New diphosphopentamolybdate (VI) (C₆H₁₄N)₄(NH₄)₂[P₂Mo₅O₂₃] · H₂O synthesis, crystal structure, experimental and theoretical studies

ALI HARCHANI* and AMOR HADDAD

Laboratory of Materials, Crystal Chemistry and Applied Thermodynamics, Faculty of Sciences Monastir,
University of Monastir, 5019 Monastir, Tunisia

*Author for correspondence (ali.harchani@gmail.com)

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Abstract. The title compound (C₆H₁₄N)₄(NH₄)₂[P₂Mo₅O₂₃] · H₂O (**1**) was obtained by solution method using ammonium molybdate tetrahydrate, phosphoric acid and cyclohexylamine reagents in aqueous solution. A single-crystal X-ray diffraction study shows that the compound crystallizes in triclinic crystal system with space group P-1 and cell constants $a = 10.7178(4)$ Å, $b = 15.0809(6)$ Å, $c = 15.7745(9)$ Å, $\alpha = 71.510(6)^\circ$, $\beta = 75.508(2)^\circ$ and $\gamma = 88.493(8)^\circ$. Also, in this article, we report results of thermal, electrochemical and spectral studies. In addition, the majority of theoretical properties were carefully studied.

Keywords. Diphosphopentamolybdate; synthesis; crystal structure; physicochemical properties; theoretical study.

1. Introduction

Polyoxometalate encompasses a wide variety of oxo-transition metal anionic clusters with complex bases. In most cases the transition metals at the base of the polyoxometalates are V (V) (polyoxovanadate), Mo (VI) (polyoxomolybdate) and W (VI) (polyoxotungstate). There are four principal types of heteropolyanions structures: Lindqvist structure, Anderson structure, Keggin structure and Dawson structure. The Strandberg family is an important class of polyoxometalate and diphosphopentamolybdates (abbreviated as {P₂Mo₅}), included in this family. Recently, a series of compounds based on diphosphopentamolybdate cluster [P₂Mo₅O₂₃]⁶⁻ through the linking of organoamine bases have been reported, such as (H₂bpp)₃[P₂Mo₅O₂₃] · H₂O [1], [(C₄N₂H₁₂)₃][P₂Mo₅O₂₃] · H₂O [2], [(C₃N₂H₁₂)₃][P₂Mo₅O₂₃] · 4H₂O [2] and (C₅H₇N₂)₆[P₂Mo₅O₂₃] [3]. This type of compound has many physicochemical properties, like electrochemical, spectral and thermal properties. Also, theoretical calculation applied to these compounds gives an idea about the characteristics of interactions, energy and electronic properties of their structures.

Theoretical studies on diphosphopentamolybdate were not systematically performed in the majority of previous works; a large number of Strandberg structures were synthesized and characterized but not theoretically studied. Herein, we

focus on semi-empirical calculations employed to study this type of compounds. Hence, in this article, firstly we report the synthesis and crystal structure of title compound. Secondly, we study the Hirshfeld surface. Thirdly, we proceed to the characterization. Finally, we discuss the theoretical calculations.

2. Experimental

2.1 Materials and measurements

For the title compound, all reagents were used without purification. The infrared (IR) spectrum of (C₆H₁₄N)₄(NH₄)₂[P₂Mo₅O₂₃] · H₂O was obtained on a Perkin-Elmer Spectrum Tow ATR-FTIR at room temperature between 4000 and 400 cm⁻¹. Thermal stability analysis was performed on a SETARAM instrument Labsys Evo (thermal gravimetric (TG)-DSC, 1600°C) in dynamic air atmosphere. Cyclic voltammetry analysis was carried out using a potentiostat with three electrodes: working electrode was glassy carbon, reference electrode was Ag–AgCl and platinum wire was a counter-electrode. A Perkin-Elmer Lambda 19 spectrophotometer was used to measure UV–Vis spectra between 200 and 800 nm in aqueous solutions.

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12034-018-1561-y>) contains supplementary material, which is available to authorized users.

2.2 Synthesis

(C₆H₁₄N)₄(NH₄)₂[P₂Mo₅O₂₃]·H₂O compound was obtained by mixing ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O (0.5 mmol, 0.618 g), phosphoric acid 85% (0.25 ml) and H₂O (25 ml) in the first step. After stirring the mixture for 30 min at room temperature, cyclohexylamine (0.3 ml) was added. All reagents were stirred for 20 min at room temperature. The solution was filtered. Several days later and at room temperature, colourless crystals were grown by slow evaporation with yield of 0.423 g (68.22%).

2.3 X-ray crystallography

A single crystal of **1** of size 0.35 × 0.41 × 0.76 mm³ was used for X-ray diffraction study at 293 K on an Enraf-Nonius CAD-4 diffractometer with Mo K α radiation (λ = 0.71073 Å). The crystal structure was solved by the Patterson method with program SHELXS-2014. This method allows the location of molybdenum and phosphorus atoms. The organic atoms except hydrogen were found using the SHELXL-2014 [4] and Crystals [5] programs by successive difference Fourier maps.

The hydrogen atoms bonded to N, C and O atoms were fixed by Crystals [5] software. The crystallographic data and structure refinements are summarized in table 1.

Table 1. Crystallographic data and structure refinements.

Empirical formula	(C ₆ H ₁₄ N) ₄ (NH ₄) ₂ [P ₂ Mo ₅ O ₂₃] · H ₂ O
Formula weight (g mol ⁻¹)	1364.46
Temperature (K)	293
Wavelength (Å)	0.71073
Space group	P-1
Unit cell dimensions	
<i>a</i> (Å)	10.7178 (4)
<i>b</i> (Å)	15.0809 (6)
<i>c</i> (Å)	15.7745 (9)
α (deg)	71.510 (6)
β (deg)	75.508 (2)
γ (deg)	88.493 (8)
Cell volume (Å ³)	2337.27 (1)
<i>Z</i>	2
Absorption coefficient (mm ⁻¹)	1.46
Crystal size (mm ³)	0.76 × 0.41 × 0.35
θ range for data collection	2.1–27.0
Measured reflections	12246
Independent reflections	10169
Data/restraints/parameters	8866/0/559
Goodness-of-fit	1.25
Final <i>R</i> indices [<i>I</i> > 3 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0445, w <i>R</i> ₂ = 0.1185
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0500, w <i>R</i> ₂ = 0.1219
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	1.88/–1.31
Max. shift	$\Delta/\sigma_{\max}$ = 0.002

3. Computational details

The semi-empirical calculations of (C₆H₁₄N)₄(NH₄)₂[P₂Mo₅O₂₃]·H₂O have been performed using the Spartan 14 V1.1.4 Wavefunction molecular modelling suite package on a personal computer [6] via PM6 semi-empirical model. The PM3 and PM6 semi-empirical models have been parameterized for most transition metals, and generally provide good results of geometry optimization [6]. Computational analyses of Hirshfeld surfaces and 2D fingerprint plots [7] were carried out using the Crystal Explorer 3.1 program [8] and TONTO [9] system.

4. Results and discussion

4.1 Description of the crystal structure

As shown in figure 1, the crystal structure of compound **1** is formed by [P₂Mo₅O₂₃]⁶⁻ anions, (C₆H₁₄N)⁺, (NH₄)⁺ cations and water molecules. The polyanion [P₂Mo₅O₂₃]⁶⁻ contains five distorted edge- and corner-sharing [MoO₆] octahedra, capped on both poles by two phosphate tetrahedra. The [PO₄] tetrahedron shares three oxygen atoms with the molybdate ring (figure 2) [10]. The hydrogen bonds of (C₆H₁₄N)⁺, (NH₄)⁺ reinforce this catenary arrangement.

Each Mo atom is surrounded by six oxygen atoms. The Mo–O distances vary between 1.688 (2) and 2.4137 (19) Å and the O–Mo–O bond angles are in the range 69.09 (7)–173.28 (9)° (supplementary table S1). It should be noted that in the structure of **1**, each [MoO₆] octahedron has four bridge oxygen atoms and two terminal oxygen atoms. The distances between phosphorus and oxygen atoms (P–O) vary in the range 1.5134 (19)–1.5729 (19) Å and O–P–O bond angles are in the range 105.11 (11)–112.82 (11)° (supplementary table S1).

In compound **1**, two ammonium cations and four cyclohexylamine cations are protonated and have +1 charge, which play an important role in the formation of the framework. There are many types of hydrogen bonds and the majority of them are formed between the terminal oxygen atoms of the diphosphopentamolybdate and the hydrogen atoms of the amine groups. N...O, C...O, O...O, N...N and C...N distances are presented in table 2. The complex network of hydrogen bonds makes the crystal structure of title compound more stable.

4.2 Optimized structure

The optimized geometry of the title compound is illustrated in supplementary figure S1. In the optimized molecular structure of title compound, as seen from supplementary table S1 and figure 3, most of the optimized and experimental bond lengths and angles values are slightly different. These differences between values may originate from the fact that

Figure 1. View of compound 1.

Figure 2. View of $[P_2Mo_5O_{23}]^{6-}$ anion.

the experimental data are obtained in the solid state, while the calculated values refer to isolated molecules without considering lattice interactions. In general, observed and calculated parameters are in good agreement.

4.3 Hirshfeld surface analysis

The Hirshfeld surfaces analysis [11] was performed to clarify the intermolecular interactions in a visual manner and to understand the role of the organic base and water molecules in structural propagation. The normalized contact distance d_{norm} is based on d_e (distance from the point to the nearest

nucleus external to the surface) and d_i (distance to the nearest nucleus internal to the surface).

The d_{norm} , d_e and d_i surfaces of $(C_6H_{14}N)_4(NH_4)_2[P_2Mo_5O_{23}] \cdot H_2O$ are shown in figure 4. For this diphosphopentamolybdate, the 3D d_{norm} surfaces were mapped over a fixed colour scale of -0.943 (red) to 1.972 (blue) and the dominant interactions between the terminal oxygen atoms of the diphosphopentamolybdate and the hydrogen atoms of the amine group can be seen in the middle of the Hirshfeld surface as the deep red areas. Also, the light red areas on the surface correspond to the $OW-H \cdots O$ interactions.

The 2D fingerprint plots (figure 5) provide us information about these intermolecular interactions. From the plots

Table 2 Hydrogen-bond geometry (Å, deg).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 $\cdots$ O11	0.889	2.085	2.935 (10)	159.62 (18)
N1—H2 $\cdots$ O1 ⁱ	0.877	1.982	2.858 (10)	176.62 (18)
N1—H3 $\cdots$ O9	0.892	1.946	2.806 (10)	161.54 (19)
N2—H15 $\cdots$ O7 ⁱⁱ	0.862	2.067	2.925 (10)	174.06 (19)
N2—H16 $\cdots$ O19	0.878	2.230	3.021 (10)	149.68 (18)
N2—H16 $\cdots$ O23	0.878	2.475	3.092 (10)	127.81 (18)
N2—H17 $\cdots$ O18 ⁱⁱⁱ	0.895	2.148	2.985 (10)	155.32 (18)
C7—H18 $\cdots$ O8 ⁱⁱ	0.996	2.386	3.139 (10)	131.76 (19)
N3—H29 $\cdots$ O18	0.961	2.376	3.261 (10)	153.0 (2)
N3—H30 $\cdots$ O14	0.957	2.026	2.981 (10)	176.0 (2)
N3—H31 $\cdots$ O8 ^{iv}	0.952	1.856	2.806 (10)	176.7 (2)
N4—H43 $\cdots$ O12 ⁱⁱ	0.943	2.093	2.779 (10)	128.5 (5)
N4—H44 $\cdots$ O23	0.945	2.005	2.944 (10)	172.1 (4)
N4—H45 $\cdots$ O17 ⁱⁱ	0.983	2.391	3.239 (10)	144.1 (3)
C19—H46 $\cdots$ O3	0.966	2.359	3.310 (10)	168.0 (6)
N5—H59 $\cdots$ N3	0.956	2.185	2.911 (10)	131.8 (2)
N6—H61 $\cdots$ O18 ^v	0.956	1.914	2.738 (10)	142.9 (6)
N6—H62 $\cdots$ O5	0.974	2.063	2.885 (10)	141.0 (5)
N6—H63 $\cdots$ O7	0.981	2.098	2.939 (10)	142.6 (5)
OW1—H65 $\cdots$ O5	0.927	2.238	2.821 (10)	120.3 (5)
OW1—H66 $\cdots$ O20 ^v	0.961	2.115	2.908 (10)	138.8 (5)
OW2—H47 $\cdots$ O20 ^v	0.954	1.922	2.669 (10)	133.4 (7)
OW2—H48 $\cdots$ O3	0.992	2.387	3.315 (10)	155.5 (7)
C20—H68 $\cdots$ N6	0.956	2.372	3.098 (10)	132.3 (4)

Symmetry codes: (i) $-x, -y+2, -z$; (ii) $-x, -y+2, -z+1$; (iii) $-x-1, -y+2, -z+1$; (iv) $x-1, y, z$ and (v) $x+1, y, z$.

it is revealed that the $H \cdots H$ (52.5%) bonding appears to be a major contributor in the crystal packing, whereas the $O \cdots H/H \cdots O$ (44.3%) and $O \cdots O$ (3.2%) contacts have their significant contribution to the total area of the surface. Also, the shape index and curvedness are illustrated in figure 5.

4.4 Vibrational study

The IR spectra of **1** (supplementary figure S2) have been recorded in the range of frequencies 4000–400 cm^{-1} , which shows many bands in the range of 3500–2900 cm^{-1} attributed to O–H stretching of water molecules, and also N–H and C–H stretching vibrations [12]. The frequencies between 1530 and 1340 cm^{-1} are assigned to the C–N and C–C stretching vibrations of the organic part [13]. Remaining bands between 1650 and 1100 cm^{-1} are associated to O–H bending of water molecules, and also N–H and C–H bending vibrations [2,14]. The compound also possesses bands in 1100–1020 cm^{-1} region attributed to $\nu(\text{P}=\text{O})$ [15]. Bands at 937, 910, 884, 797, 683, 507 and 498 cm^{-1} are ascribed to $\nu(\text{Mo}-\text{O}_i)$ and $\nu(\text{Mo}-\text{O}-\text{Mo})$ [15,16].

4.5 Thermal analysis

In order to examine the thermal stability of compound **1** their TGA and DTA were carried up to 800°C (figure 6). The TG curve for **1** exhibits three steps of mass loss. The first weight loss (31–120°C) is 1.57% (calculated is 1.32%). This weight loss corresponds to the removal of all water molecules. In this range, the DTA curve shows an endothermic peak. The second loss of 31.80% that occurs between 210 and 550°C (calculated is 31.95%) can be attributed to the decomposition of the organic amines (two endothermic peaks and one exothermic peak). The third weight loss starts after 550°C.

4.6 Electrochemical behaviour

To study the electrochemical phenomena of the title compound, the cyclic voltammetry of **1** was carried out in 0.9 M H_2SO_4 aqueous solution. Figure 7 shows the cyclic voltammogram of **1**. In the potential range from 0 to +1 V, two reversible redox peaks appear and the peak potentials

Figure 3. Correlation graphics of calculated and experimental molecular bond lengths and bond angles of $(\text{C}_6\text{H}_{14}\text{N})_4(\text{NH}_4)_2[\text{P}_2\text{Mo}_5\text{O}_{23}] \cdot \text{H}_2\text{O}$ compound.

Figure 4. Hirshfeld surfaces mapped with *dnorm*, *none*, *d_e*, *d_i*, shape index and curvedness of **1**.

$E_{1/2} = (E_{pa} + E_{pc})/2$ are +0.391 V (I) and 0.225 V (II). The two redox peaks I–I' and II–II' are attributed to two consecutive one-electron processes [14]. These mean peak potentials are in good consistency with those of known diphosphopentamolybdate. The results exhibit that the redox ability of the cluster can be maintained in $(C_6H_{14}N)_4(NH_4)_2[P_2Mo_5O_{23}] \cdot H_2O$ compound, which makes it have a potential application in electrochemistry.

4.7 UV–Vis spectra

The UV spectrum of **1** in the aqueous solution has been obtained in the range of 200–800 nm (figure 8) and reveals

two absorption peaks at 210 and 234 nm. The first at 210 nm corresponds to the charge transfer absorption of $O_t \rightarrow Mo$ LMCT bands and the second absorption peak at 234 nm is ascribed to the charge transfer $O_{b,c} \rightarrow Mo$ [17,18]. Using the limit value of absorption (270 nm) the optical energy gap (E_g) was calculated, and its value is 4.59 eV. Hence, this polyanion can be classified among insulators.

4.8 Frontier molecular orbital analysis

This analysis result is one of the important theoretical properties. Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and their energy gap

Figure 5. 2D fingerprint plots of 1.

Figure 6. The two curves corresponding to the DTA and TGA analysis of compound 1.

are very useful to determine the ability of a molecule to absorb light and they help identify the chemical stability and reactivity of the molecule [19]. Hence, it can play an important role in the electronic properties, corrosion inhibition of metal surfaces and interactions [20].

The map of frontier molecular orbitals (FMOs) of the title molecule is illustrated in figure 9. The HOMO and LUMO of our compound are localized over the Strandberg clusters. The energy values of HOMO and HOMO-1 are -9.67 and -9.70 eV, respectively. The energy values of LUMO and

Figure 7. Cyclic voltammogram of compound 1 in 0.9 mol l⁻¹ H₂SO₄ solution at a scan rate of 100 mV s⁻¹.

LUMO+1 are -0.76 and -0.50 eV, respectively. From these values, we can calculate the energy gap of the title compound. Hence, for HOMO → LUMO, $\Delta E = 8.91$ eV and for HOMO-1 → LUMO+1, $\Delta E = 9.2$ eV. The cause of the difference between the experimental and theoretical may be the effect of the isolation of the structure in the calculation. According to these results, (C₆H₁₄N)₄(NH₄)₂[P₂Mo₅O₂₃] · H₂O cannot be classified as a semiconductor.

Figure 8. UV-Vis absorption spectrum of compound 1.

To visualize relative polarity and active sites of molecules, we can use molecular electrostatic potential (MEP) and electron density (ED), because they are very effective in the investigation of the molecular structure to show the reactivity

of the molecule and it provides a visual method to study the relative polarity [21].

The 3D mapped surfaces of the MEP and ED are shown in figures 10 and 11, respectively. According to the MEP map, the different values at the surface are represented by different colours. The negative potential red regions are mainly localized over the terminal oxygen atoms of diphosphopentamolybdate anion. These regions are susceptible for electrophilic attack in the title compound. The regions around hydrogen atoms of water molecules and N-H of cyclohexylamine cation are the positive blue regions and they indicate possible sites for nucleophilic attack. There is a predominance of light green, yellow and orange regions in the MEP surfaces relative to a potential half-way between the two extreme red and blue colours.

4.9 Mulliken atomic charge

The calculation of atomic charges is one of the most important quantum mechanical calculations for many reasons. It plays a significant role in electronic structure and

Figure 9. Frontier molecular orbital plots of 1.

Figure 10. (a) Molecular electrostatic potential and (b) contours in the property range -200 to 200 kJ mol^{-1} .

molecular properties of compound such as dipole moment and polarizability [22]. Also, it is very useful to illustrate the process of equalization of transfer of charge and electronegativity in chemical reactions [23,24]. Mulliken charges were calculated by determination of the electron population of each atom as defined in the basis function. Atomic charges on the various atoms are obtained by Mulliken population analysis [19].

The atomic charges of all atoms are given in supplementary table S2. It can be seen that phosphorus P2 has the most positive Mulliken charge and oxygen O22 has the most negative charge. According to the results, it can be seen that molybdenum, phosphorus and hydrogen atoms have a positive charge. Remaining atoms, except C1, C7, C13 and C19 carbon atoms, have a negative charge.

4.10 Thermodynamic properties

The theoretical thermodynamic properties have a great importance in the materials studies. These properties provide helpful information for the study of thermodynamic energies and to estimate directions of chemical reactions according to the laws of thermodynamics in thermochemical field [25].

Figure 11. (a) Electron density and (b) contours of title compound.

Table 3. Thermodynamic properties at the PM6 level of $(\text{C}_6\text{H}_{14}\text{N})_4(\text{NH}_4)_2[\text{P}_2\text{Mo}_5\text{O}_{23}] \cdot \text{H}_2\text{O}$ at 298.15 K and 1.00 atm.

Parameters	Values
Zero point energy ZPE (kJ mol^{-1})	2460.46
Enthalpy H°	
Total (kJ mol^{-1})	2635.54
Translational (kJ mol^{-1})	3.71
Rotational (kJ mol^{-1})	3.71
Vibrational (kJ mol^{-1})	165.16
Heat capacity C_v	
Total ($\text{J mol}^{-1} \text{K}^{-1}$)	834.30
Translational ($\text{J mol}^{-1} \text{K}^{-1}$)	12.47
Rotational ($\text{J mol}^{-1} \text{K}^{-1}$)	12.47
Vibrational ($\text{J mol}^{-1} \text{K}^{-1}$)	809.36
Entropy S°	
Total ($\text{J mol}^{-1} \text{K}^{-1}$)	1344.46
Translational ($\text{J mol}^{-1} \text{K}^{-1}$)	198.93
Rotational ($\text{J mol}^{-1} \text{K}^{-1}$)	170.69
Vibrational ($\text{J mol}^{-1} \text{K}^{-1}$)	974.83

Table 4. Thermodynamic properties at different temperatures at PM6 level of $(C_6H_{14}N)_4(NH_4)_2[P_2Mo_5O_{23}] \cdot H_2O$.

T (K)	H_m° (kJ mol ⁻¹)	S_m° (J mol ⁻¹ K ⁻¹)	$C_{p,m}^\circ$ (J mol ⁻¹ K ⁻¹)
100	2723.57	707.98	413.52
200	2685.91	1072.17	646.05
298.15	2635.54	1344.47	834.31
300	2634.47	1349.14	838.14
400	2570.57	1581.74	1051.54
500	2495.99	1787.96	1229.13
600	2411.98	1970.42	1353.21
700	2319.7	2136.26	1415.97
800	2220.16	2288.79	1457.87
900	2113.96	2431.69	1497.93
1000	2003.31	2566.86	1535.98

Figure 12. Variation in thermodynamic parameters with temperature for **1**.

The thermodynamic functions at 298.15 K and 1.00 atm such as zero point energy (ZPE), enthalpy (H°), heat capacity (C_V) and the entropy (S°) for $(C_6H_{14}N)_4(NH_4)_2[P_2Mo_5O_{23}] \cdot H_2O$ are calculated and are listed in table 3. Also, the statistical thermochemical analyses are calculated from 100 to 1000 K on the basis of vibrational analysis and listed in table 4. The correlation graphs are shown in figure 12. Also, the correlation equations between these thermodynamic properties and temperature T are as follows:

$$H_m^\circ = 2738.89 - 0.11T - 7.93 \times 10^{-4}T^2 \quad (R^2 = 0.99006), \quad (1)$$

$$S_m^\circ = 29.10 + 6.29T - 6.3 \times 10^{-3}T^2 \quad (R^2 = 0.98765), \quad (2)$$

$$C_{p,m}^\circ = 24.94 + 3.35T - 2.14 \times 10^{-3}T^2 \quad (R^2 = 0.952979). \quad (3)$$

5. Conclusion

$(C_6H_{14}N)_4(NH_4)_2[P_2Mo_5O_{23}] \cdot H_2O$ has been synthesized and its structure solved by single-crystal X-ray diffraction and

characterized by spectroscopy (IR and UV spectrum). Also, the structure was optimized geometrically and in general, observed and calculated parameters are in good agreement. The Hirshfeld surface analysis was carefully studied. The thermal stability and electrochemical properties of the title compound were reported. The theoretical calculation confirms the existence of many types of hydrogen bonds and this calculation leads to several properties such as FMO, MEP, ED, Mulliken atomic charge and thermodynamic properties.

Supplementary information

CCDC 1455057 contains the supplementary crystallographic data for **1**. These data can be obtained freely via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting directly the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033).

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