Hydrothermal Syntheses and Crystal Structures of Two New Mixed-valence Vanadium Oxides $[Ni(en)_2(H_2O)_2][Ni(en)_3]_2[V_{16}O_{38}Cl] \cdot 3(H_2O)$ and $(H_3O)_2V_3O_8$

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Two vanadium oxides $[Ni(en)_2(H_2O)_2][Ni(en)_3]_2[V_{16}O_{38}Cl] \cdot 3(H_2O)$ (**1**) (en = ethylenediamine) and $(H_3O)_2V_3O_8$ (**2**) were hydrothermally synthesized and characterized by single-crystal X-ray diffraction. **1** consists of $[Ni(en)_2(H_2O)_2]^{2+}$ and $[Ni(en)_3]^{2+}$ cations, discrete $[V_{16}O_{38}Cl]^{6-}$ cluster anions and H_2O molecules, while **2** consists of anionic mixed-valent V^{5+}/V^{4+} vanadium oxide layers constructed from pairs of corner-sharing V^VO_4 tetrahedra and $V^{IV}O_5$ square pyramids, with H_3O^+ cations occupying the interlayer space. Both **1** and **2** were synthesized under the same reaction conditions but with different V/Ni molar ratios, which shows that the reactant stoichiometry of the system plays a key role in the formation of different structures in the products.

Key words: Hydrothermal Syntheses, Vanadium Oxides, Polyoxovanadates, Crystal Structure

Introduction

Vanadium oxides or polyoxovanadates have attracted much attention due to their structural diversity and potential applications in catalysis, medicine, biology, electron conductivity, magnetism, and photochemistry [1]. Vanadium is a unique element that exhibits different types of polyhedra (such as the VO_4 tetrahedron, the VO_5 square pyramid, and the VO_6 octahedron), which favor polymerization by sharing corners or edges into a wide range of cage clusters that have topological similarities to the fullerenes, as exemplified by $[V_{10}O_{28}]^{6-}$ [2], $[V_{12}O_{32}]^{4-}$ [3], $[V_{13}O_{34}]^{3-}$ [4], $[V_{15}O_{36}]^{5-}$ [5], $[V_{15}O_{42}]^{9-}$ [6], $[V_{16}O_{38}]^{n-}$ (n = 3, 7, 12) [7], $[V_{17}O_{42}]^{4-}$ [8], $[V_{18}O_{42}]^{12-}$ [9], and $[V_{34}O_{82}]^{10-}$ [10], and with structural relations to the layers of V_2O_5 [11]. These cage clusters with terminal or bridging O atoms can bind transition metal complexes or participate in intermolecular hydrogen bonds either as acceptors or donors (when they are unprotonated or protonated) to form novel extended structures with improved properties.

The hexadecavanadate cluster is a good candidate for constructing high-dimensional networks. For instance, a 3D open-framework $[\{Cu(dap)_2\}_7\{V_{16}O_{38}(H_2O)\}_2]$ is built up from $[V_{16}O_{38}(H_2O)]^{7-}$ clusters interconnected through $[Cu(dap)_2]^{2+}$ groups [12], and a 3D framework $\{V_{16}O_{38}Cl\ [Ni(en)_2]_3\}_n$ is formed from $[V_{16}O_{38}Cl]^{8-}$ clusters bridged by $[Ni(en)_2]^{2+}$ groups [13]. These examples show that hexadecavanadate clusters prefer forming higher-dimensional architectures with partly vacant $[M(amine)_2]^{2+}$ complexes (amine = en and dap), due to the small volume and the steric hindrance of such small chelating ligands. Subsequently, Peng *et al.* introduced bigger N-containing chelate ligands to the reaction system, which afforded discrete hexadecavanadates, including both $[\{L/D\text{-}Cd(H_2O)(phen)_2\}_2\{V_{16}O_{38}(Cl)\}]$ [14] and $[Cu(2,2'\text{-}bipy)_3]_2[H_4V_{16}O_{38}(Cl)] \cdot 4\,H_2O$ with a supramolecular chain [15], and $H_2[C(CH_2OH)_3NH_3]_{0.5}[Cd(phen)_3]\{[Cd\,H_2O)(phen)_2]_2(V_{16}O_{38}Cl)\}_{0.5}\{[Cd(H_2O)(phen)_2]_2(V_{16}O_{39}Cl)\}_{0.5} \cdot 2H_2O$ with a 2D supramolecular layer [16]. However, no discrete hexadecavanadates containing small chelating ligands have been reported to date.

The cations in layered vanadium oxides, which compensate the charge of the anions in the structure, can be protonated amines [17], tetra-alkylammonium ions [18], and metal cations [19]. However, layered vanadium oxides that are combined with $[H_3O]^+$ cations as counterions are still a less explored area.

In this paper, we report the synthesis and crystal structures of two new vanadium oxides $[Ni(en)_2(H_2O)_2][Ni(en)_3]_2[V_{16}O_{38}Cl] \cdot 3(H_2O)$ (**1**) and $(H_3O)_2V_3O_8$ (**2**). **1** displays a 3D supramolecular network based on the combination of discrete hexadecavanadate anions and cationic complexes with small chelating amines connected *via* intermolecular hydrogen bonds, while **2** exhibits an anionic 2D V-O layered structure constructed from VO_4 tetrahedra and VO_5 square pyramids, with counterions $[H_3O]^+$ sandwiched between the layers.

Results and Discussion

Hydrothermal methods have been utilized successfully to make a variety of solid-state oxides and organic-inorganic hybrid materials, because different solubilities of organic and inorganic precursors can thus be overcome [20]. In a specific hydrothermal process, many factors such as the type of initial reactants, pH value, temperature, solvent, reactant stoichiometry, reactant concentration, and time of reaction can influence the outcome of the reaction. In our case, the reactant stoichiometry of the system was crucial for the formation of the structure of products. When the V/Ni molar ratio was equal to 2 : 1, **1** was produced, but when the V/Ni molar ratio was elevated to 3 : 1 with other parameters unchanged, **2** was isolated. In addition, H_3BO_3 takes a role in the preparation of products as an acid buffering agent. This reagent appears to be needed in the synthesis, although it is not incorporated in the final structure.

In the IR spectrum of **1**, the stretching bands of $-NH_2$, and CH_2 groups are observed at $\nu = 3323 - 3279$ and $2928 - 2855\ cm^{-1}$, respectively, and their bending vibration bands are present at $\nu = 1597$ and $1453\ cm^{-1}$, respectively. The occurrence of these bands confirms the presence of amino groups in **1**. The absence of bands corresponding to stretching of $-NH_2$, and CH_2 groups in the spectrum of **2** demonstrated that there is no organic amine in this compound. For **2**, the broad band at $3426\ cm^{-1}$ can be assigned to O-H stretching. For **1** and **2**, the strong peaks at $986 - 968\ cm^{-1}$ can be attributed to the stretching vibrations of V=O bonds.

The crystal structure of **1** consists of $[V_{16}O_{38}(Cl)]^{6-}$ cluster anions, $[Ni(en)_2(H_2O)_2]^{2+}$ and $[Ni(en)_3]^{2+}$ cations, and H_2O molecules. The $[V_{16}O_{38}(Cl)]^{6-}$ anion exhibits a host shell structure containing one Cl^- ion in its center with approximate S_4 symmetry (Figs. 1a, 1b). The basic $\{V_{16}O_{38}\}$ shell is made up of 16 VO_5 square pyramids sharing edges and corners with 20 μ_3-oxygen atoms and 8 μ_2-oxygen atoms. The square-pyramidal geometry around the vanadium atoms V1 and V4 in four of the 16 VO_5 groups is defined by three μ_3-O atoms, one μ_2-O atom and one terminal O atom. The square-pyramidal geometry around the vanadium atoms in the remaining 12 VO_5 units is defined by one terminal O atom and four μ_3-O atoms. The V–O bond lengths [1.595(4)–1.609(3) Å for V–O_{term}, 1.798(3)–1.845(3) Å for V–O(μ_2-), and 1.835(3)–1.975(3) Å for V–O(μ_3-)] are comparable with those in $[Ni(en)_3]\{V^{IV}{}_{11}V^{V}{}_5O_{38}(Cl)[Ni(en)_2]_3\} \cdot 8.5H_2O$ [13], and $[Cu(2,2'\text{-bipy})_3]_2[H_4V_{16}O_{38}(Cl)] \cdot 4H_2O$ [15]. The 16 V atoms are arranged at the surface of the shell with radii of 3.55 ± 0.01 Å from the central Cl^- ion.

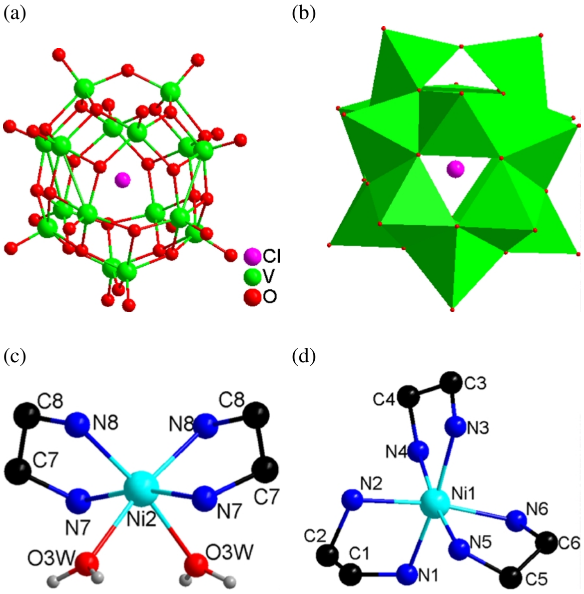

Fig. 1. Ball-and-stick (a), and polyhedral (b) representation of the $[V_{16}O_{38}Cl]$ cluster. The coordination environment of the $Ni2^{2+}$ (c) and the $Ni1^{2+}$ ion (d) (H atoms bonded to C and N atoms have been omitted for clarity).

There are two kinds of transition metal complexes as counterions in **1**: the Ni^{2+} ion in the $[Ni(en)_2(H_2O)_2]^{2+}$ cation is coordinated by four N atoms of two en ligand and two water molecules in a slightly distorted octahedron (Fig. 1c); the Ni^{2+} ion in the $[Ni(en)_3]^{2+}$ cation is bonded to six N atoms of three en ligands in a distorted octahedron (Fig. 1d). Notably, the $[Ni(en)_2(H_2O)_2]^{2+}$ cation, where two H_2O molecules instead of another strongly chelating en ligand, as

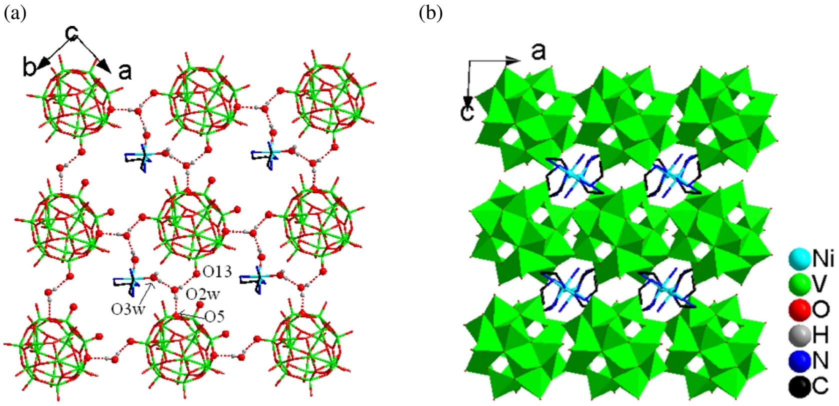

Fig. 2. (a) Part of the crystal structure of **1**, showing the formation of a (001) sheet constructed from O–H···O hydrogen bonds (ball-and-stick representation); (b) polyhedral and ball-and-stick representation of the 3D supramolecular structure of **1**. H atoms bonded to C and N atoms have been omitted for clarity.

in the $[Ni(en)_3]^{2+}$ ion, are located in *cis*-positions, are seldomly by found in polyoxovanadates. The only previous example is $[Ni(en)_2(H_2O)_2]_2[\{Ni(en)_2(H_2O)\}_2As_8V_{14}O_{42}(NO_3)][\{Ni(en)_2\}As_8V_{14}O_{42}(NO_3)] \cdot 6H_2O$ [21]. The strongly chelating en ligand binds the M^{2+} ion (M = Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, and Cu^{2+}) very strongly, generating metal complex cations $[M(en)_3]^{2+}$ as counterions, as exemplified by $[Co(en)_3]_2[V_3P_3BO_{19}][H_2PO_4] \cdot 4H_2O$ [22], $[Co(en)_3][V_3O_9] \cdot H_2O$ [22], $[Co(en)_3]_4[Mo^{V}{}_2Mo^{VI}{}_{14}V^{IV}{}_{16}O_{80}(PO_4)_2] \cdot 10H_2O$ [23], and $[Ni(en)_3]\{V_{16}O_{38}Cl\ [Ni(en)_2]_3\} \cdot 8.5H_2O$ [13].

In **1**, free water O2w atoms at (*x*, *y*, *z*) act as hydrogen bond donors, *via* H2w1 and H2w2, to atoms μ_3-O5 of the $[V_{16}O_{38}(Cl)]^{6-}$ anion at (*x*, *y*, *z*) and O13 of the $[V_{16}O_{38}(Cl)]^{6-}$ anion at $(0.5-x, 0.5+y, 1.5-z)$, generating a 2D hydrogen-bonded layered structure parallel to the (001) plane. The O2w atom accepts one hydrogen bond in an intermolecular interaction with one coordinated water molecule of a neighboring $[Ni(en)_2(H_2O)_2]^{2+}$ ion, fixing the $[Ni(en)_2(H_2O)_2]^{2+}$ ions within the 2D layered network (Fig. 2a). These layers are further interconnected by N–H···O hydrogen bonds between -NH_2 groups of $[Ni(en)_3]^{2+}$ cations and terminal O atoms of $[V_{16}O_{38}(Cl)]^{6-}$ anions leading to a three-dimensional hydrogen-bonded network structure (Fig. 2b). The O···O distances, varying from 2.796(8) to 2.882(7) Å, and the N···O distances, ranging from 3.052(6) to 3.362(5) Å, are consistent with values reported in the literature [22, 23].

Valence sum calculations [24] were made to confirm the oxidation state of the vanadium atoms. The result shows that there are nine V^{IV} and seven V^{V} (average value 4.42). The framework stoichiometry of $[V_{16}O_{38}(Cl)]$ creates a charge of −6, which is balanced by two $[Ni(en)_3]^{2+}$ and one $[Ni(en)_2(H_2O)_2]^{2+}$ cations. So **1** is formulated as $[Ni(en)_2(H_2O)_2][Ni(en)_3]_2[V^{IV}{}_9V^{V}7O_{38}Cl] \cdot 3(H_2O)$.

Single-crystal X-ray analysis indicates that the asymmetric unit of **2** contains 7 independent non-H atoms, including 2 V atoms and 5 O atoms (Fig. 3a). All atoms are located in general positions. The V atoms show two kinds of coordination modes with V–O bond lengths varying from 1.590(3) to 1.9651(15) Å for VO_5 square pyramids, and from 1.645(3) to 1.7989(11) Å for VO_4 tetrahedra. Two VO_4 tetrahedra are joined together by an O bridge to form a V_2O_7 moiety. Each V_2O_7 unit is linked to four VO_5 square pyramids *via* corner-sharing, forming a 2D V–O layer containing the pentagonal ring comprising three VO_4 tetrahedra and two VO_5 square pyramids (Fig. 3b). The network topology of the 2D V–O layer can be simplified by considering the V atoms as nodes and the μ_2-O atoms as linkers between the V nodes. As a result, an mcm topology with a vertex symbol $(5_4 \cdot 8_2)(5_3)$ is formed (Fig. 3c). The layers are stacked perpendicular to [001], and therefore the pores form tunnels running also in this direction (Fig. 3d). The shortest interlayer O···O distance is about 5.56 Å.

The structure-directing effect of the H_3O^+ cations is obvious as they are located above and below the rings of the layers (Fig. 3e). The orientation of the short V=O units parallel to the *c* axis is identical, which is significantly different from that of other layered mixed-valence vanadium oxides where they are oriented toward opposite sides of the plane of the layer [17–19]. The square pyramidally coordinated vanadium atom has an oxidation state of +4, while the tetrahedral coordination is indicative of an oxidation state of +5. This assignment of oxidation state is consistent

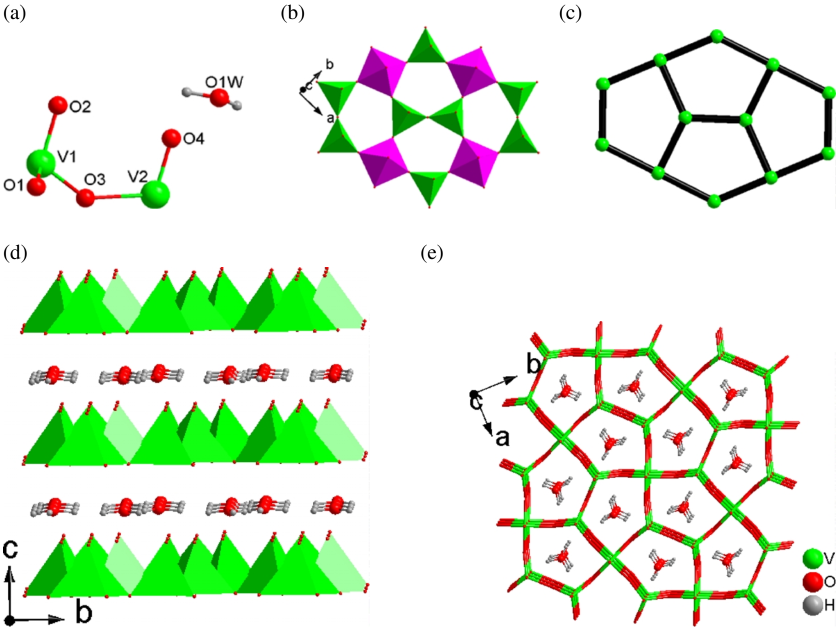

Fig. 3. (a) The asymmetric unit of **2**; (b) polyhedral representation of a 2D layer; (c) topology of the layer; (d) view down the *a* axis of **2** showing the layers (polyhedra) and H_3O^+ ions (ball-and-stick representation) in the interlayer space; (e) view down the *c* axis of **2** showing the H_3O^+ ions located above and below the rings of the layers (ball-and-stick representation).

with the overall charge balance of **2** and confirmed by the valence sum calculations [24] which gave a value of 5.12 for V1, and 4.14 for V2.

Conclusion

In summary, two new vanadium oxide derivatives $[Ni(en)_2(H_2O)_2][Ni(en)_3]_2[V_{16}O_{38}Cl] \cdot 3(H_2O)$ and $(H_3O)_2V_3O_8$ have been hydrothermally synthesized and structurally characterized. Athough some discrete hexadecavanadates have previously been reported, their cations are transition metal complexes of bigger N-containing chelate ligands, excluding steric hindrance and thus inhibiting the extension of the hexadecavanadate arrays. So **1** is a rare example of a discrete hexadecavanadate combined with a transition metal complex with small N-containing chelate ligands. Compound **2** provides an unusual example of H_3O^+ cations located between anionic vanadium oxide layers.

Experimental Section

Materials and methods

All chemicals were used as purchased without purification. Elemental analyses (C, H, and N) were performed on a PE2400 II elemental analyzer. The IR spectra were obtained on an ABB Bomen MB 102 spectrometer in the range of 4000 – 400 cm^{-1} from pressed KBr pellets.

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of **1** and **2**.

	1	**2**
Formula	$C_{16}H_{74}ClN_{16}Ni_3O_{43}V_{16}$	$H_6O_{10}V_3$
M_r	2205.46	318.87
Crystal system	monoclinic	tetragonal
Space group	$C2/c$	$P4bm$
a, Å	17.069(3)	8.8996(17)
b, Å	19.203(4)	8.8996(17)
c, Å	19.970(4)	5.577(2)
β, deg	92.73(3)	90
V, Å^3	6538(2)	441.7(2)
Z	4	2
T, K	293(2)	293(2)
Calcd. density, Mg m^{-3}	2.24	2.40
$\mu(MoK_\alpha)$, mm^{-1}	3.2	3.1
$F(000)$, e	4372	310
$2\theta_{max}$, deg	50.20	56.56
Reflns. collected / unique	17675 / 5809	2994 / 548
No. of ref. parameters	438	45
$R1$ $[I \geq 2\sigma(I)]$ / $wR2$ (all data)	0.0454 / 0.1370	0.0169 / 0.0446
GOF on F^2	1.024	1.184
x (Flack)	–	0.05(4)
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	1.79 / −1.01	0.45 / −0.38

Synthesis of $[Ni(en)_2(H_2O)_2][Ni(en)_3]_2[V_{16}O_{38}Cl] \cdot 3(H_2O)$ (1)

A mixture of NH_4VO_3 (0.2340 g, 2.00 mmol), $NiCl_2 \cdot 6H_2O$ (0.2377 g, 1.00 mmol), H_3BO_3 (0.1855 g, 3.00 mmol), en (0.8 mL), and H_2O (4 mL) was stirred for 0.5 h, sealed in a Teflon-lined steel autoclave (20 mL), kept at 145 °C for 5 d, and then cooled to r.t. Dark block-shaped crystals

Table 2. Selected bond lengths (Å), and angles (deg) for **1** and **2**.

1	Ni1–N	2.104(7) – 2.146(6)	Ni2–N	2.051(10) – 2.088(11)
	Ni2–O3W	2.143(7)	V1–O3	1.606(4) – 2.142(4)
	V2–O	1.603(4) – 1.933(4)	V3–O	1.598(4) – 1.955(4)
	V4–O	1.595(5) – 2.132(4)	V5–O	1.606(4) – 1.967(4)
	V6–O	1.606(4) – 1.961(4)	V7–O	1.602(4) – 1.973(3)
	V8–O	1.599(4) – 1.950(4)		
	N–Ni1–N(*trans*)	169.7(2) – 173.9(2)	N–Ni1–N(*cis*)	80.4(2) – 95.1(2)
	N–Ni2–N/O(*trans*)	167.8(6) – 170.9(4)	N/O–Ni2–N/O(*cis*)	85.5(4) – 100.7(6)
	O–V1–O	77.31(15) – 156.13(17)	O–V2–O	79.55(16) – 144.67(16)
	O–V3–O	80.08(15) – 144.99(16)	O–V4–O	77.99(15) – 155.01(18)
	O–V5–O	77.60(16) – 146.89(15)	O–V6–O	78.80(16) – 146.88(17)
	O–V7–O	79.18(15) – 148.70(15)	O–V8–O	79.77(15) – 145.82(16)
2	V1–O	1.645(3) – 1.7989(11)	V2–O	1.9651(15)
	O–V1–O	107.78(8) – 111.11(7)	O4–V2–O	85.04(3) – 145.78(11)

were obtained by filtration, washed with distilled water, and dried in air. Yield: *ca.* 56 % (based on NH_4VO_3). – Anal. (%): calcd. C 8.71, H 3.38, N 10.16; found C 8.65, H 3.41, N 10.20. – IR (KBr pellet, cm^{-1}): ν = 3323(m), 3279(m), 2928(m), 2855(m), 1597(m), 1505(w), 1453(m), 1318(w), 1274(w), 1094(vw), 1031(s), 968 (vs), 663(vs), 491(m).

*Synthesis of $(H_3O)_2V_3O_8$ (**2**)*

A mixture of NH_4VO_3 (0.3510 g, 3.00 mmol), $NiCl_2\cdot 6H_2O$ (0.2377 g, 1.00 mmol), H_3BO_3 (0.1855 g, 3.00 mmol), en (0.8 mL), and H_2O (4 mL) was stirred for 0.5 h, sealed in a Teflon-lined steel autoclave (20 mL), kept at 145 °C for 5 d, and then cooled to r. t. Dark block-shaped crystals were obtained by filtration, washed with distilled water, and dried in air. Yield: *ca.* 75 % (based on NH_4VO_3). – IR (KBr pellet, cm^{-1}): ν = 3426(s), 1408(m), 986(m), 815(s), 734(m), 671(m), 493(w).

X-Ray structure determinations

Data collections were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 293(2) K with a maximum 2θ value of 56.56°. The intensities were corrected for Lorentz and polarization effects. The structures were solved with Direct Methods using the SHELXS-97 program [25], and the refinement was performed against F^2 using SHELXL-97 [26]. All non-hydrogen atoms were refined anisotropically. The H atoms on C and N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters, but no H atoms associated with the free water (O1w) molecule in **2** were located from the difference Fourier map. Relevant crystal and data collection parameters and refinement results can be found in Table 1. Selected bond lengths and angles for compounds **1** and **2** are listed in Table 2.

CCDC 782216 contains the supplementary crystallographic data of **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Further details of the crystal structure investigation of **2** may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421914.

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