Unexpected Crown Thioether Complexation of Vanadium(IV): Isolation and Structural Characterisation of $[VOCl_2([9]aneS_3)]$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane)

Gerald R. Willey,* Miles T. Lakin and Nathaniel W. Alcock

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Contrary to hard and soft acid–base predictions the 'soft' crown thioether $[9]aneS_3$ forms a stable 1 : 1 coordination complex with the extremely 'hard' vanadyl ion; $[VOCl_2([9]aneS_3)]$ has a distorted octahedral structure with facial coordination (endodentate) of the trithiamacrocycle in a [2 + 1] bonding pattern, and provides the first example of a chelated high-valent group V–thioether complex.

Numerous transition metal complexes of the crown thioether $[9]aneS_3$ have been noted in the literature.[1,2] By virtue of its *endo*-conformation and the 'soft' characteristics of the trio of sulphur donor atoms, terdentate-facial coordination to class (b) transition metal ions is the dominant bonding mode associated with this particular macrocyclic ligand. Typical examples include the 2 : 1 six-coordinate metal complexes $[M([9]aneS_3)_2]^{n+}$ M = Fe; n = 2,[3] 3;[4] M = Co, Ni, Cu; n = 2,[5] and the 1 : 1 complexes which can exhibit differing metal geometries, *e.g.* $[Fe(\eta^5\text{-}C_5H_5)([9]aneS_3)]^+$ as a 'mixed-sandwich' structure,[6] $[Rh([9]aneS_3)(cod)]^+$ (cod = cycloocta-1,5-diene) and $[Rh([9]aneS_3)(C_2H_4)_2]^+$ with five-coordinate Rh^I,[7] and $[Cu(AsPh_3)([9]aneS_3)]^+$ in which Cu^I is tetrahedral.[8] Other less-common bonding modes are known, *e.g. bidentate*, $[Pt([9]aneS_3)_2]^{2+}$, square-based pyramidal,[9] and *cis*-$[PdCl_2([9]aneS_3)]$, square-planar,[10] where, in each case, one of the sulphur donor sites remains uncoordinated to the metal, and *monodentate* $[Au([9]aneS_3)_2]^+$ in which one of the $[9]aneS_3$ ligands is coordinated to Au^I *via* only one of its sulphur atoms to give a resulting tetrahedral metal geometry.[11]

In terms of Periodic Group representation the 'earliest' examples of transition metal–$[9]aneS_3$ facial complexation are to be found with the group VI elements *viz.*, Cr^{III} (d^3) $[Cr([9]aneS_3)_2][ClO_4]_3$[12] Mo^0 (d^6) $[Mo(CO)_3([9]aneS_3)]$,[13] Mo^{III} (d^3) $[MoCl_3([9]aneS_3)]$[14] and Mo^{II} (d^4) $[([9]aneS_3)$

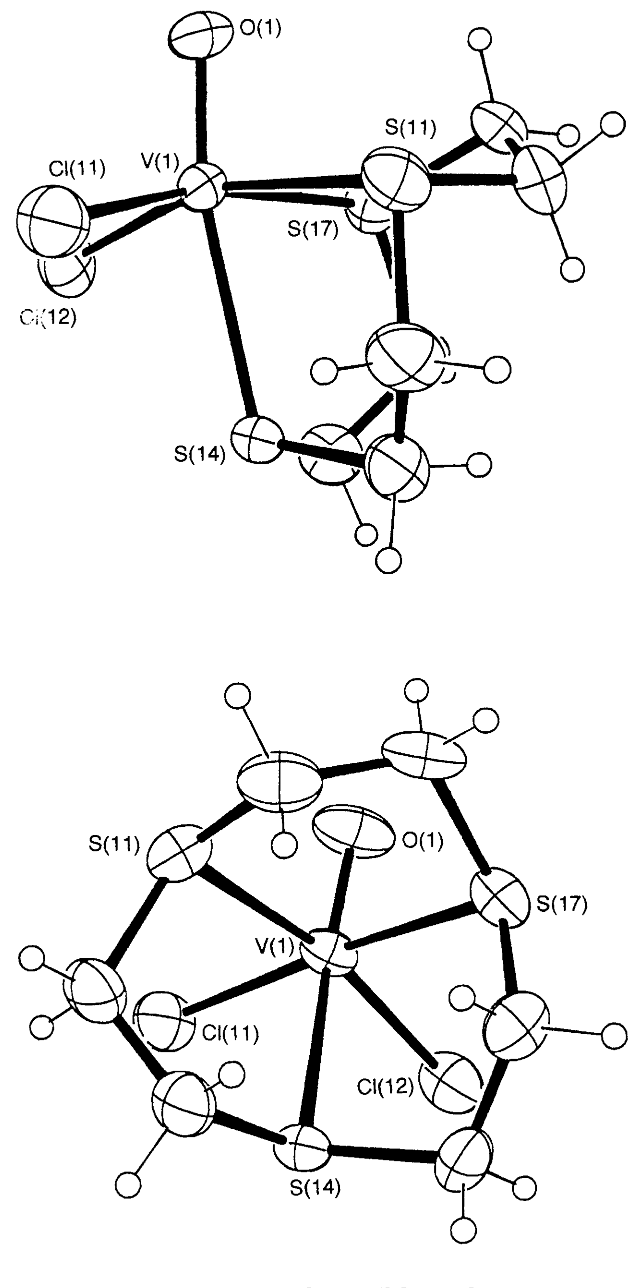

Fig. 1 Views of one molecule of $[VOCl_2([9]aneS_3)]$; mean distances: V–Cl 2.295(5), V=O 1.579(4), V–S (*trans* to O) 2.634(5), (*trans* to Cl) 2.470(5) Å

$Mo(OAc)_2Mo(MeCN)_3]^{2+}$,[12] and $[([9]aneS_3)Mo(OAc)_2Mo([9]aneS_3)]^{2+}$.[12] There are no reported complexes involving W species. For the group V elements (V, Nb, Ta) although several crown thioether–niobium(V) complexes have been reported[15] *viz*., $[NbCl_5]_2L$ and $[NbCl_5]_4L$ where L = [14]aneS_4 [16]aneS_4 and [20]aneS_4, retention of the exodentate conformation of these tetrathia ligands produces ligand bridging in preference to chelation. Thus, for example, the structure of $[(NbCl_5)_2([14]aneS_4)]$ shows symmetrical bridging of the one ligand molecule between two $NbCl_5$ units with only two of the four sulphur atoms actually involved as S-donor sites. Our isolation of $[VOCl_2([9]aneS_3)]$ in which the trithia ligand is facially bound to V^{IV} (d^1) provides the first example of a chelated crown thioether complex incorporating a high-valent 'hard' metal ion representative of this particular group.

A solution of [9]aneS_3 (0.8 g, 4.3 mmol) in acetonitrile (25 cm^3) was added dropwise to a chilled (0 °C) and stirred solution of VCl_3 (0.7 g, 4.3 mmol) in acetonitrile (50 cm^3) maintained under an atmosphere of dinitrogen. The resulting deep blue solution was stirred and intermittently heated at reflux over a period of one week. Slow removal of solvent resulted in the deposition of an azure blue semicrystalline solid which was collected by filtration, washed with n-hexane and diethyl ether and dried *in vacuo*. Recrystallisation from acetonitrile afforded beautiful, deep-blue needle crystals of the product (yield: 0.66 g, 48%) of suitable quality for X-ray diffraction studies.† Elemental analyses were satisfactory; λ_{max}/cm^{-1} (MeCN): 11 060(sh), 13 440(sh), 14 750 and 26 593; ν_{max}/cm^{-1} (mull) 356 (V–Cl) and 962 (V=O). The formation of this air-stable vanadium(IV) complex is evidently the result of oxidation–hydrolysis of a precursor vanadium(III) species by adventitious water–oxygen (VO^{2+}/V^{3+}, E° = 0.34 V).

The structure of $[VOCl_2([9]aneS_3)]$ is shown in Fig. 1. The three sulphur atoms of the crown are confacially coordinated to the $VOCl_2$ moiety giving a half-sandwich structure in which the six-coordinate vanadium(IV) (d^1) centre is approximately octahedral. In essence the somewhat rigid angular constriction imposed by the [9]aneS_3 ligand [$\angle$SVS 79.4(1)–84.3(1)°] is offset by a corresponding angular dilation within the $VOCl_2$ unit reflecting the steric requirements of the differing-sized oxygen [$\angle$OVCl mean 104·8(1)°] and chlorine [$\angle$ClVCl 95.0(1)°] atoms. A similar macrocyclic constriction–dilation effect has been observed[16] in $[ReO_3([9]aneS_3)]^+$ where $\angle$SReS (mean) = 79.5° and $\angle$OReO (mean) = 107.4°. The V=O bond distance [1.579(4) Å] lies near the lower end of the range observed for vanadyl complexes (1.55–1.68 Å). Compared with other related oxovanadium(IV)–S donor complexes, *viz*. $[VO(edt)_2]^{2-}$ (H_2edt = ethane-1,2-dithiol), V=O 1.625(2) Å, and $[VO(pdt)_2]^{2-}$ (H_2pdt = propane-1,3-dithiol), V=O 1.628(2) Å,[17] this is remarkably short and indicative of a strong multiple bond component; the associated IR ν(V=O) stretching mode appears at 962 cm^{-1} within the 'normal' range (900–1000 cm^{-1}). The V–S bond distances are irregular with a clear [2 + 1] pattern in which the sulphur atom *trans* to the vanadyl linkage [V–S 2.634(5) Å] is significantly lengthened [V–S *trans* to Cl, 2.470(5) Å]. All these V–S bond distances are long when compared with the vanadium(IV)–thiolato systems reported by Christou *et al.*:[17–19] $[VO(edt)_2]^{2-}$, V–S (mean) 2.378 Å; $[VS(SPh)_4]^{2-}$, V–S (mean) 2.391, V=S 2.078(2) Å; $[VS(edt)_2]^{2-}$, V–S (mean) 2.364, V=S 2.087(1) Å, and, even allowing that the neutral [9]aneS_3 is less basic than the thiolato anions (above), indicate the absence of any significant π-contribution to the metal-to-sulphur bonds. Thus weak (σ-only) ligand binding particularly accentuated in the *trans* V–S bond is counterbalanced by increased multiple (π) bonding in the V=O bond. The accompanying two chloride

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† *Crystal data*: $C_6H_{12}Cl_2OS_3V$, M = 318.2, monoclinic, $P2_1/c$, a = 12.328(6), b = 12.667(6), c = 14.960(11) Å, β = 90.44(5)°, U = 2337(2) $Å^3$, Z = 8, D_c = 1.81 g cm^{-3}, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 18.2 cm^{-1}, T = 290 K, R = 0.052.

Crystal character: pale blue prisms. Data were collected with a Nicolet $P2_1$ four-circle diffractometer in the ω–2θ mode. Reflections were processed using profile analysis to give 4106 unique reflections (R_{int} = 0.049), of which 2457 were considered observed [$I/\sigma(I) \geqslant 2.0$]. The crystal contains two independent molecules of $[VOCl_2([9]aneS_3)]$ whose dimensions are virtually identical. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.08 $Å^2$, inserted at calculated positions and not refined. Final refinement was on F by least-squares methods refining 235 parameters. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.00082 was used and shown to be satisfactory by a weight analysis. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ions effect charge neutralisation of the complex and have a normal V–Cl mean distance [2.295(5) Å] similar to the V–Cl distance (mean 2.308 Å) observed in $VOCl_2 (O{=}PPh_3)_2$.[20]

We thank the SERC for financial support.

Received, 28th June 1991; Com. 1/03235F

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