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Preliminary Communication

η^3-Ligation of tetrathiamacrocycles to Mo and W: structures of $[WI(CO)_3\{\eta^3\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$ and $[WI(CO)_2\{\eta^4\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$ ($Me_8[16]aneS_4$ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane)

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Abstract

Reaction of $[WI_2(CO)_3(MeCN)_2]$ with $Me_8[16]aneS_4$ gives $[WI(CO)_3\{\eta^3\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$ and $[WI(CO)_2\{\eta^4\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$, whose crystal structures have been determined; $[Mo(CO)_3(MeCN)_3]$ reacts with $[16]aneS_4$ to give $[Mo(CO)_3\{\eta^3\text{-}([16]aneS_4)\}]$.

Key words: Molybdenum; Tungsten; Thiamacrocycles; Crystal structure; Iodide; Carbonyl

The use of sulfur-donor macrocyclic ligands has increased greatly in recent times because they confer the metal–sulfur environment essential in model studies of metal-catalysed processes such as biological nitrogen fixation [1,2]. Moreover, a range of coordination geometries at the metal centre is being delineated [3]. We have recently demonstrated [4] a novel "piano-stool" geometry for a tetrathiamacrocyclic ligand in the complexes $[MX(CO)_2\{\eta^4\text{-}(Me_8[16]aneS_4)\}][MX_3(CO)_4]$ [4] (M = Mo, X = Br; M = W, X = I), and here we report the first X-ray structural characterisation of η^3-ligation for these ligands.

Treatment of two equivalents of $[WI_2(CO)_3(MeCN)_2]$ with one equivalent of 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane ($Me_8[16]aneS_4$) in CH_2Cl_2 affords two complexes, in moderate yield, which can be separated by fractional crystallisation. These are $[WI(CO)_3\{\eta^3\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$ (**1**) and $[WI(CO)_2\{\eta^4\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$ (**2**). Compound **2**, which is the major product, is a further example of piano-stool η^4-coordination by $Me_8[16]aneS_4$ (we have briefly described the structure of a molybdenum bromide analogue [4]), and its molecular structure [5*] is shown in Fig. 1. Compound **1**, on the other hand, exhibits η^3-$Me_8[16]aneS_4$ ligation (molecular structure [6*] in Fig. 2) and to our knowledge is the first structurally-characterised example of this binding mode in a mononuclear complex. A single example of η^3-ligation has been structurally demonstrated for the related macrocycle 1,4,8,11-tetrathiacyclotetradecane ($[14]aneS_4$) in the polymeric compound $[\{Cu(\mu\text{-}\eta^1\text{-}\eta^3\text{-}[14]aneS_4)\}_n]$ (the fourth sulfur binds a second metal in this complex) [7]. Compounds **1** and **2** show the expected spectroscopic properties [8*] and are clearly related in that conceptually **1** can be converted into **2** by intramolecular displacement of CO from the metal by the unligated sulfur [S(14) in Fig. 2]. These complexes therefore represent intermediates on the reaction pathway in the synthesis of $[MX_2\{\eta^4\text{-}(Me_8[16]aneS_4)\}]$ by displacement of MeCN and/or CO from $[MX_2(CO)_3(MeCN)_2]$ or $[\{MX_2\text{-}$

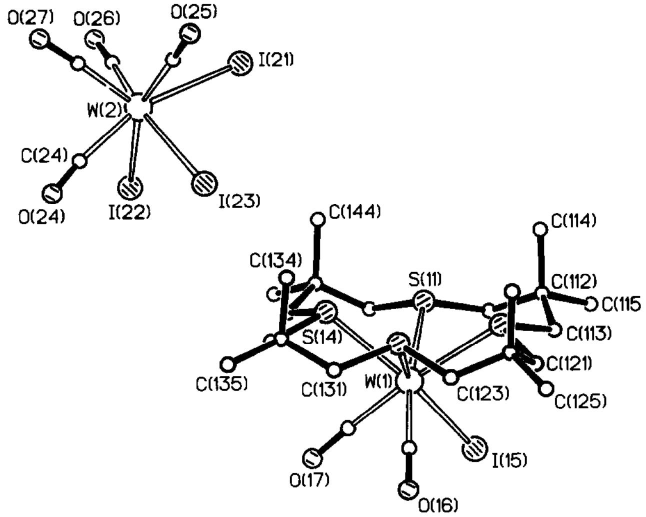

Fig. 1. Molecular structure of $[WI(CO)_2\{\eta^4\text{-}(Me_8[16]aneS_4)\}][WI_3(CO)_4]$, compound **2**.

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* Reference number with asterisk indicates a note in the list of references.

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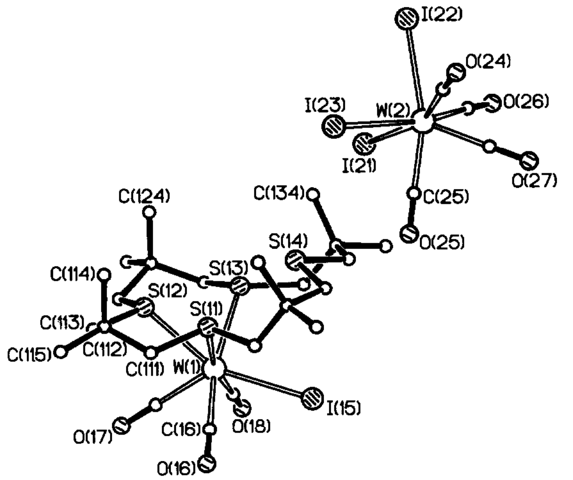

Fig. 2. Molecular structure of [WI(CO)$_3${η^3-(Me$_8$[16]aneS$_4$)}]-[WI$_3$(CO)$_4$], compound **1**.

(CO)$_4$}$_2$] with Me$_8$[16]aneS$_4$ [2,4]. It is interesting to note that reaction of [WI$_2$(CO)$_3$(MeCN)$_2$] with the acyclic trithioether 2,5,8-trithianonane (ttn) does not give the analogous [WI(CO)$_3$(η^3-ttn)]$^+$ cation, but rather a neutral complex identified by X-ray crystallography as [WI$_2$(CO)$_2$(η^3-ttn)], in which CO rather than I$^-$ has been displaced [9]. Clearly there are subtle factors controlling product formation in these reactions.

A further example of an η^3-tetrathiamacrocyclic ligand results when *fac*-[Mo(CO)$_3$(MeCN)$_3$] is treated with 1,5,9,13-tetrathiacyclohexadecane ([16]aneS$_4$) in boiling MeCN. This reaction gives the brown, poorly soluble, diamagnetic complex *fac*-[Mo(CO)$_3${η^3-([16]-aneS$_4$)}] (**3**), which has been characterised by analysis and spectroscopy [10*].

Clearly the flexibility of these versatile ligands allows a range of bonding modes to be adopted, depending upon the demands of the metal in terms of its available geometries and potential co-ligands [3]. We are extending this work to a range of other macrocyclic sulfur-donor ligands.

Acknowledgements

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References and notes

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5 Crystal data for **2**: [C$_{22}$H$_{40}$IO$_2$S$_4$W][C$_4$I$_3$O$_4$W], $M = 1452.2$, triclinic, space group $P\bar{1}$ (no. 2); $a = 11.646(1)$, $b = 13.051(3)$, $c = 14.308(2)$ Å; $\alpha = 84.345(16)°$, $\beta = 102.209(10)°$, $\gamma = 88.875(15)°$; $V = 2113.4$ Å^3; $Z = 2$; $D_{\text{calcd}} = 2.282$ g cm^{-3}; $F(000) = 1336$; μ(Mo Kα) = 86.7 cm^{-1}; λ(Mo K$\bar{\alpha}$) = 0.71069 Å. Crystals are dark green rectangular prisms; one *ca.* 0.10 mm × 0.14 mm × 0.43 mm mounted on a glass fibre in air. Diffraction intensities measured on an Enraf-Nonius CAD4 diffractometer (with monochromated radiation): 5868 unique reflections, $\theta_{\max} = 23°$, 4801 with $I > 2\sigma_I$; corrections applied for Lorentz polarisation effects, absorption, crystal deterioration (18.7% overall), and to eliminate negative net intensities. Structure determined by automated Patterson methods (G.M. Sheldrick, SHELXS program, *Acta Cryst., A46* (1990) 467). Refinement by large-block-matrix least-squares methods to $R = 0.069$ and $R_g = 0.107$ (G.M. Sheldrick, *SHELX-76, Program for crystal structure determination*, University of Cambridge, 1976; extended version, SHELXN, 1977) for 5478 reflections (with $I > \sigma_I$) weighted $w = \sigma_F^2 + 0.0200F^2)^{-1}$. Hydrogen atoms of methylene groups included with idealised parameters; those in methyl groups refined with geometrical constraints; all non-hydrogen atoms refined anisotropically. Tables of atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

6 Crystal data for **1**: [C$_{23}$H$_{40}$IO$_3$S$_4$W][C$_4$I$_3$O$_4$W], $M = 1480.2$, orthorhombic, space group $P2_12_12_1$ (no. 19); $a = 12.449(2)$, $b = 28.875(5)$, $c = 11.825(2)$ Å; $V = 4250.6$ Å^3; $Z = 4$; $D_{\text{calcd}} = 2.313$ g cm^{-3}; $F(000) = 2728$; μ(Mo Kα) = 86.3 cm^{-1}. Fragment, *ca.* 0.30 mm × 0.35 mm × 0.45 mm, of a deep red prismatic crystal mounted on a glass fibre in air. Experimental details similar to those for (**2**). In all, 4181 unique reflections measured, 3878 having $I > 2\sigma_I$; intensities corrected for absorption, and elimination of negative net intensities—no deterioration correction necessary. Refinement to $R = 0.040$ and $R_g = 0.048$ (G.M. Sheldrick, SHELX-76, *Program for crystal structure determination*, University of Cambridge, 1976; extended version, SHELXN, 1977.) for all data, weighted $w = (\sigma_F^2 + 0.00081F^2)^{-1}$. Hydrogen atoms included with geometrical constraints but with independent U_{iso}, non-hydrogen atoms all anisotropic. As in the case of **2**, supplementary data have been deposited at the Cambridge Crystallographic Data Centre.

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8 Satisfactory C and H elemental analyses have been obtained. Selected IR (KBr, ν/cm^{-1}): (**1**), 2068(s), 2036(s), 2010(sh), 1992(s), 1967(s), 1944(m) and 1924(s); (**2**), 2069(s), 2011(m), 1987(m), 1960(s), 1950(m) and 1865(s) (all CO stretch, s = strong, sh = shoulder, m = medium).

9 S.D. Harris, *Ph.D. Thesis*, 1994, University of Wales.

10 Satisfactory C and H elemental analyses obtained. Selected IR (KBr, ν/cm^{-1}): 1920(s), 1785(s) (CO stretch); ^{1}H-NMR, (Me$_2$SO-d$_6$), complex second order sets of multiplets at 1.7–1.85, 2.3–2.5 and 2.75–2.95 ppm (rel. SiMe$_4$).