Complexes of Sulphur Bis(t-butylimide) with some Transition Metals

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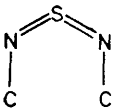
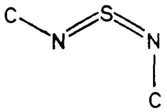
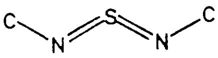
The preparation of complexes of transition metals with the new ligand sulphur bis(t-butylimide) is described. Complexes $[M(CO)_4\{S(NBu^t)_2\}]$ (I; M = Cr, Mo, and W), $[MCl_2\{S(NBu^t)_2\}_2]$ (II; M = Pd or Pt), and $[PtCl_2\{S(NBu^t)_2\}(NH_2Bu^t)]$, (III), have been characterised by analytical and spectroscopic methods. The i.r., ^1H n.m.r., and mass spectra of the complexes are discussed and structures are assigned.

SULPHUR BIS(n-BUTYLIMIDE), the first of the class of compounds of formula $(RN)_2S$, was prepared in 1956 [1] and subsequently other alkyl [2] and aryl [3] compounds were reported. It was found that tertiary-alkyl derivatives such as sulphur bis(t-butylimide) and bis(t-octylimide) were particularly thermally stable,[4] but all the compounds are subject to hydrolysis. The compounds RN=S=NR possess ylide character, $R\bar{N}{-}\overset{+}{S}{=}NR$, and many of their reactions reflect this, such as those with benzaldehyde [4] and triethyl phosphite.[5]

The structure of sulphur di-imides has been a matter of dispute; an alternative azo–alkylthio-structure has been ruled out,[3] but three possible planar conformations of the CNSNC skeleton may occur. *X*-Ray data from sulphur bis(*p*-tolylimide) has shown this compound to have the *trans–cis*-form in the solid state [6] and CNDO calculations on similar compounds also led to the conclusion that this conformation is the most stable.[7] Recent low-temperature n.m.r. studies [8] of sulphur bis(t-butylimide) and bis(methylimide) show the *trans–cis*-isomer as the most-stable isomer in solution, although another form exists for the latter compound and rapid interchange of *cis* and *trans*, non-equivalent, alkyl groups is occurring for both systems at room temperature.


cis–cis


trans–cis


trans–trans

Reactions of sulphur bis(t-butylimide) with metal complexes have been reported. Thus, reactions with $[\{(cp)Ni(CO)\}_2]$ or $(cp)_2Ni$ [9] yielded the trinuclear complex $[\{(cp)_3Ni\}_3(NBu^t)]$, reaction with $[(cp)Co(CO)_2]$ [9] yielded $[\{(cp)Co\}_2\{(Bu^tN)_2CO\}]$, $[\{(cp)Co\}_3S_2]$, and $[\{(cp)Co\}_3(CO)S]$, and reaction with $Fe(CO)_5$ [10] gave a binuclear thionitrosobutane complex $[\{(OC)_3Fe\}_2(SNBu^t)]$. Products have been isolated from reaction of sulphur bis(arylimides) and $(R_3Sn)_2O$.[11] It has also been reported that no reaction occurs between $(Bu^tN)_2S$ and the complexes $[Rh(PPh_3)_3Cl]$, $Pt(PPh_3)_4$, and $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$.[9]

In all the above reactions the sulphur ligand is cleaved or modified and no examples of the simple sulphur bis(alkylimide) as a ligand are known. We report here complexes of $(Bu^tN)_2S$ with carbonyls of chromium, molybdenum, and tungsten and with halides of palladium and platinum.

RESULTS AND DISCUSSION

Group 6A *Complexes*.—Reactions of the acetonitrile complexes $[M(CO)_{6-n}(NCMe)_n]$ ($n = 2$—3; M = Cr, Mo, or W) with $(Bu^tN)_2S$ in hexane at ambient temperature gave the respective complexes $[\{(Bu^tN)_2S\}M(CO)_4]$, (I), in fair yields as deep magenta crystals which appear green in reflected light. Properties of these complexes are listed in Table 1. The solids are freely soluble in hexane and most organic solvents. In polar solvents the solutions are lighter red in colour and in such media decomposition rapidly ensues. The solid complexes are fairly stable in air but decompose slowly on standing to give yellow-brown products, as yet uncharacterised. Molecular-weight studies of complex (I; M = Mo) in toluene and parent-ion peaks in the mass spectra of all complexes (I) showed them to be monomeric.

The main i.r.-spectral data are given in Table 2 and in the Experimental section. All complexes showed the expected four ν(CO) stretching frequencies in the solid state. In solution, in some cases, only three bands were observed of which the central absorption was broadened and this must arise from the near degeneracy of A_1 and B_1 modes of a C_{2v} species. The positions of the lower-frequency bands were quite solvent dependent, as noted for (I; M = Cr) in hexane, carbon tetrachloride, chloroform, and acetone. The band positions of these complexes were significantly higher than those of the corresponding 2,2′-bipyridyl complexes $[(bipy)M(CO)_4]$ in the same medium [12] and this would suggest that $(Bu^tN)_2S$ is a better π-acceptor than the bipy ligand. Bands in the region 950—1 300 cm^{-1} of the i.r. spectrum of $(Bu^tN)_2S$ are 1 023m, 1 060m, 1 203s, and 1 230s

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[10] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1968, **7**, 1833.

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[12] For example, see D. M. Adams, 'Metal–Ligand and Related Vibrations,' St. Martins Press, 1968.

cm^{-1}, and, by comparison with related compounds,[3,13-15] the latter two strong bands may be tentatively assigned to ν(N_2S) vibrations. In complexes (I) these bands shifted to lower frequencies [1 189m—s, 1 208 (sh) (M = Cr); 1 186m—s, 1 203 (sh) (Mo); 1 186m—s, 1 200 (sh) cm^{-1} (W)] and this may be attributed to weakening of the N–S bonds on complexation. Other tentative assignments of bands are given in the Experimental section.

TABLE 1

Analytical data and physical properties of complexes (I)—(III)

Complex	Colour	M.p. (θ_c/°C) [a]	Analyses [b]/(%) C	H	N	Other	*M* [b]
$[Cr(CO)_4\{S(NBu^t)_2\}]$ (I)	Purple	111 (decomp.)	42·9 (42·6)	5·2 (5·4)	8·5 (8·3)		338 [c] (338)
$[Mo(CO)_4\{S(NBu^t)_2\}]$ (I)	Magenta	115	37·7 (37·7)	5·1 (4·7)	7·1 (7·3)		376 [d] (382)
$[W(CO)_4\{S(NBu^t)_2\}]$ (I)	Magenta	decomp. *ca.* 65	30·6 (30·65)	3·8 (3·85)	6·3 (6·0)		470 [c] (470)
$[PdCl_2\{S(NBu^t)_2\}_2]$ (II)	Yellow	128—130	36·4 (36·5)	6·6 (6·9)	10·8 (10·65)	13·8 [e] (13·5)	545 [d] (526)
$[PtCl_2\{S(NBu^t)_2\}_2]$ (II)	Yellow	147—148	31·35 (31·3)	6·0 (5·9)	9·1 (9·1)	10·55 [f] (10·4)	560 [d] (615)
$[PtCl_2\{S(NBu^t)_2\}(NH_2Bu^t)]$ (III)	Yellow	174—175	28·1 (28·1)	5·7 (5·7)	7·9 (8·2)		520 [d] (513)

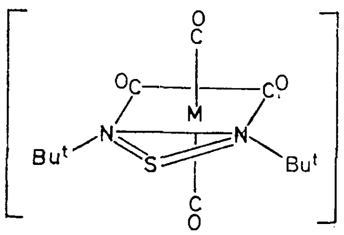
[a] Determined *in vacuo*. [b] Calculated values are given in parentheses. [c] Parent-ion peak in mass spectrum (^{52}Cr or ^{184}W). [d] In toluene solution (0·02—0·1M). [e] % Cl. [f] % S.

TABLE 2

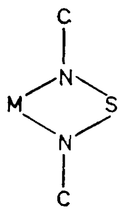
^{1}H N.m.r. and i.r. spectra (2 200—1 700 cm^{-1} of complexes (I)—(III)

Complex	^{1}H N.m.r. [a] (solvent)	I.r. (solvent)/cm^{-1}
(I; M = Cr)	8·41 ($CDCl_3$)	2 018s, 1 945vs,br, 1 888s (hexane)
	84·2 (CS_2)	2 014s, 1 938vs,br, 1 877 (CCl_4)
		2 015s, 1 940vs, *ca.* 1 927 (sh), 1 865s ($CHCl_3$)
		2 015s, 1 928vs,br, 1 860s (Me_2CO)
		2 014s, 1 929 (sh), 1 912vs, 1 848vs (KBr) [b]
(I; M = Mo)	8·40 ($CDCl_3$)	2 022s, 1 939vs, 1 927 (sh), 1 877s (CCl_4)
	8·41 (CS_2)	2 020s, 1 925 (sh), 1 907vs, 1 846vs (KBr) [b]
(I; M = W)	8·43 ($CDCl_3$)	2 023s, 1 935vs,br, 1 881s (CCl_4)
	8·44 (CS_2)	2 017s, 1 926 (sh), 1 908vs, 1 847vs (KBr) [b]
(II; M = Pd)	8·42, 8·65 (CS_2)	
(II; M = Pt)	8·15, 8·53 ($CDCl_3$)	
(III)	8·16, 8·54 ($CDCl_3$) [c]	

[a] Values in τ relative to $SiMe_4$ as internal standard; all resonances were singlets. [b] In KBr pellets. [c] At 100 MHz (22 °C): τ 8·17 (rel. intensity 9); 8·42 (2, NH_2); and 8·54 (18, two resonances, separation *ca.* 0·008 p.p.m.).



(A)



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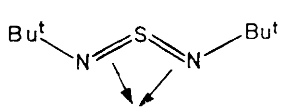

(C)

The ^{1}H n.m.r. spectra (Table 2) of complexes (I) comprised a singlet shifted 0·1—0·2 p.p.m. to low field of the free ligand (τ 8·58 in $CDCl_3$). On cooling the samples to −100 °C in CS_2 solution, no other signals were observed and little change occurred except a slight broadening and a small field shift, possibly arising from viscosity changes. Thus it appears that the t-butyl groups are in equivalent magnetic environments, unlike those in the free ligand.[8] The mass spectrum of $(Bu^tN)_2S$ has been mentioned in the literature.[7] Mass spectra of complexes (I) all showed parent-ion peaks with characteristic isotopic abundances. Fragments arising from consecutive loss of four CO groups and subsequent loss of Me groups occurred, and another strong peak can be assigned to $[M(SNBu)]^+$, a thionitroso-ion.

From the n.m.r. and other results, the most-plausible structure for complexes (I) involves a *trans–trans* $(Bu^tN)_2S$ molecule bonded to the $M(CO)_4$ fragment as in (A), forming a novel four-membered heterocyclic ring containing MNSN atoms. It is probable that the atoms depicted in (B) are coplanar as in the original geometry of the ligand; this follows from steric arguments and the fact that pyramidal N atoms should give rise to *syn-* and *anti*-isomers which might have been observed in the variable-temperature n.m.r. experiments. This

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[13] B. Cohen and A. G. MacDiarmid, *J. Chem. Soc.* (*A*), 1968, 1780.

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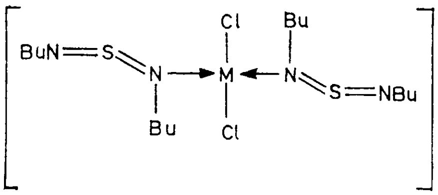
[15] J. E. Stewart, *J. Chem. Phys.*, 1959, **30**, 1259.

also follows from the 18-electron rule which is usually obeyed by low-oxidation-state Group 6A metal atoms and requires the sulphur di-imide to act as a four-electron donor and not as a diamido-ligand. It is possible that the bond to the metal involves the N=S=N π-system as in (C) and not the lone pairs of the nitrogen atoms. This cannot be definitely ruled out, but greater changes in the $\nu(N_2S)$ modes might be expected for this structure. A similar problem arises for the ligand 1,4-diazabuta-1,3-diene and it has been found that this ligand generally co-ordinates through the nitrogen atoms in carbonyl complexes.[16]

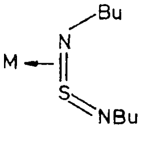
Palladium and Platinum Complexes.—Reaction of bis(benzonitrile)dichloropalladium(II) with $(Bu^tN)_2S$ in dichloromethane at ambient temperature gave the complex $[\{(Bu^tN)_2S\}_2PdCl_2]$, (II), as yellow crystals in good yield. The product is fairly soluble in saturated hydrocarbons and easily soluble in other organic solvents; it is quite stable to aerial decomposition. Reaction of bis(benzonitrile)dichloroplatinum(II) with $(Bu^tN)_2S$ even in large excess was incomplete in dichloromethane at ambient temperature and the resulting mixture of starting materials and products was difficult to separate. Heating the reaction mixture under reflux in chloroform caused complete displacement of benzonitrile from $[(PhCN)_2PtCl_2]$ and, after chromatography of the reaction mixture, two pure platinum-containing complexes were isolated as yellow crystals: $[\{(Bu^tN)_2S\}_2PtCl_2]$, analogous to (II), and another product containing a t-butylamine ligand, $[(Bu^tH_2N)PtCl_2\{S(NBu^t)_2\}]$, (III). Complexes (II; M = Pt) and (III) are soluble in most organic solvents but the former, being less polar, was eluted more readily from an alumina column. Properties of complexes (II) and (III) are listed in Table 1.

The i.r. spectra of complexes (II) were similar and characteristic bands are recorded and tentatively assigned in the Experimental section. The $\nu(N_2S)$ modes were lowered and were more widely separated than in complexes (I). Complex (III) showed three $\nu(NH)$ frequencies in the solid state, comparable to known $[(Bu^tH_2N)PtCl_2(L)]$ complexes,[17] and other bands supporting its formulation. ^1H N.m.r. spectra (Table 2) of complexes (II) showed two singlets of equal intensity, assignable to two sets of t-butyl groups, and the spectrum of (II; M = Pd) in CS_2 was unchanged except for a little broadening when the temperature was lowered to -100 °C. The Bu^t resonances were shifted to low field of the free ligand, especially in (II; M = Pt). The ^1H n.m.r. spectrum of complex (III) at 60 MHz showed two signals of relative intensities 2 : 1 (within 5%) at virtually the same chemical-shift positions as for (II; M = Pt). The higher-field resonance of relative intensity 2 arises from one t-butyl group of $(Bu^tN)_2S$ and the t-butyl group of Bu^tNH_2, shifted to low field of free Bu^tNH_2 (τ 8·83 in $CDCl_3$) by complexation. Under higher resolution at 100 MHz, the high-field signal was observed to be a doublet and a resonance due to the NH_2 protons was observed (see footnote to Table 2). It was impossible to obtain mass spectra of complexes (II) containing metal-ion fragments, but at higher temperatures fragments arising from the free ligand $(Bu^tN)_2S$ were observed. Molecular weights in toluene solution (Table 1), however, showed the complexes to be monomeric.

Complexes (II) and (III) very probably have a square-planar structure and the *cis*- or *trans*-forms (D) are consistent with the ^1H n.m.r. spectra of (II). The i.r. data cannot conclusively distinguish *cis*- or *trans*-geometry since the shoulder on $\nu(MCl)$ bands (present in KBr or Nujol) might indicate the former but could arise from a solid-state effect or from the isotopes ^{35}Cl and ^{37}Cl in a *trans*-structure. An alternative two-electron π-type interaction (E) between the metal atom and one S–N bond is possible. In complex (III) a Bu^tNH_2 ligand has replaced one $(Bu^tN)_2S$ in (II; M = Pt). The Bu^tNH_2 must be produced by cleavage of $(Bu^tN)_2S$ at the higher temperature of the formation reaction and the H atoms must derive from the solvent, probably from ethanol present in commercial chloroform.



(D) (or *cis*)



(E)

EXPERIMENTAL

The starting materials $[M(CO)_{6-n}(NCMe)_n]$ (n = 2—3; M = Cr, Mo, or W),[18] $[(PhCN)_2MCl_2]$ (M = Pd or Pt),[19] and $(Bu^tN)_2S$ [4] were made as described. All reactions were carried out under a nitrogen atmosphere. ^1H N.m.r. spectra were obtained at 60 MHz on a Perkin-Elmer R12 spectrometer operating at 35 °C unless otherwise stated, i.r. spectra on a Perkin-Elmer 457 instrument, and mass spectra at 70 eV on an A.E.I. M.S. 902 instrument.* Molecular weights were obtained using a Hewlett–Packard vapour-phase osmometer and analyses were by Alfred Bernhardt, Germany, and by Mrs. J. Brown, Heriot-Watt University.

Preparations.—*Tetracarbonyl[sulphur bis(t-butylimide)]-chromium*(0). Tris(acetonitrile)tricarbonylchromium(0) (0·6 g) [containing some bis(acetonitrile)tetracarbonylchromium(0) as judged by i.r. spectroscopy even after prolonged reaction] made *in situ* was stirred for 20 h at room temperature in hexane (30 cm^3) with $(Bu^tN)_2S$ (1 cm^3) to give a deep violet-purple solution. After evaporation to dryness the oily product was chromatographed on neutral Al_2O_3 with hexane, giving a purple eluate which yielded, after crystallisation, washing, and drying (10^{-3} mmHg), purple *needles* (0·15 g). I.r. spectrum below

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* 1 eV ≈ 1·60 × 10^{-19} J.

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[18] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

[19] F. R. Harltey, *Organometallic Chem. Rev.* (*A*), 1970, **6**, 119.

700 cm^{-1} (KBr): 674m [δ(MCO)]; 628m [δ(MCO)]; 609m [δ(MCO)]; 534w; 511m; 486w; 455m [ν(MC)]; and 419m cm^{-1} [ν(MC)]. Visible spectrum (CCl_4): 580 (ε 6·0 × 10^3) and 435 nm (ε 9·0 × 10^2 l mol^{-1} cm^{-1}). [Use of tetracarbonyl(norbornadiene)chromium(0) in place of tris(acetonitrile)tricarbonylchromium(0) in the above reaction gave a mixture of the complex and starting material which was not separable by chromatography on Al_2O_3.]

Tetracarbonyl[sulphur bis(t-butylimide)]molybdenum(0). In a similar manner to the above, tris(acetonitrile)tricarbonylmolybdenum(0) (0·6 g) and $(Bu^tN)_2S$ (1 cm^3) in hexane (30 cm^3) at room temperature yielded magenta *crystals* of the complex (*ca.* 0·15 g) after recrystallisation from hexane. (Chromatography could not be employed since decomposition occurred on the Al_2O_3 column.) I.r. spectrum below 700 cm^{-1} (KBr): 635m [δ(MCO)]; 586m [δ(MCO)]; 568m [δ(MCO)]; 530 (sh); 517m; 485w; 459w—m; 423m [ν(MC)]; 400m [ν(MC)]; 377m—s [ν(MC)]; and 357m cm^{-1} [ν(MC)].

Tetracarbonyl[sulphur bis(t-butylimide)]. This complex was obtained as magenta, needle-like, *crystals* in a reaction similar to that above. Again only rapid chromatography on a short Al_2O_3 column was possible since decomposition occurred. I.r. spectrum below 700 cm^{-1} (KBr): 608m [δ(MCO)]; 570 (sh) [δ(MCO)]; 561m [δ(MCO)]; 527 (sh); 517m; 493 (sh); 462w—m; 428 (sh) [ν(MC)]; 416m [ν(MC)]; 379m—s [ν(MC)]; and 360m cm^{-1} [ν(MC)].

Dichlorobis[sulphur bis(t-butylimide)]palladium(II). A mixture of bis(benzonitrile)dichloropalladium(0) (0·85 g) and $(Bu^tN)_2S$ (1 cm^3) in dichloromethane (30 cm^3) was left at room temperature for 20 h. After filtration the solvent was evaporated to small volume and crystallisation induced by addition of hexane. The complex (0·5 g) was obtained as yellow *crystals* which were washed with a little cold hexane and dried (10^{-3} mmHg). Characteristic i.r. bands (KBr): 2 973m [ν(CH)]; 1 180s [ν(N_2S)]; 1 148 [ν(N_2S)]; 871m; 337m [ν(PdCl)]; and 328 (sh) cm^{-1} [ν(PdCl)].

Reaction of Bis(benzonitrile)dichloroplatinum(0) *with* $(Bu^tN)_2S$.—A mixture of bis(benzonitrile)dichloroplatinum(0) (0·9 g) and $(Bu^tN)_2S$ (3 cm^3) in reagent grade chloroform (40 cm^3) was heated under reflux for 3 d. The filtered reaction mixture was pumped to dryness and the oily product chromatographed on neutral Al_2O_3. Elution with benzene separated a yellow band which was collected and subsequent crystallisation, washing, and drying of the product gave *dichlorobis[sulphur bis(t-butylimide)]platinum*(II) (0·12 g) as yellow crystals. Characteristic i.r. bands (KBr): 2 973m [ν(CH)]; 1 179s [ν(N_2S)]; 1 139s [ν(N_2S)]; 878m; 331s [ν(PtCl)]; and 321 (sh) cm^{-1} [ν(PtCl)]. Elution with dichloromethane–benzene (1 : 1) gave a second yellow band from which *dichloro[sulphur bis(t-butylimide)](t-butylamine)platinum*(II) (0·20 g) was obtained. Characteristic i.r. bands (KBr): 3 230m [ν(NH)]; 3 203m [ν(NH)]; 3 134m [ν(NH)]; 2 973m [ν(CH)]; 1 179s [ν(N_2S)]; 1 138s [ν(N_2S)]; 330m—s [ν(PtCl)]; and 320 (sh) cm^{-1} [ν(PtCl)].

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