The Preparation and *X*-Ray Structure of $V(N_3S_2)(dtbc)(phen)\cdot CHCl_3$ (dtbc = di-t-butylcatecholate, phen = phenanthroline)

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Reaction of $[V(\mu\text{-}Cl)(N_3S_2)Cl]_2$ with phenanthroline (phen) gives $V(N_3S_2)Cl_2(phen)$ (**1**) which undergoes further reaction with $2,5\text{-}Bu^t{}_2C_6H_2O_2{}^{2-}$ (di-t-butylcatecholate) to give the title compound (**2**), which is air stable and the first example of a neutral mixed ligand *tris* bidentate V^V complex to be prepared; the *X*-ray crystal structure of (**2**) is reported.

There is currently widespread interest in the synthesis of metalla–sulphur–nitrogen compounds.[1,2] Mixed ligand complexes of the type $M(S_3N)L_2$ and $M(S_2N_2)L_2$ are well established for platinum and palladium.[3–6] However, there are very few examples of mixed ligand compounds for the Groups 5 and 6 transition metals, although complexes such as $[Ph_4As][Cl_4WN_3S_2]$ containing the $S_2N_3{}^{3-}$ ligand have been prepared.[7] Soluble, readily handled, mixed ligand complexes are important as potential synthetic reagents (for transmetallation reactions), furthermore they allow the effect of the S–N ligand on the redox properties of the metal centre to be studied. There are very few vanadium complexes containing the $S_2N_3{}^{3-}$ anion, even though because of its high charge this ligand should be good at stabilising high oxidation state metal centres. Here we report on the synthesis of compounds of the type $V(N_3S_2)LL'$ [L = catecholate or 3,5-di-t-butylcatecholate (dtbc), L′ = phenanthroline (phen) or bipyridyl (bpy)], the first examples of neutral *tris* chelated complexes of V^V to be described. The new compounds have been characterised by IR, ^{51}V NMR, cyclic voltammetry, and, in the case of the title compound (**2**), by *X*-ray crystallography.

In a typical reaction $[V(\mu\text{-}Cl)(N_3S_2)Cl]_2$[8] (1.25 mmol) in CH_2Cl_2 was treated with phenanthroline (2.5 mmol) to give $V(N_3S_2)Cl_2(phen)$ (**1**) (2.2 mmol) as a brick red precipitate. Complex (**1**) (1.25 mmol) was treated with dtbc (1.25 mmol) in CH_2Cl_2. After evaporation of the solvent *in vacuo* and trituration with nitromethane, the resulting crude (**2**) (0.65 mmol) was recrystallised from $CHCl_3$ by slow diffusion of diethyl ether to give black crystals suitable for *X*-ray analysis.

$$[V(\mu\text{-}Cl)(N_3S_2)Cl]_2 + 2(\text{phen}) \rightarrow \underset{\textbf{(1)}}{2V(N_3S_2)Cl_2(\text{phen})} \quad (1)$$

$$V(N_3S_2)Cl_2(\text{phen}) + [Et_3NH]_2[Bu^t{}_2C_6H_2O_2] \rightarrow \underset{\textbf{(2)}}{V(N_3S_2)(\text{dtbc})(\text{phen})} + 2[Et_3NH]Cl \quad (2)$$

Similar reactions have also been performed using bipyridyl and catechol. All of the new compounds gave satisfactory elemental analyses and the expected IR spectra. The ^{51}V NMR (referred to $VOCl_3$) of (**1**) and (**2**) consist of broad resonances at δ 334 and 780 p.p.m., respectively.

The *X*-ray structure of (**2**)† (Figure 1) has a number of interesting features. The co-ordination of the vanadium is essentially octahedral with the angles at the metal reflecting the bite of the various ligands. The VN_3S_2 ring has non-crystallographic C_{2v} symmetry. The N_3S_2 unit is planar to within 0.008 Å with the vanadium being 0.016 Å from this plane. The N(1)–S(1) and N(3)–S(2) distances are notably shorter (by 0.06 Å) than the S(1)–N(2) and S(2)–N(2) distances indicating a significant degree of bond ordering. The V–N bonds to the phen are substantially longer than the V–N bonds to the highly charged $S_2N_3{}^{3-}$ ligand [V–N(1) 1.821(3), V–N(3) 1.820(3), V–N(21) 2.172(3), V–N(30) 2.225(4) Å] and different to each other as a consequence of the difference in the *trans* atoms [O(1) and N(1), respectively]. Similarly, the V–O distances differ [V–O(1) 1.871(2) and V–O(2) 1.990(2) Å *trans* to N(21) and N(3), respectively]. There are no significant intermolecular contacts in the crystal.

Cyclic voltammetry studies on (**2**) revealed two reversible couples [$E_{1/2}$ +0.37 and −0.77 *vs.* normal hydrogen electrode (NHE)] corresponding to V^V/V^{IV} and V^{IV}/V^{III} redox processes, respectively, indicating that the $S_2N_3{}^{3-}$ anion is, as we predicted, an extremely good ligand for the stabilisation of V^V. Both (**1**) and (**2**) are air stable as solids in marked contrast to $[V(\mu\text{-}Cl)(N_3S_2)Cl]_2$ and thus should provide useful starting materials for the synthesis of S–N containing heterocycles and new metal heterocycles.

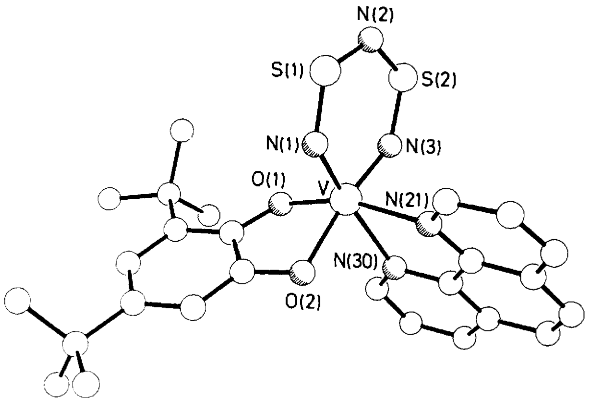

Figure 1. The *X*-ray structure of (**2**). Selected bond lengths (Å) and angles (°): V–N(1) 1.821(4), V–N(3) 1.820(3), N(1)–S(1) 1.544(4), N(3)–S(2) 1.548(4), S(1)–N(2) 1.600(4), S(2)–N(2) 1.611(4), V–N(21) 2.172(3), V–N(30) 2.225(4), V–O(1) 1.871(2), V–O(2) 1.990(2); V–N(1)–S(1) 132.7(2), N(1)–S(1)–N(2) 116.4(2), S(1)–N(2)–S(2) 124.8(3), N(2)–S(2)–N(3) 114.7(2), S(2)–N(3)–V 134.1(2), N(1)–V–N(3) 97.3(2), O(1)–V–O(2) 81.8(1), N(21)–V–N(30) 74.3(1).

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† *Crystal data* for (**2**) $C_{26}H_{28}N_5O_2S_2V\cdot CHCl_3$: monoclinic, a = 13.326(2), b = 12.926(4), c = 19.273(3) Å, β = 109.72(1)°, U = 3125 Å^3, space group $P2_1/c$, Z = 4, M = 677.0, D_c = 1.44 g cm^{-3}, $\mu(\text{Cu-}K_\alpha)$ = 66 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.047, R_w = 0.046 for 3462 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \geqslant 116°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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