In memory of S. M. Nelson

Dithiocarbamates of Tungsten(III) and Tungsten(IV)†

David A. Brown,* William K. Glass, Hani J. Toma, and W. Earle Waghorne
Chemistry Department, University College, Belfield, Dublin 4, Ireland

A series of dimeric tris(dialkyldithiocarbamato)tungsten(III) complexes, $[W_2(S_2CNR_2)_6]$ (R = Et, Pr^n, or Bu^n), and monomeric tetrakis(dialkyldithiocarbamato)tungsten(IV) complexes, $[W(S_2CNR_2)_4]$, are described, including the analogous pentamethylenedithiocarbamate complexes. Electrochemical, spectroscopic, and magnetic studies show the tris series to be dimeric, probably with a binuclear seven-co-ordinate structure, whereas the tetrakis complexes are eight-co-ordinate and monomeric. The dimeric series are effective reducing agents in non-aqueous solvents for both pyridine *N*-oxide and tetraethylammonium nitrate with preservation of the binuclear structure, whereas $[W(S_2CNEt_2)_4]$ is only effective with pyridine *N*-oxide.

Much of the current interest in the co-ordination chemistry of molybdenum stems from attempts to prepare complexes, especially those of sulphur-containing ligands, which may serve as models for biological systems and increase our understanding of industrial catalysts.[1–3] In contrast, much less attention has been given to the tungsten analogues despite the use of tungsten sulphide hydro-treating catalyst[2,3] and the recent discovery of a biological role for tungsten where it was shown capable of replacing molybdenum in *Clostridium thermoactecium* formate dehydrogenase,[4] although generally tungsten is an antagonist towards molybdenum in molybdo-enzymes.[5–7] Consequently, interest has focused on the chemistry of tungsten in its higher oxidation states (III—VI)[8] with special emphasis on tungsten(VI) dioxo[9] and tungsten(V) oxo complexes[9–13] where preparative, electrochemical, and e.s.r. studies have shown close similarities to their molybdenum analogues[14] considered as possible models for molybdo-enzymes.[7,15–17]

The dithiocarbamate ligand $(S_2CNR_2^-)$ forms a wide range of complexes with transition metals[18–21] and is an obvious candidate for the preparation of model Mo and W complexes of S-containing ligands; however, the isolation of pure Mo^{III}, Mo^{IV}, W^{III}, and W^{IV} dithiocarbamate complexes has proved to be both difficult and tenuous. $[Mo^{IV}(S_2CNMe_2)_4]$ was first reported by oxidative decarbonylation of hexacarbonylmolybdenum with *NNN′N′*-tetramethylthiuram disulphide $[Me_2NC(=S)\text{–}S\text{–}S\text{–}C(=S)NMe_2]$[22] and later by CS_2 insertion into the Me–N bond of $[Mo(NMe_2)_4]$.[23] Our first brief report of the dimeric Mo^{III} dithiocarbamates $[Mo_2(S_2CNR_2)_6]$ again involved an oxidative decarbonylation method[24] but a subsequent preparation involved $[Mo_2O_2Cl_2(H_2O)_6]$ and $Na(S_2CNEt_2)$,[25] when confirmatory *X*-ray evidence of its dimeric nature was given. However, our original report[24] was called into question by some workers[26,27] and one group only obtained the $[Mo(S_2CNR_2)_4]$ series using the oxidative decarbonylation route.[28] This confusing situation was finally resolved when it was shown that oxidative decarbonylation of both (*a*) tricarbonyl(η^6-cycloheptatriene)molybdenum in refluxing toluene in daylight and (*b*) hexacarbonylmolybdenum in refluxing toluene with rigorous exclusion of light with the corresponding tetra-alkylthiuram disulphide yield the dimeric $[Mo_2(S_2CNR_2)_6]$ series.[29,30] However, converse conditions, namely the first method with rigorous exclusion of light and the second in daylight, produce the $[Mo(S_2CNR_2)_4]$ series.[29,31] Interestingly, this work was extended recently when prolonged reaction of $[Mo(CO)_6]$ and tetraethylthiuram disulphide was shown to form first $[Mo_2(S_2CNEt_2)_6]$ and then finally the cubane-like complex $[Mo_4(\mu_3\text{-}S)_4(S_2CNEt_2)_6]$.[32]

In the case of the tungsten analogues, the existence of W^{III} dithiocarbamates was mentioned in our early report of the $[Mo_2(S_2CNR_2)_6]$ series.[24] $[W(S_2CNR_2)_4]$ (R = Et) was first reported from the reaction of $WX_4{\cdot}2MeCN$ (X = Cl or Br) and $Na(S_2CNEt_2)$ in acetonitrile;[33] subsequently, $[W^{IV}\{S_2CN(CH_2)_4\}_4]$[34] was reported. In a recent review, Dori[35] referred to unpublished work involving the preparation of $[W(S_2CNEt_2)_4]$ from $[W(CO)_3(MeCN)_3]$ and tetraethylthiuram disulphide. To the best of our knowledge, no further publication has appeared concerning the $[W(S_2CNR_2)_3]$ series since our preliminary report over 10 years ago. In the present paper, we describe in detail the synthesis of a series of dimeric tris(dithiocarbamato)tungsten(III) complexes, $[W_2(S_2CNR_2)_6]$, and a series of monomeric tetrakis(dithiocarbamato)tungsten(IV) complexes, $[W(S_2CNR_2)_4]$, together with some of their chemical and spectroscopic properties.

Experimental

All chemicals used were carefully purified and dried. All preparations and manipulations were carried out under a nitrogen atmosphere.

The electrochemistry of the complexes was studied by direct current polarography at a rotating platinum disc (diameter 0.5 cm) and by cyclic voltammetry at the same electrode. All electrochemical measurements were made using a conventional three-electrode system. The potentiostat (Thompson Electrochem model 251R) was driven by a signal generator (Hewlett Packard model 3310B); the current was monitored as the voltage drop across a measuring resistor (Jay-Jay Instruments) and the signal displayed on an X–Y recorder (Bryans Southern Instruments model 26000 A4). A platinum auxiliary electrode and aqueous saturated calomel reference electrode (s.c.e.) were used for all measurements. Tetraethylammonium hexafluorophosphate (0.1 mol dm^{-3}) was used as supporting electrolyte. Oxygen was removed from all solutions by purging with nitrogen for 10 min before measurements were made.

Mass spectra were recorded on a V.G. Micromass 7070H instrument with a Finnigan Incos Data System. Infrared spectra

---

† *Non-S.I. unit employed:* B.M. $\approx 9.274 \times 10^{-24}$ J T^{-1}.

were recorded on a Perkin-Elmer 283B spectrophotometer as 2% KBr and CsBr discs. Electronic spectra were recorded in the solid state by diffuse reflectance on a Perkin-Elmer 552 spectrophotometer using an integrating sphere attachment. Magnetic susceptibilities were measured in the solid state on a variable-temperature Gouy balance supplied by Newport Instruments using a flat-bottomed glass tube, calibrated with Hg[Co(CNS)$_4$].

Two methods were used in the preparation of these complexes: (A) photochemical oxidative decarbonylation of tricarbonyl(η^6-toluene)tungsten with $R_2NC(=S)-S-S-C(=S)-NR_2$ [R = Et (tetds), Pr^n (tptds), or Bu^n (tbtds)] or *NN'*-bis(pentamethylene)thiuram disulphide (bmptds); (B) thermal oxidative decarbonylation of the above π-complex with tetds or bmptds. Unlike the molybdenum series,[29,30] the tungsten dithiocarbamate complexes were not obtainable from reaction of [W(CO)$_6$] with the thiuram disulphide. Typical preparations are given below.

Tris(diethyldithiocarbamato)tungsten(III).—*Method A*. A mixture of [W(CO)$_3$(η^6-C$_6$H$_5$Me)] (0.005 mol) and recrystallized tetds (0.0075 mol) in dry deoxygenated benzene (100 cm^3) was irradiated under nitrogen with a u.v. lamp (Philips HPR, 125 W) until no carbonyl absorption bands were detected. After cooling to room temperature and solvent reduction to 25 cm^3, the mixture was filtered and added dropwise to (200 cm^3) dry deoxygenated hexane, with stirring under nitrogen. The dark brown product which formed was filtered off, washed with fresh aliquots of hexane, and dried under nitrogen (yield $> 70\%$).

The above procedure was also used to prepare the pentamethylene-, the di-n-propyl-, and the di-n-butyl-dithiocarbamate complexes of tungsten(III). The only difference was that after the reaction was adjudged complete, the pentamethylene derivative was filtered off directly as a fine powder. The di-n-propyl derivative was formed by removing solvent and triturating the oily residue in hexane, and the di-n-butyl derivative by removing solvent and exposing the oily residue to a high vacuum (rotary oil pump) for several hours followed by grinding under a nitrogen atmosphere.

Method B. This method was used to prepare the diethyl- and pentamethylene-dithiocarbamate derivatives. The same molar ratio as in method A was heated under reflux in toluene or benzene (100 cm^3) under nitrogen in the dark until a carbonyl-free i.r. spectrum was obtained. After cooling to room temperature, the solutions were treated as in method A.

Reaction with Pyridine N-*Oxide*.—[W$_2$(S$_2$CNEt$_2$)$_6$] (0.001 mol) and pyridine *N*-oxide (pyO, 0.005 mol) were refluxed in dichloromethane–toluene (3:1 v/v) under nitrogen. After filtration of the hot reaction mixture, the green product [W$_2$O$_3$(S$_2$CNEt$_2$)$_2$] was washed with aliquots of toluene and hexane and dried under nitrogen.

Reaction with [NEt$_4$][NO$_3$].—[W$_2$(S$_2$CNEt$_2$)$_6$] (0.001 mol) and [NEt$_4$][NO$_3$] (0.003 mol) were stirred for 1.5 h in dichloromethane (50 cm^3) under nitrogen. The solvent was removed by evaporation under vacuum, and the residue washed with toluene and water (to remove unreacted material). After dissolution in ethanol, filtration, and solvent removal, the resulting solid was washed with hexane (25 cm^3) and dried under nitrogen. The final product analyzed as [W$_2$O(NO$_2$)(S$_2$CNEt$_2$)$_6$].

In a duplicate experiment, a CH$_2$Cl$_2$ trap was used to sample the evolved gas, identified as NO from its u.v.–visible spectrum.

Tetrakis(diethyldithiocarbamato)tungsten(IV).—*Method A*. A solution of [W(CO)$_3$(η^6-C$_6$H$_5$Me)] (0.005 mol) and tetds (0.01 mol) in benzene (100 cm^3) was irradiated under nitrogen with a u.v. lamp as above. The reaction was adjudged complete when a carbonyl-free i.r. spectrum was obtained. After cooling to room temperature, the greenish brown powdery product was filtered off, washed with hexane, and dried under nitrogen (yield *ca.* 75%).

This method was also used to prepare the pentamethylene-, di-n-propyl-, and the di-n-butyl-dithiocarbamate complexes of tungsten(IV). The reaction mixture was treated differently after cooling at room temperature: the pentamethylene derivative was obtained directly as a fine powder by filtration, and the di-n-propyl derivative was formed by removing the solvent under reduced pressure, keeping the oily residue covered with hexane overnight, filtering the solid product and washing it with fresh aliquots of hexane, and subsequently drying under nitrogen. The di-n-butyl derivative was obtained by removing the solvent and leaving the oily residue under reduced pressure (oil pump) for several hours followed by trituration with hexane to give a fine powdery product.

Method B. A solution, proportions as in method A, with either acetone, toluene, or benzene as solvent was refluxed in daylight until no carbonyl absorption remained. The solution was then filtered and treated as above. The pentamethylene derivative was prepared similarly.

Reaction with Pyridine N-*Oxide*.—[W(S$_2$CNEt$_2$)$_4$] (0.001 mol) and pyO (0.005 mol) were refluxed for 2 h in toluene–dichloromethane (1:3 v/v, 50 cm^3). After cooling to room temperature, the dark brown precipitate was filtered off, washed with toluene, dried under nitrogen and analyzed as [WO(S$_2$CNEt$_2$)$_3$].

Reaction with [NEt$_4$][NO$_3$].—The reaction of [W(S$_2$CNEt$_2$)$_4$] with [NEt$_4$][NO$_3$] at room and reflux temperatures always produced oily material which could not be characterized.

Results and Discussion

The photochemical oxidative decarbonylation of tricarbonyl(η^6-toluene)tungsten with the corresponding tetra-alkylthiuram disulphide (tetds, tptds, or tbtds) in benzene under a nitrogen atmosphere yielded a series of dimeric tris(dialkyldithiocarbamato)tungsten(III) complexes [W$_2$(S$_2$CNR$_2$)$_6$] and monomeric tetrakis(dialkyldithiocarbamato)tungsten(IV) complexes [W(S$_2$CNR$_2$)$_4$] (π-complex:ligand molar ratio 1:1.5 and 1:2 respectively). Similarly, bpmtds produced [W$_2${S$_2$CN(CH$_2$)$_5$}$_6$] and [W{S$_2$CN(CH$_2$)$_5$}$_4$]. Furthermore, identical thermal oxidative decarbonylation (*a*) with a π-complex:ligand (tetds or bpmtds) molar ratio of 1:1.5 in refluxing toluene or benzene under a nitrogen atmosphere with rigorous exclusion of light produced the complexes [W$_2$(S$_2$CNEt$_2$)$_6$] and [W$_2${S$_2$CN(CH$_2$)$_5$}$_6$], and (*b*) with a molar ratio of 1:2 in refluxing acetone, toluene, or benzene under a nitrogen atmosphere in daylight yielded the complexes [W(S$_2$CNEt$_2$)$_4$] and [W{S$_2$CN(CH$_2$)$_5$}$_4$].

Thus, in contrast to the molybdenum dithiocarbamate complexes, both the tris and tetrakis tungsten series may be prepared by photochemical oxidative decarbonylation, the nature of the product depending solely on the molar ratio of reactants. However, in the corresponding thermal reaction not only must the molar ratio be carefully adjusted but rigorous exclusion of light is essential to obtain the tris complex. It is also necessary in all the above reactions to use reactants and solvents of particularly high purity. Finally, it should be noted that attempts to obtain either series from hexacarbonyltungsten were unsuccessful, in contrast to the molybdenum series.

Table 1. Characterization data for the complexes

			Analysis[a] (%)				I.r. (ν/cm^{-1})				
Complex	Colour	M.p. (°C)	C	H	N	S	ν(C$\cdots$N)	ν_{sym}(C–S)	ν_{asym}(C–S)	ν(M–S)	μ/ B.M.
$[W_2(S_2CNEt_2)_6]$	Dark brown	110—112[b]	28.7 (28.6)	4.7 (4.8)	6.5 (6.7)	30.3 (30.5)	1 513vs	1 020w	579m	349m	1.45[c]
$[W_2(S_2CNPr^n{}_2)_6]$	Dark brown	78—81[b]	35.1 (35.4)	5.7 (5.9)	5.7 (5.9)	26.8 (27.0)	1 511vs	1 011 (sh)	610m	350m	1.92[c]
$[W_2\{S_2CN(CH_2)_5\}_6]$	Dark brown	d	40.4 (40.7)	6.3 (6.8)	5.1 (5.3)	22.9 (24.1)	1 510vs	1 008w	611m	356m	1.25[c]
$[W_2\{S_2CN$-$(CH_2)_5\}_6]$	Dark brown	121—124	23.3 (23.5)	4.6 (4.5)	6.0 (6.3)	29.3 (28.9)	1 514vs	1 021m	606m	340m	1.38[e]
$[W(S_2CNEt_2)_4]$	Green-brown	152—154[b]	31.0 (30.9)	5.1 (5.2)	7.4 (7.2)	32.7 (33.0)	1 518vs	1 018w	579m	351m	1.73[e]
$[W(S_2CNPr^n{}_2)_4]$	Green-brown	108—110[b]	37.7 (37.8)	6.5 (6.3)	6.3 (6.3)	29.2 (28.8)	1 515vs	1 007 (sh)	612m	348m	1.65[e]
$[W(S_2CNBu^n{}_2)_4]$	Green-brown	93—96[b]	42.4 (43.2)	7.2 (7.2)	5.5 (5.6)	23.9 (25.6)	1 513vs	1 005m	611m	357m	1.61[e]
$[W\{S_2CN(CH_2)_5\}_4]$	Green-brown	166—170	34.8 (34.9)	4.9 (4.9)	6.6 (6.8)	32.1 (31.1)	1 519vs	1 018m	607m	342m	1.67[e]
							ν(NO)$_b$	ν(W–O$_t$)	ν_{asym}(W–O$_b$)	δ(NO)$_b$	ν_{asym}(W–O$_b$)
$[W_2O_3(S_2CNEt_2)_2]$	Green		16.3 (16.9)	2.8 (2.8)	3.8 (3.9)	16.9 (18.0)		972s	810s		445m
$[WO(S_2CNEt_2)_3]$	Dark brown		27.2 (28.0)	4.2 (4.7)	6.4 (6.5)	30.5 (29.8)		969s			
$[W_2O(NO_2)$-$(S_2CNEt_2)_6]$	Brown		27.1 (27.2)	4.6 (4.6)	7.2 (7.4)	29.3 (29.1)	1 385vs		810s	810s	445m

[a] Calculated values are given in parentheses. [b] With decomposition. [c] At 273 K. [d] Not obtainable. [e] At 263 K.

Despite the very low solubility of these complexes in aliphatic hydrocarbons and only slight solubility in some aromatic hydrocarbons such as toluene and benzene, attempts were made to crystallize the tris and tetrakis complexes from different solvents such as acetone, dichloromethane, and ethanol–light petroleum (b.p. 40—60 °C) but this only resulted in decomposition. Both series are very sensitive to oxygen both in solution and, to a lesser extent, in the solid state.

Infrared Spectra.—In the complexes $[W_2(S_2CNR_2)_6]$ and $[W(S_2CNR_2)_4]$, with tungsten formally in the oxidation states of III and IV respectively, the dithiocarbamate ligand can show both bidentate (symmetrical) and unidentate (unsymmetrical) bonding to the metal. In the former case, only one ν(C–S) stretching vibration occurs in the region 970—1 050 cm^{-1};[36] however, if two stretching vibrations are observed in this region with a separation of at least 18 cm^{-1},[37] unidentate or a mixture of uni- and bi-dentate co-ordination of the ligand may be deduced. All the W^{III} and W^{IV} dithiocarbamate complexes in the above series exhibit only one ν(C–S) band and one broad ν(C$\cdots$N) band, confirming bidentate co-ordination.

Electrochemistry.—The cyclic voltammograms (c.v.s) of the tris and tetrakis tungsten dialkyldithiocarbamate complexes show two reduction waves at $E_{\frac{1}{2}} = -0.665$ (wave 1) and -0.28 V (wave 2) and two oxidation waves at $E_{\frac{1}{2}} = +0.782$ (wave 3) and 1.03 V (wave 4) for the tris complex [Figure 1(*a*)] as against one reduction wave at $E_{\frac{1}{2}} = -0.652$ V (wave 1) and two oxidation waves at $E_{\frac{1}{2}} = +0.09$ (wave 2) and $+0.779$ V (wave 3) for the tetrakis complex [Figure 1(*b*)]. On the other hand, the polarograms of these complexes at a Pt rotating disc electrode (r.d.e.) each show one reduction and two oxidation waves (Figure 2). For the tris complex, the reduction wave appears at -0.66 V (wave 1) and the oxidation at $+0.81$ (wave 3) and 1.035 V (wave 4) [Figure 2(*a*)], while in the case of the tetrakis complex, the reduction wave appears at -0.65 V (wave 1) and the oxidation waves at $+0.08$ (wave 2) and at $+0.80$ V (wave 3) [Figure 2(*b*)]. The values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (Table 2) for all the waves in both complexes are almost equal and slightly shorter than that of a one-electron process. However, it is clear from the values of *i*/*c* (limiting current divided by concentration) that wave 1 of the tris complex is nearly twice as big as that of the other waves in both complexes. Values of ΔE_p (Table 2) reveal waves 1 and 3 in both complexes to be reversible. Further evidence for their reversibility is that no changes in peak

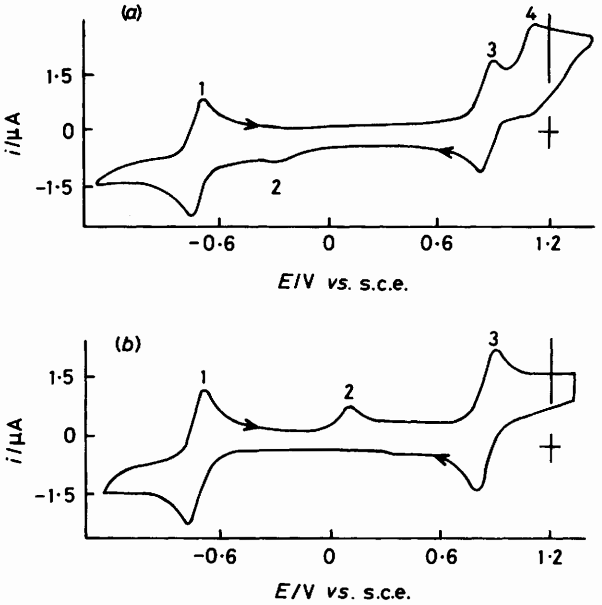

Figure 1. Cyclic voltammograms of (*a*) $[W_2(S_2CNEt_2)_6]$ and (*b*) $[W(S_2CNEt_2)_4]$

Table 2.

	Cyclic voltammetry			Rotating disc polarography		
	$E_{\frac{1}{2}}$/V	i_{pa}/i_{pc}	ΔE_p/mV	$E_{\frac{1}{2}}$/V	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$/mV	$i_d c^{-1}$/μA dm^3 mmol^{-1}
$[W_2(S_2CNEt_2)_6]$	−0.665	1.07	80	−0.66	75	1.7
	−0.28*	Irreversible				
	+0.782	1.00	75	0.81	65	0.9
	1.03*	Irreversible		1.035	70	1.05
$[W(S_2CNEt_2)_4]$	−0.652	1.04	60	−0.65	60	1.04
	0.09*	Irreversible		0.08	60	0.74
	0.779	0.95	65	0.80	70	1.14

* E_p for irreversible processes.

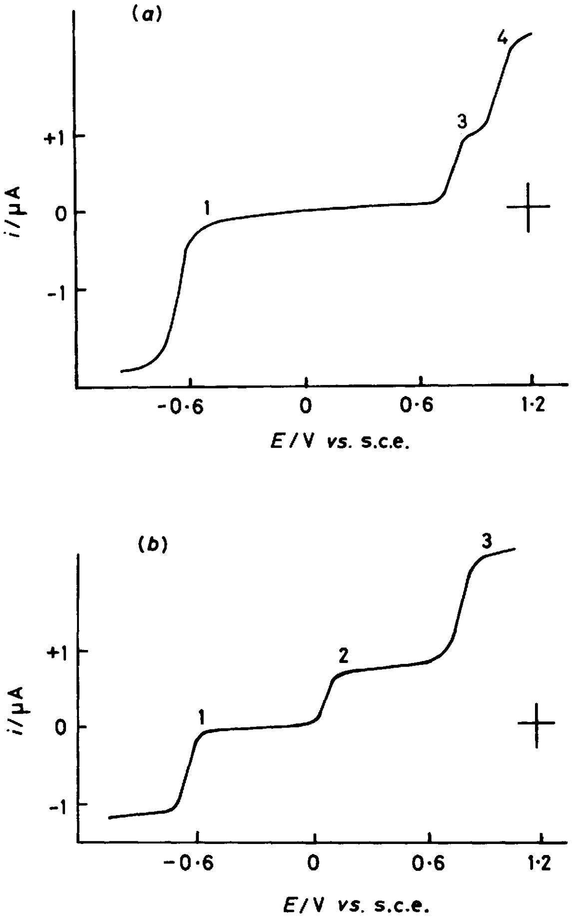

Figure 2. Rotating disc polarograms of (*a*) $[W_2(S_2CNEt_2)_6]$ and (*b*) $[W(S_2CNEt_2)_4]$

Table 3. Characteristic mass spectral data

Complex	*m/e*	Relative intensity*	Assignment
$[W(S_2CNEt_2)_4]$	776	8	$[W(S_2CNEt_2)_4]^+$
	546	20	$[W(S_2CNEt_2)_2S_2]^+$
	528	20	$[W(S_2CNEt_2)(C_3H_7NCS_2) - S_2]^+$
	264	15	$[WS_2C]^+$
$[W_2(S_2CNEt_2)_6]$			
Pathway 1	544	3	$[W(S_2CNEt_2)_2S_2]^+$
	512	20	$[W(S_2CNEt_2)_2S]^+$
	397	12	$[W(S_2CNEt_2)S_2]^+$
	353	30	$[WS_4CEt]^+$
	342	10	$[WS_4Et]^+$
Pathway 2	361	35	$[WS_2CNEt - CNS]^+$
	344	5	$[WS_2CNEt - CS]^+$
	264	3	$[WS_2C]^+$

* 100% intensity obtained for $[Et_2NCS]^+$.

positions were observed on changing the scan rate from 4×10^{-3} to 7×10^{-3} mV s^{-1}, while in doing so wave 4 of the tris complex spread out suggesting an irreversible wave. Wave 2 in the c.v. of the tetrakis complex corresponded to that of the free ligand, which showed one oxidation, at +0.09 V. This wave, in the c.v. of the tetrakis complex disappeared after controlled potential electrolysis of the solution at 1.0 V, while the other peaks in the c.v. were unaffected by the electrolysis. Thus it can be assigned to the oxidation of free ligand. This wave reappeared in the c.v. when the reduction wave 1 was included in the scan, suggesting that reduction of the complex resulted in some decomposition with liberation of the ligand. Wave 2 in the c.v. of the tris complex is due to the reduction of the decomposition product, resulting from the oxidation of the complex. Thus it is absent from the r.d.e. polarogram and from c.v.s of the complex which do not include the oxidation waves 3 and 4.

The above electrochemical studies clearly show the tris complex to have a reversible two-electron reduction wave (wave 1), a reversible one-electron oxidation wave (wave 3), and one irreversible one-electron oxidation wave (wave 4). In contrast, the tetrakis complex has a reversible one-electron reduction wave (wave 1) and a reversible one-electron oxidation wave (wave 3).

Mass Spectra.—The mass spectra of the two series of complexes showed interesting differences (Table 3). The fragmentation process for the tris complex $[W_2(S_2CNEt_2)_6]$ shows four different pathways, two involving tungsten-containing entities and the other two only the ligand. The absence of a parent molecular-ion peak together with the presence of two fragmentation paths for the tungsten-containing species is in accord with a dimeric structure. In contrast, the tetrakis complex $[W(S_2CNEt_2)_4]$ gave a molecular-ion peak and only two fragmentation pathways, one for the ligand and another for the tungsten-containing species, proving both its monomeric nature and illustrating the difference from the tris series.

Magnetic Moments.—The low values of the magnetic moments of the tris complexes, with the exception of Pr^n, ranging from 1.2 to 1.4 B.M. (Table 1) are indicative of the presence of at most one unpaired electron per tungsten atom with some spin coupling presumably occurring between the W centres in the dimer. Certainly, for a d^3 system, the magnetic moments are incompatible with a simple monomeric octahedral structure. Diamagnetic dimeric tungsten(III) complexes are well known;[38] the diamagnetism is explained by the formation of a triple bond through overlap of the metal d_{z^2} orbitals, to form a σ bond, and the metal d_{xz}/d_{yz} orbitals, to form π bonds, giving the configuration $\sigma^2\pi^4$. The low magnetic moments for the complexes $[W_2(S_2CNR_2)_6]$ probably arise, not from a weakening of the above type of interaction which might be expected to lead to formation of a single W–W σ bond and a d^2 configuration at the W atom, but rather by formation of a binuclear seven-co-ordinate tungsten(III) complex of either capped trigonal prismatic (c.t.p.) or pentagonal bipyramidal (p.b.) structure.

The values of 1.65—1.7 B.M. (Table 1) for the magnetic moments of the d^2 eight-co-ordinate W^{IV} complexes $[W(S_2CNR_2)_4]$, which in theory should be diamagnetic, may be explained by the presence of paramagnetic impurities and/or air oxidation of the product during manipulation and magnetic susceptibility measurements. Similar behaviour occurs for the Mo^{IV} complexes $[Mo(S_2CNR_2)_4]$ which show magnetic moments of up to 1.3 and 1.4 B.M. for R = Pr^n and Bu^n respectively,[31] although n.m.r. and e.s.r. results indicated an eight-co-ordinate diamagnetic species.[31]

Electronic Spectra.—The solid-state reflectance electronic spectra of the complexes $[W_2(S_2CNR_2)_6]$ exhibit five *d–d* transition bands in the region 14 200—27 900 cm^{-1} (14 200, 16 800, 19 200, 21 400, and 27 900 cm^{-1}). This behaviour is more complex than expected for octahedral metal complexes but it is consistent with a seven-co-ordinate W^{III} complex with c.t.p. rather than p.b. geometry.[39–43] In contrast, the electronic spectra of the complexes $[W(S_2CNR_2)_4]$ show six bands in the region 13 600—26 700 cm^{-1} (13 600, 14 200, 16 600, 18 200, 21 300, and 23 800 cm^{-1}) consistent with a square-antiprismatic structure.[44,45]

Reduction Reactions.—The reaction of $[W_2(S_2CNEt_2)_6]$ with pyridine *N*-oxide in a refluxing toluene–dichloromethane mixture resulted in the oxidation of W^{III} to W^{IV} and preservation of the binuclear structure of the parent tris complex by forming $[W_2O_3(S_2CNEt_2)_2]$, through abstraction of oxygen from the pyridine *N*-oxide. The appearance of bands at 445, 810, and 972 cm^{-1} in the i.r. spectrum (Table 1), which are absent in the parent complex, may be attributed to $\nu_{sym}(W–O_b)$, $\nu_{asym}(W–O_b)$, and $\nu(W–O_t)$ stretching vibrations respectively (b = bridging, t = terminal). A study on the mono- and di-oxo-bridged systems showed their vibrational frequencies to be strongly sensitive to the M–O–M bond angle.[46] It also revealed that ν_{asym} of the monobridged system appears at least 215 cm^{-1} to high frequency of ν_{sym}, with the difference increasing as the angle approaches linearity, while the corresponding differences in the dioxo-bridged systems appear over a narrower range. In another study[47] it was concluded that ν_{sym} in the linear bridged system is i.r.-inactive. Therefore $[W_2O_3(S_2CNEt_2)_2]$ has a non-linear mono-oxo-bridged system with the tungsten atoms four-co-ordinate [Figure 3(*a*)].

The identical reaction of $[W(S_2CNEt_2)_4]$ with pyridine *N*-oxide resulted in the oxidation of W^{IV} to W^V and the formation of $[WO(S_2CNEt_2)_3]$ as a dark brown solid and again reduction of the substrate to pyridine. In addition to the bands present in the parent tetrakis complex, this compound shows a band at 969 cm^{-1} (Table 1) which is assigned as the $\nu(W–O_t)$ terminal stretching vibration. However, it shows no additional bands at *ca.* 450 and 750—820 cm^{-1} where the $\nu_{sym}(W–O_b)$ and $\nu_{asym}(W–O_b)$ vibrations occur respectively. Thus, a structure [Figure 3(*b*)] in which the tungsten atom is seven-co-ordinate may be suggested.

Finally, reaction of $[W_2(S_2CNEt_2)_6]$ with $[NEt_4][NO_3]$ in dichloromethane at room temperature yielded $[W_2O(NO_2)(S_2CNEt_2)_6]$. The i.r. spectrum of this compound shows two bands in the $\nu_{sym}(C–S)$ region with a splitting of *ca.* 18 cm^{-1} (1 001 and 1 019 cm^{-1}) and therefore the mode of chelation of the ligand is a mixture of uni- and bi-dentate.[37] The occurrence of a new band at 1 385 cm^{-1} may be attributed to a bridging (NO) group.[48] Both the $\nu_{asym}(W–O_b)$ and $\delta(ONO)$ appear in the 800 cm^{-1} region. Consequently, the band at 810 cm^{-1} is assigned to these modes in the complex, superposition occurring. Moreover, the band at 445 cm^{-1} is assigned to the $\nu_{sym}(W–O_b)$ stretching vibration. From the above i.r. studies, a binuclear structure in which the tungsten atoms are bridged by both μ-oxo and μ-NO_2 groups may be suggested for $[W_2O(NO_2)(S_2CNEt_2)_6]$ [Figure 3(*c*)].

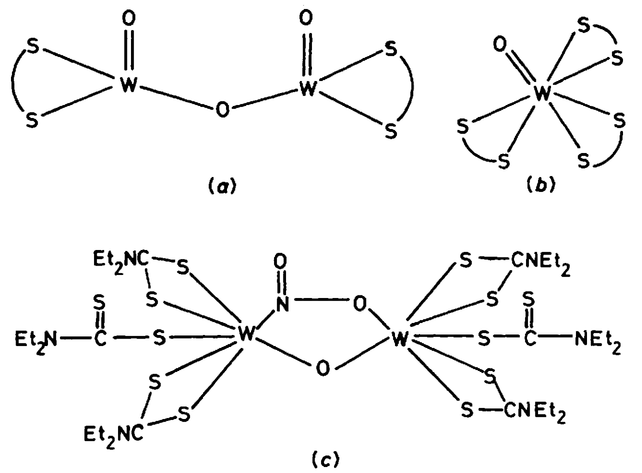

Figure 3. Proposed structures of (*a*) $[W_2O_3(S_2CNEt_2)_2]$, (*b*) $[WO(S_2CNEt_2)_3]$, and (*c*) $[W_2O(NO_2)(S_2CNEt_2)_6]$ (not to scale)

Conclusions

The electrochemical, magnetic, and mass spectroscopic studies described above show that the W^{III} and W^{IV} dithiocarbamate complexes prepared here are dimeric and monomeric respectively. Their i.r. spectra confirm bidentate co-ordination of the ligand in both series. The magnetic moment results for the complex $[W_2(S_2CNR_2)_6]$ rule out octahedral co-ordination and are consistent with a seven-co-ordinate tungsten(III) structure with either c.t.p. or p.b. geometry, the former being more consistent with the observed electronic spectra. In contrast, the spectroscopic results of the complexes $[W(S_2CNR_2)_4]$ are consistent with a square antiprismatic structure with the tungsten atom being eight-co-ordinate as observed in the closely related $[W(S_2CNEt_2)_4Br]$.[49]

Finally, the oxidation–reduction reactions show clearly that the complexes $[W_2(S_2CNR_2)_6]$ are more effective reducing agents in non-aqueous solutions than the complexes $[W(S_2CNR_2)_4]$, with the former complexes preserving their binuclear nature during the reaction.

Acknowledgements

Microanalyses were performed by the Microanalytical Laboratory, University College Dublin (U.C.D. Chemical Services Unit). We should also like to thank Mr. Peter Caplan for the mass spectra (U.C.D. Mass Spectroscopy Centre).

References

1 E. I. Stiefel, in 'Molybdenum and Molybdenum Containing Enzymes,' ed. M. P. Coughlan, Pergamon Press, Elmsford, New York, 1980, p. 41.

2 H. F. Barry and P. C. H. Mitchell (eds.), Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum, Climax Molybdenum Co., Ann Arbor, Michigan, 1982.

3 E. I. Stiefel and R. R. Chianelli, in 'Nitrogen Fixation,' eds. A. Muller and W. E. Newton, Plenum Press, New York, 1983, pp. 341—369.

4 I. Yamamoto, T. Saiki, S. M. Shiu, and L. G. Ljungdahl, *J. Biol. Chem.*, 1983, **258**, 1826.

5 L. G. Ljungdahl, *Trends Biochem. Sci.*, 1976, **1**, 63.

6 E. J. Hewitt and B. A. Newton, in 'Molybdenum and Molybdenum Containing Enzymes,' ed. M. P. Coughlan, Pergamon Press, New York, 1980, p. 273.

7 J. L. Johnson and K. V. Rajagopalan, *J. Biol. Chem.*, 1976, **251**, 5505.

8 Z. Dori, *Prog. Inorg. Chem.*, 1981, **28**, 239.

9 C. A. Rice, P. M. H. Kroneck, and J. T. Spence, *Inorg. Chem.*, 1981, **20**, 1996.

10 G. J-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chim. Acta*, 1976, **19**, L67.

11 G. J-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chim. Acta*, 1980, **41**, 49.

12 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta*, 1974, **11**, 223.

13 W. Levason, C. A. McAuliffe, and F. P. McCullough, jun., *Inorg. Chem.*, 1977, **16**, 2911.

14 R. D. Taylor, J. P. Street, M. Minelli, and J. T. Spence, *Inorg. Chem.*, 1978, **17**, 3207.

15 R. A. D. Wentworth, *Coord. Chem. Rev.*, 1976, **18**, 1.

16 S. P. Cramer, *Adv. Inorg. Bioinorg. Mech.*, 1983, **2**, 259.

17 R. C. Bray, in 'Molybdenum Chemistry of Biological Significance,' eds. W. E. Newton and S. Otsuka, Plenum Press, New York and London, 1980, p. 117.

18 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.

19 D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11**, 233.

20 R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12**, 295.

21 R. P. Burns, F. P. McMullough, and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 211.

22 R. N. Jowitt and P. C. H. Mitchell, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 39.

23 D. C. Bradley and M. H. Chisholm, *J. Chem. Soc. A*, 1971, 2741.

24 D. A. Brown, B. J. Corden, W. K. Glass, and C. J. O'Daly, Proceedings of the 16th International Conference on Coordination Chemistry, Toronto, 1972, p. 676.

25 P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 1975, 110.

26 A. Nieuwpoort, H. M. Claessen, and J. G. M. Van der Linden, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 869.

27 J. Willemse and J. J. Steggerda, and C. P. Keijzers, *Struct. Bonding (Berlin)*, 1976, **28**, 91.

28 A. Nieuwpoort and J. J. Steggerda, *J. R. Netherlands Chem. Soc.*, 1976, **95**, 250.

29 D. A. Brown, W. K. Glass, and K. S. Jasim, *Inorg. Chim. Acta*, 1980, **45**, L97.

30 D. A. Brown, W. K. Glass, and K. S. Jasim, in ref. 2, p. 156.

31 K. S. Jasim, Ph.D. Thesis, National University of Ireland, 1982.

32 T. C. N. Mak, K. S. Jasim, and C. Chieh, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 377.

33 J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 441.

34 T. M. Brown and J. N. Smith, *J. Chem. Soc., Dalton Trans.*, 1972, 1614.

35 Z. Dori, *Prog. Inorg. Chem.*, 1981, **28**, 239; unpublished work.

36 F. Bonati and R. Ugo, *J. Organomet. Chem.*, 1967, **10**, 257.

37 D. A. Brown, W. K. Glass, and M. A. Burke, *Spectrochim. Acta, Part A*, 1976, **32**, 137.

38 M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, 1978, **11**, 356.

39 L. O. Gilpatrick and L. M. Toth, *Inorg. Chem.*, 1974, **13**, 2242.

40 D. Nicholls, T. A. Ryan, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1974, 635.

41 G. R. Rossman, F. D. Tsay, and H. B. Gray, *Inorg. Chem.*, 1973, **12**, 824.

42 S. T. Spees, J. R. Perumareddi, and A. W. Adamson, *J. Am. Chem. Soc.*, 1968, **90**, 6626.

43 J. R. Wason and D. R. Lorenz, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 617.

44 J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, 1962, **37**, 17.

45 B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476.

46 R. W. Wing and K. P. Callahan, *Inorg. Chem.*, 1969, **8**, 871.

47 B. Jezowska-Trzebiatowska, *Pure Appl. Chem.*, 1971, **27**, 89.

48 N. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 4th edn., Wiley, New York, 1978.

49 J. G. Wijnhoven, *Cryst. Struct. Commun.*, 1973, **2**, 637.

Received 22*nd December* 1986; *Paper* 6/2459