Dithiocarbamato- and Carbonyldithiocarbamato-complexes of Rhenium-(I), -(III), -(IV), and -(V) †

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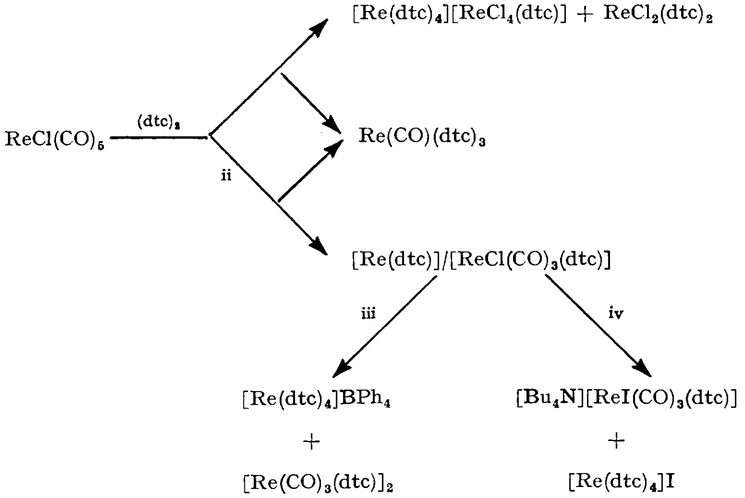
Dithiocarbamato-complexes of rhenium such as $Re(CO)(S_2CNR_2)_3$ (R = Me, Et, $PhCH_2$), $ReCl_2(S_2CNR_2)_2$ (R = Et, $PhCH_2$), and $Re_2O_2S\{S_2CN(PhCH_2)_2\}_4$, and complex ions such as $[Re(S_2CNEt_2)_4]^+$ and $[Re(CO)_3(S_2CNEt_2)X]^-$ (X = Cl, I), have been prepared by interaction of $Re(CO)_5Cl$ and thiuram disulphides.

Interaction of $Tl(S_2CNEt_2)$ and $Re(CO)_5Cl$ leads to $[Re(CO)_3(S_2CNEt_2)]_2$ which is easily cleaved by CO, pyridine, and PPh_3 to $Re(CO)_3(S_2CNEt_2)(L)$.

The reaction of $ReCl_4(PPh_3)_2$ with $[Et_2NCS_2]_2$ leads to $[Re_2Cl_2(Et_2NCS_2)_5]Cl_2$ as well as $ReCl_2(S_2CNEt_2)_2$ and $[Re(S_2CNEt_2)_4]^+$.

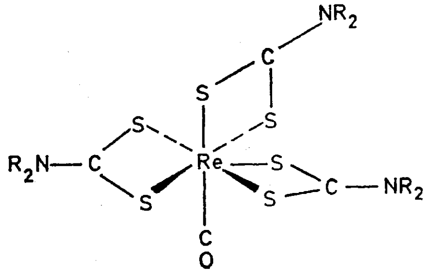
PREVIOUS studies[1,2] on rhenium dithiocarbamato-complexes have been extended. Spectroscopic data for new compounds are collected in the Table. The electrochemistry of certain of the compounds will be described separately.



SCHEME 1 dtc = diethyldithiocarbamate. Reagents: i, in benzene; ii, in acetone; iii, $NaBPh_4$ in acetone; iv, $Bu^n{}_4N$, NaI, in acetone

Interaction of Tetra-alkylthiuram Disulphides with Rhenium Carbonyl Chlorides.—Scheme 1 summarises the principal reactions investigated. The main products from the interaction of pentacarbonylchlororhenium(I) with $[R_2NCS_2]_2$ (R = Me, Et, and $PhCH_2$) in acetone, tetrahydrofuran, toluene, *etc.*, are brown crystalline compounds of stoicheiometry $Re(CO)(S_2CNR_2)_3$. For R = Et, the same product is also obtained from $Re_2Cl_2(CO)_8$, $Re_2(CO)_{10}$, and $ReCl(CO)_3(PPh_3)_2$. The compounds are monomeric and diagmagnetic and have only one C–O stretching frequency. Although we originally[2] believed them to be dicarbonyls on the basis of the only really critical analyses, *i.e.* of oxygen, which were in excellent agreement with calculated values, subsequent *X*-ray diffraction study[3] of the diethyldithiocarbamate showed the compound to be the seven-co-ordinate monocarbonyl with a distorted pentagonal bipyramidal structure (I). The high oxygen analyses on different samples at different times were due[4] to a wrong blank determination and to wrong processing.

The i.r. spectra of the complexes in regions characteristic for co-ordinated dithiocarbamate showed a single



(I)

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† No reprints available.

[1] J. F. Rowbottom and G. Wilkinson, *J.C.S. Dalton*, 1972, 826.

[2] J. F. Rowbottom and G. Wilkinson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 675.

[3] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, submitted for publication.

[4] Dr. G. Reuter, Alfred Bernhardt Mikroanalytisches Laboratorium, personal communication.

Infrared [a] and nuclear magnetic resonance [b] spectral and analytical data for rhenium dithiocarbamate complexes

						Found (%)								Required (%)							
	ν(CO)	ν(CN)	$\nu(CS_2)$	Other bands [e]	τ Values	C	H	N	Hal	O	Re	S	*M*	C	H	N	Hal	O	Re	S	*M*
$Re(CO)(S_2CNMe_2)_3$	1878s	1540s	1005m 975m		6·9 CH_3	20·9	3·3	7·0		3·8	34	31·0	540	20·9	3·2	7·3		2·8	32·4	33·5	574
$Re(CO)(S_2CNEt_2)_3$	1870s	1505s	1015m 995m	390m 355m 330w (ReS)	6·5 quartet CH_2 8·9 triplet CH_3	29·2	4·6	6·4		2·6	27	28·2	690	29·2	4·6	6·4		2·4	28·3	29·2	658
$Re(CO)(S_2CNP_2CH_2)_3$	1870s	1480s	1025m 990m,br		2·5 [f] Ph 5·0 CH_2	53·3	4·0	3·7					930	53·6	4·1	4·1					1030
$[Re(CO)_3(S_2CNEt_2)]_2$	2030s 2005s 1955s 1920s	1520s	1000m 980m			23·5	2·4	3·2		10·6			830	23·0	2·4	3·3		11·5			836
$Re(CO)_4(S_2CNEt_2)$	2090m [c] 1995s 1982s 1945s 1915w	1510s	995m (980sh)					3·0					460			3·1					446
$Re(CO)_3(S_2CNEt_2)(PPh_3)$	2010s 1922s 1905s 1894s	1499s	995m			46·4	3·8	1·8	[5·0P]				690	45·9	3·7	2·1	[4·6P]				680
$Re(CO)_3(S_2CNEt_2)(C_5H_5N)$	1998m 1910s 1890s (1850sh)	1508s	993m			31·2	3·1	2·8					470	31·4	3·0	2·8					497
$[Re(S_2CNEt_2)_4][Re(CO)_3Cl(S_2CNEt_2)]$	1995m 1895s 1885s 1860s,br	1520s 1495s	999m			27·5	4·2	5·6		4·1		25·7		27 3	4·1	5·7		3·9		26·0	
$[Re(S_2CNEt_2)_4][Re(CO)_3Cl(S_2CNEt_2)],C_6H_6$	1995m 1895s 1885s 1860s,br	1520s 1495s	999m	675s (C_6H_6) 390w 342m (ReS) 290w 260w (ReCl)	2·7 singlet CH 6·6 quartet CH_2 8·9 triplet CH_3	31·4	4·2	5·2	2·6	3·5	29			31·2	4·3	5·3	2·7	3·7	28·4		
$[Bu^n_4N][Re(CO)_3I(S_2CNEt_2)]$	1999m 1960m 1895s 1865s	1498s	1010w [d] 990w 985w	390w 350w (ReS)		36·0	5·5	3·6	16·5	6·4		9·1		36·6	5·8	3·6	16·1	6·1		8·1	
$[Bu^n_4N][Re(CO)_3(Cl)(S_2CNEt_2)]$	1995m [e] 1890s,br 1860s,br																				
$[Re(S_2CNEt_2)_4]BPh_4$		1518s	1025w [d] 1000w 965w			48·5	5·5	4·9						48·1	5·5	5·1					
$[Re(S_2CNEt_2)_4]I_3$		1522s	1025w [d] 1000w 975w			21·0	3·5	5·1	34·3					20·7	3·6	4·8	32·9				
$[Re(S_2CNEt_2)_4]I$		1530s	1000w			26·9	4·4	6·3	14·4					26·5	4·4	6·2	14·0				
$[Re(S_2CNEt_2)_4]Cl$		1525s	1000w		6·1 quartet CH_2 9·2 triplet CH_3	30·2	4·8	6·7	4·1					29·5	4·9	6·8	4·4				
$[Re(S_2CNEt_2)_4][ReCl_4(S_2CNEt_2)]$		1520s	1000m (970sh)	390w 370w 350w (ReS) 315s 298s (280sh) (ReCl)		24·1	3·8	5·7	10·8		40	27·5		23·9	4·0	5·6	11·3		29·7	25·5	
$[Re_2Cl_8(S_2CNEt_2)_5]Cl_3$		1525s	995m	362m (ReS) (295sh) 287s (270sh) (ReCl)		24·6	4·2	5·8	11·8					23·9	4·0	5·6	11·3				
$ReCl_2(S_2CNEt_2)_2$		1535s	1000m	355m 338m (ReS) 305s 287m (ReCl)		21·6	3·6	5·1	13·0			23·4	580	21·7	3·6	5·1	12·8			23·1	553
$ReCl_2\{S_2CN(PhCH_2)\}_2$		1515s	1020m [d] 1000m 985m			44·8	3·8	3·2					960	45·0	3·8	3·5	8·9				801
$Re_2O_2S\{S_2CN(PhCH_2)_2\}_4$		1505s	1020w [d] 995w	895s (Re=O) 448m 435m (ReS_b) 315m 290w (ReS)	2·5 (C–H) [f] 5·0 (CH_2)	47·3	3·7	3·8		4·2		17·9	1700	47·2	3·7	3·7		2·1		18·9	1524
$ReOCl\{S_2CN(PhCH_2)_2\}_2$		1515s	1000m	970s (Re=O)																	
$Re_2O_3\{S_2CN(PhCH_2)_2\}_4$		1490s,br	980m	958m (Re=O) 650s (Re–O–Re) 300m,sh 290m (ReS)		48·0	3·6	3·5						47·7	3·7	3·7					

[a] Nujol and hexachlorobutadiene mulls. [b] Significant peaks only shown in cm^{-1}. [c] Dichloromethane solution; Me_4Si reference. [d] Hexane solution. [e] All bands in this region included. Tentative assignments made on the basis of comparison between relevant spectra. [f] Acetone solution.

strong C–N stretch typical of bidentate dithiocarbamate; in the C–S region two medium bands were observed both in mulls and in solution. The second band evidently arises because of the non-equivalence of the sulphur atoms in the dithiocarbamate group that has one S *trans* to CO, as the two Re–S distances are significantly different. The compounds are remarkably inert and can be recovered unchanged after even prolonged treatment with refluxing pyridine, molten triphenylphosphine, sodium ethoxide in ethanol, hydrogen chloride in ethanol, u.v. irradiation in benzene, and prolonged heating at 200 °C. The molybdenum compound,[5a] $Mo(NO)(S_2CNMe_2)_3$, is isoelectronic with these rhenium compounds and evidently has a pentagonal bipyramidal structure as is known for $Mo(NO)(S_2CNBu_2)_3$.[5b] At 25° multiple CH_3 resonances were observed which collapse to a singlet at elevated temperatures. By contrast the rhenium complexes ($R = Me$, Et, $PhCH_2$) are non-rigid and show only single CH_3 and normal ethyl and benzyl resonances at 30° and the methyl and ethyl compounds show no change from -70 to $+90°$. In this temperature range, the alkyl groups are evidently equivalent. The reason for this difference from the molybdenum compound is not clear but it is of interest that in several seven-co-ordinate dithiocarbamates, $TiX(S_2CNR_2)_3$, the methyl and ethyl groups also remain equivalent.[6] Since a mechanism involving dissociation would imply greater chemical reactivity than is found for the rhenium compounds, a non-bond breaking path is presumably involved.

A second product from the interaction of $ReCl(CO)_5$ and $[Et_2NCS_2]_2$ in acetone is a golden-brown crystalline solid of stoicheiometry $Re_2Cl(CO)_3(Et_2NCS_2)_5$. On recrystallisation from acetone–benzene, a benzene solvate was obtained. The presence of benzene was shown by analysis and i.r. and n.m.r. spectroscopy, the latter being consistent with one benzene per five dithiocarbamate groups. The chloride is a 1 : 1 electrolyte in nitromethane[7] ($\Lambda_M = 86{\cdot}5\ \Omega^{-1}\ cm^2\ mol^{-1}$; *c* 10^{-3}M) but since no rational structure with a univalent dirhenium cation can be accommodated, rhenium must be present in both cation and anion. These ions could be separated and identified.

From acetone solutions of the chloride, sodium tetraphenylborate gives black crystals of the diamagnetic complex $[Re(S_2CNEt_2)_4][BPh_4]$. This too is a 1 : 1 electrolyte in nitromethane ($\Lambda_M = 84{\cdot}2\ \Omega^{-1}\ cm^2\ mol^{-1}$; *c* 10^{-3}M). The i.r. spectrum shows only one C–N and one C–S stretch assignable to bidentate dithiocarbamate and since the compound is diamagnetic, the cation is evidently the eight-co-ordinate rhenium(V) ion $[Re(S_2CNEt_2)_4]^+$. As far as we are aware the only other examples of[8] eight-co-ordinate Re^V are $[Re(diars)_2Cl_4]^+$ and $[Re(CN)_8]^{3-}$.

During the reaction with sodium tetraphenylborate, sodium chloride and a dimeric rhenium carbonyl (which had been obtained in other ways as discussed later) separated. This reaction hence appears to be:

$$[Re(S_2CNEt_2)_4][ReCl(CO)_3S_2CNEt_2] + NaBPh_4 \longrightarrow$$
$$[Re(S_2CNEt_2)_4]BPh_4 + \tfrac{1}{2}[ReS_2CNEt_2(CO)_3]_2 + NaCl$$

Although we have not been able to isolate the chloro-anion, the corresponding iodo-species can be obtained. When the parent complex is treated with n-butylammonium iodide and sodium iodide in acetone, pale cream crystals of the salt $[Bu^n{}_4N][ReI(CO)_3(S_2CNEt_2)]$ are obtained. This is diamagnetic as expected for Re^I and is a 1 : 1 electrolyte in nitromethane ($\Lambda_M = 104{\cdot}8\ \Omega^{-1}\ cm^2\ mol^{-1}$; *c* 5×10^{-3}M). The cation also can be obtained from the solution as black crystals of the iodide $[Re(S_2CNEt_2)_4]I$ ($\Lambda = 115\ \Omega^{-1}\ cm^2\ mol^{-1}$; *c* 2×10^{-3}M in $MeNO_3$). Interaction of this iodide with an acetone solution of $Bu^n{}_4NCl$ leads to $[Re(S_2CNEt_2)_4]Cl$. The position and number of C–O stretching frequencies in the anion and of the C–N and C–S bands in both anion and cation in the separate complexes correspond to those in the parent compound which is hence $[Re(S_2CNEt_2)_4][ReCl(CO)_3S_2CNEt_2]$. The ν(CN) band in $[Re(S_2CNEt_2)_4]^+$ occurs at higher frequency (1520 cm^{-1}) than that in the anion (1495 cm^{-1}), which is consistent with the differing oxidation states of the metal.

The cation can also be obtained as $[Re(S_2CNEt_2)_4]I_3$ from the products of the reaction of $ReI(CO)_3(PPh_3)_2$ with $[Et_2NCS_2]_2$ and can be isolated as the tetraphenylborate from the products of interaction of $ReCl_4(PPh_3)_2$ and $[Et_2NCS_2]_2$.

The interaction of $ReCl(CO)_5$ and $[Et_2NCS_2]_2$ in benzene, while giving mainly $Re(CO)(S_2CNEt_2)_3$, gives a by-product different from that formed in acetone, as just described. A brown tarry solid separates and on recrystallisation from acetone brown needles of stoicheiometry $Re_2Cl_4(S_2CNEt_2)_5$ are obtained. This substance is a 1 : 1 electrolyte in nitromethane ($\Lambda_M = 89\ \Omega^{-1}\ cm^2\ mol^{-1}$; *c* $0{\cdot}5 \times 10^{-3}$M) but unlike the previous salt it is paramagnetic ($\chi_g = 4{\cdot}0 \times 10^{-6}$ c.g.s.u. at 297 K). The i.r. spectrum indicates bidentate dithiocarbamate. Separation of the cation as before gives $[Re(S_2CNEt_2)_4][BPh_4]$ identical with that obtained previously. Although attempts to separate the anion have failed, the initial product is clearly $[Re^V(S_2CNEt_2)_4][Re^{IV}Cl_4(S_2CNEt_2)]$. Other data are consistent with this formulation. The complex has Re–Cl stretches (Table) and the magnetic moment calculated on this formulation, $\mu_{eff} = 3{\cdot}7$ B.M. (297 K) is consistent with rhenium(IV), d^3 spin-free for the anion.

A third product, $Re(S_2CNEt_2)_2Cl_2$, can also be isolated from the reaction in benzene. It forms red crystals, is monomeric in benzene, non-conducting in nitromethane, and is paramagnetic with $\mu_{eff} = 2{\cdot}9$ B.M. at 297 K.

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[5] (*a*) B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1969, 1668; R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994; (*b*) T. F. Brennan and I. Bernal, *Chem. Comm.*, 1970, 138.

[6] E. C. Alyea, B. S. Ramaswamy, A. N. Bhat, and R. C. Fay, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 399.

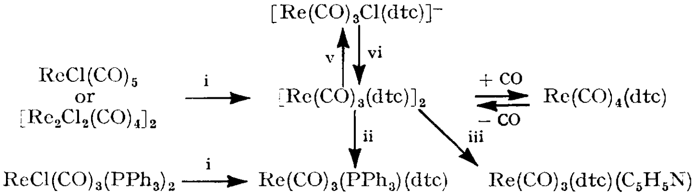
[7] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[8] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' John Wiley and Sons, London, 1972, 3rd edn.

The i.r. spectrum indicates bidentate dithiocarbamate, and has two Re–Cl stretching frequencies. The complex is evidently the octahedral *cis*-dichlorobis(diethyldithiocarbamato)rhenium(IV), *cis*-$ReCl_2(S_2CNEt_2)_2$.

This complex can also be obtained from the products of the interaction in benzene of $ReCl_4(PPh_3)_2$ and the thiuram disulphide. The dibenzyl dithiocarbamato-analogue $ReCl_2[S_2CN(CH_2Ph)_2]_2$ is obtained by interaction of $ReCl(CO)_5$ with tetrabenzylthiuram disulphide as red crystals with physical properties similar to those of the ethyl complex.

The benzylthiuram reaction however also gives other products as shown by chromatography on alumina. One is the dark brown seven-co-ordinate $Re(CO)\{S_2CN(PhCH_2)_2\}_3$. A third complex that forms brown diamagnetic needles has stoicheiometry $Re_2O_2S[S_2CN(CH_2Ph)_2]_4$ and is a dimer in $CHCl_3$. In addition to the expected dithiocarbamate bands there is a strong band in the i.r. region at 895 cm^{-1} assignable as ν(Re=O). Since there is no strong broad band at *ca.* 670 cm^{-1} in the region characteristic of the bridge in the linear $(O{=}Re)_2O$ group[1] in $[O{=}Re(S_2CNR_2)]O$, this third complex is probably the sulphur-bridged dimer $[O{=}Re(S_2CNR_2)]S$. Two bands at 448 and 435 cm^{-1} in the i.r. spectrum of the sulphur bridged dimer may be due to the Re–S–Re group as these bands do not appear in the spectrum of the oxygen-bridged species.



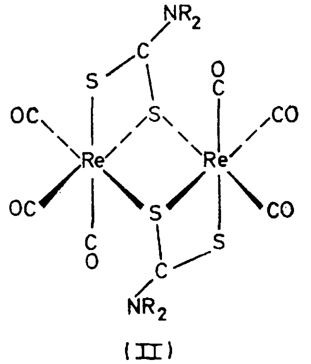
SCHEME 2 i, Tl(dtc); ii, PPh_3; iii, pyridine; iv, $NaBPh_4$; v, LiCl and $Bu^n{}_4NCl$

Interaction of Thallium Dithiocarbamates with Rhenium Carbonyl Chlorides.—The dimeric compound, $[Re(CO)_3(S_2CNEt_2)]_2$, referred to earlier, and the related complexes $Re(CO)_3(S_2CNEt_2)(L)$ (L = CO, py, PPh_3) are formed in the reactions in Scheme 2. The dimer is quite readily cleaved by triphenylphosphine, pyridine, carbon monoxide, and chloride ion so that it seems unlikely to contain a Re–Re bond and indeed this is also suggested by the ready formation from $[Re(CO)_3Cl(S_2CNEt_2)]^-$ discussed earlier. This anion was also detected spectroscopically in the hexane extract from the products of interaction of the dimer with LiCl and $[Bu^n{}_4N]Cl$ in acetone.

Rather similar dimers with other dithio-acids have been described, *viz*, $[(Et_2PS_2)Re(CO)_3]_2$ [9] and $[(PhCS_3)Re(CO)_3]_2$ [10] as well as $(Et_2PS_2)Re(CO)_4$,[9] $RCS_2Re(CO)_4$,[11] and $(Et_2PS_2)Re(CO)_3L$ [12] (L = PPh_3, $AsPh_3$, $SbPh_3$, py) and for the dimeric compounds a sulphur-bridged structure was proposed.

The dithiocarbamate dimer probably has the structure (II) where one of the S atoms of the CS_2 moiety links the metal atoms as in zinc[13] and cadmium[14] diethyldithiocarbamates. Rhenium(I) is thus octahedral as usual and the splitting of the ν(CS) band in the i.r. spectrum (Table) can be accounted for. However, the i.r. criterion is by no means well established.

(*a*) A split ν(CS) has been interpreted[15a] as indicating unidentate S_2CNR_2 in a well defined case. (*b*) A split ν(CS) is found as above in $Re(CO)(S_2CNR_2)_3$ where one sulphur is '*trans*' to CO and hence inequivalent. (*c*) The zinc and cadmium diethyldithiocarbamates $[M(S_2CNEt_2)_2]_2$ whose structures have been determined by *X*-ray methods do not show a split ν(CS) but only single bands at *ca.* 990 cm^{-1}. In $Tl(S_2CNEt_2)_3$ in a Nujol mull there is a splitting,[15b] but in *solution* there is only *one* band at *ca.* 980 cm^{-1}. In these cases, of course, no other ligands are present that might cause splitting due to inequivalent sulphur atoms.



(II)

It may be noted in respect of $[Re(CO)_3(S_2CNEt_2)]_2$ that the ν(CN) band at 1520 cm^{-1} is higher than in unidentate dithiocarbamates (1460—1470 cm^{-1}).[16] The compound also has four C–O stretching frequencies as in $[ReX(CO)_3(S_2CNEt_2)]^-$ (X = Cl, I) and $Re(CO)_3(PPh_3)(S_2CNEt_2)$ and also in $[(PhCS_3)Re(CO)_3]_2$ in hexane.

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[9] E. Lindner and K. Matejcek, *J. Organometallic Chem.*, 1971, **29**, 283.

[10] W. Hieber and W. Rohm, *Chem. Ber.*, 1962, **102**, 2787.

[11] E. Lindner and R. Grimmer, *J. Organometallic Chem.*, 1970, **25**, 493.

[12] E. Lindner and H. Berke, *J. Organometallic Chem.*, 1972, **39**, 145.

[13] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 898.

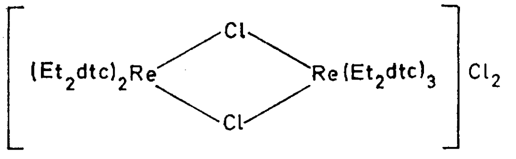
[14] A. Domenicano, L. Torelli, A. Vaciago, and L. Zambonelli, *J. Chem. Soc.* (*A*), 1968, 1351.

[15] (*a*) F. Bonati and R. Ugo, *J. Organometallic Chem.*, 1967, **10**, 257; (*b*) F. Bonati, S. Cenini, and R. Ugo, *ibid.*, 1967, **9**, 395.

[16] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 1966, 476.

The compound $Re(CO)_4(S_2CNEt_2)$ loses carbon monoxide when heated in benzene and the dimer $[Re(CO)_3(S_2CNEt_2)]$ separates from solution.

Interaction of Tetraethylthiuram Disulphide with Bis(triphenylphosphine)tetrachlororhenium(IV).— Interaction of $ReCl_4(PPh_3)_2$ with $(Et_2NCS_2)_2$ in refluxing benzene gives a red solution and an insoluble brown powder. The solution contains $ReCl_2(S_2CNEt_2)_2$ identical with the product from $ReCl(CO)_5$ and thiuram disulphide discussed above. The power on crystallisation from methylene dichloride gives brown needles of stoicheiometry $Re_2Cl_4(S_2CNEt_2)_5$. These are insoluble in acetone but dissolve in nitromethane where the conductivity ($\Lambda_M = 153\ \Omega^{-1}\ cm^2\ mol^{-1}$; $c\ 10^{-3}$M) is that of a 1 : 2 electrolyte. Electrophoresis on paper using solutions of n-butylammonium perchlorate in dichloromethane as supporting electrolyte shows the presence of a brown cation and a colourless anion which can be shown to be chloride. The complex can be formulated as (III) with octahedral Re^{IV} and eight-co-ordinate Re^{V}.



(III)

The magnetic susceptibility corresponds to a moment for the Re^{IV} atom of $\mu_{eff} = 3{\cdot}3$ B.M. at 297 K. The i.r. band at 287 cm^{-1} which has two shoulders can be assigned to the metal bridging chlorine system.

When $ReCl_4(PPh_3)_2$ and thiuram disulphide are refluxed in acetone, brown solutions are obtained from which $[Re(S_2CNEt_2)_4]^+$ is obtained.

EXPERIMENTAL

Analyses were by the Microanalytical Laboratory, Imperial College, and by A. Bernhardt, W. Germany. Infrared spectra were recorded on Perkin-Elmer 457 and Unicam SP 200 instruments. Molecular weights were measured on a Perkin-Elmer–Hitachi model 115 osmometer. N.m.r. spectra were obtained on Perkin-Elmer R14 (100 MHz) and R12A (60 MHz) spectrometers.

All reactions were carried out under oxygen-free nitrogen. The following were prepared by published methods $ReCl(CO)_5$,[17] $Re_2(CO)_8Cl_2$,[18] $ReCl_4(PPh_3)_2$,[19] and $[Et_2NCS_2]_2$.[20] $ReOCl[S_2CN(CH_2Ph)_2]_2$ and $Re_2O_3[S_2CN(CH_2Ph)_2]_4$ were prepared by the methods used for the analogous ethyl complexes published previously.[1]

Interaction of Pentacarbonylchlororhenium(I) *and Tetraethylthiuram Disulphide in Acetone*.—An acetone (80 cm^3) solution of $[Et_2NCS_2]_2$ (5 g), and $ReCl(CO)_5$ (2 g) was refluxed for 6 h. The dark brown solution was evaporated under reduced pressure and the residual brown mass extracted with ether (3 × 30 cm^3) to leave a brown solid. This brown solid was extracted with refluxing benzene (30 cm^3) to leave a golden-brown solid (1·23 g, 36%) which was recrystallised from acetone–ether to give brown plates of the salt $[Re(S_2CNEt_2)_4][Re(CO)_3(S_2CNEt_2)Cl]$. Recrystallisation of this substance from acetone–benzene solution gave brown plates of the benzene solvate $[Re(S_2CNEt_2)_4][Re(CO)_3(S_2CNEt_2)Cl],C_6H_6$. Concentration of the above benzene extract followed by addition of ether gave brown crystals of $Re(CO)(S_2CNEt_2)_3$ (1·1 g, 27%).

Interaction of Pentacarbonylchlororhenium(I) *and Tetraethylthiuram Disulphide in Benzene*.—A benzene (50 cm^3) solution of $ReCl(CO)_5$ (1 g) and $[Et_2NCS_2]_2$ (2·8 g) was refluxed for 7 h, cooled, and set aside at *ca.* 10° for 12 h. The brown deposit was collected and recrystallised from acetone–benzene to give brown needles of the salt $Re_2(S_2CNEt_2)_5Cl_4$ (0·15 g, 8%). The red-brown filtrate was concentrated to 25 cm^3 and set aside for 3 days to give red crystals of the *complex* $Re(S_2CNEt_2)Cl_2$ (0·14 g, 9·3%); these were recrystallised from acetone. The second filtrate was then treated with ether to give brown crystals of the *complex* $Re(CO)(S_2CNEt_2)_3$ (1·2 g, 63%). This was dissolved in acetone, transferred to an alumina column, and eluted with ether–acetone (1 : 1).

Carbonyltris(dimethyldithiocarbamato)rhenium(III).— An acetone (60 cm^3) solution of $[Me_2NCS_2]_2$ (1·44 g) and $ReCl(CO)_5$ (0·724 g) was refluxed for 4 h, cooled, and filtered. The residue was recrystallised from acetone to give the *product* as brown crystals (0·8 g, 66%).

Interaction of Pentacarbonylchlororhenium(I) *and Tetrabenzylthiuram Disulphide in Benzene*.—A benzene (30 cm^3) solution of $[(PhCH_2)_2NCS_2]_2$ (2·25 g) and $ReCl(CO)_5$ (0·5 g) was refluxed for 1 h, cooled, and filtered. Ether (60 cm^3) was added to the filtrate which, after rejection of the residue, was concentrated to 20 cm^3 when a further 30 cm^3 of ether was added. The red solid which separated during 2 days was recrystallised from acetone to give red crystals (0·05 g, 5%) of the *complex* $Re[S_2CN(CH_2Ph)_2]_2Cl_2$. Further concentration of the filtrate and addition of ether gave a brown powder which was recrystallised twice from acetone to give brown crystals of the *complex* $Re(CO)[S_2CN(CH_2Ph)_2]_3$ (0·42 g, 29%).

The mixture was refluxed for 5 h and then evaporated; the residue was then dissolved in acetone (10 cm^3). The acetone solution was transferred to an alumina column and eluted with acetone–ether (1 : 1); the red-brown solution was concentrated and treated with ether to give a brown powder. Recrystallisation from acetone gave the *complex* $Re_2O_2S[S_2CN(CH_2Ph)_2]_4$ as brown needles (0·22 g, 20%).

Tetrakis(diethyldithiocarbamato)rhenium(V) *Tetraphenylborate*.—An acetone (30 cm^3) solution of $[Re(S_2CMEt_2)_4][Re(CO)_3(S_2CNEt_2)Cl]$ (0·27 g) and $NaBPh_4$ (0·07 g) was refluxed for 2 h, cooled, and the white solid collected. Addition of ether to the filtrate gave dark brown needle-like crystals of the *complex* (0·12 g, 50%). The white residue was extracted with refluxing benzene. Concentration and cooling of the benzene extract gave cream crystals of $[Re(CO)_3(Et_2dtc)]_2$.

Tetrabutylammonium Tricarbonyliodo(diethyldithiocarbamato)rhenate(I).—An acetone (10 cm^3) solution of $[Re(S_2CNEt_2)_4][Re(CO)_3(S_2CNEt_2)Cl]$ (0·7 g), $Bu^t{}_4NI$ (0·2 g), and NaI (0·81 g) was refluxed for 2 h and cooled. Ether (15 cm^3) was added to the mixture which was then set aside

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[20] R. Rothstein and K. Binovic, *Rec. trav. Chim.*, 1954, **56**, 75.

overnight. Dark brown crystals were collected and recrystallised from acetone to give the iodide Re(S$_2$CNEt$_2$)$_4$I (0·2 g, 40%).

The filtrate was evaporated to dryness and the remaining solid was extracted with dichloromethane. Addition of ether to the extract and cooling for 24 h gave white crystals of the *salt* [Bu$^n{}_4$N][Re(CO)$_3$(S$_2$CNEt$_2$)I] (0·1 g, 22%).

Tetrakis(dithiocarbamato)rhenium(v) *Tri-iodide*.—A benzene (30 cm^3) solution of ReI(CO)$_3$(PPh$_3$)$_2$ (0·6 g) and [Et$_2$NCS$_2$]$_2$ (0·6 g) was refluxed for 1¼ h, cooled, filtered, treated with ether (60 cm^3), and set aside overnight to give dark brown crystals of the *compound* (0·1 g, 13%). Concentration of the remaining solution gave the complex Re(CO)(S$_2$CNEt$_2$)$_3$ (0·1 g, 20%).

Bis-μ-(diethyldithiocarbamato)-bis[tricarbonylrhenium(I)].—*Method* (A). A benzene (40 cm^3) solution of [Re(CO)$_4$Cl]$_2$ (0·86 g) and Tl(S$_2$CNEt$_2$) (0·91 g) was refluxed for 8 h and then filtered whilst hot; the residue was extracted with hot benzene (30 cm^3). The benzene solution was concentrated (20 cm^3) and cooled to give the *complex*, [Re(CO)$_3$(S$_2$CNEt$_2$)]$_2$, as cream crystals (0·73 g, 80%).

Method (B). A benzene (30 cm^3) solution of ReCl(CO)$_5$ (0·36 g) and Tl(S$_2$CNEt$_2$) (0·35 g) was refluxed for 14 h, and then filtered whilst hot; the filtrate was set aside to give the *complex* (0·22 g, 52%).

Tetracarbonyl(diethyldithiocarbamato)rhenium(I).—Carbon monoxide was bubbled through a suspension of [Re(CO)$_3$(S$_2$CNEt$_2$)]$_2$ (0·21 g) in benzene (30 cm^3) at 40° for 6 h to give a clear solution. The benzene was evaporated under reduced pressure at 40°. The solid residue was extracted with light petroleum (b.p. 60—80°; 3 × 20 cm^3) and the extract was concentrated (10 cm^3) to give the *complex* as white crystals (0·12 g, 55%).

Tricarbonyl(diethyldithiocarbamato)(pyridine)rhenium(I).—A benzene (20 cm^3) solution of pyridine (1 cm^3) and [Re(CO)$_3$(S$_2$CNEt$_2$)]$_2$ (0·4 g) was refluxed for 2 h, cooled, and filtered. The filtrate was concentrated (10 cm^3) and light petroleum (b.p. 60—80°; 20 cm^3) was added to give a white solid. This solid was recrystallised from benzene–light petroleum to give the *complex* as white crystals (0·25 g, 53%).

Tricarbonyl(triphenylphosphine)(diethyldithiocarbamato)-rhenium(I).—*Method* (A). A benzene (20 cm^3) solution of ReCl(CO$_3$)(PPh$_3$) (0·28 g) and Tl(S$_2$CNEt$_2$) (0·21 g) was refluxed for 1 h and then filtered whilst hot; the filtrate was concentrated (5 cm^3). Addition of light petroleum (b.p, 60—80°; 15 cm^3) gave white crystals of the *complex* (0·12 g. 55%).

Method (B). A benzene solution (10 cm^3) of [Re(CO)$_3$(Et$_2$dtc)]$_2$ (0·43 g) and PPh$_3$ (0·3 g) was refluxed for 1½ h, cooled, and ether added to give the complex (0·53 g, 76%).

Interaction of Bis(triphenylphosphine)tetrachlororhenium(IV) *with Tetraethylthiuram Disulphide*. (A) A benzene (50 cm^3) solution of (Et$_2$NCS$_2$)$_2$ (1·4 g) and ReCl(PPh$_3$)$_2$ (1 g) was refluxed for 18 h, cooled, and filtered. The brown residue of the *salt* Re$_2$Cl$_4$(Et$_2$NCS$_2$)$_5$ (0·33 g, 38%) was collected. The red filtrate was concentrated to 20 cm^3 and ether (50 cm^3) was added to give the *complex* ReCl$_2$(S$_2$CNEt$_2$)$_2$ as red crystals (0·24 g, 37%).

(B) An acetone (30 cm^3) solution of [Et$_2$NCS$_2$]$_2$ (1·26 g) and ReCl$_4$(PPh$_3$)$_2$ (0·9 g) was refluxed for 1½ h. The solvent was removed under reduced pressure and replaced by benzene (30 cm^3). The solution was refluxed for *ca*. 24 h, cooled, and filtered. The brown residue was collected and recrystallised from dichloromethane–ether (1 : 1) to give the *salt* [Re$_2$Cl$_4$(S$_2$CNEt$_2$)$_5$] as brown needles (0·23 g, 30%). The filtrate was treated with NaBPh$_4$ (0·36 g) and refluxing continued for 3 h when the mixture was evaporated and the remaining solid dissolved in acetone. The acetone extract was concentrated and treated with ether to give the *salt*, [Re(S$_2$CNEt$_2$)$_4$]BPh$_4$, as dark brown crystals (0·3 g, 26%).

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