A Zigzag Chain Structure of a 3-Thiapentane-1,5-dithiolato Vanadium Complex linked by Lithium Ions

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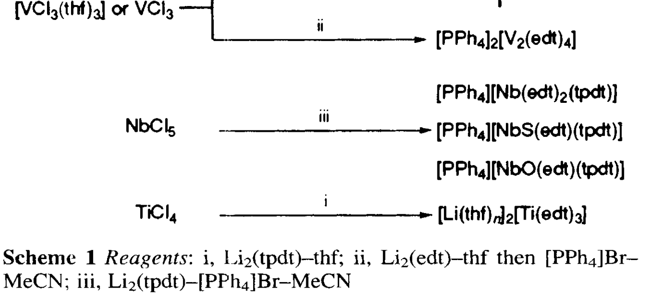
The homoleptic 3-thiapentane-1,5-dithiolato vanadium(III) complex [Li(thf)][V(tpdt)$_2$] **1** is synthesized and structurally characterized which reveals that **1** has an intriguing zigzag chain structure in the solid state where lithium cations bridge the tpdt sulfurs.

We previously reported the synthesis of a series of homoleptic alkanedithiolato complexes of Nb^{V}, Ta^{V}[1] and U^{IV},[2] and found that ethane-1,2-dithiolate (edt) in [M(edt)$_3$]$^-$ (M = Nb, Ta) was transformed to 3-thiapentane-1,5-dithiolate (tpdt) resulting in formation of [MS(edt)(tpdt)]$^-$.[3] Furthermore, treatment of NbCl$_5$ with Li$_2$(tpdt), followed by a cation exchange with [PPh$_4$]Br, caused a facile C–S bond cleavage, and gave rise to [PPh$_4$][Nb(edt)$_2$(tpdt)],[4] [PPh$_4$][NbS(edt)(tpdt)] and [PPh$_4$][NbO(edt)(tpdt)].[5] As an outgrowth of our interest in the behaviour of dithiolates at electron-deficient transition-metal centres, we have examined reactions of [VCl$_3$(thf)$_3$] and VCl$_3$ with Li$_2$(edt) and Li$_2$(tpdt) (Scheme 1). Here we report on such reactions, focussing mainly on the synthesis and characterization of [Li(thf)][V(tpdt)$_2$] **1** which has an intriguing polymeric structure in the solid state.

A thf solution (40 ml) of [VCl$_3$(thf)$_3$] (7.0 mmol) was added dropwise to a slurry of Li$_2$(tpdt) (15 mmol) in thf (50 ml) at 0 °C. After stirring at room temp. for 1 h, the reaction mixture was filtered to remove insoluble materials, and then the resulting reddish brown solution was concentrated. On standing for 3 days at −20 °C we obtained [Li(thf)][V(tpdt)$_2$] **1** as a hygroscopic dark brown microcrystalline solid in 43% yield; a rare example of a homoleptic thiolate complex of vanadium.[6–8] An analogous reaction of VCl$_3$ with Li$_2$(tpdt) gave **1** in a similar yield. Crystals of **1** suitable for X-ray analysis were formed by cooling its thf solution very slowly to −50 °C for several days. Complex **1** is not very soluble in MeCN, in contrast to high solubility of [A][M(edt)$_3$] [A=Li(thf)$_4$, PPh$_4$, or NEt$_4$; M=Nb, Ta] and [PPh$_4$][Nb(edt)$_2$(tpdt)].

The local coordination geometry and an overall view of **1** are given in Fig. 1, along with selected bond distances.† As shown in Fig. 1(*a*), there are two crystallographically independent vanadium sites, each of which is surrounded by six sulfur atoms in an approximately octahedral array. The average V–S(thiolate) distance is 2.372 Å, within the range expected for V–S single bonds and comparable to those of the V^{III}–S distances in [V(SNC$_9$H$_6$)$_3$] (2.364 Å)[6] and [PPh$_4$]$_2$[V$_2$(edt)$_4$] (2.381 Å).[7] However these bond lengths are slightly shorter than the sum of the ionic radii of V^{III} and S^{-II} (2.48 Å),[9] so that there may be a π-bonding character in these bonds. The V–S(thioether) distances (av. 2.535 Å) are longer than the V–S(thiolate) distances. In the nearly octahedral coordination geometry, the two thioether type sulfurs, as expected occupy *cis*-positions.



Scheme 1 *Reagents*: i, Li$_2$(tpdt)–thf; ii, Li$_2$(edt)–thf then [PPh$_4$]Br–MeCN; iii, Li$_2$(tpdt)–[PPh$_4$]Br–MeCN

Lithium cations bridge the [V(tpdt)$_2$]$^-$ anions in two different ways, as shown in Fig. 1(*b*). Li(1) and Li(3) coordinate to three thiolate sulfurs of each [V(tpdt)$_2$]$^-$, while Li(2) is bound to only one thiolate sulfur of each complex anion. Li(1) and Li(3) assume octahedral coordination geometry with a mean Li–S distance of 2.651 Å; on the other hand, Li(2) is tetrahedral with coordination completed by two thf molecules; the Li–S distance (av. 2.48 Å) is notably shorter than for Li(1) and Li(3). As a consequence, complex **1** has a unique zigzag chain geometry in the solid state, with {[V(tpdt)$_2$]–Li–[V(tpdt)$_2$]–Li(thf)$_2$} as a repeating unit. In the polymeric structure, all the thiolate sulfurs are inequivalent, and atoms S(1) and S(11) which interact with the two lithiums have the longest V–S(thiolate) bond lengths, while the lithium-free sulfurs [S(4) or S(8)] show the shortest V–S bond lengths.

The far-IR and Raman spectra of **1** give bands arising from the V–S stretching vibrations at 308 and 340 cm^{-1} (far-IR), and

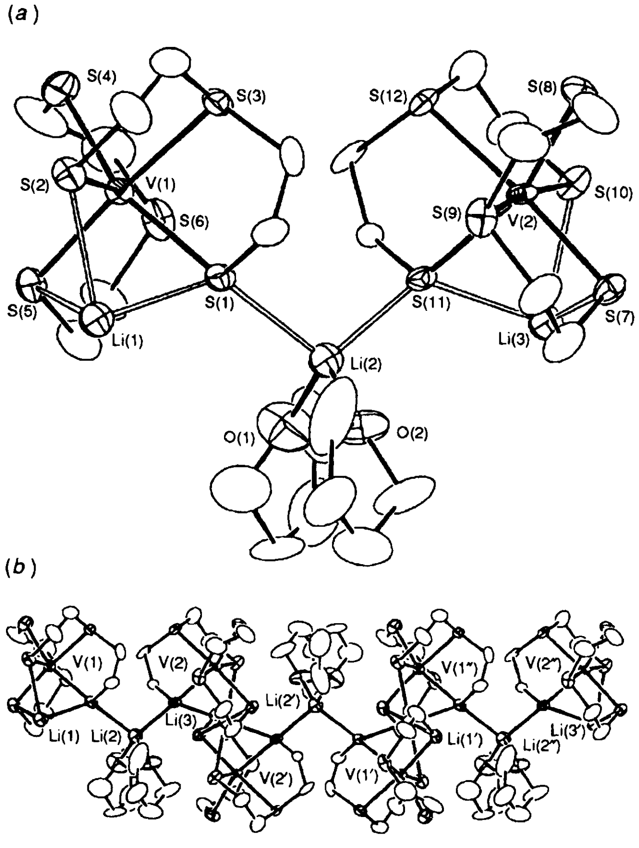


Fig. 1 Local coordination geometry at vanadium (*a*) and overall linear chain structure (*b*) of [Li(thf)][V(tpdt)$_2$] **1** showing 50% thermal ellipsoids. Selected bond distances (Å) : V(1)–S(1) 2.441(5), V(1)–S(2) 2.365(6), V(1)–S(3) 2.507(5), V(1)–S(4) 2.336(6), V(1)–S(5) 2.350(6), V(1)–S(6) 2.555(6), V(2)–S(7) 2.359(5), V(2)–S(8) 2.319(5), V(2)–S(9) 2.547(6), V(2)–S(10) 2.371(6), V(2)–S(11) 2.433(5), V(2)–S(12) 2.530(5), Li(1)–S(1) 2.691(6), Li(1)–S(2) 2.680(5), Li(1)–S(5) 2.604(5), Li(2)–S(1) 2.54(4), Li(2)–S(11) 2.42(4), Li(3)–S(7) 2.632(4), Li(3)–S(10) 2.599(6), Li(3)–S(11) 2.698(6).

326 and 335 cm^{-1} (Raman). In the UV–VIS spectrum in MeCN, there are two absorptions at 315 nm (ε = 4400 dm^3 mol^{-1} cm^{-1}) and 473 (1800) assignable to sulfur → vanadium charge-transfer transitions. The ^{1}H NMR spectrum in CD_3CN is featureless owing to the paramagnetic nature of **1**. Interestingly, the electronically analogous molybdenum congener [Mo(tpdt)$_2$] is diamagnetic.[10] The coordination geometry around the d^2 Mo^{IV} centre is trigonal prismatic, contrasting to the nearly octahedral d^2 V^{III} geometry of **1**.

From the reaction of [VCl_3(thf)$_3$] or VCl_3 with Li_2(edt) in thf, we were able to isolate only the known binuclear vanadium(III) complex, [V_2(edt)$_4$]$^{2-}$. Both [V_2(edt)$_4$]$^{2-}$ and **1** are stable in dmf at 100 °C and in boiling thf, respectively, and no C–S bond cleavage was observed. In the case of the $NbCl_5$–Li_2(tpdt)–PPh_4Br–MeCN reaction system at room temp. a facile C–S bond rupture was found to occur, and [M(edt)$_3$]$^-$ (M = Nb, Ta) isomerized to [MS(edt)(tpdt)]$^-$ in dmf at 70–100 °C. We have also found that the reaction of $TiCl_4$ with Li_2(tpdt) in thf or MeCN at room temp. gave rise to [Ti(edt)$_3$]$^{2-}$ in high yields.[11,12] Early transition metals have been known to occasionally activate C–S bonds,[13] and it seems that C–S bond cleavage is caused more readily by metals with higher acidity. In this respect, the reaction between $MoCl_5$ and H_2tpdt giving Mo(tpdt)$_2$, albeit in a low yield is intriguing. Further studies are needed to elucidate the mechanism of C–S bond activation by early transition metals.

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† *Crystal structure analysis* of **1**: $C_{24}H_{48}Li_2O_2S_{12}V_2$, M = 869.13 single crystal, 0.55 × 0.35 × 0.40 mm^3, triclinic, space group $P\bar{1}$ a = 12.66(2), b = 16.63(3), c = 9.610(9) Å, α = 103.4(1), β = 105.49(8), γ = 75.9(1)°, V = 1860(4) Å^3, Z = 2, D_c = 1.551 Mg m^{-3}. Data collection with a Rigaku AFC5R diffractometer; Mo-Kα radiation, ω scans, 2θ = 4–50.5°, 6997 measured reflections, 6649 independent, 4008 observed [$I > 3.0\sigma(I)$], empirical absorption correction based on azimuthal scans. Solution and refinement with the TEXSAN package of the Molecular Structure Corporation (direct methods); all non-hydrogen atoms except for lithiums were refined anisotropically and the hydrogen atoms on tpdt were placed in calculated positions; atoms Li(1) and Li(3) lie on inversion centres while Li(2) is at a general position; full-matrix refinement with 409 parameters led to R = 0.099 and R_w = 0.112, GOF = 3.76.

Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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