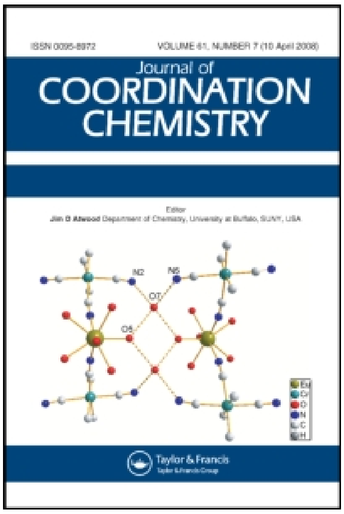

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A NEW PERSPECTIVE ON VANADYL TARTRATE DIMERS. PART II. STRUCTURE AND SPECTROSCOPIC PROPERTIES OF CALCIUM VANADYL TARTRATE TETRAHYDRATE

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A NEW PERSPECTIVE ON VANADYL TARTRATE DIMERS. PART II. STRUCTURE AND SPECTROSCOPIC PROPERTIES OF CALCIUM VANADYL TARTRATE TETRAHYDRATE

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The calcium vanadyl tartrate complex $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$ has been synthesized and characterized by spectroscopic methods. Its crystal structure was solved by X-ray methods. The compound is monoclinic, space group $P2_1/c$, with $a = 8.0282(5)$, $b = 17.1568(8)$, $c = 7.6113(3)$Å, $\beta = 94.269(4)°$ and $Z = 4$. The structure consists of centrosymmetric vanadyl tartrate dimers, $[(VO)(d,l\text{-}C_4H_2O_6)]_2^{4-}$, and calcium cations placed between them. As a result, dimers form chains in the [101] direction. Neighbouring chains are linked by the coordination of the calcium ion to the oxygen atom of a vanadyl group of a different chain, thus forming a two-dimensional structure. Different layers are linked by hydrogen bonds. Spectroscopic studies show the existence of intra-dimeric interactions between vanadium atoms.

KEYWORDS: Vanadyl, tartrate, calcium, crystal structure, EPR

INTRODUCTION

In the last decade superconductivity research activities have been mainly focused on systems containing copper and alkaline earth ions.[1,2] However, since 1989 only a few new copper oxide systems have been characterized. This fact has spurred scientific research in new directions.[3] In this way, antiferromagnetism and spin values of one-half seem to have a relationship with high-T_c superconductivity.[4] Therefore, oxides of type M-V-O (M = Ca, Sr, Ba) are of particular interest when the vanadium cation has a d^1 electronic configuration.[5,6]

A great deal of attention is also being paid to related techniques of sample preparation.[7] Synthesis of mixed oxide systems are generally based upon the ceramic method. Heterobimetallic complexes of alkaline earth vanadium(IV) systems are of potential value in this context because they contain well-defined

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V(IV):M(II) ratios and after adequate thermal treatment mixed oxides can be obtained.[8]

In neutral aqueous solution, the tetranegative tartrate anion can chelate an alkaline earth cation and a vanadyl ion simultaneously to yield a metallo-organic precursor with general formula $[M(VO)(C_4H_2O_6)(H_2O)_x]$.[9] Although these tartrates have not been much studied,[10] the structural, magnetic and optical properties of alkali and ammonium vanadyl tartrates have been extensively investigated, $M_4[(VO)(C_4H_2O_6)]_2 \cdot x\ H_2O$ (M = Na, Rb, Cs, NH_4^+).[11-14] The compounds obtained exhibit a dimeric structure, each vanadyl group being coordinated by two tartrate ligands. The nature of the complexes is also dependent on the optical isomers of tartrate involved.[15] In this way, the racemic *d,l*-tartrate mixture exhibits a *cis* coordination about the vanadium atom, but the *d,d*- isomer has a *trans* configuration. In this paper, we report the crystal structure and spectroscopic properties of the calcium oxovanadium(IV) tartrate complex of formula $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$.

EXPERIMENTAL

Synthesis

The complex $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$ was obtained from a mixture of the sodium salt, $Na_4[(VO)(d,l\text{-}C_4H_2O_6)]_2 . 12\ H_2O$,[10] and $CaCl_2$ solutions in a diffusion device. After 48 hours, brown prismatic crystals suitable for X-ray structure determination were collected and washed with water, acetone and ether and dried over P_2O_5. Anal; calcd. for $CaVO_{11}C_4H_{10}$: V, 15.7; C. 14.8; H, 3.1%. Found: V, 15.8; C. 14.5; H, 3.3%.

Physical measurements

Infrared spectra were obtained with KBr pellets in the 4000–400 cm^{-1} region, using a Nicolet FT-IR 740 spectrophotometer. Reflectance spectra were measured on a Perkin Elmer lambda 9 spectrophotometer at room temperature in the 6000–40000 cm^{-1} range.

E.S.R. spectra were recorded on a Bruker E.S.P. 300 spectrometer, equipped with a standard Oxford low-temperature device, operating at X band frequencies and calibrated by an NMR probe for the magnetic field, and by using the signal of DPPH (diphenylpicrylhydrazyl) for frequency.

Crystallographic data collection and structure determination

A single crystal of dimensions 0.20 × 0.16 × 0.05 mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and using MoKα radiation at room temperature. Accurate unit cell parameters were derived from least-squares refinement of the setting angles of 25 reflections in the range $10 < 2\theta < 25°$. Lattice and data collection parameters are given in Table 1. Intensities and angular positions of four standard reflections were

Table 1 Crystal data, data collection and structure refinement details for $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$.

Crystal Data	
Formula	$CaVO_{11}C_4H_{10}$
Mol. wt (g)	325.14
System	Monoclinic
Space Group	$P2_1/c$
a (Å)	8.0282(5)
b (Å)	17.1568(8)
c (Å)	7.6113(3)
β (°)	94.269(4)
V (Å^3)	1045.4(3)
Z	4
$\rho_{obs.}$ (g cm^{-3})	2.05(2)
$\rho_{calc.}$ (g cm^{-3})	2.07
μ(MoKα), cm^{-1}	14.47
F(000)	660
Data Collection	
Radiation, MoKα (Å)	0.71069
Scan type	$\omega/2\theta$
θ Range (°)	1–30°
Check reflections	3-3-1, 162, 251, 32-1
No. measured reflections	3043
Interval h, k, l	10, 24, ±11
Refinement	
No. variables	186
Selection	$I \geq 2.5\ \sigma(I)$
No. unique reflections	2619
$w = 1/[\sigma^2\|F_0\| + p\|F_0\|^2]$	$p = 0.0047$
$R = (\Sigma\|\|F_0\| - \|F_c\|\|)/(\Sigma\|F_0\|)$	0.028
$R_w = [\Sigma w(\|F_0\| - \|F_c\|)^2/\Sigma w\|F_0\|^2]^{1/2}$	0.033
$(\Delta\rho)_{min}$ (e$^-$ Å^{-3})	−0.38
$(\Delta\rho)_{max}$ (e$^-$ Å^{-3})	0.64

measured every hour and these showed no decrease nor misalignment during data collection. The data were corrected for Lorentz and polarization effects. Some 3043 reflections were measured in the range $1 < \theta < 30°$; 2619 were considered as observed ($I \geq 2.5\sigma(I)$).

The crystal structure was solved by the Patterson method using scattering factors and anomalous dispersion parameters taken from *International Tables for X-ray Crystallography.*[16] The positions of the vanadium and calcium atoms were found by sharpened Patterson functions (SHELX-86[17]). Successive Fourier synthesis (SHELX-76[18]) located all other non-hydrogen atoms. The calculations were made initially with isotropic, then with anisotropic thermal parameters. Hydrogen atoms were located by means of different Fourier synthesis. Hydrogen atoms coordinates were refined with restricted distances (1.01Å) to the bonded oxygen and carbon atoms. Refinement converged to a standard R value of 0.028 and $R_w = 0.033$. Final fractional atomic coordinates and equivalent temperature factors are listed in Table 2.

Table 2 Fractional atomic coordinates (× 10^5) and equivalent temperature factors ($Å^2$) for $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$.

Atom	x/a	y/b	z/c	B^*_{eq}
V	31422(3)	7175(1)	8999(3)	1.28(1)
Ca	9314(3)	10972(2)	-47965(3)	1.46(1)
O(1)	65701(16)	23077(7)	-1234(20)	2.69(3)
O(2)	7069(14)	-1998(6)	-33810(14)	1.85(2)
O(3)	42329(13)	16117(7)	-1921(15)	1.98(2)
O(4)	17461(14)	6307(6)	-13915(15)	1.71(2)
O(5)	53180(13)	5830(6)	20412(15)	1.87(2)
O(6)	27346(14)	3842(6)	9141(12)	1.69(2)
O(7)	20037(15)	11383(7)	22950(16)	2.14(3)
O(1w)	38264(18)	6836(9)	-44485(20)	3.34(4)
O(2w)	22744(15)	21387(7)	-31163(16)	2.33(3)
O(3w)	-2868(17)	22459(8)	-60957(20)	3.08(3)
O(4w)	-16406(16)	13000(8)	65418(18)	2.63(3)
C(1)	57806(17)	17462(9)	3530(20)	1.74(3)
C(2)	65409(17)	11288(8)	16161(18)	1.50(3)
C(3)	20727(18)	-7102(8)	-6818(19)	1.46(3)
C(4)	14212(17)	-671(8)	-19111(18)	1.41(3)

* $B_{eq} = 8/3\pi^2\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

RESULTS AND DISCUSSION

Description of the structure

Selected interatomic bond distances and angles are given in Table 3. The crystal structure contains tetranegative dimeric anions, $[(VO)(d,l\text{-}C_4H_2O_6)]_2{}^{4-}$, and calcium cations arranged between them (see Fig. 1).

The dimeric tetranegative anions consist of two vanadyl groups chelated by two tartrate ligands. As found in all structures of *d,l*-tartrate-bridged vanadyl dimeric complexes, the anion lies about a symmetry centre, giving a *cis* coordination geometry about the vanadium atom. The coordination polyhedron of the vanadium

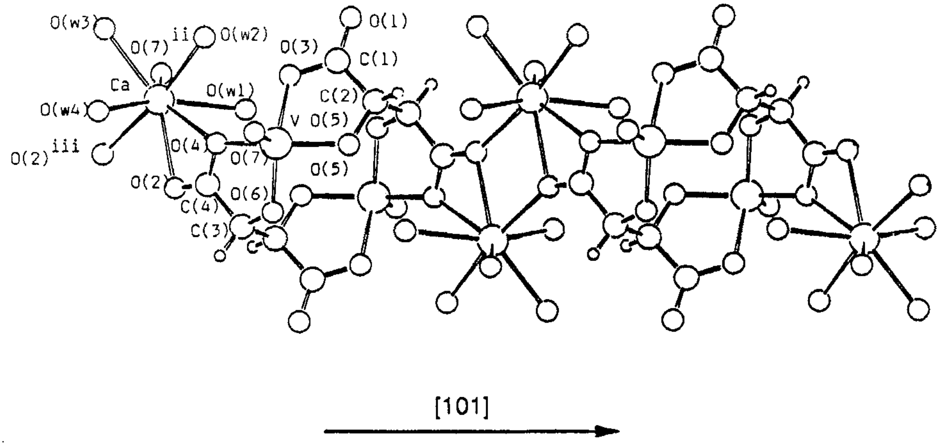

Figure 1 Chains of dimer molecules in the [101] direction.

Table 3 Selected bond distances (Å) and angles (°) for $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$.

*Vanadium and calcium coordination spheres**			
V-O(3)	1.980(1)	V-O(4)	2.007(1)
V-O(5)	1.906(1)	V-O(6)	1.918(1)
V-O(7)	1.621(1)	V-V^{i}	4.1767(3)
V-V^{ii}	7.611(2)		
O(3)-V-O(4)	85.90(5)	O(3)-V-O(5)	82.31(5)
O(3)-V-O(6)	147.87(5)	O(3)-V-O(7)	102.62(6)
O(4)-V-O(5)	145.13(5)	O(4)-V-O(6)	81.22(4)
O(4)-V-O(7)	107.25(5)	O(5)-V-O(6)	91.67(5)
O(5)-V-O(7)	107.31(5)	O(6)-V-O(7)	109.30(6)
V-O(3)-C(1)	116.4(1)	V-O(4)-C(4)	115.16(9)
V-O(5)-C(2)	116.40(8)	V-O(6)-C(3)	116.17(8)
O(7)-V-V^{i}	158.16(3)		
Ca-O(4)	2.745(1)	Ca-O(2)	2.485(1)
Ca-O(2)^{iii}	2.399(1)	Ca-O(7)^{ii}	2.435(1)
Ca-O(w1)	2.426(1)	Ca-O(w2)	2.405(1)
Ca-O(w3)	2.382(2)	Ca-O(w4)	2.395(1)
O(4)-Ca-O(7)^{ii}	142.31(4)	O(4)-Ca-O(2)	49.40(3)
O(4)-Ca-O(2)^{iii}	116.15(4)	O(7)-Ca-O(2)	117.52(4)
O(7)-Ca-O(2)^{iii}	73.06(4)	O(2)-Ca-O(2)^{iii}	67.762(4)
Average values in tartrate ligand			
C-C	1.53(1)	C-O(carboxyl)	1.29(1)
C-O(hydroxyl)	1.408(4)	C=O	1.23(1)
C-H	0.9981(3)		
C-C-C	107.0(8)	C-C-O(carboxyl)	122.7(1)
C-C-O(hydroxyl)	110.1(7)	C-C=O	114(1)
Hydrogen bonds			
O(w2)···O(7)^{iv}	2.982(2)	O(w3)···O(1)^{v}	2.789(2)
O(w3)···O(w2)^{iv}	2.860(2)	O(w4)···O(1)^{vi}	3.017(2)

* Symmetry codes: *i* = 1−*x*, −*y*, −*z*; *ii* = *x*, *y*, *z*−1; *iii* = −*x*, −*y*, −*z*−1; *iv* = *x*−1, 1/2−*y*, *z*−1/2; *v* = *x*, 1/2−*y*, *z*−1/2.

atom is a distorted square pyramid, comprising two hydroxyl oxygen atoms [V-O(3), O(4); 1.980(1), 2.007(1)Å] and two carboxyl oxygen atoms [V-O(5), O(6); 1.906(1), 1.918(1)Å]. The coordination sphere is completed with the oxygen atom of the vanadyl group [V-O(7); 1.621(1)Å] which occupies the axial position. The vanadium atom is displaced from the basal plane by 0.578(1)Å. Distortion of the polyhedron from an ideal trigonal bipyramid ($\Delta = 0$) towards a square pyramid ($\Delta = 1$) has been calculated by the Muetterties-Guggenberger method,[19] yielding a value of $\Delta = 0.98$ (Table 4). Therefore, the coordination geometry about the vanadium atoms has a symmetry close to C_{4v}. Vanadium atoms have an intradimeric distance of 4.1767(3)Å and a O = V-V^{i} angle of 158.16(3)°. As a result, both vanadyl groups are parallel but not co-linear.

Each calcium atom is bonded to two tartrate groups of different dimers [Ca-O(2), O(4), O(2)^{iii}; 2.485(1), 2.745(1), 2.399(1)Å]. Thus, infinite chains in the [101] direction of the type $\text{-}2Ca\text{-}[(VO)(d,l\text{-}C_4H_2O_6)]_2\text{-}2Ca\text{-}[(VO)(d,l\text{-}C_4H_2O_6)]_2\text{-}2Ca\text{-}$ are formed (see Fig. 1). Neighbouring chains are linked by the coordination of the oxygen atom of a vanadyl group to the calcium cation [Ca-O(7)^{ii}; 2.435(1)Å] (similar bonding has been found in the analogous barium compound[9]). As a consequence, the presence of calcium in the crystal structure of the title compound implies the formation of layers (see Fig. 2). In these layers, dimers of different

Table 4 Distortion, Δ*, of the VO_5 coordination polyhedron in $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$ between the ideal trigonal bipyramid (TBP) and square pyramid (SP) geometries.

Dihedral angle	TBP	VO_5	SP
δa_1	101.5	[O(7)-O(5)-O(6)-O(4)] 119.1	121.8
δa_3	101.5	[O(7)-O(3)-O(5)-O(4)] 119.4	121.8
δa_4	101.5	[O(7)-O(4)-O(3)-O(5)] 119.6	121.8
δa_6	101.5	[O(7)-O(6)-O(4)-O(5)] 122.7	121.8
δa_2	101.5	[O(3)-O(4)-O(7)-O(6)] 72.2	73.9
δa_5	101.5	[O(3)-O(7)-O(5)-O(6)] 74.4	73.9
δe_1	53.1	[O(4)-O(3)-O(7)-O(5)] 75.9	73.9
δe_2	53.1	[O(4)-O(7)-O(6)-O(5)] 75.1	73.9
δe_3	53.1	[O(6)-O(4)-O(5)-O(3)] 2.9	0
Δ	0	0.98	1

$$\Delta^* = \left|\frac{(\delta a_1 + \delta a_3 + \delta a_4 + \delta a_6) - 406.0}{182.7}\right| + \left|\frac{(\delta a_2 + \delta a_5) - 203.0}{248.4}\right| + \left|\frac{(\delta e_1 + \delta e_2) - 106.2}{187.2}\right| + \left|\frac{\delta e_3 - 53.1}{477.1}\right|.$$

chains are stacked along the *c* axis. The coordination sphere of the calcium atom is completed by four water molecules [Ca-O(w1), O(w2), O(w3), O(w4); 2.426(1), 2.405(1), 2.382(2), 2.395(1)Å] yielding a final coordination number of 8 with square antiprismatic geometry. Distortion of this polyhedron has been evaluated by the Brown and Shannon method.[20] The calculated factor, $\Delta = 21 \times 10^{-4}$, is in good agreement with a slightly distorted geometry. As can be seen in Figure 3, the tartrate

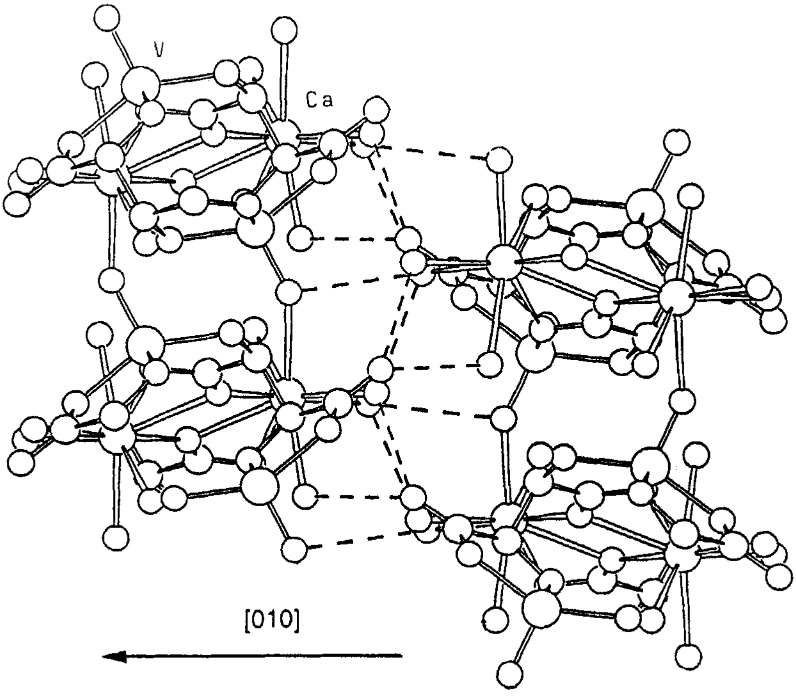

Figure 2 Schematic view of the layer arrangement of $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$ along [101].

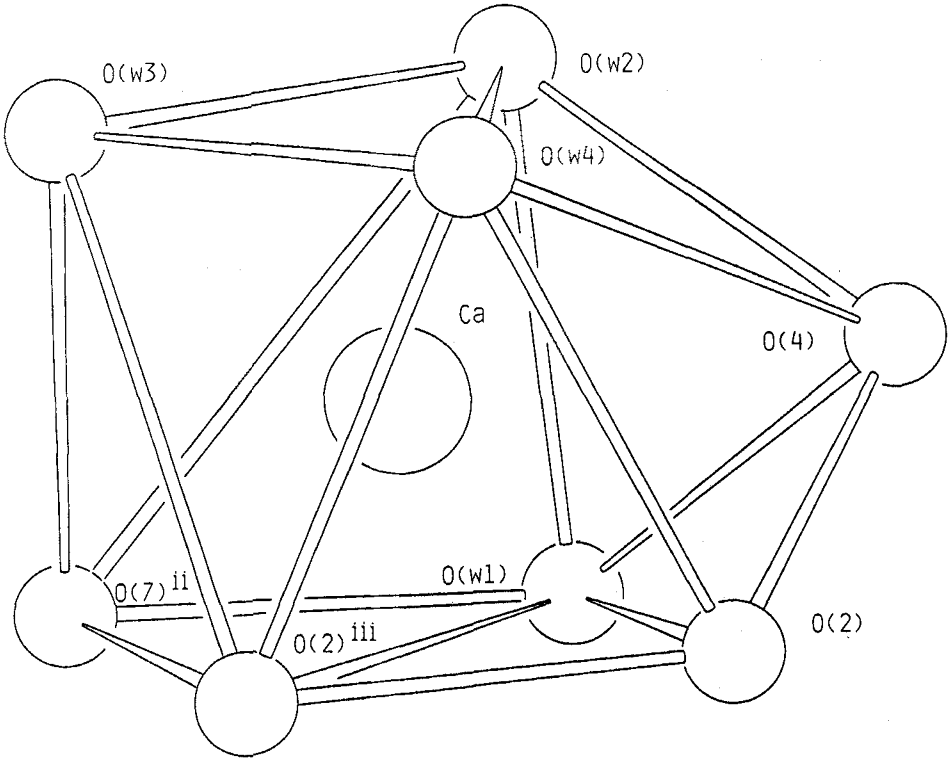

Figure 3 Coordination polyhedron of the Ca atom.

oxygen O(4) contributes most to the distortion of the polyhedron.

Finally, attention is drawn to the arrangement of the layers. They are linked by four hydrogen bonds between water molecules and the oxygen atoms of the tartrate ligand. In this sense, the water molecule H(7)-O(w3)-H(8) is bonded to two oxygens [O(w3)$\cdots$O(1)^{iv}, O(w2)^{v}; 2.789(2), 2.860(2)Å; $iv = x - 1$, $1/2 - y$, $z - 1/2$; $v = x$, $1/2 - y$, $z - 1/2$]. Another hydrogen bond is present between the water molecule H(5)-O(w2)-H(6) and the oxygen of the vanadyl group [O(w2)$\cdots$O(7)^{v}; 2.982(2)Å]. The fourth link occurs between the H(9)-O(w4)-H(10) water molecule and the oxygen atom O(1) of a neighbouring layer [O(w4)$\cdots$O(1)^{vi}; 3.017(2)Å; $vi = x - 1$, $1/2 - y$, $z + 1/2$].

Infrared spectroscopy

Interest in the infrared spectrum of the title compound lies in the bands corresponding to the vanadyl cation and the carboxyl and hydroxyl groups of the ligand. The spectrum shows analogies with the *d,l*-tartaric acid.

The band observed at 1630 cm^{-1} can be assigned to the stretching vibration of the carbonyl group. In the range 1400–1050 cm^{-1} bands corresponding to C-O single bonds can be observed at 1360 cm^{-1} and 1080 cm^{-1} corresponding to ν(C-O) of the carboxyl and hydroxyl groups, respectively.

The absence of the band due to the δ_{ip}(OH) absorption of the alcohol group is in agreement with the loss of all -OH protons as observed in the crystal structure. This band appears at 1450 cm^{-1} in the free ligand and has been also observed in vanadyl tartrate complexes where the V:L ratio is 1:2, $M(VO)(d,l\text{-}C_4H_2O_6)_2 \cdot n\ H_2O$ (M = Ca, Sr).[8]

The vanadyl group stretching vibration is clearly split into two bands. The band (centered at 970 cm^{-1}, split at 960 and 990 cm^{-1}) cannot be assigned to non-equivalent vanadyl groups[21] as can be deduced from the crystal structure. This splitting has been also observed in the corresponding compound of barium[9] and is related to the coordination of the oxygen atom of the vanadyl group to the alkaline earth atom.

Reflectance spectroscopy

The reflectance spectrum of the title compound shows three bands at 13700, 19000 and 22300 cm^{-1}. Assignment of these bands has been made following the Ballhausen and Gray model for the $[VO(H_2O)_5]^{2+}$ cation.[22] The maxima appearing in the electronic spectra of the complex have been ascribed to transitions $^2B_2 \rightarrow {}^2E(I)$, 13700 cm^{-1}; $^2B_2 \rightarrow {}^2B_1$, 19000 cm^{-1} and $^2B_2 \rightarrow {}^2A_1$, 22300 cm^{-1}. These results are in good agreement with those observed for complexes of alkali vanadyl *d,l*-tartrates. However, it is important to note the difference with the *d,d*-tartrate dimers in which the distorted trigonal bipyramidal environment of the vanadium atoms lifts the $d_{zx} - d_{yx}$ degeneracy, thus giving rise to four active bands.[10]

Electron spin resonance spectroscopy

The X-band spectrum of a polycrystalline sample shows a mean isotropic signal with g = 1.986, corresponding to a $\Delta Ms = \pm 1$ allowed transition (see Fig. 4). A weak signal is also observed with $g \cong 4$. This signal is associated with a forbidden $\Delta Ms = \pm 2$ transition, thus giving evidence of the existence of intra-dimeric interactions between vanadium atoms.

Taking into account the V-V distance obtained in the crystal structure, a calculation of the value of the dipolar interaction using the point-dipole approximation for an axially symmetric system[23] has been made. The value of zero-field-splitting obtained, D = 0.0352 cm^{-1}, is in good agreement with those observed for other related compounds (see Table 5).

Several attempts have been made to dilute the compound to search for the

Table 5 ESR data for spin-coupled dimeric vanadyl tartrate complexes.

Compound	g	D(cm^{-1})	Ref.
$Na_4[(VO)(d,l\text{-}C_4H_2O_6)]_2 \cdot 12H_2O$	1.972	0.0334	13
$Na_4[(VO)(d\text{-}C_4H_2O_6)]_2 \cdot 6H_2O$	1.973	0.0335	13
$[Ba(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$	1.980	0.0343	9
$[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$	1.986	0.0352	this work

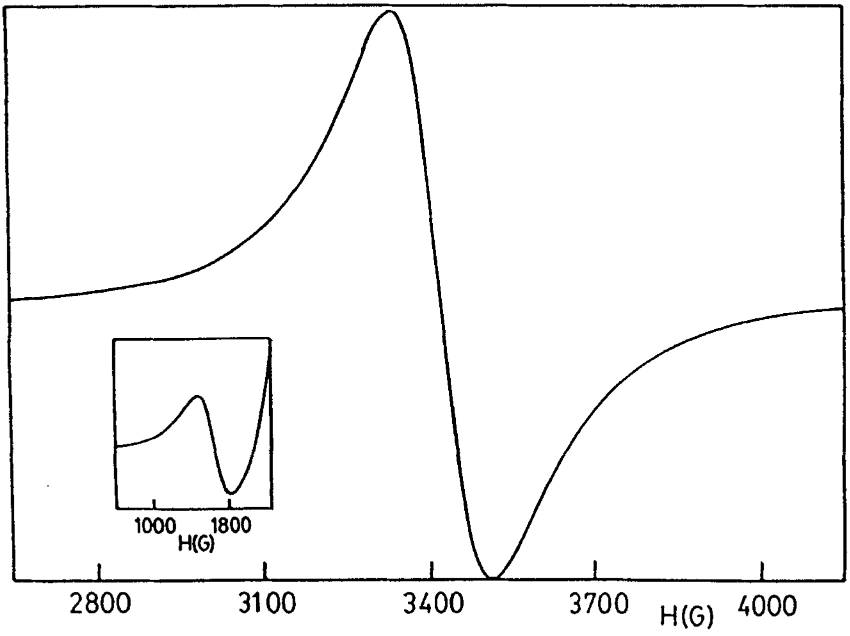

Figure 4 X band e.s.r. spectrum of a powdered sample of $[Ca(VO)(d,l\text{-}C_4H_2O_6)(H_2O)_4]$.

resolution of the axial local structure. All have failed both in solution and solid states. The signal could not be improved even at low temperature.

The covalence factor of a vanadyl compound can be evaluated with the expression:

$$g = g_e - \frac{4\lambda_{VO}\langle K\rangle^2}{3}\left(\frac{2}{\Delta_1}+\frac{1}{\Delta_2}\right)$$

where λ_{VO} is the free ion spin-orbit coupling constant (248 cm^{-1} for the vanadyl ion), $\langle K\rangle$ the covalence factor and Δ_1, Δ_2 correspond to the electronic transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E(I)$, respectively, as obtained from the reflectance spectra. The value calculated, $\langle K\rangle = 0.53$, is similar to that for other vanadyl compounds ($\cong 0.55$) and shows the high covalence of the V-O bonds in this complex.

The synthesis of suitable crystals for X-ray structure determination cannot be perfomed by common methods only diffusion techniques gave adequate crystals. The dimeric entities present in this compound are centrosymmetric and similar to those observed in alkali vanadyl *d,l*-tartrates. The presence of the calcium atom in the crystal structure favours the formation of layers constituted by chains of dimers. The neighbouring chains are linked by the calcium cation. Hydrogen bonds exist between neighbouring layers. The covalence of vanadium-oxygen bonds is slightly higher than observed in other vanadyl-tartrate compounds. Finally, it is of note that the dipolar interactions between vanadium atoms of the dimer in these alkaline earth compounds are of similar magnitude to those observed for related alkali and ammonium complexes.

Acknowledgements

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Supplementary Material

Full lists of anisotropic thermal parameters, H atom positions, H bonding parameters and observed and calculated structure factors are available from T.R.

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