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Synthesis and structural characterization of diammonium bis[octaaquastrontium] decavanadate dehydrate $(NH_4)_2[Sr(OH_2)_8]_2 .V_{10}O_{28}.2H_2O$

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Abstract: The title compound, $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ **1** , has one $[V_{10}O_{28}]^{6-}$ anion, two $[Sr(H_2O)_8{}^{2+}]$ cation, two NH_4^+ cation and two water molecules. The crystal structure of diammonium bis[octaaquastrontium] decavanadate dihydrate has been determined by single-crystal X-ray diffraction in the space group P-1. The centrosymmetric polyanion $[V_{10}O_{28}]^{6-}$ consists of five independent $[VO_6]$ octahedra sharing edges and has approximate D_{2h} symmetry. The compound is a classical isomer of decavanadate clusters, in which two centrosymmetrically related cyclic $\{V_5O_{14}\}$ units are linked by bridging oxygen atoms. NH_4^+ and $Sr(H_2O)_8^{2+}$ acting as charge-compensating cations and space-filling structural subunits, are connected to the $[V_{10}O_{28}]^{6-}$ clusters by a complex network of hydrogen interactions via water molecules.

Key words: Decavanadate, crystal structure, cyclic voltammetry

INTRODUCTION

Polyoxometalate (POM) compounds are a great interest due to a wide variety of their applications in many different fields, such as chemical catalysis, surface sciences and pharmacologiy [1]. In our investigations, the understading of the interactions of POMs in biological media and their putative enzyme inhibition mechanism is of particularly interest. Among these compounds, decavanadates are especially attractive since vanadium is important for biological metabolism [2]. Decavanadate is formally a $[V_{10}O_{28}]^{6-}$ polyanion with a cage structure giving rise to fascinating supramolecular architectures in the solid state [3].

The decavanadate anion, $[V_{10}O_{28}]^{6-}$, is a very stable and typical isopolyanion species of vanadium. Since its structure was reported by Evans [4], crystal structures of many salts have been characterized, e.g. $Cs_4[H_2V_{10}O_{28}].4H_2O$ [5] ,$(NH_4)_4Na_2[V_{10}O_{28}].10H_2O$ [6], $K_2[Zn(H_2O)_6]_2[V_{10}O_{28}].4H_2O$[4], $(NH_4)_2[Co_2[V_{10}O_{28}].16H_2O$[7], $[Na(H_2O)_3]_2[Ni(H_2O)]_2[V_{10}O_{28}].4H_2O$[8], $Na_4[Ni(H_2O)_6][V_{10}O_{28}].17H_2O$[9]. $CuNa_4V_{10}O_{28}{\cdot}23H_2O$ [10], $K_2[Co(H_2O)_6]_2[V_{10}O_{28}].4H_2O$ [11] and $Mg_2Na_2V_{10}O_{28}{\cdot}20H_2O$ [12], containing both transition metal complex and ammonium (or alkali metal) cation.

In the course of our research on the synthesis and structural characterization of novel materials containing POMs we came across the title compound $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ **1.**

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EXPERIMENTAL

1. Preparation of $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ 1

All chemicals were purchased from Aldrich and used without further purification. $Sr(NO_3)_2$ (4 mmol) and NH_4VO_3 (1 mmol) were dissolved in distilled water (20 mL) for 30 min, the pH of the solution was adjusted to 4 using a 5M aqueous solution in HCl, and the resulting mixture was stirred thoroughly for one hour. One week later, oranges crystals were grown by slow evaporation at room temperature. The EADX spectrum (figure 1) of the product confirm the formation of $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ **1**.

2. X-ray structure determination

The compound is stable under ambient conditions and one single crystal was carefully selected and glued on the end of a glass capillary. The intensities of the diffraction data were measured using an Enraf-Nonius CAD-4 diffractometer with monochromated graphite Mo Ka radiation ($\lambda = 0.71073$ Å) [13] at 293 K. The numbers of collected and independent reflections were respectively, 9597 and 7887. Unit cell dimensions were obtained by least-square refinement of the angular settings in the $2.01° < \theta < 26.07°$. The reflections were corrected for Lorentz and polarization effects; an empirical absorption correction was also applied using Ψ-scan data. The structure was successfully developed in the centrosymmetric space group P-1, solved by Patterson method using SHELXS-97 [14] and refined with anisotropic temperature factors for non-hydrogen atoms, by full matrix least-squares based on F^2 using SHELXL-97[14]. The positions of the hydrogen atoms were determined from a difference Fourier map and were refined isotropically. The final full-matrix least-squares refinement on F^2converged with R = 0.033 and $wR(F^2) = 0.0856$ for 6160 unique observed reflexions [$I > 2\sigma(I)$]. Further details of the X-ray structural analysis are given in (Table I).

Table I Crystal data and structure refinement parameters for $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$

Empirical formula	$(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$.
Formula weight ($g\ mol^{-1}$)	1420.95
Temperature (K)	298(2)
Wavelength (A°)	0.71073
Space group	P-1
Unit cell dimensions	
a (Å)	10.351(1)
b (Å)	12.621(1)
c (Å)	15.154(1)
α (°)	110.67(1)
β (°)	97.56(1)
γ (°)	95.75(1)
Cell volume ($A^{\circ 3}$)	**1813.1(3)**
Z	2
Absorption coefficient (mm^{-1})	5.496
Crystal size (mm^3)	0.20x0.15x0.10
θ range for data collection (°)	2.01-26.07
Reflections (collected/unique)	
Parameters	614
Goodness-of-fit	1.021
R indices [$I>2\sigma(I)$]	$\mathbf{R_1}$=0.034, $\mathbf{wR_2}$=0.086
R indices (all data)	R_1=0.053, wR_2=0.093
$\Delta\rho_{max}/\Delta\rho_{min}$ ($eA^{\circ 3}$)	0.823/-0.521

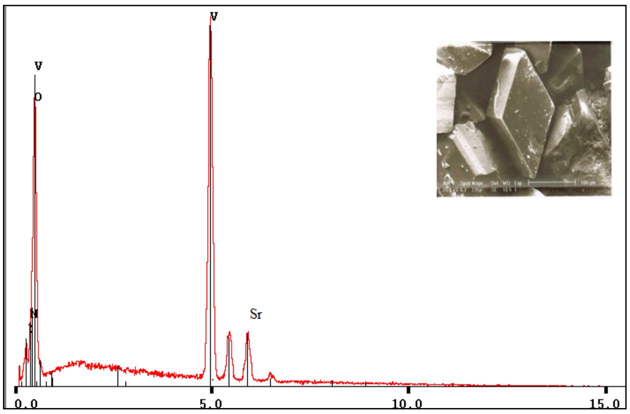

Figure 1 EADX patterns of $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ **1**

3. Infrared spectroscopy

Infrared spectra (KBr pellets; 4000-400 cm^{-1}) were recorded at a room temperature on either a Nicolet 470 FTIR spectrophotometer.

4. UV-Vis Spectroscopy

UV-Vis spectra were measured using a Perkin-Elmer Lambda 19 spectrophotometer in the 180-800 nm range using aqueous solutions.

5. Cyclic voltammetric studies

The cyclic voltammetry (CV) electrochemical measurements were carried out on CHI 660B electrochemical analyzer at room temperature. A three electrode electrochemical cell was used with a platinum as the working electrode, a platinum gauze as the counter and a saturated calomel electrode (SCE) reference electrode.

RESULTS AND DISCUSSION

1. Structure description of compound 1

As show in (figure 2), each formula unit of **1** includes one cluster of $[V_{10}O_{28}]^{6-}$anion, two $Sr(H_2O)_8^{2+}$ cations, two NH_4^+ cations and two water molecules. The centrosymmetric $V_{10}O_{28}$ cluster is composed of ten $[VO_6]$ octahedra combined via shared edges and has approximate D_{2h} symmetry. In the title anion, the oxygen atoms can be classified into four groups by the type of coordination, viz. O_t, O_b, O_c, and O_h, where O_t represents a terminal O atom bound to a V atom, O_b represents a doubly bridging O atom bound to two V atoms, O_c represents a triply bridging O atom bound to three V atoms, and O_h represents a central O atom coordinated to six V atoms.

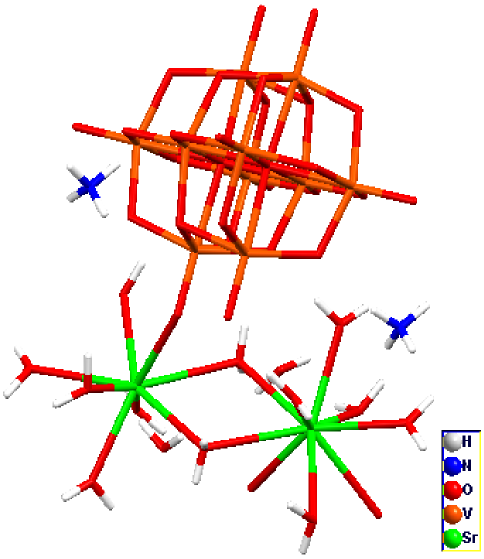

Figure. 2 Structure unit of $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ **1**

Table II Bond distances (A°) for the compound **1**

V1—O4	1.690 (3)	V6—O20	1.618 (3)
V1—O9	1.691 (3)	V6—O25	1.806 (3)
V1—O13	1.912 (3)	V6—O19	1.828 (3)
V1—O22	1.934 (3)	V6—O11	1.986 (3)
V1—O1	2.102 (3)	V6—O13	2.007 (3)
V1—O14	2.104 (3)	V6—O1	2.229 (3)
V2—O21	1.601 (3)	V7—O6	1.601 (3)
V2—O16	1.820 (3)	V7—O26	1.809 (3)
V2—O19	1.862 (3)	V7—O2	1.832 (3)
V2—O26	1.884 (3)	V7—O22	1.984 (3)
V2—O4	2.053 (3)	V7—O27	2.029 (3)
V2—O1	2.346 (3)	V7—O1	2.242 (3)
V3—O28	1.597 (3)	V8—O10	1.619 (3)
V3—O5	1.835 (3)	V8—O15	1.817 (3)
V3—O24	1.878 (3)	V8—O17	1.822 (3)
V3—O15	1.876 (3)	V8—O11	1.992 (3)
V3—O7	2.039 (3)	V8—O13	2.016 (3)
V3—O14	2.351 (3)	V8—O14	2.228 (3)
V4—O12	1.590 (3)	V9—O3	1.597 (3)
V4—O5	1.860 (3)	V9—O2	1.847 (3)
V4—O23	1.873 (3)	V9—O16	1.856 (3)
V4—O17	1.873 (3)	V9—O25	1.895 (3)
V4—O9	2.035 (3)	V9—O18	2.042 (3)
V4—O14	2.310 (3)	V9—O1	2.328 (3)
V5—O18	1.684 (3)	V10—O8	1.618 (3)
V5—O7	1.699 (3)	V10—O24	1.819 (3)
V5—O27	1.921 (3)	V10—O23	1.826 (3)
V5—O11	1.935 (3)	V10—O27	1.981 (3)
V5—O1	2.105 (3)	V10—O22	2.004 (3)
V5—O14	2.118 (3)	V10—O14	2.228 (3)

Symmety codes : (i) x, y−1, z; (ii) −x, −y−1, −z; (iii) x, y+1, z.

The V…V distances are in the range 3,0560 (2) - 3,1179(1) Å, four types of V-O bond length are in the ranges 1,590(2) - 1,618(2) Å (Ot), 1,912(2) - 2,029 (2) Å (Oc), 1,690(2) - 2,052(2) Å (Ob) and 2,101 (2) - 2,351(2) Å (Oh) (Table II). The bonds lengths and angles of $[V_{10}O_{28}]^{6-}$ show similar trends to those found in the reference literature. The framework of $[V_{10}O_{28}]^{6-}$ has been studied in detail previously by Evans [15].

The hydrated Sr^{2+} cations are coordinated by eight water molecules, forming distorted polyhedral (figure 3). The Sr -O bond length distances are ranging from 2.544 (3) to 2.843 (4) Å.

Hydrogen bonds occur between the polyanion, strontium polyhedral and the ammonium ion in the compound. (figure 4) shows the hydrogen-bonding interactions on compound **1**. The water molecules form hydrogen bonds with O atoms of the decavanadate group; there are also N-H…OW hydrogen-bond interactions. All of the O atoms on the surface of the decavanadate anion form hydrogen bonds with water molecules, except for atoms O1, O8, O14 and O20. Hydrogen bonds of the compound **1** are listed in (Table III).

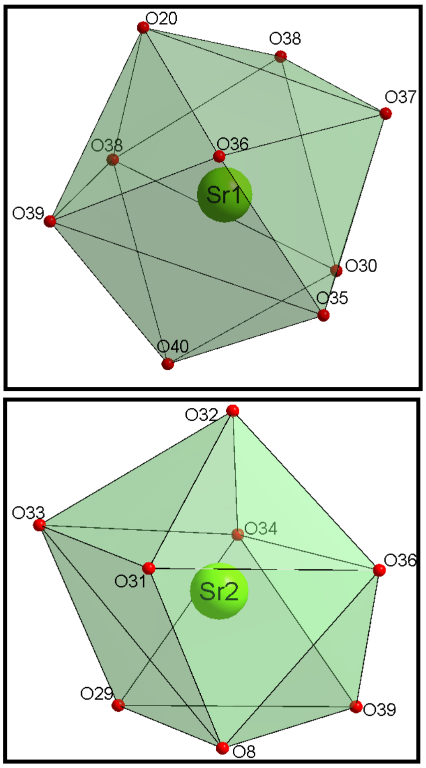

Figure.3 The strontium environments.

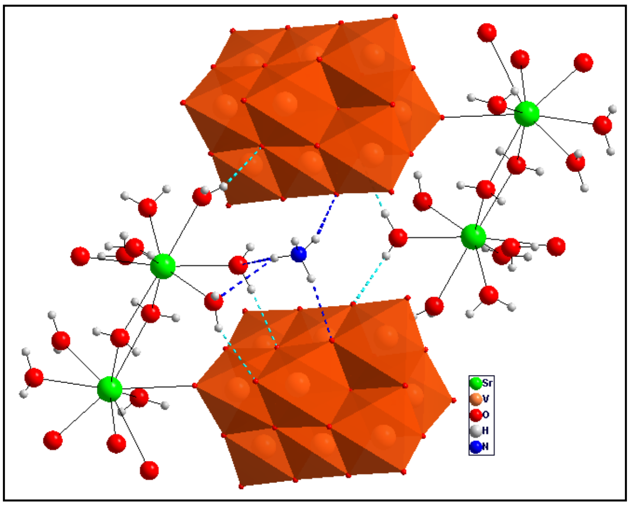

Figure.4 Hydrogen bonds between clusters.

2. Infrared spectroscopy

The FT-IR spectra of the diammonium bis [octaaquastrontium] decavanadate dihydrate is presented in (figure 5).The strong band at 966 cm^{-1} in the IR spectrum of **1** is due to the stretching vibration of the V=O groups of $[V_{10}O_{28}]^{6-}$ clusters [17], those at 837, 750 and 588 cm^{-1} can be attributed to (V–O) and (V–O –V). Broad bands around 3523 cm^{-1} could be assigned to asymmetric and symmetric O–H stretching modes of lattice water [18-21]. Whereas, the bands around 1625 cm^{-1} can be

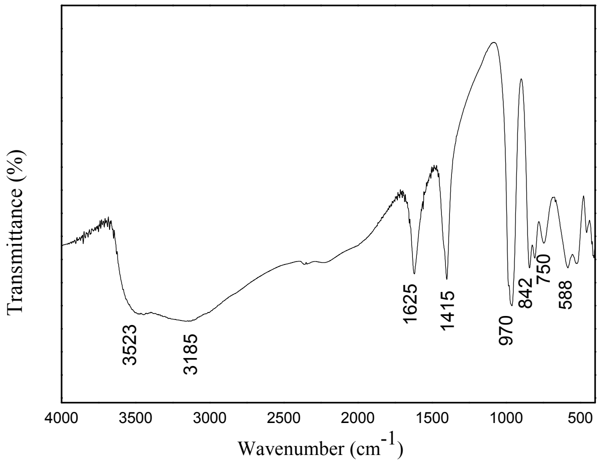

Figure.5 IR spectrum of compound **1**.

ascribed to the H–O–H bending modes. The broad absorption observed in the region around 3185 cm^{-1} and the peak at 1423 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the tetrahedral ammonium cation.

3. UV-Vis Absorption Spectra

The UV-Vis spectrum of the compound **1** was measured at room temperature. The electronic spectrum show in (figure 6), displays two absorption bands centered at 232 and 268 nm which can be attributed to $O_t \rightarrow V$

Table III Hydrogen bonds for the title compound **1**

D—H···A	D—H	H···A	D···A	D—H···A
O29—H291···O5^{iv}	0.85	2.10	2.913	160
O29—H292···O23	0.85	2.42	2.969	123
O29—H292···O24	0.85	2.36	3.010	134
O30—H301···O21^{v}	0.85	2.10	2.884	155
O30—H302···O11^{vi}	0.85	2.00	2.841	173
O31—H311···O23^{vii}	0.85	1.84	2.686	174
O31—H312···O33^{vii}	0.85	2.24	3.028	155
O32—H321···O9^{vii}	0.85	2.02	2.866	173
O32—H322···O13^{i}	0.85	1.99	2.825	167
O32—H322···O4^{i}	0.85	2.61	3.152	122
O33—H332···O28^{iv}	0.85	2.16	2.999	168
O33—H331···O22^{vii}	0.86	1.97	2.799	163
O34—H341···O10^{i}	0.84	2.04	2.784	148
O34—H342···O5^{iv}	0.85	2.07	2.867	158
O35—H351···O16^{v}	0.85	1.97	2.813	175
O35—H352···O6	0.85	2.01	2.844	168
O36—H361···O19^{i}	0.85	1.88	2.697	162
O36—H362···O2W	0.85	2.10	2.869	150
O36—H362···O35	0.85	2.60	3.042	114
O37—H372···O25^{i}	0.84	2.48	3.121	134
O37—H372···O16^{i}	0.84	2.59	3.402	162
O37—H371···O35	0.84	2.61	3.160	125
O38—H381···O1W	0.85	1.95	2.752	157
O38—H382···O25^{vi}	0.85	1.81	2.634	163
O39—H392···O24	0.85	2.03	2.835	159
O39—H391···O1W	0.85	2.02	2.806	153
O40—H401···O18^{vi}	0.85	2.19	2.987	156
O40—H402···O27	0.85	2.00	2.837	169

continued on next page ...

... from previous page **Table III** Hydrogen bonds for the title compound **1**

D—H···A	D—H	H···A	D···A	D—H···A
N1—H12···O26^{v}	0.85	2.00	2.839	170
N1—H13···O7^{vi}	0.85	2.06	2.894	169
N1—H11···O30	0.85	2.36	3.083	143
N1—H11···O40	0.85	2.53	3.206	137
N1—H11···O35	0.85	2.58	3.154	123
N1—H14···O2	0.85	1.99	2.813	165
N2—H21···O34^{vii}	0.85	2.43	3.013	126
N2—H21···O32^{vii}	0.85	2.40	3.146	148
N2—H22···O4	0.86	2.04	2.841	156
N2—H23···O15^{viii}	0.86	2.09	2.917	164
N2—H24···O17^{ix}	0.85	2.03	2.858	165
O1W—H2W1···O2W^{x}	0.85	2.42	2.884	115
O1W—H1W1···O12^{iv}	0.85	2.30	2.806	119
O2W—H1W2···O3^{v}	0.85	2.01	2.823	160
O2W—H2W2···O31	0.86	2.18	2.955	151

Symmetry codes: (i) x, y−1, z; (iv) −x, −y, −z+1; (v) −x+1, −y, −z; (vi) −x, −y, −z; (vii) −x+1, −y, −z+1; (viii) x+1, y, z; (ix) −x+1, −y+1, −z+1; (x) x−1, y, z.

BVS calculations [16] revealed that all the vanadium atoms have valence sums ranging from 5.002 to 5.009, with an average value of 5.007, close to the ideal value of 5 for V^{v}. The calculated average value of strontium (+II) atoms is 2.008 and 2.02.

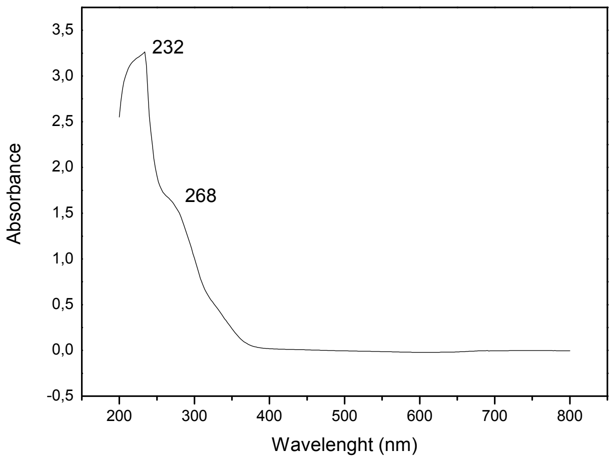

Figure.6 UV-Vis absorption spectrum of compound **1.**

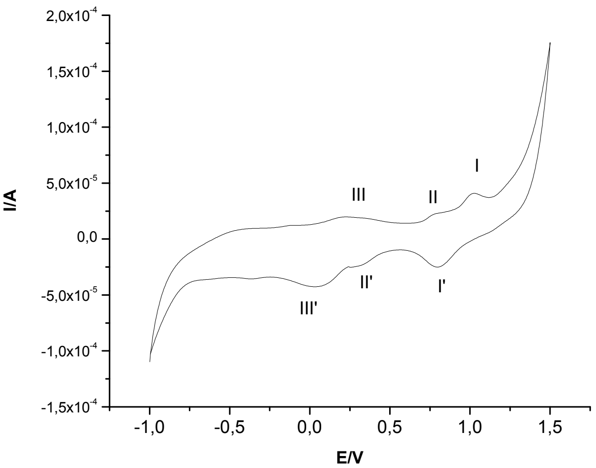

Figure.7 The Cyclic Voltammogram of **1** in distilled water at a scan rate of 50 mV s^{-1}

and $O_{b,c}\rightarrow V$ charge transfers of decavanadate [22].

4. Electrochemical Behavior

To determinate the redox properties of the compound **1**, Pt electrodes were used as the working electrode and counter electrode, the reference electrode was a Ag/AgCl electrode. As shown in (figure 7), the cyclic voltammetric behavior for **I** in distilled water exhibit three pairs of redox peak in the potential range from +1.5 to -1.0 V at scan rate 50 mV.s^{-1} which may correspond to the processes of V(IV)/V (V) [23-24]. The peak potentials [$E_{1/2}$ = (Epa+Epc)/2] are respectively 0.899, 0.525 and 0.125 V. The values of peak-to-peak separation between the corresponding anodic and cathodic peaks (ΔEp) are 0.239 (I-I'), 0.35 (II-II') and 0.21 (III-III').

CONCLUSION

To summarize, a new ammonium strontium salt of decavanadate, formulated as $(NH_4)_2[Sr(H_2O)_8]_2[V_{10}O_{28}].2H_2O$ **1**, have been successfully synthesized. The physicochemical characterization using UV and IR are reported. **1** presents a 3D network, where the decavanadate anions are linked to $[Sr(H_2O)_8]^{2+}$ group and $[NH_4]^+$ via hydrogen bonds. Cyclic voltammetry curves indicated three redox processes.

SUPPLEMENTARY MATERIAL

Further details concerning the crystal structure investigation are free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033**.** The depository number CCDC 983352

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