$, 161—166; and $L^4\cdot 2I_2$, 80 °C.

The adduct $L^4\cdot I_2$ was prepared similarly except that iodine was added to L^4 in a 1 : 1 mol ratio.

The compounds $[L''][I_3]_2$ ($L'' = L^8$ *or* L^9). These were obtained by similar methods of which the following is typical. To L^5 (0.24 g, 1 mmol) dissolved in $CHCl_3$ (15 cm^3) was added slowly iodine (0.762 g, 3 mmol) dissolved in $CHCl_3$ (150 cm^3). A dark red-violet complex immediately precipitated and this was washed with $CHCl_3$, hexane, and diethyl ether. For L^6, precipitation occurred on reduction of the volume of $CHCl_3$. The yield of $[L^9][I_3]_2$ was 60% while that of $[L^8][I_3]_2$ was 40%. The former compound has a m.p. of 154—158 °C.

The compound $[L^9][Br_5]$. To L^5 (10 g, 0.046 mol) dissolved in $CHCl_3$ (120 cm^3) was added over 5 min a solution of bromine (19.2 g, 0.12 mol) dissolved in $CHCl_3$ (100 cm^3). A deep orange solid precipitated and was filtered off and washed with $CHCl_3$ and diethyl ether. The yield was 90% and the m.p. was *ca.* 138 °C. The compound fumed in air, and in acetone a light yellow solid of approximate composition $[L^9][Br_2]$ was isolated. A brief report of $[L^9][Br_5]$ has appeared in the literature.[32]

The complexes $[L''][FeCl_4]_2$ ($L'' = L^8$, L^9, L^{12}, *and* L^{13}). These were obtained following the method of Tamminen and Hjelt.[13] A typical preparation is described. To L^6 (1.46 g, 0.005 mol) dissolved in diethyl ether (or chloroform) (40 cm^3) was added anhydrous iron(III) chloride (3.25 g, 0.02 mol) dissolved in diethyl ether (40 cm^3). A black precipitate formed, which was filtered off and repeatedly washed with chloroform until yellowish crystals were left, yield 1.2 g, m.p. 150 °C with decomposition at 130 °C. M.p.s: $[L^9][FeCl_4]_2$, 150; $[L^{12}][FeCl_4]_2$, 140—150; and $[L^{13}][FeCl_4]_2$, *ca.* 150 °C. For the last complex there was less contamination with by-products in its preparation.

The complexes $[CuCl_2(S_2CNR_2)]$ (R = Me *or* Et). These copper(III) derivatives were prepared by similar methods of which the following is typical. To $CuCl_2\cdot 2H_2O$ (0.7 g, 4 mmol) dissolved in acetone (*ca.* 80 cm^3) was added slowly L^6 (0.20 g, 0.7 mmol) dissolved in acetone (15 cm^3). The solution became reddish and after *ca.* 15 min red-brown crystals of $[CuCl_2(S_2CNEt_2)]$ appeared, which were filtered off and washed with acetone and diethyl ether, yield 0.3 g, m.p. 130 °C. For $[CuCl_2(S_2CNMe_2)]$, L^5 (*ca.* 0.12 g, 0.5 mmol) dissolved in acetone (20 cm^3) was added to $CuCl_2\cdot 2H_2O$ (1.0 g, 6 mmol) dissolved in acetone (100 cm^3). The red-brown precipitate had a m.p. of 140 °C.

The complex $[CuCl(S_2CNMe_2)]$. Compound L^5 (0.24 g, (1 mmol) dissolved in $CHCl_3$ (*ca.* 10 cm^3) was added slowly to $CuCl_2\cdot 2H_2O$ (2.0 g, 12 mmol) dissolved in ethanol (*ca.* 80 cm^3). A brown-green complex precipitated (0.15 g) and this was washed thoroughly with ethanol, $CHCl_3$, and diethyl ether. An alternative preparation was achieved by the addition of $Na[S_2CNMe_2]\cdot H_2O$ (0.179 g, 1 mmol) dissolved in ethanol (15 cm^3) to $CuCl_2\cdot 2H_2O$ (2.0 g, 12 mmol) dissolved in ethanol (25 cm^3) and $CHCl_3$ (5 cm^3) whereupon the product precipitated (0.14 g) and was washed as above.

The complex $[CuCl(S_2CNEt_2)]$. Compound L^6 (0.2 g) dissolved in $CHCl_3$ (8 cm^3) was added slowly to $CuCl_2\cdot 2H_2O$ (1.5 g) dissolved in ethanol (35 cm^3). On leaving to stand overnight, dark greenish black crystals of the product were isolated (0.076 g) and these were washed with cold ethanol and diethyl ether. The m.p. was 176 °C.

The complexes $[Cu(S_2CNR_2)_2][BF_4]$ (R = Me *or* Et). These were prepared by similar methods of which the following is typical. To $Cu[BF_4]_2\cdot 6H_2O$ (1.03 g, 3 mmol) dissolved in acetone (10 cm^3) was added L^6 (0.29 g, 1 mmol) in acetone (5 cm^3). Diethyl ether was slowly added to the resulting green solution and a green precipitate of $[Cu(S_2CNEt_2)_2][BF_4]$ appeared after 1 h with cooling. When left overnight, a light yellow precipitate of $Cu[S_2CNEt_2]$ contaminated the product. The green product could be recrystallised from acetone on addition of diethyl ether or benzene, yield *ca.* 0.16 g, m.p. 142—144 °C. The complex $[Cu(S_2CNMe_2)_2][BF_4]$ was prepared when L^5 (0.15 g, 0.6 mmol) in acetone (15 cm^3) was added to $Cu[BF_4]_2\cdot 6H_2O$ (1.03 g, 3 mmol) in acetone (10 cm^3). From the green solution, dark brownish red microcrystals of the product (0.1 g) appeared. An alternative preparation of this complex was the addition of $Na[S_2CNMe_2]\cdot 2H_2O$ (0.179 g, 1 mmol) to $Cu[BF_4]_2\cdot 6H_2O$ (1.03 g, 3 mmol) in a total volume of 30 cm^3 of acetone.

The complexes $[Ni(S_2CNMe_2)_3]X$ ($X = BF_4^-$ *or* Cl^-). To $Ni[BF_4]_2\cdot 6H_2O$ (1.05 g, 3 mmol) dissolved in acetone (*ca.* 12 cm^3) was added L^5 (0.24 g, 1 mmol) in chloroform (12 cm^3). After *ca.* 20 min dark brownish red crystals of $[Ni(S_2CNMe_2)_3][BF_4]$ precipitated. These were filtered off and washed with acetone and diethyl ether, yield 0.25 g, decomposed >320 °C. The preparation of $[Ni(S_2CNMe_2)_3]Cl$ was similar except that $NiCl_2\cdot 6H_2O$ was used, and the product was precipitated by the addition of diethyl ether to give a blackish red product. This was contaminated with a little $[Ni(S_2CNEt_2)_2]$ into which it converted slowly in the solid state by the action of light, as well as in solution (*e.g.* MeCN) on warming.

The complex $[Fe(S_2CNMe_2)_3][ClO_4]$. To $Fe[ClO_4]_2\cdot 6H_2O$ (0.72 g, 2 mmol) dissolved in acetone (10 cm^3) was added L^5 (0.12 g, 0.5 mmol) dissolved in chloroform (5 cm^3). Blackish green crystals of the product (0.07 g) were filtered off after a few hours, and washed with acetone and diethyl ether.

The complexes $[L''][CoCl_4]$ ($L'' = L^8$ *or* L^9). These were prepared by similar methods of which the following is typical. To $CoCl_2\cdot 6H_2O$ (1.9 g, 8 mmol) dissolved in acetone (*ca.* 55 cm^3) was added L^5 (0.48 g, 2 mmol) dissolved in chloroform (15 cm^3). After 35 min a blue-green precipitate was filtered off, washed thoroughly with acetone,

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chloroform, and diethyl ether, and dried *in vacuo*, yield 0.13 g. By reduction in volume of the green filtrate, $[Co(S_2CNMe_2)_3]$ was isolated and characterised. For $[L^8][CoCl_4]$ the yield was only 0.04 g; $[Co(S_2CNEt_2)_3]$ was obtained from the green mother liquor.

The Reaction of $Co[BF_4]_2 \cdot 6H_2O$ *with* L^5.—To $Co[BF_4]_2 \cdot 6H_2O$ (1.0 g, 3 mmol) dissolved in acetone (18 cm^3) was added L^5 (0.24 g, 1 mmol) in chloroform (12 cm^3). After a series of colour changes a white precipitate was isolated from a green solution. The yield was *ca.* 20 mg and the compound decomposed after a couple of days. From the i.r. spectrum (see Discussion section) we suggest that $[L^9][BF_4]_2$ may have been formed.

We thank Professor N. Curtis for use of the Cahn electrobalance for the measurement of magnetic moments, and the New Zealand Universities Grants Committee for a grant towards instrumental facilities.

[6/1455 *Received, 26th July,* 1976]