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Unusual formation and crystal structure of a new stable dinuclear vanadium(v) amino–imino–acetal

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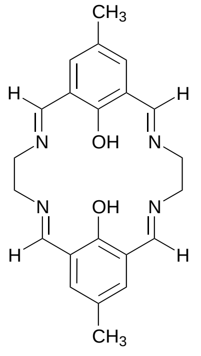
Unusual formation of a new imino–amino–acetal as a dimeric complex of VO_2^+ revealed dramatically how difficult it can be to form stable macrocyclic dinuclear complexes of VO_2^+ and VO^{2+}.

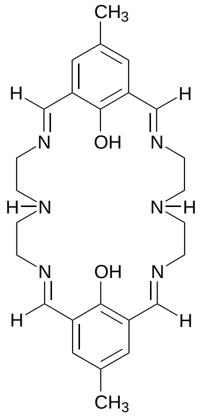
Whereas predictability is desirable in the synthetic chemistry and electronic properties of vanadium compounds achieving it has, in important respects, been elusive. For example, a large collection of macrocyclic chelates is now available,[1] but the number of dinuclear macrocyclic vanadium compounds remains inexplicably small.[1–3] There ae several synthetic reports in which the formation of vanadium-(III), -(IV), -(V), their mixtures, or mononuclear species is unusually persistent.[4] Understanding of the factors governing the electronic coupling in $V^{III}–V^{III}$, $V^{IV}–V^{IV}$ or $V^{V}–V^{IV}$ is also poor.[2–5] This dearth of clear ideas in these areas is a limiting factor in the design and development effort of new vanadium biological and industrial catalysts as well as suitable models for those already in use.[6,7] Our synthetic activity in vanadium chemistry reflects our recent interest in potential insulin mimics,[8] which is a response to the large diabetic population in Jamaica (roughly 18% of the 15 years old and over population).[9] We have unsuccessfully explored the possibility of forming dinuclear vanadium complexes of the 2:2 macrocycles $[L^1]^{2-}$ and $[L^2]^{2-}$, although the dinuclear complex of $[L^3]^{2-}$ has been reported.[2] However, unusual formation of chelate $[L^4]^-$ and the ammonium salt, $H_2dien{\cdot}SO_4$ (dien = 3-azapentane-1,5-diamine) was persistent.

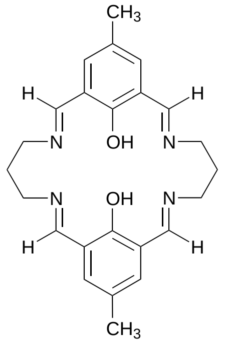
Herein, we report the preparation and crystal and molecular structure of a new stable dinuclear complex of VO_2^+ with a new acyclic ligand $[L^4]^-$, $[(VO_2L^4)_2]$ **1** (Figs. 1 and 2), and hydrogen-bonding stabilization of $H_2dien{\cdot}SO_4$ (Fig. 3).

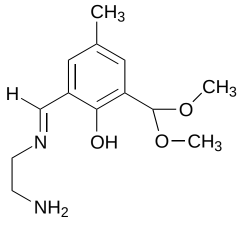
The interaction of VO^{2+} salts (chloride or sulfate), 2.6-diformyl-*p*-cresol and ethane-1,2-diamine in methanol (95%) yields an unexpected acetal as a crystalline compound of VO_2^+ after heating for 3 d at 55 °C in a 250 cm³ conical flask open to the atmosphere.† Compound **1** is not, however, obtained when the reaction is carried out in the presence of hydrogen peroxide and forms slowly in low yield after 4 weeks in a nitrogen atmosphere indicating that molecular oxygen is important in the formation of the VO_2^+ species from VO^{2+}. Conducting the experiment in an oxygen atmosphere did not result in significantly increased yields compared to air but the compound formed in 1 d. Consistent with oxidation state V for the pair of vanadium centres, compound **1** is diamagnetic. When heated to 473 K, crystals of compound **1** decompose to a green paramagnetic product, the elemental analysis of which (C, 42.0; H, 4.35; N, 9.65%) is consistent with loss of the acetal functionalities. The magnetic moment of the product [*ca.* 1.5 μ_B ($\approx 1.39 \times 10^{-23}$ J T^{-1}) assuming a stoichiometry of $C_{20}H_{26}N_4O_9V_2$] suggests the formation of a $V^{V}–V^{IV}$ complex. The infrared spectrum of this paramagnetic product is dominated by C=N absorptions; more detailed studies are in progress.

Whereas the reasons for the preference of **1** for 2:2 (aldehyde:diamine) cyclic or 2:1 acyclic products are unclear, the formation of the acyclic vanadium acetal complex is very


H_2L^1


H_2L^2


H_2L^3


HL^4

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† Synthesis of compound **1**. 2,6-Diformyl-*p*-cresol (0.08 g, 0.5 mmol) in methanol (50 cm³) was added to vanadyl sulfate (0.08 g, 0.5 mmol) (or 0.5 mmol vanadyl chloride) in methanol (40 cm³) and the resulting solution was heated at 55 °C for 1 h. A solution of ethane-1,2-diamine (0.06 g, 0.5 mmol) in methanol (10 cm³) was then added and the cloudy mixture obtained was further heated at 55 °C for 3 d. During this time the 250 cm³ flask containing the reaction mixture was loosely covered with Parafilm and aluminium foil. The denser golden yellow hexagonal platelets of **1** were isolated from the cloudy reaction mixture by repeated decanting/washing with the mother-liquor. Yield 0.04 g (12%) (Found: C, 46.55; H, 5.7; N, 8.75. $C_{26}H_{38}N_4O_{10}V_2$ requires C, 46.7; H, 5.7; N, 8.4%). IR (cm^{-1}): 1640 (C=N), 3150–3200 (NH_2), 960 (V=O) and 840 (V=O···V).

Synthesis of $H_2dien{\cdot}SO_4$. The procedure described above was repeated using 5-azapentane-1,3-diamine with vanadyl sulfate and $H_2dien{\cdot}SO_4$ was isolated as light yellow needles in 25% yield. Crystals suitable for X-ray crystallography were obtained by carrying out the reaction in a nitrogen atmosphere (Found: C, 24.40; H, 7.65; N, 20.25. $C_4H_{15}N_3O_4S$ requires C, 24.4; H, 7.7; N. 20.1%). IR (cm^{-1}): 3200 (NH) and 1140 (SO_4^{2-}).

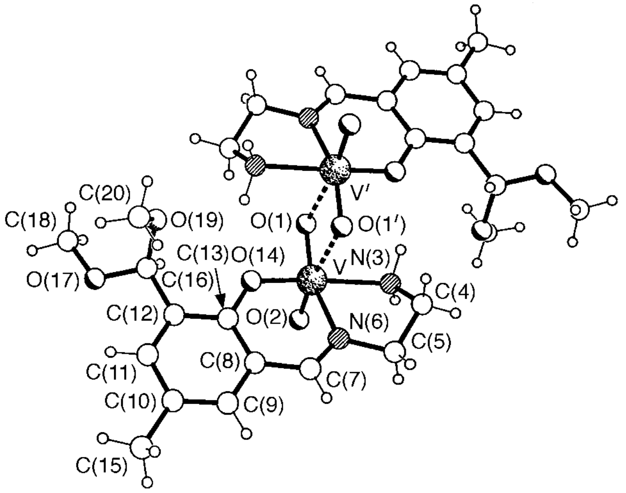

Fig. 1 Molecular structure of the $[(VO_2L^4)_2]$ dimer

unusual under the relatively vigorous reaction conditions employed.[10] The new acetal is attractive as a potentially good source of new vanadium ionophores derived from chemical manipulations involving the reactive NH_2 and $C(OCH_3)_2$ sites. Better understanding of V–V interactions in such new ionophores could facilitate the design and preparation of new types of vanadium compounds, especially those exhibiting tunable electronic behaviour.[11]

Since a 2:2 macrocyclic dinuclear VO^{2+} complex is formed[2] from the reduced chelate $[L^3]^{2-}$ we attempted to form a Schiff-base complex using a more flexible amine, 3-azapentane-1,5-diamine (dien). This time no well defined condensation iminic product was isolated; instead the hydrogen-bond stabilized hydrolytic product $H_2dien{\cdot}SO_4$ was formed (Fig. 3) when vanadyl sulfate was used.

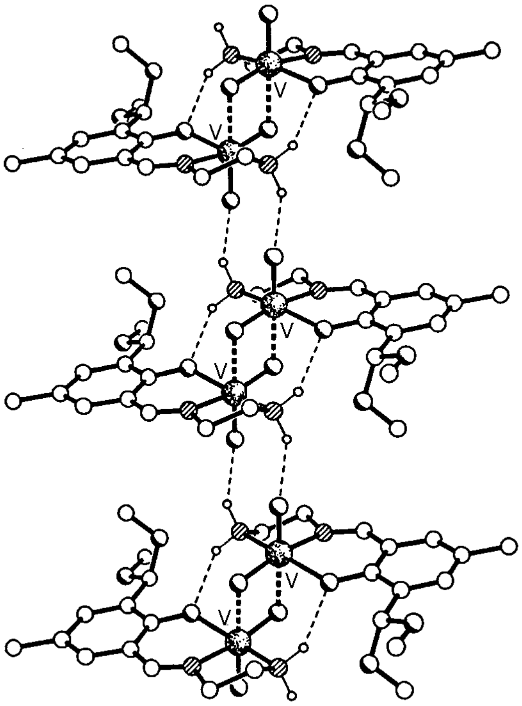

Fig. 2 Hydrogen bonded chain of $[(VO_2L^4)_2]$ dimers in the crystallographic *b* direction

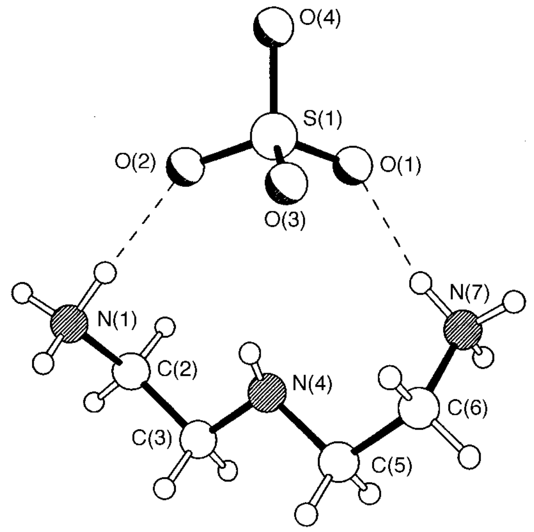

Fig. 3 Structure of $H_2dien{\cdot}SO_4$

The X-ray analysis of **1**‡ reveals (Fig. 1) the formation of a C_i-symmetric oxo-bridged dimeric structure with each Schiff-base ligand being tridentate and binding to each vanadium centre *via* amine [N(3)] and imine [N(6)] nitrogen and the phenolate oxygen [O(14)] atoms. The co-ordination at vanadium is distorted octahedral with bond angles at V^{5+} in the ranges 75.7(1)–106.1(1) and 155.4(1)–171.8(1)° (for the bridging oxygen *trans* to the terminal oxo). The V–N [2.133(3), 2.160(3) Å] and V–O (phenoxy) [1.908(3) Å] distances are normal for the respective vanadium(V)-imino, -amino and -phenolate linkages.[10] The terminal V=O (oxo) distance at 1.612(3) Å is again typical of such vanadium(V) bonds. The μ-O distances are markedly asymmetric with V–O(1) 1.675(2) and V–O(1′) 2.270(2) Å. Consistent with considering the vanadium centre as being five-co-ordinate and adapting a conventional square-pyramidal geometry[13] in which the vanadium is displaced (0.32 Å) out of the plane of the four basal atoms, O(1), N(3), N(6) and O(14), towards the apical oxo-atom O(2), **1** is formulated as a dimer, $[(VO_2L^4)_2]$. The dimeric complex (V···V′ 3.08 Å) is further stabilized by a pair of N–H···O hydrogen bonds between one of the amino N–H hydrogen atoms on one ligand and the phenoxy-oxygen atom of the other and *vice versa* (N···O, H···O distances 3.00, 2.12 Å, N–H···O angle 150°). Adjacent dimers are linked *via* pairs of N–H···O hydrogen bonds between the other amino N–H hydrogen atom of one dimer and the terminal oxo oxygen atom [O(2)] of another dimer and *vice versa* to form hydrogen-bonded chains of dimers (Fig. 2) that extend in the crystallographic *b* direction (N···O, H···O distances 2.93, 2.10 Å, N–H···O angle 141°).

The transformation of the aldehyde functionality into an acetal $[L^4]^-$, which is normally less favoured than the formation of iminic linkages,[10] and the unexpected hydrolytic product

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‡ *Crystal data*. Compound **1**. $C_{26}H_{38}N_4O_{10}V_2$, platy yellow needles, size 0.10 × 0.33 × 0.73 mm, monoclinic, $P2_1/c$, $a = 15.609(2)$, $b = 7.757(1)$, $c = 14.029(2)$ Å, $\beta = 111.18(2)°$, $U = 1583.9(4)$ Å^3, $Z = 2$, $M = 668.5$, $D_c = 1.402$ g cm^{-3}, $D_m = 1.38$ g cm^{-3}, μ(Mo-Kα) = 0.65 mm^{-1}, $F(000) = 696$, $T = 293$ K.

$H_2dien{\cdot}SO_4$. $C_4H_{15}N_3O_4S$, clear prisms, size 0.13 × 0.11 × 0.11 mm, monoclinic, $P2_1/n$, $a = 6.875(1)$, $b = 6.927(1)$, $c = 18.865(3)$ Å, $\beta = 97.46(1)°$, $U = 890.8(2)$ Å^3, $Z = 4$, $M = 201.3$, $D_c = 1.501$ g cm^{-3}, μ(Cu-Kα) = 3.18 mm^{-1}, $F(000) = 432$, $T = 293$ K. Data for both compounds were measured on a Siemens P4 diffractometer using for **1** graphite-monochromated Mo-Kα radiation, for $H_2dien{\cdot}SO_4$ Cu-Kα radiation and ω scans. The structures were solved by direct methods and were refined using the SHELXTL program system[12] to give for **1** $R1 = 0.0466$, $wR2 = 0.1156$ for 1732 independent observed reflections $[|F_o| > 4\sigma(|F_o|), \theta \leqslant 23°]$; for $H_2dien{\cdot}SO_4$ $R1 = 0.0435$, $wR2 = 0.1273$ for 1274 independent observed reflections $[|F_o| > 4\sigma(|F_o|), \theta \leqslant 62°]$. Data for both compounds were not corrected for absorption effects. The positions of the hydrogen atoms were located in Δ map and idealized; they were assigned isotopic thermal parameters $U(H) = 1.2\ U_{eq}$ (C or N) and allowed to ride on their parent C or N atoms. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/435.

$H_2dien \cdot SO_4$ of 5-azapentane-1,3-diamine reveal most dramatically how very difficult it is for VO^{2+} and VO_2^+ species to form stable macrocyclic dinuclear complexes.[1–3]

Acknowledgements

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