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COMMUNICATION

From a versatile arsenotungstate precursor to a large lanthanide-containing polyoxometalate-carboxylate hybrid

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A large, lanthanide-containing polyoxometalate-carboxylate hybrid $K_{14}Li_4H_{20}[As_6W_{58}O_{206}Ce_4(pydc)_2(H_2O)_6] \cdot 44H_2O$ (1**), $H_2pydc = \text{pyridine-2,3-dicarboxylic acid}$ was synthesized from the versatile precursor $[As_2W_{19}O_{67}(H_2O)]^{14-}$ through combined disassembly and reassembly processes. The novel macroanion in **1** is constituted of two identical subunits with the formula $[As_3W_{29}O_{103}Ce_2(pydc)(H_2O)_3]^{19-}$.**

Among the multitude of polyoxometalate (POM) structural motifs, the lanthanide (Ln)-containing tungstoarsenates have been attracting increasing attention because they offer particularly interesting features, such as magnetism, luminescence, sorption and catalysis. In this research field, the simple materials $Na_2WO_4 \cdot 2H_2O$ and As_2O_3 or the precursor $[AsW_9O_{33}]^{9-}$ have often been used to assemble various POM-based Ln clusters, such as $[As_{12}W_{148}O_{524}Ce_{16}(H_2O)_{36}]^{76-}$,^{1a} $[Gd_6As_6W_{65}O_{229}(OH)_4(H_2O)_{12}(OAc)_2]^{38-}$,^{1b} $[Yb_{10}As_{10}W_{88}O_{308}(OH)_8(H_2O)_{28}(OAc)_4]^{40-}$,^{1b} $[Ce_4As_4W_{44}O_{151}(\text{alanine})_4(OH)_2(H_2O)_{10}]^{12-}$,^{1c} $[K\{Eu(H_2O)_2(AsW_9O_{33})\}_6]^{35-}$,^{1d} the series $[Cs\{Ln_6As_6W_{63}O_{218}(H_2O)_{14}(OH)_4\}]^{25-}$ ($Ln = Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, \text{ and } Er^{III}$),^{1e} and so on. Whereas, POM-based analogues containing other Ln cations cannot be prepared *via* similar synthetic route. To achieve this aim, new versatile POM building blocks must be explored. The dilacurary polyanion $[As_2W_{19}O_{67}(H_2O)]^{14-}$ (abbreviated to $\{As_2W_{19}\}$) as an important and versatile precursor, which was proposed by Tourné in the 1970,² and then its structural characterization was reported by Kortz,³ can combine Ln cations forming some large and unpredictable tungstoarsenates, for example the clusters $\{As_4W_{38}Tb_8\}$,⁴ $\{As_4W_{41}Nd_3\}$,⁵ $\{As_4W_{44}Ln_6\}$,⁶ $\{As_5W_{40}Ln_4\}$,⁷ $\{As_6W_{42}Y_6\}$,⁸ $\{As_{12}W_{124}Gd_8\}$,⁹ $\{As_{16}W_{164}Ln_{16}\}$,¹⁰ and their properties such as magnetism and photoluminescent have also been studied. However, in these reported compounds, little work has been devoted to the organic-inorganic Ln-containing tungstoarsenates.^{4,6,7} As a result, the design of novel organic-inorganic analogues remains a challenge. Herein we report the synthesis and structural characterization of a large Ln-containing POM-carboxylate hybrid $K_{14}Li_4H_{20}[As_6W_{58}O_{206}Ce_4(pydc)_2(H_2O)_6] \cdot 44H_2O$ (**1**), $H_2pydc = \text{pyridine-2,3-dicarboxylic acid}$.

The synthesis of **1** was achieved in a one-pot reaction starting from 1:2.4:3 ratio of $\{As_2W_{19}\} : CeCl_3 \cdot 7H_2O : H_2pydc$ in the presence of

$LiCl$.¹¹ Compared with those Ln-based tungstoarsenates originated from the precursor $\{As_2W_{19}\}$,⁴⁻¹⁰ we found that pH value, organic ligand and Ln cation all play important roles in the formation and crystallization of them. Firstly, the pH value of **1** was adjusted to 6 with 1M LiOH, which is higher than that of other representative tungstoarsenates.⁴⁻¹⁰ Parallel experiments revealed that too high and too low pH value of the system all could not lead to the formation of **1**. Secondly, when the H_2pydc was replaced by pyridine-2,5-dicarboxylic acid, a series of Ln-based POM-carboxylate compounds $[Ln_2(H_2O)_6\{As_2W_{19}O_{68}\}\{WO_2(C_7NO_4H_4)\}_2]^{8-}$ were isolated, which have been prepared in another article. Thirdly, when the Ce^{3+} cation was replaced by other Ln cations in the same condition, no analogues were isolated. Therefore, systematic exploration on this system still remains a great interest to us, and this work is in progress. Furthermore, it should be noted that: (1) the presence of Li^+ appears to promote the formation of **1**, probably as a consequence of the increased solubility of the polyanion building blocks, instances of similar structural dependence on the cation have been reported for POMs;^{4,12} (2) during the evaporation process of the resulting solution, plenty of precipitates were generated continually, which should be filtered without delay, otherwise, no crystals formed. This is because nucleophilic polyoxoanions are liable to form precipitates rather than crystals when they react with oxyphilic Ln^{III} ions under conventional aqueous solutions; similar phenomenon has been previously encountered.¹³

The precursor $\{As_2W_{19}\}$ is essential for the synthesis of **1**, this dilacurary POM consists of two $[AsW_9O_{33}]^{9-}$ subunits that are connected by a WO_6 octahedron and its flexible isomerization behaviour at low pH values in combination with alkali cations is a good prerequisite for the formation of large Ln-containing POMs.^{4,9} In the preparation of **1**, the precursor $\{As_2W_{19}\}$ must undergo a series of disassembly reassembly processes that are highly sensitive to variation in reaction conditions, giving rise to compounds that contain $\{\alpha-AsW_9O_{33}\}$ POM subunits held together by other structural components, including extra tungstate fragments that have arisen from partial decomposition of the precursor. Balanced chemical reaction for the formation of **1** is presented in eqs 1.

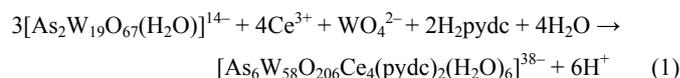


Figure 1 insert here

Figure 1. (a) Polyhedral and ball-and-stick representation of the macroanion $[\text{As}_6\text{W}_{58}\text{O}_{206}\text{Ce}_4(\text{pydc})_2(\text{H}_2\text{O})_6]^{38-}$ in **1**, symmetry transformation: $A = 1-x, -y, 1-z$; (b) Polyhedral and ball-and-stick representation of $\{\text{Ce}_2\text{As}_3\text{W}_{29}\}$ subunit in **1**. $\{\text{WO}_6\}$ in $\{\alpha\text{-AsW}_9\text{O}_{33}\}$ unit, yellow/green/purple octahedra; all the lattice water molecules, H^+ , K^+ have been omitted for clarity.

Single crystal X-ray diffraction analysis indicates that **1** consists of a macro polyoxoanion $[\text{As}_6\text{W}_{58}\text{O}_{206}\text{Ce}_4(\text{pydc})_2(\text{H}_2\text{O})_6]^{38-}$, 44 lattice water molecules, 14 counter K^+ ions and 20 protons based on charge balance. The large, POM-carboxylate polyanion $[\text{As}_6\text{W}_{58}\text{O}_{206}\text{Ce}_4(\text{pydc})_2(\text{H}_2\text{O})_6]^{38-}$ in **1** is constructed from two identical subunits with the formula $[\text{As}_3\text{W}_{29}\text{O}_{103}\text{Ce}_2(\text{pydc})(\text{H}_2\text{O})_3]^{19-}$ (abbreviated to $\{\text{Ce}_2\text{As}_3\text{W}_{29}\}$), which are linked together by four Ce–O–C bonds constituting a staggered pattern (Figure 1a, Figure S1). The macro polyoxoanions $[\text{As}_6\text{W}_{58}\text{O}_{206}\text{Ce}_4(\text{pydc})_2(\text{H}_2\text{O})_6]^{38-}$ connect each other by K^+ ions building a beautiful 3D structure (Figure S2). In **1**, each $\{\text{Ce}_2\text{As}_3\text{W}_{29}\}$ cluster contains two Ce^{3+} , a pydc ligand and a $\{\text{As}_3\text{W}_{29}\}$ building block, which can be compared to $\{\text{As}_3\text{W}_{30}\}$ building block in $[\text{As}_6\text{W}_{65}\text{O}_{217}(\text{H}_2\text{O})_7]^{26-}$ reported by Kortz.³ However, there are significant differences from it: (1) $\{\text{As}_3\text{W}_{30}\}$ is constructed from an $\{\alpha\text{-AsW}_9\text{O}_{33}\}$ unit and two $\{\beta\text{-AsW}_9\text{O}_{33}\}$ units, whereas $\{\text{As}_3\text{W}_{29}\}$ in **1** contains three identical $\{\alpha\text{-AsW}_9\text{O}_{33}\}$ units; (2) the $\{\alpha\text{-AsW}_9\text{O}_{33}\}$ unit and two $\{\beta\text{-AsW}_9\text{O}_{33}\}$ units in $\{\text{As}_3\text{W}_{30}\}$ connect each other by three additional tungsten atoms forming a closed structure, but in $\{\text{As}_3\text{W}_{29}\}$, three identical $\{\alpha\text{-AsW}_9\text{O}_{33}\}$ units are linked to each other through two tungsten atoms (W(10) and W(20)) and a cerium atom (Ce(1)) (Figure 1b). It is notable that two cerium cations in **1** exhibit distinct geometry configurations. $\text{Ce}(1)^{3+}$ is in a distorted monocapped square-antiprismatic geometry (Figure 2a), which is defined by six terminal oxygen atoms from a $\{\text{As}_3\text{W}_{29}\}$ cluster [Ce(1)–O: 2.503(16)–2.600(16) Å], a carboxyl oxygen atom [Ce(1)–O: 2.545(18) Å] and a nitrogen atom [Ce(1)–N: 2.66(2) Å] from a pydc ligand, and a terminal water ligand [Ce(1)–O: 2.508(19) Å]. Differently, $\text{Ce}(2)^{3+}$ is ten-coordinate and adopts a distorted, bicapped square-antiprismatic geometry (Figure 2b), which bonds to four terminal oxygen atoms from a $\{\text{As}_3\text{W}_{29}\}$ cluster [Ce(2)–O: 2.408(16)–2.464(15) Å], four carboxyl oxygen atoms [Ce(2)–O: 2.648(18)–2.678(19) Å] from two pydc ligands, and two terminal water ligands [Ce(2)–O: 2.602(18)–2.628(16) Å]. Bond valence sum calculations¹⁴ are consistent with tungsten (VI) and cerium (III), and no localized protonation of the oxo ligands on the POM.

The X-ray powder diffraction pattern of **1** is in good agreement with the simulated pattern based on the single-crystal solution (Figure 3a), indicating the phase purity of the product. The differences in intensity may be due to the preferred orientation of the

Figure 2 insert here

Figure 2. (a) Monocapped square-antiprismatic geometry of $\text{Ce}(1)^{3+}$ in **1**; (b) bicapped square-antiprismatic geometry of $\text{Ce}(2)^{3+}$ in **1**, symmetry transformation: $A = 1-x, -y, 1-z$.

powder samples.

In the IR spectrum of compound **1** (Figure 3b), characteristic vibration patterns in the low-wavenumber region ($\nu < 1000 \text{ cm}^{-1}$) derived from the polyoxoanion frameworks are observed. The peak at 946 cm^{-1} can be assigned to the W=O stretching vibration, peaks at 865 and 793 cm^{-1} correspond to the two types of W–O–W stretching vibrations, and the peak at 716 cm^{-1} can be assigned to the W–O(–As) stretch.⁷ These characteristic peaks are redshifted by $3\text{--}35 \text{ cm}^{-1}$ in comparison with the precursor $\{\text{As}_2\text{W}_{19}\}$ ($951, 891/796$ and 751 cm^{-1}). The most likely reason for this is that the rare metal complexes have stronger interactions with the oxygen atoms of the

polyoxoanion, which impairs the W–O bond, reduces the W–O bond force constant, and leads to the decrease of the W–O vibration frequency. Additionally, the resonances at $1394\text{--}1467 \text{ cm}^{-1}$ and $1557\text{--}1629 \text{ cm}^{-1}$ are assigned to the symmetric stretching vibration and asymmetric stretching vibration of the carboxylate groups,^{12b} which have a shift to some extent comparing with free H_2pydc ligand, indicating that the free H_2pydc ligand coordinate to the Ce^{3+} cation. From Figure 3b, we found that the characteristic vibration frequencies of **1** were distinct with those of $\text{Na}_9[\alpha\text{-AsW}_9\text{O}_{33}] \cdot 19\text{H}_2\text{O}$ ($933, 900, 780$ and 722 cm^{-1}), though the macro polyoxoanions $[\text{As}_6\text{W}_{58}\text{O}_{206}\text{Ce}_4(\text{pydc})_2(\text{H}_2\text{O})_6]^{38-}$ in **1** is constructed from six identical $\{\alpha\text{-AsW}_9\text{O}_{33}\}$ units.

The UV spectrum of **1** displays two weak peaks at about 220 and 250 nm (Figure 3c), which are associated with the charge-transfer bands corresponding to $\text{O}_t \rightarrow \text{W}$ and $\text{O}_{b,c} \rightarrow \text{W}$, respectively, suggesting the presence of the polyoxoanions.

The thermal property of **1** was measured in an N_2 flow with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 25 to $800 \text{ }^\circ\text{C}$. The TG curve of **1** (Figure 3d) indicates two weight-loss steps, which are associated with the loss of lattice water molecules, coordination water molecules, constitutional water molecules, pydc ligands and As_2O_3 with a total loss of 12.02 % (calcd. 11.91 %). The first weight loss of 5.34 % between 25 and $336 \text{ }^\circ\text{C}$ corresponds to the loss of 44 lattice water molecules and 6 coordination water molecules (calcd. 5.36 %). On further heating, the materials lose weight continuously during the second step with a combined weight loss of 6.68 % from 336 to $800 \text{ }^\circ\text{C}$, which corresponds to the decomposition of 2 pydc ligands, 10 constitutional water molecules and 3 As_2O_3 molecules (calcd. 6.55 %).

Conclusions

In conclusion, from the versatile precursor $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ through combined disassembly and reassembly processes, a large, Ln-containing POM-carboxylate hybrid $\text{K}_{14}\text{Li}_4\text{H}_{20}[\text{As}_6\text{W}_{58}\text{O}_{206}\text{Ce}_4(\text{pydc})_2(\text{H}_2\text{O})_6] \cdot 44\text{H}_2\text{O}$ (**1**) was obtained. The novel macroanion in **1** consists of two identical subunits with the formula $[\text{As}_3\text{W}_{29}\text{O}_{103}\text{Ce}_2(\text{pydc})(\text{H}_2\text{O})_3]^{19-}$, which are linked together by four Ce–O–C bonds constituting a staggered pattern. Effort to explore systematic strategy and prepare other novel organic-inorganic Ln-containing POM is presently underway and will be reported in due course.

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Notes and references

Figure 3 insert here

Figure 3. (a) Comparison of the simulated and experimental XRD patterns of **1**; (b) the IR spectra of the precursor {As₂W₁₉}, free H₂pydc ligand, Na₉[α-AsW₉O₃₃]·19H₂O and **1**; (c) the UV spectrum of **1**; (d) the TG curve of **1**.

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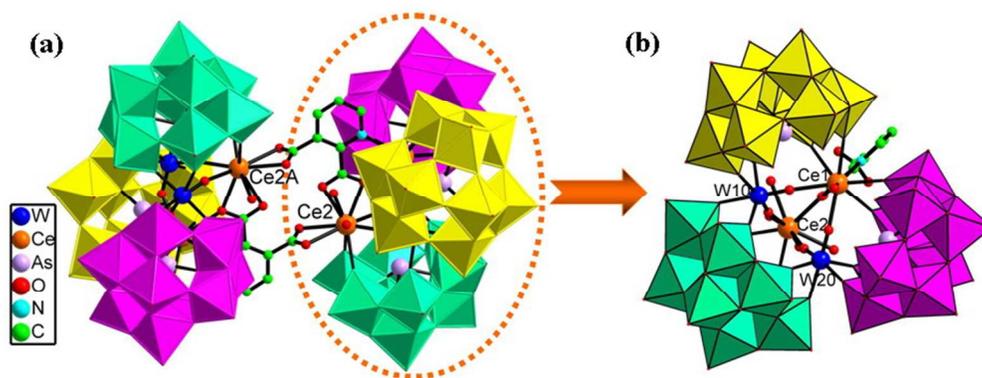
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† Footnotes Crystal data for **1**: C₁₄H₁₂₆N₂O₂₆₄As₆Ce₄K₁₄Li₄W₅₈, *M_r* = 16794.86, triclinic space group *P*-1, *a* = 19.568 (2), *b* = 20.952 (2), *c* = 23.623 (3) Å, *α* = 74.831 (2), *β* = 86.481 (2), *γ* = 64.269 (2)°, *V* = 8405.6 (16) Å³, *Z* = 1, *T* = 296 (2) K, *D_c* = 3.249 g cm⁻³, *μ* = 21.122 mm⁻¹, *G*OOF = 1.078. Of 43355 total reflections collected, 29459 were unique (*R_{int}* = 0.0809). *R₁* [*I* > 2σ(*I*)] = 0.0796, *wR₂* = 0.1833. Intensity data for **1** were collected on Bruker CCD Apex-II diffractometer with Mo *K*α radiation (λ = 0.71073 Å) at 296 K. The structure **1** was resolved by direct methods using the SHELXTL-97 program package.¹⁵ The remaining atoms were found from successive full-matrix least-squares refinements on *F*² and Fourier syntheses. Lorentz polarization and empirical absorption corrections were applied. All the nonhydrogen atoms were anisotropically refined, except for all the lattice water molecules. The integral water molecules were located from the difference Fourier map, but the disordered solvent water molecules are determined by the result of TGA analysis. No hydrogen atoms associated with the water molecules were located from the difference Fourier map. Positions of the hydrogen atoms attached to the carbon atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. Absorption effects were empirically applied. 4 Li⁺ ions are determined based on the result of elemental analysis. CCDC reference number 1012904. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

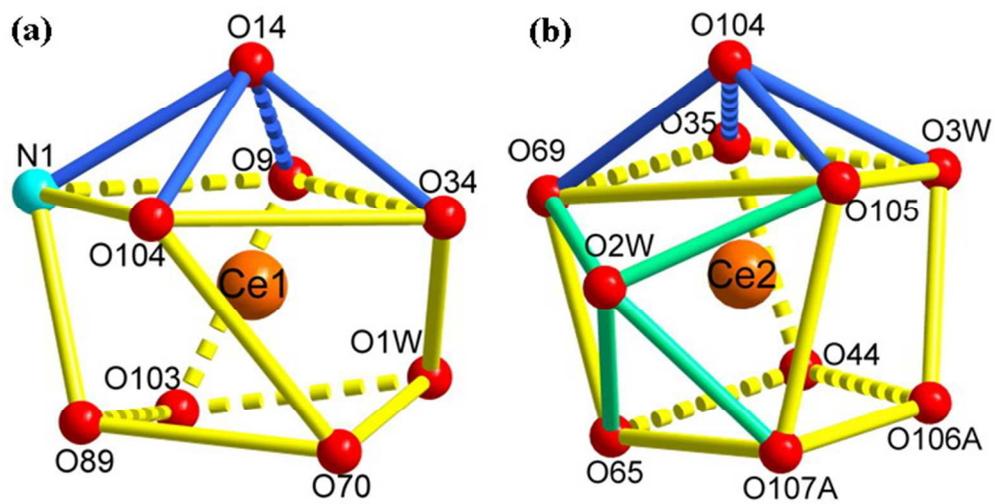
Electronic Supplementary Information (ESI) available: X-ray crystallographic file in CIF format for **1**; ball-and-stick representation of the macroanion [As₆W₅₈O₂₀₆Ce₄(pydc)₂(H₂O)₆]³⁸⁻ in **1**; wires and sticks representation of the 3D structure of **1**; the selective bond length of **1**; the bond valence sum calculations of W, As and Ce atoms in **1**. See DOI: 10.1039/c000000x/

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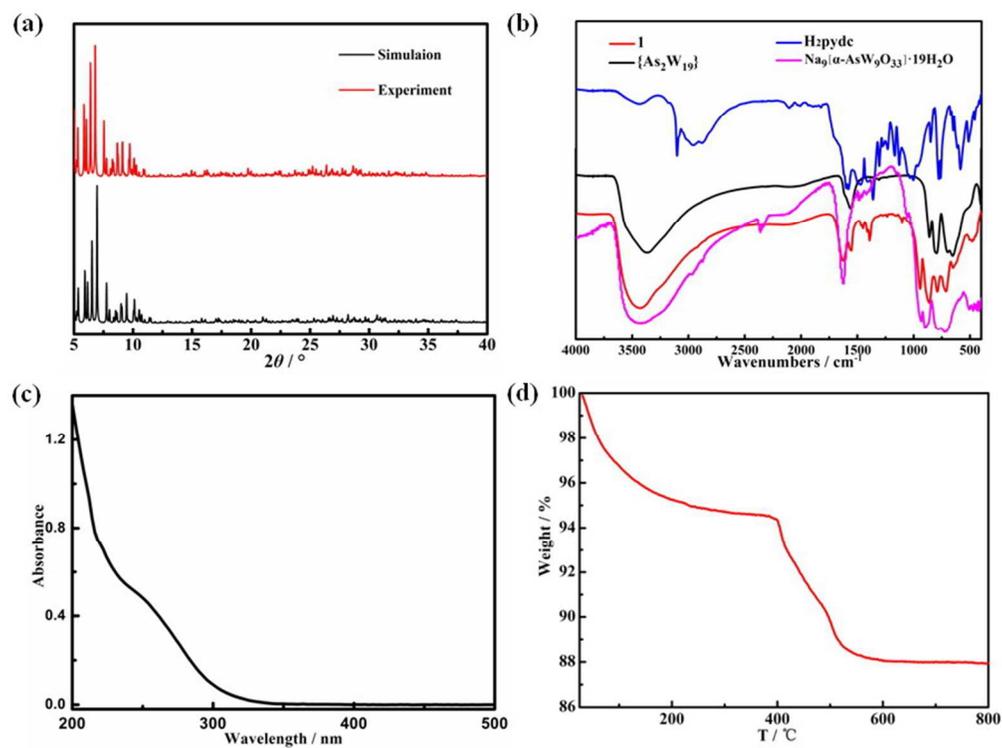
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- Synthesis of **1**: CeCl₃·7H₂O (1.12 g, 0.30 mmol) and H₂pydc (0.42 g, 0.375 mmol) were successively dissolved in 15 mL H₂O, then K₁₄[As₂W₁₉O₆₇(H₂O)] (0.66 g, 0.125 mmol) and LiCl (0.10 g, 2.36 mmol) were added. The pH was adjusted to 6 with 1M LiOH. The resulting mixture was heated (60 °C) for 1 h and filtered after cooling. Slow concentration at room temperature led to the formation of yellow block single crystals about 5 weeks, which were collected by filtration and dried in air (yield ca. 35.46 % based on CeCl₃·7H₂O). Anal. Calcd for **1**, C₁₄H₁₂₆N₂O₂₆₄As₆Ce₄K₁₄Li₄W₅₈ (16794.86): C 1.00, H 0.76, N 0.17, K 3.26, Li 0.17, As 2.68, Ce 3.34, W 63.49. Found: C 1.05, H 0.72, N 0.19, K 3.20, Li 0.18, As 2.49, Ce 3.43, W 62.99. Selected IR (KBr, cm⁻¹): 3435 (br), 1629 (s), 1557 (m), 1467 (w), 1454 (w), 1415 (w), 1394 (m), 1105 (w), 946 (s), 865 (s), 793 (s), 716 (s), 655(m), 482(w).
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247x95mm (96 x 96 DPI)



201x102mm (96 x 96 DPI)



237x176mm (96 x 96 DPI)