Cation–anion interactions in bis(±)*trans*-2-aminocyclohexylammonium tetrathiotungstate, 1,7-diazonia-4-aza-heptane tetrathiotungstate and 1,5-diazonia-9-aza-nonane tetrathiotungstate

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Dedicated to Prof. Dr. Y.S. Prahalad on the occasion of his 60th birthday.

Abstract

The reaction of $(NH_4)_2[WS_4]$ with (±)*trans*-1,2-diaminocyclohexane (*trans*-1,2-cn), bis(2-aminoethyl)amine (dien) and bis(3-aminopropyl)amine (dipn) leads to the formation of the organic ammonium tetrathiotungstates (*trans*-1,2-cnH)$_2$[WS$_4$] (**1**), (dienH$_2$)[WS$_4$] (**2**) and (dipnH$_2$)[WS$_4$] (**3**) [*trans*-1,2-cnH is (±)*trans*-2-aminocyclohexylammonium; dienH$_2$ is 1,7-diazonia-4-aza-heptane; dipnH$_2$ is 1,5-diazonia-9-aza-nonane] in good yields. The title complexes **1**–**3** react with [Ni(en)$_3$]$^{2+}$ (en = ethylenediamine) forming the highly insoluble complex [Ni(en)$_3$][WS$_4$]. The structure of the complexes **1**–**3** can be described as consisting of tetrahedral [WS$_4$]$^{2-}$ dianions which are linked to the monoprotonated cation of *trans*-1,2-cn in **1** and the diprotonated cations of dien and dipn in **2** and **3**, with the aid of weak hydrogen bonding interactions. The difference between the longest and the shortest W–S bond lengths Δ is 0.0104, 0.0170 and 0.0173 Å in **1**, **2** and **3**, respectively. A comparative study of the structural features of several tetrathiotungstates is presented and the interactions between the organic cations and the tetrathiotungstate anions are discussed in terms of the magnitude of Δ, the difference between the longest and the shortest W–S bond distances.
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1. Introduction

The chemistry of Mo/W–S complexes is currently a frontier area of research owing to the use of the group VI metal sulfides in hydrodesulfurization catalysis [1] and the importance of layered metal disulfides in nanomaterials [2]. The soluble sulfides of the group VI metals W and Mo [3–5] are a unique class of compounds with a wide range of metal to sulfur stoichiometries, metal oxidation states, coordination geometries and bonding modes of the sulfido ligands. The use of $(NH_4)_2[WS_4]$ as a precursor for the soft

synthesis of WS$_2$ nanotubes [6,7] is an important reason for the current interest in the chemistry of tetrathiotungstate. Li and coworkers have reported that the direct pyrolysis of bis(cetyltrimethylammonium) tetrathiotungstate leads to the formation of bulk quantities of uniform WS$_2$ nanotubules [8], indicating the importance of organic ammonium salts of [WS$_4$]$^{2-}$ in material applications. The simplest mononuclear W–S compound ammonium tetrathiotungstate $(NH_4)_2[WS_4]$, known from the days of Berzelius [9], has been used as a starting material for the synthesis of a variety of di-, tri- and polynuclear W–S complexes [3,4]. From a structural point of view, the acentric tetrahedral [WS$_4$]$^{2-}$ unit can be used as a building block to create non-centrosymmetric materials by an appropriate

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choice of cation. The WS_4 tetrahedron is flexible and can exist in a variety of structural environments as evidenced by the structural characterization of several $[WS_4]^{2-}$ complexes with different counter ions [10–18]. In many of these compounds, the WS_4 tetrahedron is slightly distorted with one or two of the W–S bonds elongated, which has been attributed to S···H interactions between $[WS_4]^{2-}$ and the organic ammonium cation. Our work with $[WS_4]^{2-}$ has shown that organic amines can be used as cationic handles to distort the WS_4 tetrahedron [17]. In order to understand the importance of H-bonding interactions in the structural chemistry of tetrathiotungstates, we are investigating the reactions of $[WS_4]^{2-}$ with several amines, which differ in terms of their steric bulk and the number of potential donor H atoms. In the present work, we wish to describe the spectroscopic and structural characterization of three new tetrathiotungstates obtained by the reaction of $(NH_4)_2[WS_4]$ with the cyclic diamine $(\pm)trans$-1,2-diaminocyclohexane ($trans$-1,2-cn) and the acyclic triamines bis-(2-aminoethyl)amine (dien) and bis(3-aminopropyl)amine (dipn). The title compounds constitute three additions to the growing list of structurally characterized tetrathiotungstates. The availability of structural information for several tetrathiotungstates permits us to make a comparative study of the structural features, the details of which are described in this paper.

2. Experimental

2.1. Materials and methods

The organic amines $trans$-1,2-cn, dien, dipn and the solvents were used as obtained from commercial sources with analytical purity. $(NH_4)_2[WS_4]$ was prepared by a literature method [19]. The details of the instrumentation used for the elemental analysis, IR, Raman and UV–Vis spectroscopy are the same as described in our previous reports [16,17].

2.2. Synthesis of organic ammonium tetrathiotungstates 1–3

$(NH_4)_2[WS_4]$ (348 mg, 1 mmol) was dissolved in 15 mL of distilled water containing a few drops of aqueous ammonia, and filtered. To the clear yellow filtrate $trans$-1,2-cn (0.3 mL) was added in drops at room temperature and the reaction mixture was kept for crystallization. After a day, yellow blocks of compound **1** slowly crystallized. The crystals were isolated by filtration, washed well with ice-cold water (5 ml), isopropanol (10 mL) and ether (10 mL) and dried under vacuum. The yield of the product was 400 mg. The use of dipn and dien instead of ($trans$-1,2-cn) in the above procedure afforded complexes **2** and **3** in 60% yield. All the complexes are quite stable in air.

($trans$-1,2-cnH)$_2$[WS$_4$] **1**: *Anal*. Calc. for $C_{12}H_{30}N_4WS_4$: C, 26.57; H, 5.58; N, 10.33; S, 23.64. Found: C, 26.38; H, 5.49; N, 10.08; S, 22.65%.

IR data: 3309, 3239, 3095, 2939, 2856, 1581, 1498, 1443, 1398, 1229, 1126, 1002, 965, 847, 583, 521, 482 (v_1), 465 (v_3), 429, 409, 329, 286, 214, 136, 102 cm^{-1}; Raman data: 481 (v_1), 464 (v_3), 193 (v_4), 178, 168 cm^{-1}.

UV–Vis data in nm (ε in mol^{-1} 1 cm^{-1}) 393 (18 437), 277 (23 802), 219 (24 375).

(dienH$_2$)[WS4] **2**: *Anal*. Calc. for $(C_4H_{15}N_3WS_4)$: C, 11.51; H, 3.60; N, 10.07; S, 30.74. Found: C, 11.63; H, 3.52; N, 9.94; S, 28.15%.

IR data: 3243, 3054 (br), 1563, 1547, 1513, 1458, 1365, 1297, 1279, 1257, 1203, 1162, 1122, 1107, 1094, 1026, 980, 959, 933, 866, 824, 797, 789, 770, 750, 627, 479 (v_1) , 464 (v_3), 443, 357, 324, 243, 185 (v_4), 99 cm^{-1}; Raman data: 481 (v_1), 460 (v_3), 359, 188 (v_4) cm^{-1}.

UV–Vis data in nm (ε in mol^{-1} 1 cm^{-1}) 393 (15 858), 280 (17 459), 220 (19 244).

(dipnH$_2$)[WS$_4$] **3**: *Anal*. Calc. for $(C_6H_{19}N_3WS_4)$: C, 16.18; H, 4.30; N, 9.44; S, 28.80. Found: C, 16.36; H, 4.26; N, 9.933; S, 29.12%.

IR data: 3275, 3235, 2993, 1573, 1518, 1460, 1420, 1380, 1284, 1208, 1083, 1040, 989, 922, 868, 823, 755, 478 (v_1), 461 (v_3), 292, 258, 233, 188 (v_4) cm^{-1}; Raman data: 477 (v_1), 458 (v_3), 188 (v_4) cm^{-1}.

UV–Vis data in nm (ε in mol^{-1} 1 cm^{-1}) 393 (12 441), 277 (18 114), 217 (21 122).

2.3. Crystal structure determination

Intensity data were collected on a STOE Imaging Plate Diffraction System for compound **1** and on an AED-II four-circle diffractometer for compounds **2** and **3**, using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The raw intensities were corrected for Lorentz, polarization effects. All structures were solved with direct methods using SHELXS-97 [20] and refinement was done against F^2 using SHELXL-97 [21]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in the difference map but were positioned with idealized geometry and refined isotropically using a riding model. In compound **2** the N atom of dien is disordered due to symmetry. The structure can also be solved and refined in the non-centrosymmetric space group $Pmn2_1$. In this case no disorder is present but the absolute structure cannot be determined (Flack x-parameter 0.5) and strong correlation of the atomic coordinates of the symmetry related atoms occur. When the structure was checked for higher symmetry using Platon, the space group $Pmmn$ was selected. Therefore this space group was chosen. Intensity data were additionally collected at low temperature (170 K) using a different crystal to check whether the disorder is dynamic or static in nature. However the disorder persists even at low temperature and no indications were found for a symmetry change. In the present contribution we describe only the room temperature data because the quality of the structure model was much better than that of the low temperature data set. The technical details of data acquisition and some selected refinement results are summarized in Table 1.

Table 1
Technical details of data acquisition and selected refinement results for **1**–**3**

Compound	1	2	3
Formula	$C_{12}H_{30}N_4S_4W$	$C_4H_{15}N_3WS_4$	$C_6H_{19}N_3WS_4$
Temperature (K)	293	293	293
Wavelength (pm)	71.073	71.073	71.073
Space group	*C*2/*c*	*Pmmn*	*Pca*2$_1$
a (Å)	19.3669(13)	11.559(1)	13.8110(8)
b (Å)	9.4959(5)	7.2424(6)	7.5327(6)
c (Å)	11.3836(7)	7.4956(5)	13.4999(7)
β (°)	107.713(7)		
Volume (Å^3)	1994.3(2)	627.50(9)	1404.45(16)
Z	4	2	4
μ (mm^{-1})	6.210	11.48	8.791
F(000)	1072	396	856
Molecular weight (g/mol)	542.49	417.28	445.33
D_{calc} (g cm^{-3})	1.807	2.402	2.106
Crystal size (in mm)	0.13, 0.09, 0.07	0.11, 0.09, 0.08	0.1, 0.09, 0.08
h k l Range	−27/27;−13/13;−16/16	−15/15;−9/8;−9/1	−19/3;−10/4;−18/3
2*θ* Range	3°–60°	3°–56°	3°–60°
Reflections collected	11 868	3620	4895
Reflections unique	2978	859	2582
Data ($F_o > 4\sigma(F_o)$)	2675	812	2019
R_{int}	0.0369	0.0257	0.0350
Minimum/maximum transmission	0.3399/0.4861	0.2088/0.3116	0.1431/0.4355
Δ*ρ* (e/Å^3)	−1.336/1.191	−0.66/0.40	−1.051/1.200
Parameters	98	42	130
R_1 [$F_o > 4\sigma(F_o)$][a]	0.0305	0.0131	0.0218
WR_2 for all unique data	0.0740	0.0323	0.0531
Goodness-of-fit	1.102	1.128	1.006

[a] $R_1 = \sum \|F_o| - F_c\| / \sum |F_o|$.

3. Results and discussion

3.1. Synthesis and reactivity studies

The title compounds **1**–**3** were synthesized by a base promoted cation exchange method wherein the stronger organic bases *trans*-1,2-cn and the acyclic triamines dien and dipn replace the weak ammonia from the ammonium cation of $(NH_4)_2[WS_4]$. The complexes analyzed satisfactorily for the proposed formula containing the well-known $[WS_4]^{2-}$ anion in association with the monoprotonated cation of *trans*-1,2-cn in **1** and the diprotonated cations of dien and dipn in **2** and **3**. In an earlier report we have shown that the use of the polyamine tren (tren is tris(2-aminoethylamine)) results in the formation of $(trenH_2)^{2+}[WS_4]^{2-}$ [16]. In the present work, it is interesting to note that the terminal primary amine groups are protonated in **2** unlike in the related triamine dipropylenetriamine (dipn) in **3** where the protonation of the central secondary amine functionality and one of the terminal N atoms is observed. It has been reported that WO_3 dissolves in aqueous dien leading to the formation of the hexacoordinated neutral complex $[WO_3(dien)]$ where dien functions as a neutral tridentate ligand [22]. The neutral compound is highly water soluble and forms $(dienH_2)[WO_4]$ in solution. While $(dienH_2)[WO_4]$ exists only in solution, the corresponding tetrathio analogue **2** can be crystallized as a stable solid indicating the difference in the chemistry of oxo- and thiotungstates. The formation of **2** can be attributed to the weak H-bonding interactions (see the structure description) between the organic cation and $[WS_4]^{2-}$. Our efforts to prepare the neutral trithio complex $[WS_3(dien)]$ by the reaction of WS_3 with dien were not successful as WS_3 does not dissolve in aqueous dien unlike WO_3. Furthermore, our attempts to obtain a 1:1 $[WS_4]^{2-}$ complex containing the diprotonated cation of *trans*-1,2-cn or a 2:3 $[WS_4]^{2-}$ complex of the fully protonated dipn and dien by changing the reaction stoichiometries were not successful. It is well documented that $[WS_4]^{2-}$ can function as a bidentate ligand and bis(tetrathiotungstato) complexes of the type $[Ni(WS_4)_2]^{2-}$ are well known [3]. The availability of $[WS_4]^{2-}$ together with a N-donor ligand like dien suggested that the title complexes can be used to form S-bridged mixed ligand heterobimetallic complexes. Accordingly the reaction of the title complexes with $[Ni(H_2O)_6]Cl_2$ in aqueous ammonia were investigated. The use of ammonia was to facilitate the deprotonation of the organic cations. These reactions did not afford any mixed ligand complexes. However the reaction of the title complexes **1**–**3** under identical conditions with $[Ni(en)_3]^{2+}$ resulted in the formation of the highly insoluble complex $[Ni(en)_3][WS_4]$ in high yields. The complex $[Ni(en)_3][WS_4]$ has earlier been isolated under solvothermal conditions [12] and its facile formation indicates that $[WS_4]^{2-}$ is a weaker ligand as compared to en.

3.2. Description of crystal structures

Compound **1** crystallizes in the monoclinic space group $C2/c$ and is isostructural with the corresponding Mo analogue [23]. The substitution of Mo by W in **1** yields slightly larger unit cell parameters, which can be explained by the larger size of W. The asymmetric unit of **1** consists of the monoprotonated cation of *trans*-1,2-cn, which adopts a chair confirmation, and the $[WS_4]^{2-}$ anion (Fig. 1). The organic cation is located in a general position while the anion is situated on a twofold axis. The WS₄ tetrahedron is moderately distorted (S–W–S angles: 108.04(6)–110.89(5)°; average: 109.47°). The W–S bond lengths (2.1874(11)–2.1978(10) Å) have a mean value of 2.1926 Å (Table 2). The geometric parameters of **1** are in good agreement with those reported for other materials like (enH₂)[WS₄] (en = ethylenediamine) [13] and (1,3-pnH₂)[WS₄] (1,3-pn = 1,3-propanediamine) [14]. Two of the bond lengths are shorter while the other two are longer than the average W–S bond length of 2.1926 Å. As a result of the H-bonding interactions, the cations and anions in **1** are organized in a rod-like manner along [100] with the ammonium groups of *trans*-1,2-cn always pointing towards
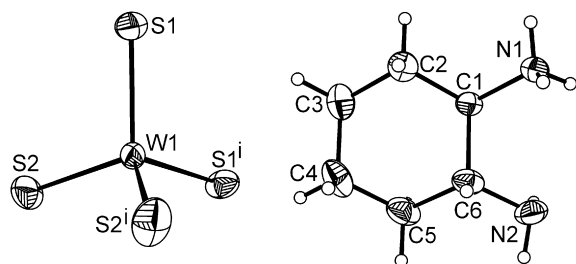
the S atoms of the anion. Hence, the sequence along this direction is $\cdots[WS_4]^{2-}$-*trans*-1,2-cnH-*trans*-1,2-cnH-$[WS_4]^{2-}\cdots$. The special arrangement of the constituents may be viewed as layers within the (001) plane. Along [010] and [001] the anions and cations each form individual stacks. Each anion is surrounded by six cations and five short S⋯H contacts ranging from 2.675 to 2.969 Å (Table 3) are observed, which are shorter than the sum of the van der Waals radii of S and H [24]. The shortest S⋯H contact of 2.675 Å and another at 2.769 Å observed for S1 can probably explain the elongation of the W–S1 bond. Although three S⋯H contacts are observed for S2, the W–S2 bond is slightly shorter at 2.1874(11) Å, which may be due to the longer S⋯H distances as well as the smaller values of the N–H⋯S angles. In addition, a very short N–H⋯N contact at 2.029 Å is observed which joins the cations to form pairs. The crystal packing diagram of the resulting hydrogen bonding network in **1** is shown in Fig. 2. The difference between the longest and shortest W–S bond Δ in **1** is 0.0104 Å and is indicative of little distortion. This value is much less compared to the Δ value of 0.0385 Å observed earlier for (pipH₂)[WS₄] (pip is piperazine) [16].

Compound **2** crystallizes in the orthorhombic space group *Pmmn* and its structure consists of the $[WS_4]^{2-}$ anion and the $(dienH_2)^{2+}$ cation, both of which are located in special positions (Fig. 3). Four of the S–W–S angles are 109.4(1)°, the other two being 109.2(1)° and 110.1(1)°, indicating very little distortion. The W–S bond lengths vary from 2.172(1) to 2.189(1) Å (mean W–S bond length: 2.1805 Å) (Table 4). The geometric parameters are in good agreement with those for other organic ammonium tetrathiotungstates like **1** or (enH₂)[WS₄]. The W–S bonds show a pattern with two short (2.172(1) Å) and two longer (2.189(1) Å) values. In all, three short S⋯H contacts ranging from 2.531 to 2.968 Å are observed (Table 5). Interestingly the central secondary N atom is not involved in H-bonding. The single short contact of 2.765 Å is accompanied by a N–H⋯S angle of 140.76°, which may account for the shorter W–S2 bond, while the shortest contact of 2.531 Å accompanied by the largest N–H⋯S bond angle can explain the elongation of the W–S1 bond. The S⋯H interactions join adjacent WS₄ tetrahedra into layers extending in the (001) plane (Fig. 4). The difference between the longest and the shortest W–S bond Δ is 0.0170 Å and is slightly larger than that observed for **1**

Fig. 1. Crystal structure of the anion (left) and cation (right) in (*trans*-1,2-cnH)₂(WS₄) (**1**) with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) −x + 1, y, −z + 1/2].

Table 2
Selected geometric parameters (Å, °) for (*trans*-1,2-cnH)₂[WS₄] (**1**)

W(1)–S(2)	2.1874(11)	W(1)–S(1)ⁱ	2.1978(10)
W(1)–S(2)ⁱ	2.1874(11)	W(1)–S(1)	2.1978(10)
S(2)–W(1)–S(2)ⁱ	108.33(7)	S(2)–W(1)–S(1)	109.35(4)
S(2)–W(1)–S(1)ⁱ	110.89(5)	S(2)ⁱ–W(1)–S(1)	110.89(5)
S(2)ⁱ–W(1)–S(1)ⁱ	109.35(4)	S(1)ⁱ–W(1)–S(1)	108.04 (6)

Symmetry transformations used to generate equivalent atoms: ⁱ−x + 1, y, −z + 1/2.

Table 3
Hydrogen-bonding geometry (Å, °) for (*trans*-1,2-cnH)₂[WS₄] (**1**)

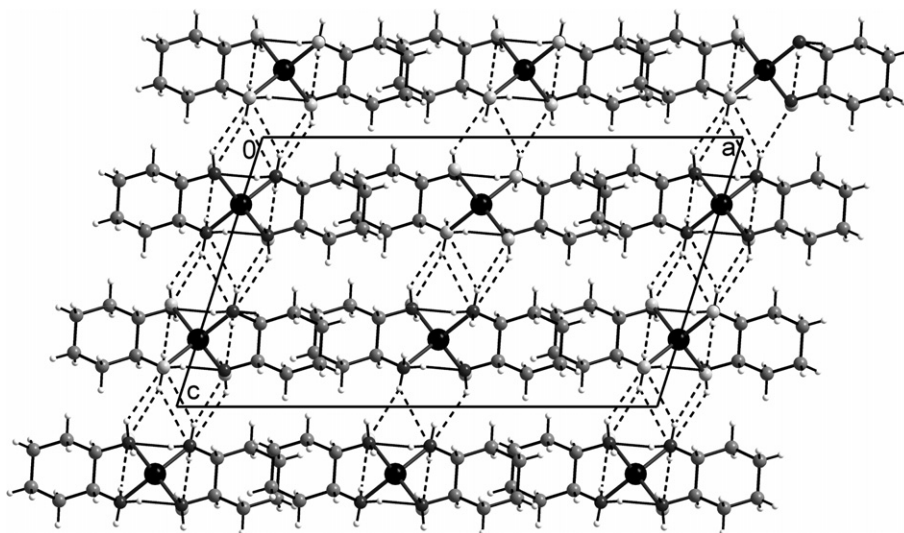| D–H⋯A	d(D–H)	d(H⋯A)	d(D⋯A)	∠DHA	Symmetry code
N1–H1⋯S1	0.890	2.769	3.596	155.19	−x + 1, −y + 1, −z
N1–H1⋯S2	0.890	2.872	3.472	126.10	−x + 1, −y + 1, −z
N1–H2⋯N2	0.890	2.029	2.911	171.02	−x + 1, y, −z + 1/2
N1–H3⋯S1	0.890	2.675	3.538	163.69	−x + 1, y − 1, −z + 1/2
N2–H1⋯S2	0.890	2.969	3.786	153.47	
N2–H2⋯S2	0.890	2.741	3.433	135.58	x, −y + 1, z + 1/2

Fig. 2. Crystal packing diagram of **1** with a view along the *b* axis showing the H-bonding network running along the *c* axis (hydrogen bonding is shown as dashed lines).

but is quite less compared to the Δ value of 0.0385 Å observed earlier for (pipH$_2$)[WS$_4$] [16].

Compound **3** crystallizes in the orthorhombic non-centrosymmetric space group $Pca2_1$ and its structure consists of discrete diprotonated dipn cations (dipnH$_2$)$^{2+}$ and
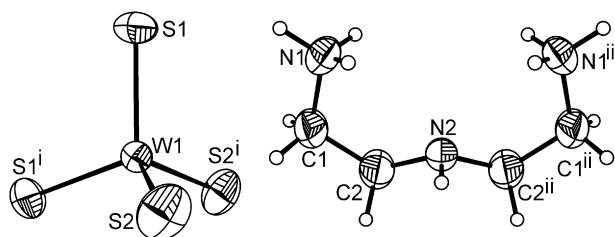

Fig. 3. Crystal structure of the anion (left) and cation (right) in (dienH$_2$)[WS$_4$] (**2**) with labelling and displacement ellipsoids drawn at the 50% probability level [symmetry codes: (i) $-x + 3/2$, $-y + 1/2$, z (ii) $-x + 1/2$, $-y + 1/2$, z].

Table 4
Selected geometric parameters (Å, °) for (dienH$_2$)[WS$_4$] (**2**)

W(1)–S(2)^i	2.172(1)	W(1)–S(1)	2.189(1)
W(1)–S(2)	2.172(1)	W(1)–S(1)^i	2.189(1)
S(2)^i–W(1)–S(2)	109.2(1)	S(1)–W(1)–S(1)^i	110.1(1)
S(2)^i–W(1)–S(1)	109.4(1)	S(2)^i–W(1)–S(1)^i	109.4(1)
S(2)–W(1)–S(1)	109.4(1)	S(2)–W(1)–S(1)^i	109.4(1)

Symmetry transformations used to generate equivalent atoms: $^i-x + 3/2$, $-y + 1/2$, z.

[WS$_4$]$^{2-}$ anions (Fig. 5), with all atoms being located in general positions. One of the primary N atoms and the central secondary N atom are protonated, unlike in **2**. Again, the WS$_4$ tetrahedron is slightly distorted (S–W–S angles: 108.90(6)–110.23(5)°; average: 109.47°) with W–S bond lengths from 2.188(2) to 2.2053(12) Å (mean value: 2.195 Å) (Table 6). The geometric parameters are in close agreement with those for other organic ammonium tetrathiotungstates like **2** or (tmenH$_2$)[WS$_4$] (tmen = N,N,N',N'-tetramethylethylenediamine) [14]. Extended H-bonding interactions produce a three-dimensional network (Fig. 6). The cations and [WS$_4$]$^{2-}$ anions are stacked in rods along [0 0 1] to form a pseudo-hexagonal array. Along [1 0 0] and [0 1 0] cations and anions alternate. In the (0 1 0) plane a layer like arrangement is found with the anions being located in the pockets formed by three neighboring cations. A very short N3–H⋯N1 contact of 1.896 Å links the cations into a chain running along the *c* axis. Every anion is surrounded by four different cations and eight short S⋯H distances ranging from 2.532 to 2.958 Å (Table 7) indicate weak S⋯H bonding, with all H atoms attached to the N atoms being involved in H-bonding unlike in **2**. The difference between the longest and shortest W–S bond Δ is 0.0173 Å and is quite small compared to the Δ value (0.0385) observed earlier for (pipH$_2$)[WS$_4$]. In general the W–S bond lengths tend to be longer when the S⋯H contacts are shorter and the N–H⋯S angles are less acute [14–17]. In the present compound the shortest S⋯H

Table 5
Hydrogen-bonding geometry (Å, °) for (dienH$_2$)[WS$_4$] (**2**)

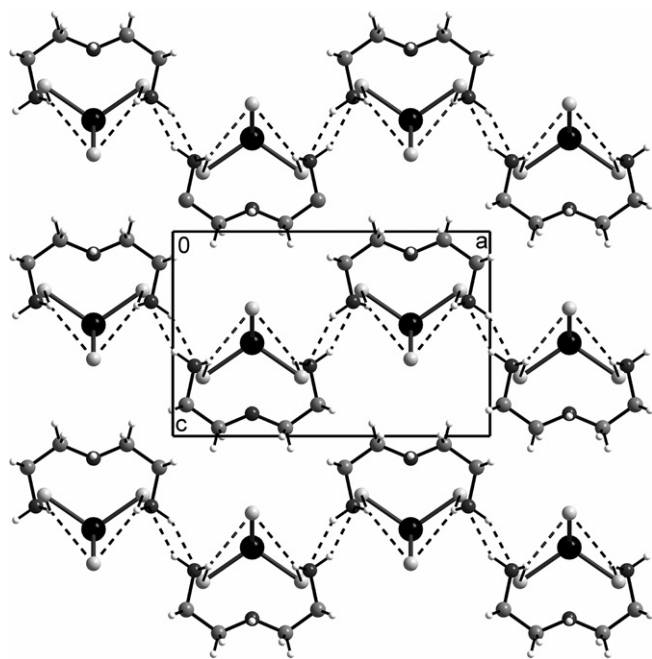| D–H⋯A	d(D–H)	d(H⋯A)	d(D⋯A)	∠D–HA	Symmetry code
N1–H1⋯S1	0.890	2.531	3.344	152.13	
N1–H2⋯S2	0.890	2.765	3.500	140.74	$x - 1/2$, $y + 1/2$, $-z + 1$
N1–H2 ⋯S1	0.890	2.968	3.657	135.61	$-x + 1$, $-y + 1$, $-z + 1$

Fig. 4. Crystal packing diagram of **2** with a view along the *b* axis showing the H-bonding network (hydrogen bonding is shown as dashed lines).

contact of 2.532 Å is accompanied by the shortest W–S3 bond. The reason for this is not clear. It is to be noted that no structurally characterized $[WS_4]^{2-}$ compound containing a protonated primary amine (N3), a protonated secondary amine (N2) and a free primary amine (N1) has so far been reported. Hence a possible explanation may be the type of N–H···S interactions are probably different in view of the differing nature of the amine groups. In addition, the very strong N3–H···N1 interaction may weaken the S···H interaction. For a better understanding more examples with the above-mentioned situation are needed
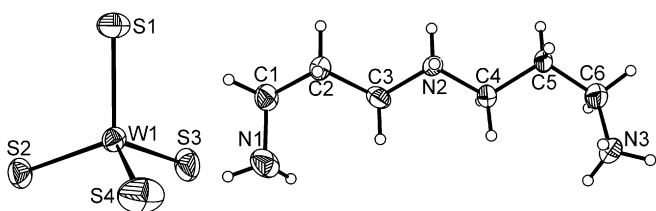

Fig. 5. Crystal structure of the anion (left) and cation (right) in $(dipnH_2)[WS_4]$ (**3**) with labelling and displacement ellipsoids drawn at the 50% probability level.

Table 6
Selected geometric parameters (Å, °) for $(dipnH_2)[WS_4]$ (**3**)

W(1)–S(3)	2.1882(22)	W(1)–S(4)	2.1950(21)
W(1)–S(2)	2.1935(13)	W(1)–S(1)	2.2053(12)
S(3)–W(1)–S(2)	108.90(7)	S(3)–W(1)–S(1)	109.40(8)
S(3)–W(1)–S(4)	109.21(8)	S(2)–W(1)–S(1)	110.23(5)
S(2)–W(1)–S(4)	109.83(9)	S(4)–W(1)–S(1)	109.25(7)

and synthesis and characterization of such tetrathiotungstates are under way in our laboratories.

3.3. Spectral studies

A combination of UV–Vis, infrared and Raman spectroscopic techniques has been employed to characterize the compounds. The electronic spectra recorded in water exhibit bands at around 393, 280 and 220 nm. These peak positions are almost identical within experimental error to the corresponding ammonium or organic ammonium salts [3,16] and can be assigned to the charge transfer transitions of the $[WS_4]^{2-}$ moiety [3]. The mid IR up to 500 cm^{-1} exhibit several signals which can be attributed to the absorptions of the organic cations. Unlike the IR spectra of the previously reported compounds $(pipH_2)[WS_4]$, $(enH_2)[WS_4]$ etc., which exhibit a broad signal at around 3000 cm^{-1} for the N–H vibrations, more signals are observed in the N–H region (3300–3000 cm^{-1}) in **1**–**3**. This can be attributed to the presence of both free and protonated amine functionalities. For **1** the ν_{N-H} absorptions occur at around 3309 (s), 3239 (s) and 3054 (br) cm^{-1}. Similarly the bands at 3243 (s) and 3054 (br) cm^{-1} in **2** and the signals at 3309 (s), 3239 (s) and 3094 (br) cm^{-1} in **3** can be assigned to the N–H vibrations. The free tetrahedral $[WS_4]^{2-}$ anion is expected to show four normal modes of vibrations viz. $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$ [25]. All four vibrations are Raman active while only ν_3 and ν_4 are infrared active. The usefulness of IR spectra for the characterization of the tetrathiotungstates is well documented in the literature as the metal–sulfur vibrations appear as characteristic signals below 500 cm^{-1} [26]. When the T_d symmetry of WS$_4$ is lowered to C_{2v}, as in $[Ni(WS_4)_2]^{2-}$ where $[WS_4]^{2-}$ functions as a bidentate ligand, it has been shown that this leads to a splitting of the triply degenerate $\nu_3(F_2)$ vibration of the W–S bond [25,26]. In $[Ni(WS_4)_2]^{2-}$ the W–S bond to the bridging S atom is long (W–S–Ni) and the W–S bond to terminal S atom is short (2.151 Å). In our compounds the longer W–S distances are always observed when strong S···H bonding interactions are present, and the W–S bond length distribution indicates a slight distortion of the tetrahedra. A splitting of the W–S vibration (Fig. 7) was observed in $(pipH_2)[WS_4]$ [16] which shows a difference of $\Delta = 0.0385$ Å between the longest and the shortest W–S bonds. However for **1**–**3** no such splitting is observed in the IR spectra. The symmetric stretching vibration ν_1 is observed as a shoulder along with the strong absorption due to the asymmetric mode of ν_3. In the Raman spectra of all the three compounds an intense signal is observed around 480 cm^{-1} indicating that the weak signal around the same frequency in the IR spectra should be due to the symmetric stretching mode. The asymmetric stretching vibration ν_3 in **1**–**3** occurs as a sharp signal at around 460 cm^{-1} along with a very weak band at about 480 cm^{-1} and these spectra do not show the characteristic splitting pattern observed in $(pipH_2)[WS_4]$ whose Δ value is more than twice that of the title complexes. The
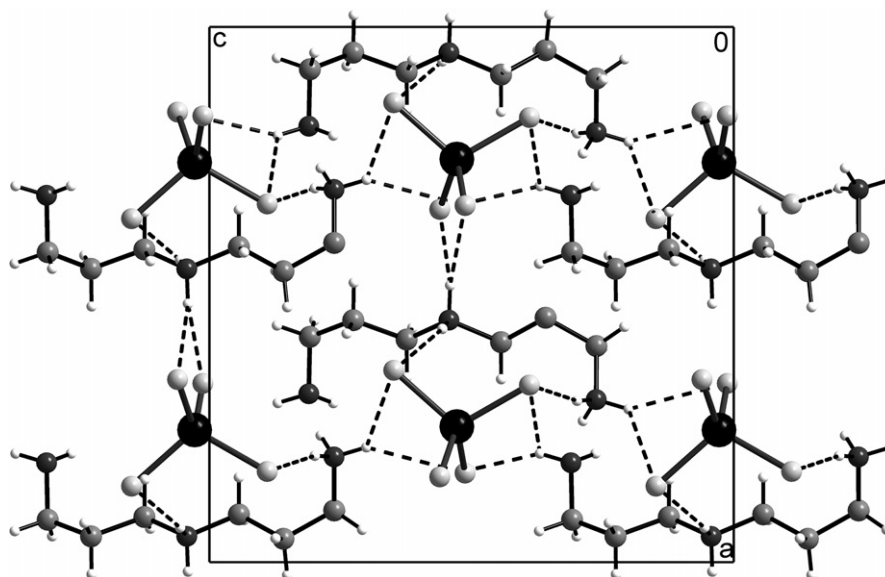
Fig. 6. Crystal packing diagram of **3** with a view along the *b* axis showing the extended H-bonding network (hydrogen bonding is shown as dashed lines).

Table 7
Hydrogen-bonding geometry (Å, °) for (dipnH$_2$)[WS$_4$] (**3**)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA	Symmetry code
N1–H2...S2	0.890	2.779	3.587	151.73	$-x + 3/2, y - 1, z + 1/2$
N1–H2...S3	0.890	2.806	3.361	121.76	$-x + 3/2, y - 1, z + 1/2$
N2–H1...S4	0.900	2.639	3.494	159.08	
N2–H2...S2	0.900	2.660	3.401	140.20	$x - 1/2, -y + 1, z$
N2–H2...S1	0.900	2.741	3.446	135.98	$x - 1/2, -y + 1, z$
N3–H1...S3	0.890	2.532	3.408	167.95	
N3–H2...S1	0.890	2.675	3.470	149.35	$-x + 3/2, y, z - 1/2$
N3–H2...S4	0.890	2.958	3.534	124.07	$-x + 3/2, y, z - 1/2$
N3–H3...N1	0.890	1.899	2.768	165.06	$-x + 3/2, y, z - 1/2$

signals due to the degenerate v_2 and v_4 vibrations occur at around 190 cm^{-1} in **1–3**.

3.4. Comparative study of the structural features of tetrathiotungstates

Tetrathiotungstates containing different cations like the fully inorganic (NH$_4$)$^+$, Rb$^+$, cationic metal complexes like [Ni(tren)$_2$]$^{2+}$, [Ni(en)$_3$]$^{2+}$ and [Mn(en)$_3$]$^{2+}$ and a variety of organic ammonium cations like (enH$_2$)$^{2+}$, (dienH$_2$)$^{2+}$ are known. The isolation and structural characterization of [WS$_4$]$^{2-}$ with these different cations indicates the flexibility of the tetrathiotungstate ion to exist in different structural environments. It is to be noted that of the 20 tetrathiotungstates listed in Table 8 only the [WS$_4$]$^{2-}$ complexes derived from [Ni(en)$_3$]$^{2+}$, en, N-Me-en and dipn crystallize in non-centrosymmetric space groups. In addition to Rb$_2$[WS$_4$], where the mean Rb$\cdot\cdot\cdot$S distance has been reported to be 3.5466 Å, the compounds [(Et)$_4$N]$_2$[WS$_4$] and [(Pr)$_4$N]$_2$-[WS$_4$], which contain the fully alkylated organic ammonium cations, do not show any H-bonding interactions between the anion and cation [27]. All the other complexes exhibit weak H-bonding interactions between the cation

and [WS$_4$]$^{2-}$. A comparative study of the structural parameters of 20 different tetrathiotungstates is presented here to explain the importance of the S$\cdot\cdot\cdot$H bonding interactions in the structural chemistry of tetrathiotungstates. In all compounds the average S–W–S angles are very close to the ideal tetrahedral value. The average value of the W–S distance ranges from 2.1788 Å in [Mn(en)$_3$][WS$_4$] to 2.195 Å in **3**. It is also noted that the difference Δ between the longest and the shortest W–S bond ranges from 0.0092 Å in (enH$_2$)[WS$_4$] to 0.0542 in [Ni(tren)$_2$][WS$_4$]. The compound [Ni(tren)$_2$][WS$_4$] is different compared with the organic ammonium tetrathiotungstates because it shows the shortest W–S distance of 2.1580 Å and also the maximum $\Delta = 0.0542$, even though the shortest S$\cdot\cdot\cdot$H contact is observed for this complex at a distance of 2.73 Å. We note that in [Ni(tren)$_2$][WS$_4$] the N atom of tren is not protonated, unlike in the organic ammonium compounds, but is linked to Ni(II). This indicates that the nature of the N–H$\cdot\cdot\cdot$S contacts in [Ni(tren)$_2$][WS$_4$] are probably different from those in the organic ammonium tetrathiotungstates. The same argument is applicable for the N–H$\cdot\cdot\cdot$S contacts in the other two cationic complexes, namely [Ni(en)$_3$][WS$_4$] and [Mn(en)$_3$][WS$_4$].
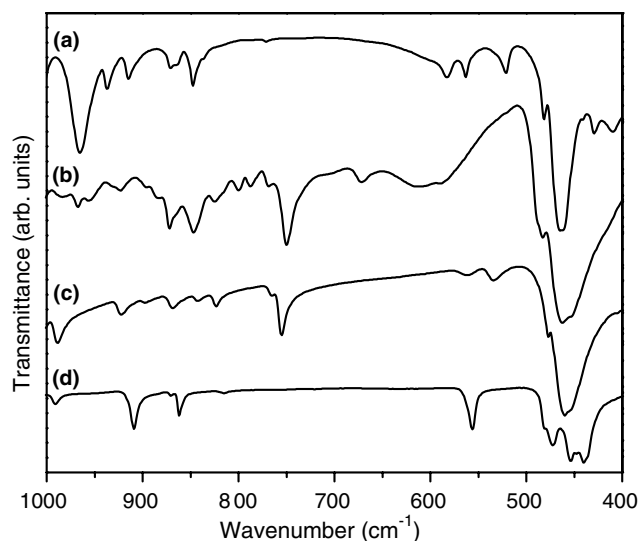
Fig. 7. Infrared spectra of (a) (*trans*-1,2-cnH)$_2$[WS$_4$], (b) (dienH$_2$)[WS$_4$], (c) (dipnH$_2$)[WS$_4$] and (d) (pipH$_2$)[WS$_4$].

In the organic ammonium [WS$_4$]$^{2-}$ complexes, including the fully protonated (NH$_4$)$_2$[WS$_4$], the longest W–S bonds range from 2.2147 in (pipH$_2$)[WS$_4$] to 2.189 Å in (dienH$_2$)[WS$_4$] **2**. Furthermore, the shortest S···H contacts in all organic ammonium tetrathiotungstates are in a very narrow range of 2.31 Å for (N-Me-enH$_2$)[WS$_4$] (N-Me-en is *N*-methylethylenediamine) to 2.68 Å in **1** and **3**. The difference between the longest and shortest W–S bonds can probably be taken as a measure of the distortion of the [WS$_4$]$^{2-}$ tetrahedron. In an earlier report [17] we have shown that when the Δ value is larger than 0.033 Å a split-

ting of the W–S vibration is seen in the IR spectra. From the analysis of the structural features certain trends emerge. The substitution of one H by a methyl group in en to N-Me-en results in the increase of Δ, indicating the role of methyl groups in enhancing distortion. The same effect is also observed for the pair of cations 1,3-pn and (*N,N'*-dm-1,3-pn). It is of interest that when all H atoms in en are replaced by methyl groups, as in tmen, the experimental value for Δ is larger than that for en but smaller than that for N-Me-en by 0.01 Å. In all compounds listed in Table 8 (pipH$_2$)[WS$_4$] is unique as the cation is derived from a cyclic amine in which the N atoms are part of the ring. In the present work, the Δ value for compound **1** is 0.0104 Å and the cation in **1** is derived from the amine *trans*-1,2-cn where the –NH$_2$ functional groups are attached to a six membered ring.

The Δ values of the two organic ammonium tetrathiotungstates [(Et)$_4$N]$_2$[WS$_4$] (Et is ethyl) and [(Pr)$_4$N]$_2$[WS$_4$] (Pr is propyl) without N–H···S bonds are nearly identical (0.0184 and 0.0175 Å, respectively) [27] and the average is about 0.0180 Å. The usefulness of this value is that the observed difference Δ in the W–S bond lengths in these compounds is due to effects other than H-bonding interactions, i.e., they are probably of electrostatic nature. Interestingly, in the title compounds the values for Δ are 0.0104, 0.0170 and 0.0173 Å for **1**, **2** and **3**, respectively, and these values are smaller than or equal to that found for the fully alkylated organic ammonium tetrathiotungstates indicating that the H-bonding interactions do not show a pronounced influence in the title compounds to cause distortion in terms of the observed W–S bond

Table 8
Comparative structural parameters of tetrathiotungstates

Compound	Space group	W–S (long) in Å	W–S (short) in Å	Difference Δ in Å	W–S average in Å	S...H short in Å	References
(NH$_4$)$_2$[WS$_4$]	*Pnma*	2.2090	2.1856	0.0234	2.1905	2.57	[18]
Rb$_2$[WS$_4$]	*Pnma*	2.2053	2.1710	0.0343	2.1878		[10]
[Ni(tren)$_2$][WS$_4$]	*P2$_1$/c*	2.2122	2.1580	0.0542	2.1872	2.73	[11]
[Ni(en)$_3$][WS$_4$]	*Pna2$_1$*	2.190	2.162	0.028	2.1808	2.587	[12]
[Mn(en)$_3$][WS$_4$]	*Pbca*	2.189	2.168	0.021	2.1788	2.503	[12]
(enH$_2$)[WS$_4$]	*P2$_1$2$_1$2$_1$*	2.1943	2.1851	0.0092	2.1893	2.43	[13]
(N-Me-enH$_2$)[WS$_4$]	*P2$_1$2$_1$2$_1$*	2.2064	2.1727	0.0337	2.1919	2.31	[17]
(tmenH$_2$)[WS$_4$]	*P2$_1$/n*	2.1995	2.1772	0.0223	2.1891	2.56	[14]
(1,3-pnH$_2$)[WS$_4$]	*P2$_1$/c*	2.1946	2.1798	0.0148	2.1903	2.43	[14]
(*N,N'*-dm-1,3-pnH$_2$)[WS$_4$]	*P2$_1$/n*	2.1992	2.1771	0.0221	2.1931	2.42	[17]
(1,4-bnH$_2$)[WS$_4$]	*P$\bar{1}$*	2.2030	2.1799	0.0231	2.1918	2.39	[17]
(trenH$_2$)[WS$_4$] · H$_2$O	*P2$_1$/c*	2.1997	2.1739	0.0258	2.1904	2.46	[16]
(mipaH)$_2$[WS$_4$]	*C2/c*	2.2126	2.1792	0.0334	2.1940	2.47	[17]
(pipH$_2$)[WS$_4$]	*P2$_1$/c*	2.2147	2.1762	0.0385	2.1937	2.39	[16]
(1,4-dmpH$_2$)[WS$_4$]	*Pbca*	2.2136	2.1781	0.0355	2.1943	2.64	[15]
[(Et)$_4$N]$_2$[WS$_4$]	*P2$_1$/n*	2.2030	2.1846	0.0184	2.1919		[27]
[(Pr)$_4$N]$_2$[WS$_4$]	*C2/c*	2.2009	2.1834	0.0175	2.1935		[27]
(*trans*-1,2-cnH)$_2$[WS$_4$]	*C2/c*	2.1978	2.1874	0.0104	2.1926	2.68	this work
(dienH$_2$)[WS$_4$]	*Pmmn*	2.189	2.172	0.0170	2.1805	2.54	this work
(dipnH$_2$)[WS$_4$]	*Pca2$_1$*	2.2053	2.188	0.0173	2.195	2.68	this work

Abbreviations. tren, tris(2-aminoethyl)amine; en, ethylenediamine; N-Me-en, *N*-methylethylenediamine; tmen, *N,N,N',N'*-tetramethylethylenediamine; 1,3-pn, 1,3-propanediamine; *N,N'*-dm-1,3-pn, *N,N'*-dimethyl-1,3-propanediamine; 1,4-bn, 1,4-butanediamine; mipa, monoisopropylamine; pip, piperazine; 1,4-dmp, 1,4-dimethylpiperazine; Et, ethyl; Pr, *n*-propyl.

distances. The infrared spectral observations are also indicative of a similar behavior. Hence the cation–anion interactions in the title compounds can be classified as weak interactions.

4. Conclusions

The reaction of $(NH_4)_2[WS_4]$ with the cyclic diamine *trans*-1,2-cn and the acyclic triamines bis(2-aminoethyl)amine (dien), bis(3-aminopropyl)amine (dipn) results in the formation of organic ammonium tetrathiotungstates **1**–**3**. The title complexes react with $[Ni(en)_3]^{2+}$ to form the highly insoluble complex $[Ni(en)_3][WS_4]$. The structures of **1**–**3** consist of tetrahedral $[WS_4]^{2-}$ anions which are linked to partially protonated organic ammonium cations with the aid of weak N–H···S interactions. The importance of these weak interactions can be evidenced especially in the case of compound **2** as the corresponding oxo analogue has been reported to exist only in solution [22]. Unlike WO_3, which dissolves in aqueous dien, WS_3 does not dissolve in dien indicating the differing nature of oxo and thio analogues of W. The complexes exhibit distinct W–S bond lengths and the observed Δ values are comparable to those observed in tetralkylammonium tetrathiotungstates. A comparative study of the structural features of 20 tetrathiotungstates indicates that tetrathiotungstates are less prone to pack in non-centrosymmetric space groups.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 601986 (**1**), CCDC 601987 (**2**) and CCDC 601988 (**3**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 122 3336 033 or email: deposit@ccdc.cam.ac.uk.

References

[1] S.E. Skrabalak, K.E. Suslick, J. Am. Chem. Soc. 127 (2005) 9990.
[2] R. Tenne, M. Homyonfer, Y. Feldman, Chem. Mater. 10 (1998) 3225.
[3] A. Müller, E. Diemann, R. Jostes, H. Bögge, Angew. Chem., Int. Ed. Engl. 20 (1981) 934.
[4] T. Shibhahara, Coord. Chem. Rev. 123 (1993) 73.
[5] D. Coucouvanis, Adv. Inorg. Chem. 45 (1998) 1.
[6] M. Nath, A. Govindaraj, C.N.R. Rao, Adv. Mater. 13 (2001) 283.
[7] J. Chen, S.L. Li, F. Gao, Z.L. Tao, Chem. Mater. 15 (2003) 1012.
[8] Y.D. Li, X.L. Li, R.R. He, J. Zhu, Z.X. Deng, J. Am. Chem. Soc. 124 (2002) 1411.
[9] J.J. Berzelius, Poggendorffs Ann. Phys. Lpz. 8 (1826) 277.
[10] J. Yao, J.A. Ibers, Acta Crystallogr., Sect. E 60 (2004) i10.
[11] J. Ellermeier, R. Stähler, W. Bensch, Acta Crystallogr., Sect. C 58 (2002) m70.
[12] J. Ellermeier, Ph.D. Dissertation, University of Kiel, Germany, 2002.
[13] B.R. Srinivasan, S.N. Dhuri, C. Näther, W. Bensch, Acta Crystallogr., Sect. E 58 (2002) m622.
[14] B.R. Srinivasan, S.N. Dhuri, C. Näther, W. Bensch, Acta Crystallogr., Sect. C 59 (2003) m124.
[15] B.R. Srinivasan, S.N. Dhuri, C. Näther, W. Bensch, Acta Crystallogr., Sect. E 59 (2003) m681.
[16] B.R. Srinivasan, S.N. Dhuri, M. Poisot, C. Näther, W. Bensch, Z. Anorg. Allg. Chem. 631 (2005) 1087.
[17] B.R. Srinivasan, C. Näther, S.N. Dhuri, W. Bensch, Monats. Chem. 137 (2006) 397.
[18] B.R. Srinivasan, M. Poisot, C. Näther, W. Bensch, Acta Crystallogr., Sect. E 60 (2004) i136.
[19] J.W. McDonald, G.D. Friesen, L.D. Rosenhein, W.E. Newton, Inorg. Chim. Acta 72 (1983) 205.
[20] G.M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1994.
[21] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, 1997.
[22] R.S. Taylor, P. Gans, P.F. Knowles, A.G. Sykes, J. Chem. Soc., Dalton 24 (1972).
[23] B.R. Srinivasan, C. Näther, W. Bensch, Acta Crystallogr., Sect. C 62 (2006) m98.
[24] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[25] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., John Wiley, New York, 1997.
[26] K.H. Schmidt, A. Müller, Coord Chem. Rev. 14 (1974) 115.
[27] M. Poisot, C. Näther, W. Bensch, Z. Naturforsch (in press).