

## A polymeric oxovanadium(IV) pyromellitate complex

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The reaction of oxovanadium(IV) sulphate with 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) in the presence of potassium carbonate yields a polymeric complex,  $K_2[VO(pyr)] \cdot 6H_2O$  (**I**) [pyr = pyromellitate(4-) ion]. The PM3(tm) calculations and IR spectroscopy suggest that the polymeric structure of **I** consists of  $-V-pyr-$  chains formed by the 1,4- or 1,5-bridging by the pyr ions. The chains are additionally cross-linked by the chelate function of one of the  $COO^-$  groups of the pyr ion. Magnetic measurements do not reveal the presence of antiferromagnetic coupling between the V centers.

*Key words:* oxovanadium(IV) complexes, pyromellitic acid, polymeric structure, PM3(tm) calculations.

Oxovanadium(IV) complexes with dicarboxylic acids have been prepared and characterized for a number of acids, such as oxalic, citric, tartaric, phthalic and their homologues.<sup>1-8</sup> The carboxylato anions in these complexes are coordinated in two ways – either like a bidentate chelate group or like a bridge between two vanadium atoms thus forming discrete units or binuclear/polynuclear species are formed, respectively. In the case of the oxalato anion both arrangements are found,<sup>1</sup> whereas the phthalate anion (pht) bridges the V atoms forming a binuclear complex,<sup>4</sup>  $K_2[(VO)_2(pht)_2(OH)_2(H_2O)_2] \cdot 6H_2O$ .

The aim of this work was to examine the coordination arrangements that can arise in the oxovanadium(IV) – pyromellitate system, as the pyr ions are potentially capable of functioning as mono-, bi-, tri-, and tetradentate ligands. To this end, a  $VO^{2+}$ -pyr complex was prepared, isolated and characterized, the preparation involving the reaction of an aqueous solution of  $VOSO_4$  with partially neutralized pyromellitic acid.

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## EXPERIMENTAL

Powder X-ray diffraction analysis was performed on a Siemens-D 500 diffractometer using the Ni-filtered  $\text{CuK}\alpha$  radiation and a scintillation counter, at a scanning rate of  $0.02^\circ 2\theta/\text{s}$ .

Magnetic measurements were carried out at room temperature on a Sherwood Scientific Ltd. magnetic balance (model MSB-MK1) using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. The molar magnetic susceptibility was corrected for the diamagnetism of the constituents. The formula  $\mu_{\text{eff}} = 801 (\chi_{\text{m}}^{\text{corr}} T)^{1/2}$  was used to relate the effective magnetic moment,  $\mu_{\text{eff}}$  (in  $\mu_{\text{B}}$ ), and  $\chi_{\text{m}}^{\text{corr}}$  (in  $\text{cm}^3 \text{mol}^{-1}$ ),  $T$  being the temperature in K.

The infrared spectrum was obtained using KBr pellets ( $4000\text{--}600 \text{ cm}^{-1}$ ) on a Bomem MB-100 FTIR spectrophotometer.

Thermal analysis measurements were performed using a Stanton thermoanalyser. The sample was heated from  $30$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen flow.

The diffuse reflectance spectrum was obtained on a Beckman DK-1 A spectrophotometer using  $\text{MgO}$  as an internal standard.

*Synthesis*

To a solution of  $\text{VOSO}_4 \cdot 5 \text{H}_2\text{O}$  ( $2.54 \text{ g}$ ,  $1.0 \times 10^{-2} \text{ mol}$ ) and pyromellitic acid ( $2.54 \text{ g}$ ,  $1.0 \times 10^{-2} \text{ mol}$ ) in  $200 \text{ cm}^3$  of water a solution of  $\text{K}_2\text{CO}_3$  (about  $2 \text{ g}$ ) in  $40 \text{ cm}^3$  of water was added under stirring at room temperature. A blue solution was obtained ( $\text{pH} \approx 3$ ) which was allowed to stand at room temperature for a day until a crop of blue crystals was isolated. The product, after washing with water, was dried in air yielding  $3.0 \text{ g}$  of crystals ( $60\%$ ). Anal. Found (mas. %): C, 23.40; H, 2.69; K, 15.34; V (spectrophotometrically), 9.95. Calcd. for  $\text{C}_{10} \text{H}_{14} \text{O}_{15} \text{K}_2 \text{V}$ : C, 23.86; H, 2.80; K, 15.54; V, 10.12.

## RESULTS AND DISCUSSION

The blue crystalline product (**I**) separates out of an aqueous solution of vanadyl sulphate and pyromellitic acid, partially neutralized by potassium carbonate upon standing at room temperature. Elemental analysis yields the composition of **I** as  $\text{K}_2\text{VO}(\text{pyr}) \cdot 6\text{H}_2\text{O}$ . The product is insoluble in all common solvents, which suggests that **I** has a polymeric structure.

The powder diffractogram shows that **I** is a crystalline material. It contains numerous reflections suggesting a low symmetry of the crystals. That the symmetry is low is further indicated by the fact that an attempt to determine the unit cell parameters of **I**, by analyzing the powder diffracton data using the crystallographic program TREOR,<sup>9</sup> was not successful.

Structural data on polymeric pyromellitate complexes are generally still quite scarce. Therefore, in order to obtain some guideline regarding the energetics of various possible modes of bridging by the pyr ion, semi-empirical quantum-mechanical PM3(tm)<sup>10</sup> calculations were carried out on a range of model binuclear first row transition metal-pyromellitate complexes,  $[\text{H}_2\text{O}]_5\text{M-pyr-M}(\text{H}_2\text{O})_5$  ( $\text{M} = \text{divalent transition metal ion}^*$ ). The calculations show that, at the optimized geometries of the model complexes, bridging through the  $\text{COO}^-$  groups at the 1 and 4

\* The  $\text{VO}^{2+}$  ion itself was not included in the calculations since the "PC Spartan Plus" program used<sup>10</sup> has not yet been parameterized for vanadium.

positions on the aromatic ring is by about 120 kJ/mol and by only about 10 kJ/mol more favorable than 1,2- and 1,5-bridging, respectively. This means that the polymeric structure of **I**, as suggested by its insolubility, can be practically attained by chain formation through either 1,4- or 1,5-bridging by the pyr ions. Any crosslinking of such chains must inevitably involve the additional presence of the less favorable 1,2-bridging component.

Magnetic susceptibility measurement shows that **I** has an effective magnetic moment per vanadium(IV),  $\mu_{\text{eff}} = 1.70 \mu_{\text{B}}$ . This is in accordance with the spin-only value ( $\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$ ) and indicates the absence of intramolecular magnetic coupling of the  $d^1-d^1$  centers. This does not, however, preclude the polymeric structure of the complex, because of the relatively great distance between any two V centers bridged by pyromellitate anions. Namely, PM3(tm) calculations show that, at the optimized geometries of the model  $[(\text{H}_2\text{O})_5\text{M}-\text{pyr}-\text{M}(\text{H}_2\text{O})_5]$  complexes, the M...M distance is about 9.2 Å, 8.6 Å, and 6.9 Å for the 1,4-, 1,5-, and 1,2-bridging modes, respectively. In  $\text{VO}^{2+}$  complexes in which antiferromagnetic coupling is observed, the V...V distance is considerably shorter. For example, in the bis-acetato bridged  $[\text{L}_2(\text{VO})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$  and bis-hydroxo bridged  $[\text{L}'_2(\text{VO})_2(\mu\text{-OH})_2]^{2+}$  species, which have room temperature  $\mu_{\text{eff}}$  values of 1.60 and 1.20  $\mu_{\text{B}}$ , respectively, the V...V distances are 4.08 Å and 3.03 Å, respectively.<sup>11,12</sup>

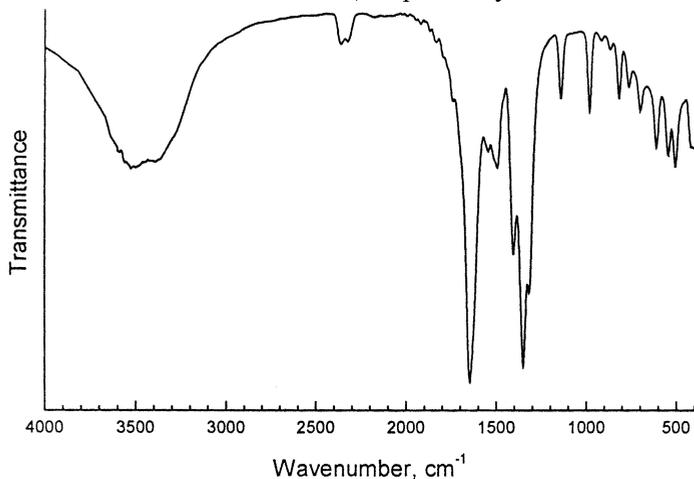


Fig. 1. Infrared spectrum of  $\text{K}_2[\text{VO}(\text{pyr})]\cdot 6\text{H}_2\text{O}$ .

The IR spectrum **I** (Fig. 1) exhibits a strong absorption at  $976 \text{ cm}^{-1}$ , corresponding to the  $\text{V}=\text{O}$  stretching vibration typical<sup>13</sup> of vanadyl complexes. The broad strong bands centered at  $3550 \text{ cm}^{-1}$  and  $3375 \text{ cm}^{-1}$  can be assigned to lattice water.<sup>14</sup> The IR spectrum unambiguously shows that no non-ionized COOH groups are present in **I**, because a strong absorption at  $1700 \text{ cm}^{-1}$ , characteristic of pyromellitic acid, is not found. This is somewhat unexpected since the synthesis of **I** was performed using only partially neutralized pyromellitic acid.

The IR spectrum shows the presence of both coordinated as well as free  $\text{COO}^-$  groups. The very strong absorptions at  $1645\text{ cm}^{-1}$  [ $\nu_{\text{as}}(\text{COO}^-)$ ] and  $1349\text{ cm}^{-1}$  [ $\nu_{\text{s}}(\text{COO}^-)$ ] correspond to the ionized carboxyl groups in the complex. The difference between the symmetric and antisymmetric vibrations  $\Delta\nu = 296\text{ cm}^{-1}$  is much larger than  $\Delta\nu$  found in the spectrum of  $\text{K}_4\text{pyr}$  ( $\Delta\nu = 195\text{ cm}^{-1}$ ). This is a strong indication<sup>15</sup> of the monodentate coordination mode for these carboxylate groups, and implies a bridging function of the pyr ligand between two vanadium centers. The medium intensity absorptions at  $1492\text{ cm}^{-1}$  and  $1315\text{ cm}^{-1}$  ( $\Delta\nu = 177\text{ cm}^{-1}$ ) can be assigned to ionized, but non-coordinated<sup>15</sup> carboxylate groups. In addition, there are medium intensity absorptions at  $1541\text{ cm}^{-1}$  and  $1404\text{ cm}^{-1}$ ; the  $\Delta\nu$  value ( $137\text{ cm}^{-1}$ ) in this case corresponds to the  $\text{COO}^-$  groups that have a chelate function.<sup>15</sup> All this suggests that **I** contains not only chains consisting of V centers interconnected by the 1- and 4- $\text{COO}^-$  groups of the pyr ion, but also that the chains themselves are interconnected. This is schematically shown in Fig. 2, in which the label "1" refers to the 1- and 4- $\text{COO}^-$  groups, label "2" to the ionized but non-coordinated  $\text{COO}^-$  group, and label "3" to the chelate  $\text{COO}^-$  group. The latter group belonging to one chain chelately coordinates a V center on an adjacent chain. In that way, each V center has an approximate square-pyramidal coordination geometry, the double-bonded O atom being at the apex of the pyramid. The square-pyramidal geometry is proposed here because it is very characteristic of  $\text{VO}^{2+}$  complexes.<sup>13</sup> It should be added that octahedral geometry around the V atom cannot be entirely precluded. However, since the TG results show (vide infra) that water molecules are not coordinated to vanadium, octahedral geometry would only imply an even greater degree of cross-linking of the polymeric chains.

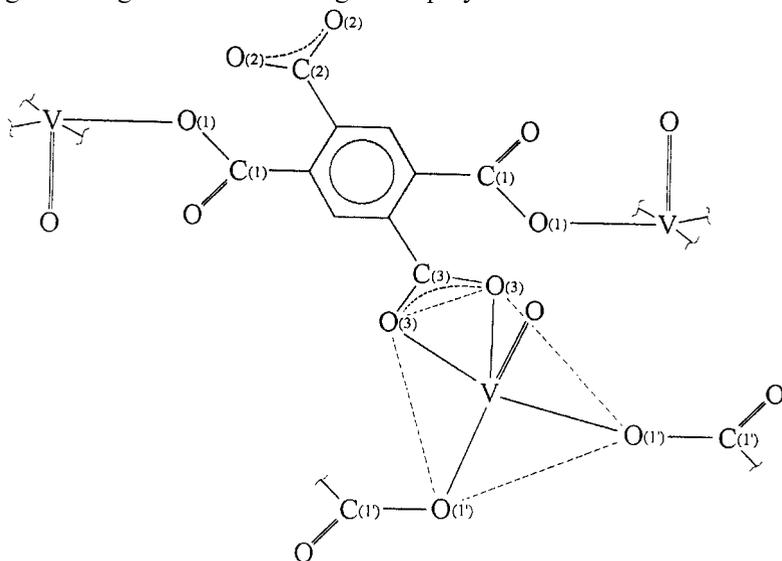


Fig. 2. Schematic view of the proposed polymeric chain structure of  $\text{K}_2[\text{VO}(\text{pyr})] \cdot 6\text{H}_2\text{O}$ . The unprimed and primed labels refer to atoms on two adjacent chains, the latter being interconnected by the  $\text{COO}^-$  group carrying the label "3".

The electronic spectra of most square-pyramidal oxovanadium(IV) complexes exhibit three bands in the 330–1000 nm range. These are essentially intra d shell transitions, but their exact assignment has long been the subject of controversy due to the presence of a strong  $\pi$  component in the V=O bond.<sup>16,17</sup> Three absorption maxima are also observed in the diffuse reflectance spectrum of I: at 850 nm, 594 nm and 379 nm, the latter absorption occurring as a shoulder on the intense charge transfer band of the oxovanadium(IV) species. This can be compared to the maxima at 780 nm, 580 nm, and 390 nm found<sup>18</sup> for [VO(acac)], the latter being a typical square-pyramidal oxovanadium(IV) complex (acac = acetylacetonate ion).

The thermogravimetric curve of I (Fig. 3) shows that dehydration begins slightly above room temperature. Six water molecules escape by 105 °C (calcd.: 21.48 mass%, found: 21.22%). The fact that water is lost at comparatively low temperatures strongly suggests that the water molecules are not coordinated to vanadium, but that they reside in the lattice (as also indicated above by the IR spectrum).

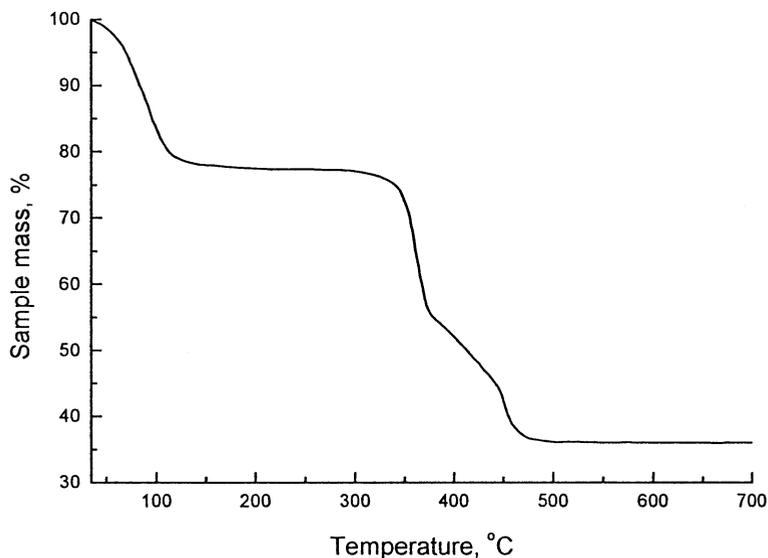


Fig. 3. Thermogravimetric curve of  $K_2[VO(pyr)] \cdot 6H_2O$ .

Following the release of water, there is a rather broad temperature range on the TG curve (up to 350 °C) in which only one carbon monoxide molecule is lost (calcd.: 5.56 mass %, found: 5.71%); this probably originates from the non-coordinated  $COO^-$  group. Next, between 350 °C and 363 °C there is a sharp decline on the TG curve that can be assigned to the departure of three more CO molecules (calcd.: 16.70 mass %, found: 16.31%), probably coming from the coordinated  $COO^-$  groups. The final thermal decomposition of the pyr ion occurs in the 363–475 °C range in at least two stages, the overall result being the loss of three additional CO molecules and one  $H_2O$  molecule (calcd.: 20.28 mass%, found: 20.54%). The residue above 475 °C corresponds to the mixture  $K_2O + VC + 2C$  (calcd. residue: 35.98%, found: 36.22%).

In conclusion, oxovanadium(IV) ions with pyromellitate anions form the complex  $K_2[VO(pyr)] \cdot 6H_2O$  having a polymeric structure, in which the pyr ligand exhibits both monodentate as well as chelate behavior.

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### ИЗВОД

#### ПОЛИМЕРНИ ОКSOВANAДИЈУМ(IV)-ПИРОМЕЛИТАТНИ КОМПЛЕКС

ДУШАНКА Д. ВАСОВИЋ И ЂОРЂЕ СТОЈАКОВИЋ

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Реакција између оксованадијум(IV)-сулфата и 1,2,4,5-бензентетракарбоксилне киселине (пиромелитне киселине) у присуству калијум-карбоната даје полимерни комплекс  $K_2[VO(pyr)] \cdot 6H_2O$  (**I**) [pyr = пиромелитат(4-)–јон]. Прорачуни методом РМЗ(tm) као и ИЦ-спектроскопија указују да се полимерна структура једињења **I** састоји од ланаца –V–pyr–V–pyr– насталих преомошћавањем помоћу pyr јонана преко положаја 1,4- или 1,5-. Ланци су додатно међусобно повезани хелатним деловањем једне од  $COO^-$  група pyr јона. Магнетна мерења не показују присуство антиферромагнетског купловања између V центара.

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