Monatshefte für Chemie 137, 397–411 (2006)
DOI 10.1007/s00706-005-0456-y

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

On the Importance of H-Bonding Interactions in Organic Ammonium Tetrathiotungstates[#]

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Received August 16, 2005; accepted (revised) October 5, 2005

Summary. Four new organic ammonium tetrathiotungstates (*N–Me–en*H_2)[WS_4] (**1**), (*N,N′-dm*-1,3-*pn*H_2)[WS_4] (**2**), (1,4-*bn*H_2)[WS_4] (**3**), and (*mipa*H)$_2$[WS_4] (**4**), (*N–Me–en*H_2 = *N*-methylethylenediammonium, *N,N′-dm*-1,3-*pn*H_2 = *N,N′*-dimethyl-1,3-propanediammonium, 1,4-*bn*H_2 = 1,4-butanediammonium, and *mipa*H = monoisopropylammonium) were synthesized by the base promoted cation exchange reaction and characterized by elemental analysis, infrared, *Raman*, UV-Vis and ^{1}H NMR spectroscopy as well as single crystal X-ray crystallography. The structures of **1**–**4** consist of $[WS_4]^{2-}$ tetrahedra which are linked to the organic ammonium cations via N–H···S hydrogen bonding. The strength and number of the S···H interactions affect the W–S bond lengths as evidenced by distinct short and long W–S bonds. The IR spectra exhibit splitting of the W–S vibrations, which can be attributed to the distortion of the $[WS_4]^{2-}$ tetrahedron. From a comparative study of several known tetrathiotungstates it is observed that a difference of more than 0.033 Å between the longest and shortest W–S bonds in a tetrathiotungstate will result in the splitting of the asymmetric stretching vibration of the W–S bond.

Keywords. Organic ammonium tetrathiotungstates; N–H···S Hydrogen bonds; Distortion; WS_4 tetrahedron.

Introduction

The chemistry of Mo/W–S complexes is an area of intense research investigations owing to the use of the group VI metal sulfides in hydrodesulfurization catalysis (HDS) [1] and the emerging importance of the layered metal disulfides in nanomaterials [2]. The soluble sulfides of the group VI metals W and Mo [3–5] are a

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[#] Dedicated to Prof. Dr. *S. Venkateswaran* on the occasion of his 67th birthday 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. In the context of nanomaterials, the reported synthesis of WS_2 nanotubes from the gas phase reaction between WO_{3-x} and H_2S in a reducing atmosphere by *Tenne* and coworkers [6, 7] has added an entire new dimension to metal sulfide chemistry. The use of $(NH_4)_2[WS_4]$ as precursor for the soft synthesis of WS_2 nanotubes [8, 9], is an important reason for the current interest in the chemistry of tetrathiotungstate. Recently *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 [10]. This report indicates the emerging importance of organic ammonium salts of $[WS_4]^{2-}$ in material applications.

It has been well demonstrated that the tetrahedral $[WS_4]^{2-}$ unit is an important building block that can be used to prepare several W–S complexes [3, 4]. From a structural point of view $[WS_4]^{2-}$ is an interesting as well as an important motif due to its flexibility to exist in a variety of structural environments as evidenced by the structural characterization of several $[WS_4]^{2-}$ complexes with different counter ions in our earlier work [11–16]. In almost all these complexes, the WS_4 tetrahedron is slightly distorted with one or two of the W–S bonds elongated, which has been explained on the basis of the strength and numbers of $S\cdots H$ interactions between $[WS_4]^{2-}$ and the organic cation. In our research, we are investigating the synthesis and structural characterization of organic ammonium tetrathiotungstates [11–14] and tetrathiomolybdates [17, 18] and have already shown that a rich chemistry of tetrathiotungstates can be developed by suitably changing the H-bonding interactions between the organic cation and $[WS_4]^{2-}$ [16]. In the present work, we wish to describe the synthesis, spectroscopic, and X-ray structural characterization of four new tetrathiotungstates obtained by the reaction of $(NH_4)_2[WS_4]$ with the amines *N*-methylethylendiamine (*N–Me–en*), *N*,*N'*-dimethyl-1,3-propanediamine (*N*,*N'*-*dm*-1,3-*pn*), 1,4-butanediamine (1,4-*bn*), and monoisopropylamine (*mipa*). The amines used in this work differ in terms of the steric bulk as well as the number of potential H-bonding donors. The importance of the resulting H-bonding interactions in the structural aspects of organic ammonium tetrathiotungstates is discussed in this paper.

Results and Discussions

Description of the Crystal Structures

Complex **1** crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with all atoms in general positions (Fig. 1 top). The geometric parameters of **1** are in good agreement with those in other tetrathiotungstates like *e.g.* $(enH_2)[WS_4]$ (*en* = ethylenediamine) [11]. The $[WS_4]^{2-}$ tetrahedron is slightly distorted and the W–S bonds vary from 2.1727(15) to 2.2064(14) Å (average: 2.1919 Å) (Table 1). Two of the bonds are shorter while the other two are longer than the average value. This feature can be explained based on the strength and number of $S\cdots H$ bonding interactions. The resulting hydrogen bonding network is shown in Fig. 1 bottom. Seven $S\cdots H$ contacts ranging from 2.308 to 2.915 Å (Table 2) are observed in **1**, less than the nine contacts in $(enH_2)[WS_4]$ (range: 2.43 to 3.0 Å) [11] which can be

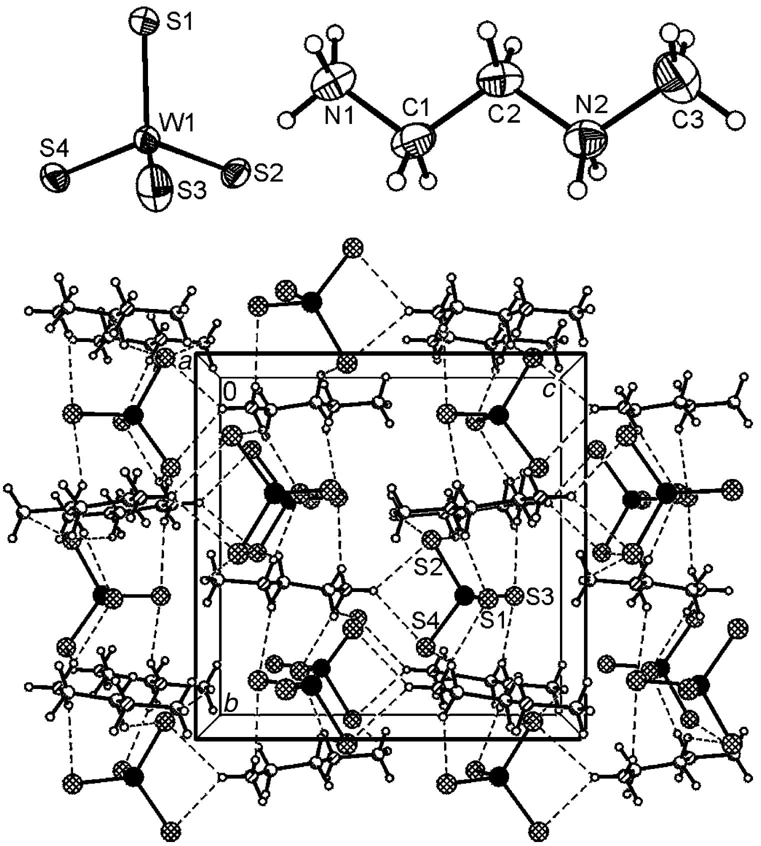

Fig. 1. Crystal structure of compound **1** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with view in the direction of the crystallographic *a*-axis (bottom; hydrogen bonding is shown as dashed lines)

attributed to the replacement of one H atom bound to N(2) by a CH_3 group. All S···H distances in **1** are shorter than 3.00 Å which is the sum of the *van der Waals* radii of S and H, and six of them are shorter by about 0.30 Å indicating strong interactions [19]. The S(1), S(3), and S(4) atoms have two short contacts each while S(2) has only one such contact. The single short contact with a relatively long S···H distance of 2.685 Å is accompanied by a small N–H–S angle (134.57°)

Table 1. Selected geometric parameters (Å, °) for (*N–Me–en*H_2)[WS_4] (**1**)

W(1)–S(2)	2.1727 (15)	N(1)–C(1)	1.476 (8)
W(1)–S(4)	2.1850 (14)	C(1)–C(2)	1.513 (9)
W(1)–S(3)	2.2037 (15)	C(2)–N(2)	1.475 (8)
W(1)–S(1)	2.2064 (14)	N(2)–C(3)	1.501 (8)
S(2)–W(1)–S(4)	110.64 (6)	S(2)–W(1)–S(1)	109.27 (6)
S(2)–W(1)–S(3)	108.28 (6)	S(4)–W(1)–S(1)	108.97 (6)
S(4)–W(1)–S(3)	109.73 (6)	S(3)–W(1)–S(1)	109.93 (6)
N(1)–C(1)–C(2)	110.2 (5)	C(2)–N(2)–C(3)	111.7 (6)
N(2)–C(2)–C(1)	110.6 (5)		

Table 2. Hydrogen-bonding parameters (Å, °) for (*N–Me–en*H$_2$)[WS$_4$] (**1**)

D–H···*A*	*d*(D–H)	*d*(H···A)	*d*(D···A)	<DHA	Symmetry code
N1–H1···S1	0.940	2.383	3.290	161.91	$x - 1/2, -y + 3/2, -z + 1$
N1–H1···S4	0.940	2.915	3.404	113.75	$x - 1/2, -y + 3/2, -z + 1$
N1–H2···S4	0.940	2.650	3.376	134.46	
N1–H2···S2	0.940	2.685	3.411	134.57	
N1–H3···S3	0.940	2.536	3.259	133.90	$-x + 1/2, -y + 1, z - 1/2$
N2–H1···S3	0.940	2.388	3.198	144.18	$x - 1/2, -y + 3/2, -z + 1$
N2–H2···S1	0.940	2.308	3.222	163.91	$-x + 3/2, -y + 1, z - 1/2$

and may explain the shortest W–S(2) bond of 2.1727(15) Å. In contrast, the two shortest S···H separations (2.308 and 2.383 Å) accompanied by the largest N–H···S angles (163.91 and 161.91°) can account for the longest W–S(1) distance of 2.2064(14) Å. The intermediate W–S bond lengths of 2.1850 and 2.2037 Å can be similarly explained based on the strengths of the H-bonding interactions. The difference between the longest and the shortest W–S bond Δ is 0.0337 Å and is considerably larger than the difference observed in (*en*H$_2$)[WS$_4$] (0.0092 Å).

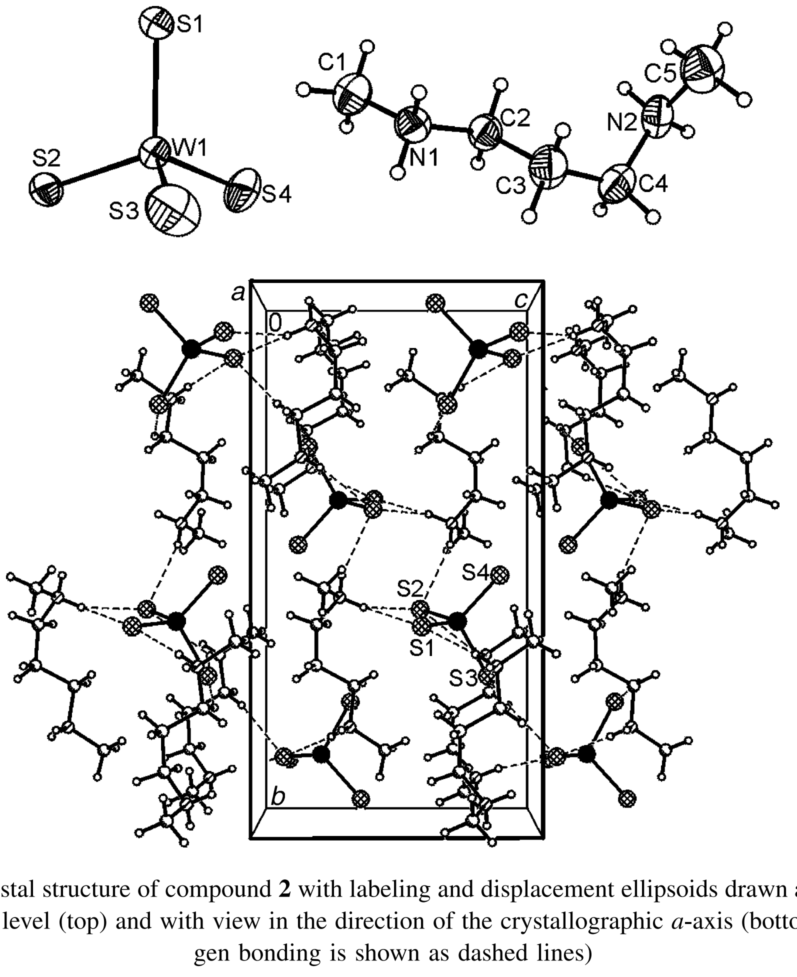

Fig. 2. Crystal structure of compound **2** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with view in the direction of the crystallographic *a*-axis (bottom; hydrogen bonding is shown as dashed lines)

Table 3. Selected geometric parameters (Å, °) for (N,N'-dm-1,3-pnH$_2$)[WS$_4$] (**2**)

W(1)–S(4)	2.1771 (14)	N(1)–C(2)	1.462 (7)
W(1)–S(3)	2.1980 (15)	C(2)–C(3)	1.520 (7)
W(1)–S(2)	2.1982 (12)	C(3)–C(4)	1.496 (9)
W(1)–S(1)	2.1992 (12)	C(4)–N(2)	1.503 (8)
C(1)–N(1)	1.468 (7)	N(2)–C(5)	1.466 (8)
S(4)–W(1)–S(3)	109.26 (7)	S(4)–W(1)–S(1)	109.60 (6)
S(4)–W(1)–S(2)	109.93 (6)	S(3)–W(1)–S(1)	109.64 (6)
S(3)–W(1)–S(2)	109.09 (6)	S(2)–W(1)–S(1)	109.30 (5)
C(2)–N(1)–C(1)	115.0 (5)	C(4)–C(3)–C(2)	113.7 (5)
N(1)–C(2)–C(3)	109.9 (4)	C(3)–C(4)–N(2)	114.2 (5)
C(5)–N(2)–C(4)	117.3 (5)		

This feature indicates that the further alkylation of an organic diamine can increase the distortion of the WS$_4$ tetrahedron.

Complex **2** crystallizes in space group $P2_1/n$ and contains tetrahedral $[WS_4]^{2-}$ dianions and (N,N'-dm-1,3-pnH$_2$)$^{2+}$ counter cations (Fig. 2 top). As in **1**, the $[WS_4]^{2-}$ tetrahedron is slightly distorted (W–S bonds: 2.1771(14)–2.1992(12) Å, average: 2.1931 Å) and geometric parameters are comparable to that in (1,3-pnH$_2$)[WS$_4$] (1,3-pn = 1,3-propanediamine) [13]. Three of the W–S bonds are longer than the mean value while the fourth W–S bond is shorter (Table 3). The elongation of the three W–S bonds is accompanied by short N–H···S contacts ranging from 2.424 to 2.960 Å (Table 4) and all distances are shorter than the sum of the *van der Waals* radii of S and H. The extended H bonding network is depicted in Fig. 2 bottom. The S···H distances are comparable to those in the related complex (1,3-pnH$_2$)[WS$_4$] (2.43 to 2.81 Å). S(2) has three S···H contacts, S(1) two, and S(3)/S(4) each have one such interaction. The W–S(4) bond is very short at 2.1771(14) Å which may be induced by the weak S···H interaction (2.96 Å) and the small N–H···S(4) angle of 131.21°. Also the W–S(3) bond of 2.1980 Å can be explained on the basis of a single S···H contact at 2.479 Å and the N–H···S angle of 154.59°. The W–S(1) distance of 2.1992(12) Å is the longest bond and is associated with the shortest S···H separation (2.424 Å) and the largest N–H···S angle of 175.62°. Although S(2) has three S···H contacts the W–S(2) distance is slightly shorter than W–S(1), which can be explained on the basis of two longer S···H separations with smaller N–H···S angles. The value for Δ is 0.0221 Å and is larger than that observed for

Table 4. Hydrogen-bonding parameters (Å, °) for (N,N'-dm-1,3-pnH$_2$)[WS$_4$] (**2**)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<DHA	Symmetry code
N1–H1···S3	0.900	2.479	3.314	154.59	$x-1, y, z$
N1-H1···S2	0.900	2.895	3.458	122.12	$x-1, y, z$
N1–H2···S1	0.900	2.424	3.322	175.62	
N2–H1···S2	0.900	2.556	3.351	147.70	$-x+3/2, y+1/2, -z+3/2$
N2–H1···S4	0.900	2.960	3.617	131.21	$-x+3/2, y+1/2, -z+3/2$
N2–H2···S1	0.900	2.596	3.390	147.56	$x-1/2, -y+1/2, z-1/2$
N2–H2···S2	0.900	2.811	3.431	127.23	$x-1/2, -y+1/2, z-1/2$

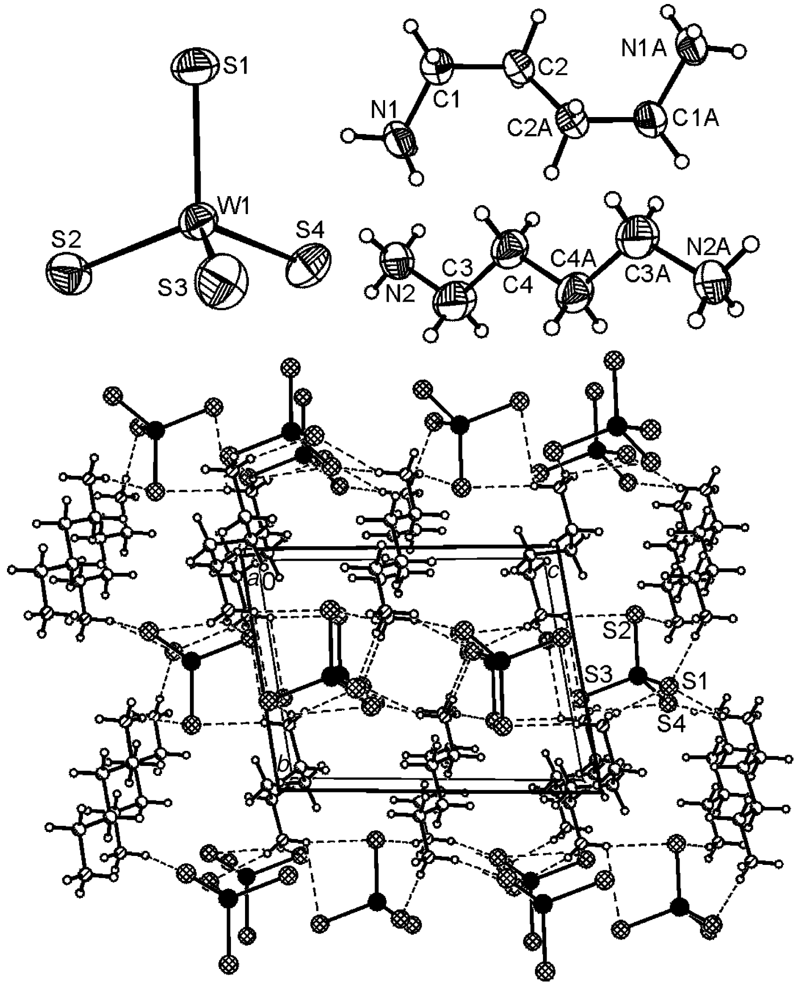

Fig. 3. Crystal structure of compound **3** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with view in the direction of the crystallographic *a*-axis (bottom; hydrogen bonding is shown as dashed lines)

(1,3-*pn*H_2)[WS_4] (0.0148 Å) indicating the role of the methyl groups to enhance the distortion of the $[WS_4]^{2-}$ tetrahedron.

Complex **3** crystallizes in space group $P\bar{1}$ with two crystallographically independent cations which are located on centres of inversion (Fig. 3 top). Its structure is built up of discrete (1,4-*bn*$H_2)^{2+}$ cations and tetrahedral $[WS_4]^{2-}$ anions connected to each other *via* hydrogen bonding interactions (Fig. 3 bottom). Bond lengths and angles of (1,4-*bn*$H_2)^{2+}$ (Table 5) are in good agreement with data for (1,4-*bn*H_2)[CrO_4] [20]. The $[WS_4]^{2-}$ tetrahedron is moderately distorted and W–S bonds vary from 2.1799(8) to 2.2030(8) Å (average: 2.1918 Å) (Table 5), being comparable with values in other tetrathiotungstates [11, 13]. Two W–S bonds are longer and the other two are comparatively shorter than the mean W–S distance. Nine S···H distances (range: 2.387–3.002 Å) (Table 6) are observed. We note that six are shorter than the sum of the S and H *van der Waals* radii by about 0.35 Å. S(1) and S(4) are involved in three short S···H bonds while S(2) has two such short

Table 5. Selected geometric parameters (Å, °) for (1,4-*bn*H_2)[WS_4] (**3**)

W(1)–S(1)	2.1799 (8)	C(2)–C(2A)	1.516 (6)
W(1)–S(3)	2.1820 (10)	C(3)–C(4)	1.483 (5)
W(1)–S(4)	2.2024 (9)	C(1)–C(2)	1.514 (4)
W(1)–S(2)	2.2030 (8)	N(2)–C(3)	1.482 (4)
N(1)–C(1)	1.486 (4)	C(4)–C(4A)	1.514 (6)
S(1)–W(1)–S(3)	109.70 (4)	S(1)–W(1)–S(4)	108.63 (4)
S(3)–W(1)–S(4)	109.91 (4)	S(1)–W(1)–S(2)	109.49 (3)
S(3)–W(1)–S(2)	109.09 (3)	S(4)–W(1)–S(2)	110.01 (4)
N(1)–C(1)–C(2)	111.8 (3)	C(1)–C(2)–C(2A)	113.4 (4)
N(2)–C(3)–C(4)	112.7 (3)	C(3)–C(4)–C(4A)	112.6 (4)

Table 6. Hydrogen-bonding parameters (Å, °) for (1,4-*bn*H_2)[WS_4] (**3**)

D–H···*A*	*d*(D–H)	*d*(H···A)	*d*(D···A)	<DHA	Symmetry code
N1–H1A···S4	0.890	2.444	3.304	162.48	$-x+1, -y+1, -z+2$
N1–H1B···S3	0.890	2.578	3.411	156.11	$-x+2, -y+1, -z+2$
N1–H1B···S1	0.890	2.938	3.469	119.91	$-x+2, -y+1, -z+2$
N1–H1C···S2	0.890	2.473	3.322	159.66	
N2–H2A···S4	0.890	2.388	3.278	179.02	$-x+1, -y+1, -z+1$
N2–H2B···S2	0.890	2.387	3.255	164.97	$-x+2, -y+1, -z+1$
N2–H2B···S1	0.890	3.002	3.426	111.18	$-x+2, -y+1, -z+1$
N2–H2C···S4	0.890	2.654	3.347	135.47	
N2–H2C···S1	0.890	2.720	3.419	136.31	

contacts. As in the other compounds the longest W–S bond (W–S(2): 2.2030 Å) is found for the shortest S···H contacts (S(2)···H: 2.387 and 2.473 Å) accompanied by large N–H···S angles (164.97 and 159.66°). Despite the fact that S(4) exhibits three short contacts (range: 2.388 to 2.654 Å) the W–S(4) bond is shorter than W–S(2). An explanation is that one of the interactions is weak due to the smaller N–H···S angle of 135.47°. Although S(1) has three hydrogen bonds the W–S(1) bond is the shortest (2.1799 Å) which may be caused by the relatively long S···H distances (2.720–3.002 Å) and small N–H···S angles (Table 6) indicating weak interactions. The single short S···H contact (2.578 Å) accompanied by a N–H···S angle of 156.11° observed for S(3) which is shorter than any of the three S(1)···H contacts can account for the slightly longer W–S(3) bond length of 2.1820(10) Å. The value for Δ is 0.0231 Å which may be responsible for the appearance of a broad W–S vibration in the IR spectrum (see below).

Compound **4** crystallizes in space group $C2/c$ and consists of (*mipa*H)$^+$ cations and $[WS_4]^{2-}$ anions (Fig. 4 top). The amine group in **4** is protonated and functions as a monocation whereas in **1**–**3** both amine functionalities are protonated. The S–W–S angles indicate a small distortion of the tetrahedron. The W–S bond lengths vary from 2.1792(13) to 2.2126(12) Å with an average of 2.1940 Å (Table 7). The pattern of W–S bond lengths shows two shorter and two longer bonds than the average value. The reason for the elongation of W–S(4) is that S(4) has three strong

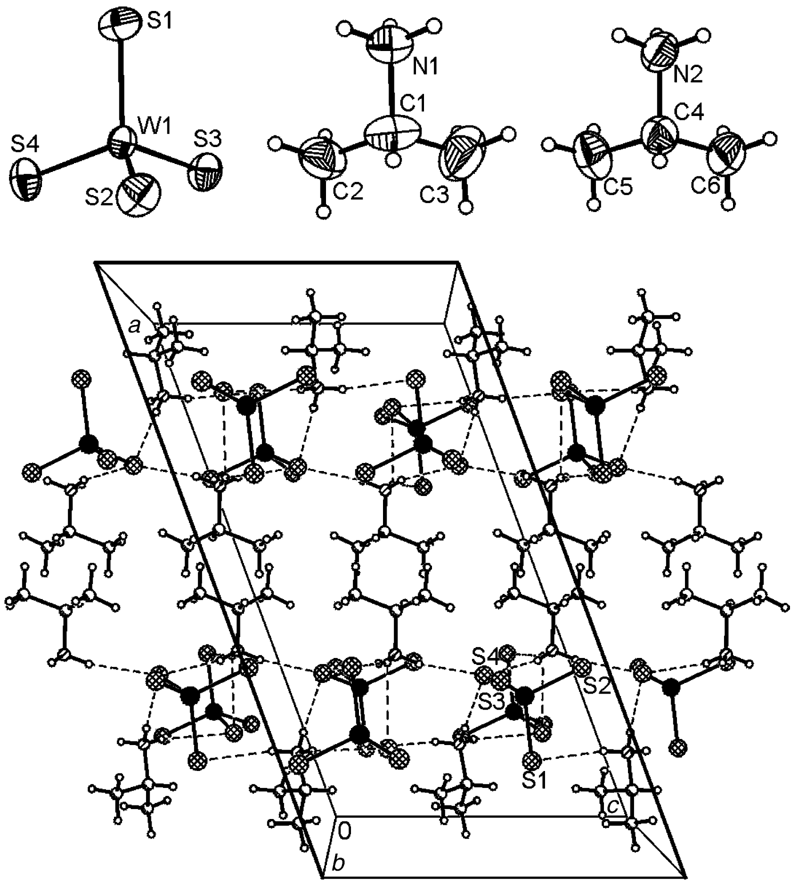

Fig. 4. Crystal structure of compound **4** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with view in the direction of the crystallographic *b*-axis (bottom; hydrogen bonding is shown as dashed lines)

Table 7. Selected geometric parameters (Å, °) for $(\mathit{mipa}\mathrm{H})_2[\mathrm{WS}_4]$ (**4**)

W(1)–S(2)	2.1792 (13)	C(1)–C(3)	1.465 (10)
W(1)–S(3)	2.1805 (12)	C(1)–C(2)	1.514 (9)
W(1)–S(1)	2.2038 (14)	N(2)–C(4)	1.501 (7)
W(1)–S(4)	2.2126 (12)	C(4)–C(6)	1.497 (8)
N(1)–C(1)	1.497 (7)	C(4)–C(5)	1.510 (8)
S(2)–W(1)–S(3)	109.28 (5)	S(2)–W(1)–S(4)	108.88 (5)
S(2)–W(1)–S(1)	109.28 (6)	S(3)–W(1)–S(4)	110.03 (5)
S(3)–W(1)–S(1)	109.30 (5)	S(1)–W(1)–S(4)	110.05 (6)
C(3)–C(1)–N(1)	109.7 (6)	C(6)–C(4)–N(2)	107.4 (5)
C(3)–C(1)–C(2)	112.8 (6)	C(6)–C(4)–C(5)	114.4 (5)
N(1)–C(1)–C(2)	109.7 (5)	N(2)–C(4)–C(5)	108.4 (5)

H bonds (Table 8) which weaken the bond to W. On the other hand, W–S(2) is the shortest bond because S(2) has only two weak contacts to H atoms and one $S(2)\cdots H$ is very long and has a remarkably low angle of 110.77°. The cations

Table 8. Hydrogen-bonding parameters (Å, °) for (*mipa*H)[WS_4] (**4**)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<DHA	Symmetry code
N1–H1···S4	0.890	2.490	3.355	164.11	
N1–H2···S4	0.890	2.555	3.424	165.66	$x, -y+1, z-1/2$
N1–H3···S1	0.890	2.612	3.473	163.21	$-x+1/2, -y+3/2, -z+1$
N1–H3···S3	0.890	2.882	3.349	114.34	$-x+1/2, -y+3/2, -z+1$
N2–H1···S3	0.890	2.675	3.439	144.52	$-x+1/2, y-1/2, -z+3/2$
N2–H1···S2	0.890	2.885	3.571	135.05	$-x+1/2, y-1/2, -z+3/2$
N2–H2···S4	0.890	2.468	3.348	169.86	
N2–H3···S1	0.890	2.561	3.438	168.64	$x, -y+1, z-1/2$

and anions are linked *via* nine N–H···S interactions (Fig. 4 bottom) and all the S···H distances are shorter than the sum of the *van der Waals* radii of S and H. S(4) is involved in three hydrogen bonds, while S(1), S(2), and S(3) have two such contacts each. It is to be noted that the value for $\Delta = 0.0334$ Å is large and explains the distortion of the $[WS_4]^{2-}$ tetrahedron. The cations and anions are arranged in a layer-like fashion with the anions and cations alternating along the *a*-axis (Fig. 4 bottom).

Spectral Studies

A combination of UV-Vis, infrared, and *Raman* spectroscopic techniques has been employed to characterize compounds **1**–**4**. The electronic spectra of the complexes 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. The observed chemical shifts in the ^{1}H NMR spectra (see Experimental) of **1**–**4** are in the normal range expected for the organic moieties.

The mid IR of **1**–**4** (up to 500 cm^{-1}) exhibit several signals which can be assigned to the absorptions of the amines. In the IR, the N–H absorption region is broad and shifted to lower wavenumbers as compared to the free amines. This feature can be explained due to the change of the amine groups to ammonium ions in the title complexes and also due to the hydrogen bonding interactions between the organic cations and the anions. In **1**, the N–H stretching vibration is observed at 3059 cm^{-1} while in **2** at 3006 cm^{-1}. Similar trends are observed in **3** and **4** with N–H vibrations occurring at 3004 and 3050 cm^{-1} respectively. For the free tetrahedral $[WS_4]^{2-}$ anion four characteristic bands $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ are expected [21]. All four bands are *Raman* active whereas only ν_3 and ν_4 are infrared active. When $[WS_4]^{2-}$ functions as a bidentate ligand, as in $[Ni(WS_4)_2]^{2-}$, the symmetry is reduced to C_{2v} and it has been shown that this leads to a splitting of the triply degenerate $\nu_3(F_2)$ vibration of the W–S bond [21, 22]. In **1** and **4** the W–S vibrations centered at around 450 cm^{-1} are split (Fig. 5) due to a lowering of the symmetry of the tetrahedra. 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 the terminal S atom is short (2.151 Å). In our compounds the longer W–S distances are always observed when

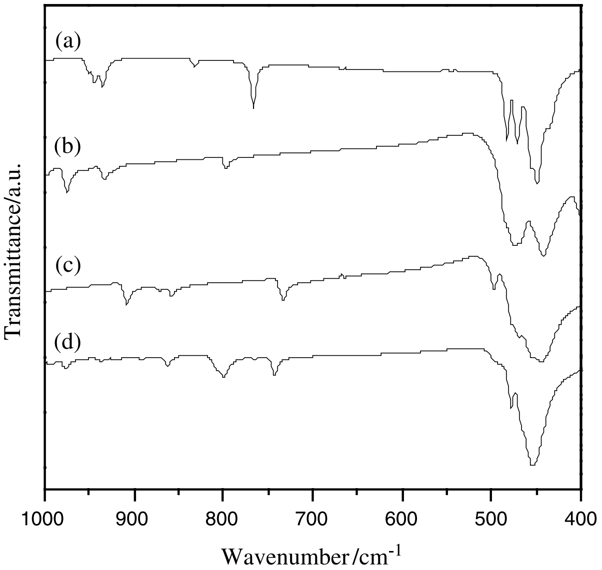

Fig. 5. IR spectra of (a) (*N–Me–en*H_2)[WS_4] (**1**), (b) (*mipa*H)$_2$[WS_4] (**4**), (c) (1,4-*bn*H_2)[WS_4] (**3**), (d) (*N,N′-dm*-1,3-*pn*H_2)[WS_4] (**2**)

strong S$\cdots$H bonding interactions are present, and the W–S bond length distribution indicates a slight distortion of the tetrahedra. A similar observation was made in our earlier work on organic ammonium tetrathiotungstates. A splitting of the W–S vibration was observed in (*pip*H_2)[WS_4] (*pip* = piperazine) [16] which shows a difference of $\Delta = 0.0385$ Å between the longest and the shortest W–S bonds. In the two compounds (*N–Me–en*H_2)[WS_4] (**1**) and (*mipa*H)$_2$[WS_4] (**4**) with $\Delta \approx 0.03$ Å a clear splitting of the W–S vibrations occurs. In contrast, the two complexes (*N,N′-dm*-1,3-*pn*H_2)[WS_4] (**2**) and (1,4-*bn*H_2)[WS_4] (**3**) show only a broad W–S vibration in accordance with the smaller values for Δ. In **2**, three of the W–S bond lengths are around 2.1992 Å and the shortest W–S bond is 2.1771 Å ($\Delta = 0.0221$ Å) indicating that the symmetry is reduced to C_{3v}. Hence, only a broad signal centered around 454 cm^{-1} with a shoulder at 479 cm^{-1} is observed. The medium intense signal at around 498 cm^{-1} in **3** originates from the cation and not from $[WS_4]^{2-}$ as the same feature is also observed in (1,4-*bn*H_2)[CrO_4] and (1,4-*bn*H_2)Cl_2. The assignment of the IR band in **1** to **4** at around 188 cm^{-1} for the ν_4 vibration gains credence from the observation of a strong signal in the *Raman* spectra at around 188 cm^{-1}. The assignment of the *Raman* signals in **1**–**4** at around 479 and 449 cm^{-1} for ν_1 and ν_3 respectively is in agreement with the reported data [3, 21].

Comparative Study of the Structural Features of Tetrathiotungstates

A comparative study of the structural parameters of several known tetrathiotungstates (Table 9) has been made with a view to understand the importance of the S$\cdots$H bonding interactions to induce the elongation of the W–S bond lengths. The isolation and structural characterization of $[WS_4]^{2-}$ with different cations ranging from

Table 9. Comparative structural parameters of tetrathiotungstates

Compound	S–W–S average in °	W–S (long) in Å	W–S (short) in Å	Difference Δ in Å	W–S average in Å	S···H short in Å	Ref.
$(NH_4)_2[WS_4]$	109.42	2.2090	2.1856	0.0234	2.1905	2.57	[15]
$Rb_2[WS_4]$	109.46	2.2053	2.1710	0.0343	2.1878	–	[23]
[Ni(*tren*)$_2$][WS_4]	109.47	2.2122	2.1580	0.0542	2.1872	2.73	[12]
(*en*H_2)[WS_4]	109.47	2.1943	2.1851	0.0092	2.1893	2.43	[11]
(1,3-*pn*H_2)[WS_4]	109.47	2.1946	2.1798	0.0148	2.1903	2.43	[13]
(*tmen*H_2)[WS_4]	109.47	2.1995	2.1772	0.0223	2.1891	2.56	[13]
(*tren*H_2)[WS_4] · H_2O	109.47	2.1997	2.1739	0.0258	2.1904	2.46	[16]
(*pip*H_2)[WS_4]	109.47	2.2147	2.1762	0.0385	2.1937	2.39	[16]
(1,4-*dmp*H_2)[WS_4]	109.46	2.2136	2.1781	0.0355	2.1943	2.64	[14]
(*N–Me–en*H_2)[WS_4] (**1**)	109.47	2.2064	2.1727	0.0337	2.1919	2.31	This work
(*mipa*H)$_2$[WS_4] (**4**)	109.47	2.2126	2.1792	0.0334	2.1940	2.47	This work
(*N,N′-dm*-1,3-*pn*H_2) [WS_4] (**2**)	109.47	2.1992	2.1771	0.0221	2.1931	2.42	This work
(1,4-*bn*H_2)[WS_4] (**3**)	109.47	2.2030	2.1799	0.0231	2.1918	2.39	This work

Abbreviations used: *tren* = tris(2-aminoethyl)amine; *en* = ethylenediamine; 1,3-*pn* = 1,3-propanediamine; *tmen* = *N,N,N′,N*-tetramethylethylenediamine; *pip* = piperazine; 1,4-*dmp* = 1,4-dimethylpiperazine

$(NH_4)^+$, Rb^+, [Ni(*tren*)$_2$]$^{2+}$ (*tren* = tris(2-aminoethyl)amine), (*en*H_2)$^{2+}$, (*pip*H_2)$^{2+}$, (*N–Me–en*H_2)$^{2+}$, *etc.* indicates the flexibility of the tetrathiotungstate ion to exist in different structural environments. In all these compounds the average value of the S–W–S angles is very close to the ideal tetrahedral value. All complexes listed in Table 9 exhibit cation-anion interactions in the form of S···Rb as in $Rb_2[WS_4]$ [23] or S···H–N as in all the other compounds. In $Rb_2[WS_4]$ the mean Rb···S distance has been reported to be 3.5466 Å. The average value of the W–S distance ranges from 2.1872 Å in [Ni(*tren*)$_2$][WS_4] to 2.1943 Å in (1,4-*dmp*H_2)[WS_4] (1,4-*dmp* = 1,4-dimethylpiperazine). It is also noted that the difference between the longest and the shortest W–S bond ranges from 0.0092 Å in (*en*H_2)[WS_4] to 0.0542 Å 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 $\Delta = 0.0542$ Å, even though the shortest S···H contact is observed for this complex with a distance of 2.73 Å. It is to be noted that in [Ni(*tren*)$_2$][WS_4] the N atom of *tren* is not protonated unlike in the organic ammonium compounds but linked to Ni(II). This indicates that the strengths of the N–H···S contacts in [Ni(*tren*)$_2$][WS_4] are probably different from those in the organic ammonium tetrathiotungstates. In the organic ammonium $[WS_4]^{2-}$ complexes including $(NH_4)_2[WS_4]$, the longest W–S bonds scatter in a very small range from 2.2147 Å in (*pip*H_2)[WS_4] to 2.1943 Å in (*en*H_2)[WS_4]. Furthermore, the shortest S···H contacts in all organic ammonium tetrathiotungstates are in a very narrow range of 2.31 Å in **1** to 2.64 Å in (1,4-*dmp*H_2)[WS_4]. The shortest S···H distance of 2.31 Å in **1** is observed for the H atom attached to N which carries two alkyl groups indicating the importance of steric features for the structural distortion. It appears that the difference between the longest and shortest W–S distances is an important factor and this difference can probably be taken as a measure of the distortion of the $[WS_4]^{2-}$ tetrahedron. In the title compounds the $[WS_4]^{2-}$ tetrahedron is distorted with one or more of the W–S bonds being elongated. The strongest distortion is observed in **1** and **4** which show a splitting of the W–S vibrations in the IR spectra. In both compounds as well as in our previously reported (*pip*H_2)$[WS_4]$ the value for Δ is larger than 0.03 Å, whereas in **2** and **3** the values for Δ are 0.0221 and 0.0231 Å respectively and only a broadening of the W–S vibrations occurs in their IR spectra.

Conclusions

Four new organic ammonium tetrathiotungstates have been synthesized by the base promoted cation exchange reaction and characterized by chemical analysis, spectroscopic methods, and single crystal structure determination. The most interesting structural feature is a considerable distortion of the $[WS_4]^{2-}$ tetrahedra due to S···H interactions yielding distinct W–S bond lengths. All complexes exhibit several short S···H distances which are quite shorter than the sum of the *van der Waals* radii of S and H. The distortion of the tetrahedron is clearly seen in the IR spectra as a splitting or broadening of the W–S stretching vibrations. From the comparative study of several tetrathiotungstates it is observed that a difference Δ of more than 0.033 Å in an organic ammonium tetrathiotungstate leads to a pronounced distortion of the $[WS_4]^{2-}$ tetrahedron as evidenced in the splitting of the W–S asymmetric vibration in the infrared spectrum. In the complexes **1** and **2** which contain the N-methylated cations (*N–Me–en*H_2)$^{2+}$ and (*N,N′-dm*-1,3-*pn*H_2)$^{2+}$ the value for Δ is considerably larger than the values for the unalkylated cations (*en*H_2)$^{2+}$ and (1,3-*pn*H_2)$^{2+}$ indicating that alkyl groups enhance the distortion of the tetrahedron. It will be of interest to understand such effects especially the role of alkyl groups by using differently substituted amines. Efforts in this direction are underway in our laboratories.

Experimental

Materials and Methods

The organic amines *N–Me–en*, *N,N′-dm*-1,3-*pn*, 1,4-*bn*, *mipa*, and the solvents were used as obtained from commercial sources with analytical purity. $(NH_4)_2[WS_4]$ was prepared by literature method [24]. Proton NMR spectra were collected in DMSO-d_6. The details of the base promoted cation exchange method used for the synthesis of **1**–**4** as well as the procedure used for the elemental analysis, NMR, IR, *Raman*, and UV-Vis spectroscopy were the same as described in our previous reports [17, 18].

*Preparation of Complexes **1** to **4***

$(NH_4)_2[WS_4]$ (348 mg, 1 mmol) was dissolved in 10 ml distilled water and filtered. To the clear yellow filtrate *N–Me–en* (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** started appearing in the mother liquor. The crystals were isolated by filtration, washed well with ice-cold water (2 ml), isopropanol (10 ml), and ether (10 ml). The compound was dried under *vacuo*. Yield of product was 300 mg. The use of other organic amines such as *N,N′-dm*-1,3-*pn*, 1,4-*bn*, and *mipa* instead of *N–Me–en* in the above procedure resulted in the formation of the organic ammonium compounds **2**, **3**, and **4** respectively in good yields. All compounds were analyzed satisfactorily.

Spectroscopy

(*N–Me–en*H$_2$)[WS$_4$] (**1**): IR (KBr): $\bar{\nu} = 3059$ (br), 2961, 1454, 1116, 1026, 935, 766, 484, 471, 450 (ν_3), 258, 183 (ν_4), 158, 127 cm^{-1}; *Raman*: $\bar{\nu} = 480$, 473 (ν_1), 454 (ν_3), 444, 412, 200, 181 (ν_2), 169 cm^{-1}; UV-Vis (water): $\lambda_{\max} = 393$, 278, 220 nm; ^{1}H NMR (300 MHz, DMSO-*d$_6$*): $\delta = 2.32$ (s, 3H), 2.69 (t, 2H, $J = 5.9$ Hz), 2.79 (t, 2H, $J = 3.1$ Hz) ppm.

(*N,N′-dm*-1,3-*pn*H$_2$)[WS4] (**2**): IR (KBr): $\bar{\nu} = 3006$ (br), 2775, 1561, 1487, 1461, 1432, 1123, 1068, 1040, 1013, 1007, 973, 865, 800, 743, 479, 454 (ν_3), 189 (ν_4) cm^{-1}; *Raman*: $\bar{\nu} = 479$ (ν_1), 468, 457 (ν_3), 416, 295, 197, 188 (ν_4), 175 cm^{-1}; UV-Vis (water): $\lambda_{\max} = 393$, 281, 220 nm; ^{1}H NMR (300 MHz, DMSO-*d$_6$)*: $\delta = 1.91$ (p, 2H, $J = 7.5$ Hz), 2.56 (s, 6H), 2.96 (t, 4H, $J = 7.6$ Hz) ppm.

(1,4-*bn*H$_2$)[WS$_4$] (**3**): IR (KBr): $\bar{\nu} = 3004$ (br), 2903, 1567, 1466, 1436, 1375, 1323, 1255, 1086, 1017, 908, 858, 733, 498, 479, 446 (ν_3), 214, 188 (ν_4), 150, 112, 96, 88 cm^{-1}; *Raman*: $\bar{\nu} = 478$ (ν_1), 449 (ν_3), 187 (ν_2) cm^{-1}; UV-Vis (water): $\lambda_{\max} = 393$, 281, 220 nm; ^{1}H NMR (300 MHz, DMSO-*d$_6$*): $\delta = 2.74$, 2.44 ppm.

(*mipa*H)$_2$[WS$_4$] (4): IR (KBr): $\bar{\nu} = 3050$, 2772, 2661, 2562, 2433, 1892, 1577, 1458, 1366, 1201, 1155, 975, 933, 476, 442 (ν_3), 397, 193 (ν_4), 122 cm^{-1}; *Raman*: $\bar{\nu} = 483$ (ν_1), 458 (ν_3), 400,

Table 10. Technical details of data acquisition and selected refinement results for compounds **1–4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_3H_{12}N_2S_4W$	$C_5H_{16}N_2S_4W$	$C_4H_{14}N_2S_4W$	$C_6H_{20}N_2S_4W$
Temperature/K	293	293	293	293
a/Å	7.890(1)	7.259(1)	7.189(1)	20.404(2)
b/Å	11.831(2)	18.562(1)	8.182(1)	14.081(1)
c/Å	11.972(2)	9.734(1)	10.634 (2)	11.268(1)
α/°	–	–	79.65 (1)	–
β/°	–	90.28(1)	81.66 (1)	110.28(1)
γ/°	–	–	83.54 (1)	–
Volume/Å^3	1117.5(3)	1311.5(2)	606.4(2)	3036.8(4)
Space group	$P2_12_12_1$	$P2_1/n$	P-1	C2/c
Z	4	4	2	8
μ/mm^{-1}	11.028	9.405	10.17	8.127
F(000)	728	792	380	1664
MW/g · mol^{-1}	388.24	416.29	402.26	432.33
D_c/g · cm^{-3}	2.308	2.108	2.203	1.891
hkl range	−11/4	−10/10	0/10	−28/28
	−16/1	−26/24	−11/11	−19/19
	−16/1	−13/13	−14/14	−15/15
2θ range	3°–60°	3°–60°	3°–60°	3°–60°
Refl. collected	3184	17112	3795	16917
Refl. unique	2646	3884	3534	4486
Data ($Fo > 4\sigma(Fo)$)	2492	3231	3259	3365
$R_{\text{int.}}$	0.0479	0.0297	0.0130	0.0519
Min/Max transm.	0.1858/0.2621	0.1926/0.3926	0.1727/0.3800	0.2291/0.4174
$\Delta\rho$ [e/Å^3]	−1.238/1.124	−1.843/1.836	−0.76/0.61	−1.664/1.222
Parameters	92	110	103	125
$R1$ [$Fo > 4\sigma(Fo)$]^a	0.0234	0.0305	0.0180	0.0312
$wR2$ for all data	0.0601	0.0778	0.0436	0.0820
Goodness of fit	1.032	1.047	1.089	0.999

[a] $R1 = \Sigma\|Fo| - |Fc\|/\Sigma|Fo|$

188 (ν_2) cm^{-1}; UV-Vis (water): $\lambda_{max} = 393$, 281, 220 nm; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.09$ (d, 6H, $J = 6.9$ Hz), 3.20 (m, H, $J = 6.5$ Hz) ppm.

Crystal Structure Determination

Intensity data were collected on an AED-II four-circle diffractometer for the compounds **1** and **3**, and on an Imaging Plate Diffraction System (Fa. STOE) for compounds **2** and **4**, using graphite monochromated Mo–K$_\alpha$ radiation. All structures were solved with direct methods using SHELXS-97 [25] and refinement was done against F^2 using SHELXL-97 [26]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in a difference map but were positioned with idealized geometry and refined isotropically using a riding model. The absolute structure of compound **1** was determined and is in agreement with the selected setting (*Flack* x-parameter: −0.003(11)). The technical details of data acquisition and some selected refinement results are summarized in Table 10.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 280575 (**1**), CCDC 280576 (**2**), CCDC 280577 (**3**), and CCDC 280578 (**4**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

B. R. S. thanks the Department of Science and Technology (DST), New Delhi for financial support under SR/S1/IC-41/2003. *W. B.* acknowledges the financial support by the State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (DFG). The authors thank Frau *Uschi Cornelissen* for recording the vibrational spectra. The Department of Chemistry, Goa University is supported by the University Grants Commission, New Delhi under the Special Assistance Program (SAP). *W. B.* and *B. R. S.* thank the DST, New Delhi and Deutscher Akademischer Austauschdienst (DAAD) Bonn, for the sanction of a DST-DAAD (PPP) project.

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