

Synthesis, Spectroscopic and X-Ray Structure Characterisation of Bis(tetramethylammonium), Bis(tetraethylammonium) and Bis(tetrapropylammonium) Tetrathiotungstates

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The three new tetraalkylammonium tetrathiotungstates $((\text{Me})_4\text{N})_2[\text{WS}_4]$ (**1**), $((\text{Et})_4\text{N})_2[\text{WS}_4]$ (**2**) and $((\text{nPr})_4\text{N})_2[\text{WS}_4]$ (**3**) were prepared *via* a direct salt substitution using $(\text{NH}_4)_2[\text{WS}_4]$ as starting material. Compound **1** crystallises in the chiral orthorhombic space group $P2_12_12_1$ with $a = 8.9433(4)$, $b = 15.5658(9)$ and $c = 37.279(2)$ Å. Compound **2** crystallises in space group $P2_1/n$ with lattice parameters $a = 16.6695(12)$, $b = 9.3415(6)$, $c = 16.9965(13)$ Å and $\beta = 117.185(15)^\circ$. The third compound **3** crystallises in space group $C2/c$ with the lattice parameters $a = 32.440(2)$, $b = 13.8453(6)$, $c = 15.0563(10)$ Å and $\beta = 109.19(7)^\circ$. The structures of all compounds consist of slightly distorted $[\text{WS}_4]^{2-}$ tetrahedra and tetraalkylammonium cations which are packed in different ways. One interesting observation is that the disorder of parts of the alkyl groups decreases with increasing chain length. The IR and Raman spectra show the vibrations of the $[\text{WS}_4]^{2-}$ tetrahedron with a slight shift with increasing alkyl chain length. The most prominent IR-band of the $[\text{WS}_4]^{2-}$ tetrahedra is broad but not split, indicating that the distortion of the tetrahedra is small.

Key words: Crystal Structure, Tetrathiotungstates, IR and Raman Spectroscopy

Introduction

The production of clean transport fuels by hydrotreating and specially deep hydrodesulfurization (HDS) has recently gained attention due to the introduction of new environmental legislation regarding fuel specifications [1, 2]. In order to meet the specifications there is an increased need to understand and consequently improve HDS catalysts. Alumina is the most widely used support material for preparing HDS catalysts due to its good mechanical and textural properties. However, one of its disadvantages is the strong interaction with metal precursors in the catalysts preparation step, which makes the complete sulfidisation of supported metal oxides difficult [3–5]. On the other hand, carbon has been probed as alumina replacement, and several studies [3–10] have demonstrated that carbon supported MoS_2 , $(\text{Co/Ni})\text{Mo(W)}$ sulphide catalysts show a HDS activity superior to that of the alumina supported counterparts. This high activity can be attributed to an enhanced dispersion of catalytically active species.

Recently, Alonso *et al.* have reported that very efficient carbon containing MoS_2 and WS_2 catalysts are

produced by the *in situ* decomposition of precursors during HDS of DBT [11]. In a previous report results of the synthesis of MoS_2 catalysts by the thermal decomposition of tetraalkyl tetrathiomolybdates were presented [12]. Moreover, the role of structural carbon for the activity of HDS catalysts was investigated and the results of a profound study gave evidences that a critical C content is essential for a high performance of such catalysts [13]. For MoS_2 based catalysts we demonstrated that the C content of the active material can be determined by the C content of the $(\text{R})\text{MoS}_4$ precursors (R = organic ammonium ions) [12]. With respect to W-S chemistry it was demonstrated recently that the well known ammonium tetrathiotungstate is a useful precursor for the soft synthesis of WS_2 nanotubes [14, 15]. In another report the suitability of bis(cetyltrimethylammonium) tetrathiotungstate as a precursor for the formation of bulk quantities of uniform WS_2 nanotubes was reported [16]. In the meantime about 20 different tetrathiotungstates with different cations as charge balancing ions were reported in the literature [17–26]. The present contribution is part of our ongoing investigations aimed to the synthesis of active and efficient MoS_2 and

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

Compound	1	2	3
Formula	C ₈ N ₂ H ₂₄ WS ₄	C ₁₆ N ₂ H ₄₀ WS ₄	C ₂₄ N ₂ H ₅₆ WS ₄
MG [g/mol]	460.38	572.59	684.80
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ /n	<i>C</i> 2/ <i>c</i>
Temperature [K]	293	293	293
Wavelength [Å]	0.71073	0.71073	0.71073
<i>a</i> [Å]	8.9433(4)	16.6695(12)	32.440(2)
<i>b</i> [Å]	15.5658(9)	9.3415(6)	13.8453(6)
<i>c</i> [Å]	37.279(2)	16.9965(13)	15.0563(10)
β [°]	90	117.185(15)	109.19(7)
<i>V</i> [Å ³]	5189.7(5)	2354.3(3)	6386.7(7)
<i>Z</i>	12	4	8
μ [mm ^{−1}]	7.139	5.26	3.89
<i>F</i> (000)	2688	1152	2816
<i>D</i> _{calc} [g cm ^{−3}]	1.768	1.615	1.424
Crystal size [mm]	0.14, 0.09, 0.05	0.15, 0.11, 0.06	0.16, 0.12, 0.08
2 θ Range [°]	2–22	5–56	5–56
Collected reffs	26540	22976	31153
Unique reflections	6609	5644	7615
Data [<i>F</i> o > 4 σ (<i>F</i> o)]	5191	4265	5779
<i>R</i> _{int}	0.0884	0.0410	0.0534
$\Delta\rho$ [e/Å ³]	−2.224/1.664	−1.047/1.067	−0.708/0.526
Parameters refined	364	225	318
<i>R</i> 1 [<i>F</i> o > 4 σ (<i>F</i> o)] ^a	0.0567	0.0294	0.0300
<i>wR</i> 2 for all unique data	0.1483	0.0744	0.0664
Goodness of fit	1.169	1.034	1.034
BASF parameter	0.43(4)	–	–

^a *R*1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

WS₂ catalysts, and its Ni/Co promoted versions. For a full characterisation of the precursor materials and an understanding of the chemical reactivity the crystal structures of the compounds should be known. One interesting observation in the tetrathiotungstate chemistry with organic cations as charge balancing ions is the fact that no structural data are available with fully alkylated amines. In this contribution the syntheses, crystal structures and spectroscopic data of three new tetraalkylammonium tetrathiotungstates (R₄N)₂WS₄ (R = methyl, ethyl, propyl) are presented.

Experimental Section

Synthesis

The synthesis of the tetraalkylammonium salts (R₄N)₂MoS₄ has been reported by McDonald [27]. Later this method was improved by Alonso [28]. In the present work, a modified version of the last method was used and crystals were grown from a very dilute solution. The amines and the solvents were used as obtained from commercial sources. (NH₄)₂WS₄ was prepared as reported in the literature [27]. Freshly prepared (NH₄)₂WS₄ (5 mmol) was dissolved in wa-

Table 2. Selected geometric parameters (Å, °) for ((Me)₄N)₂-[WS₄] (**1**).

W(1)-S(1)	2.187(8)	W(2)-S(7)	2.079(7)
W(1)-S(2)	2.162(8)	W(2)-S(8)	2.176(7)
W(1)-S(3)	2.196(8)	W(3)-S(9)	2.219(10)
W(1)-S(4)	2.192(10)	W(3)-S(10)	2.202(9)
W(2)-S(5)	2.165(9)	W(3)-S(11)	2.199(8)
W(2)-S(6)	2.155(8)	W(3)-S(12)	2.182(8)
S(2)-W(1)-S(1)	109.0(4)	S(7)-W(2)-S(8)	108.5(4)
S(2)-W(1)-S(4)	108.0(4)	S(6)-W(2)-S(8)	109.5(4)
S(1)-W(1)-S(4)	112.5(4)	S(5)-W(2)-S(8)	110.7(4)
S(2)-W(1)-S(3)	109.6(4)	S(12)-W(3)-S(11)	109.8(4)
S(1)-W(1)-S(3)	109.1(3)	S(12)-W(3)-S(10)	108.1(3)
S(4)-W(1)-S(3)	108.6(4)	S(11)-W(3)-S(10)	108.4(4)
S(7)-W(2)-S(6)	109.5(4)	S(12)-W(3)-S(9)	111.0(3)
S(7)-W(2)-S(5)	108.6(4)	S(11)-W(3)-S(9)	110.2(4)
S(6)-W(2)-S(5)	110.1(4)	S(10)-W(3)-S(9)	109.3(4)

ter (30 ml) and stirred. (R₄N)Br (10 mmol) was dissolved in a solution of NaOH (10 mmol) in 30 ml water and stirred. The first solution was added to the second and the mixture was stirred for 30 min. Afterwards, the solution was kept undisturbed over ice to obtain the red crystalline products. The solid was filtered off and was washed with cold water and ethanol. 80% Yield. These compounds are stable on air.

Characterisation

A CHN-O RAPID combustion analyser from Heraeus was used to determine the content of C, H, N and S, using zinc sample holders with 2–3 mg per sample, heated up to 1000 °C under oxygen atmosphere. Compound **1**: calcd. C 20.9, H 5.21, N 6.08; found C 20.7, H 5.15, N 5.90; compound **2**: calcd. C 33.57, H 6.98, N 4.89; found C 33.42, H 6.93, N 4.89; compound **3**: calcd. C 42.13, H 8.18, N 4.09; found C 42.08, H 8.25, N 4.04.

Far IR spectra (80–500 cm^{−1}) were measured on a Bruker IFS 66 spectrometer in pressed polyethylene disks. MIR spectra (450–3000 cm^{−1}) were recorded in a ATI Mattson Genesis spectrometer. The samples were ground with dry KBr into fine powders and pressed into transparent pellets. Raman spectra were measured from 100 to 3500 cm^{−1} in a Bruker IFS 66 Fourier Transform Raman spectrometer.

Structure refinement details

Single crystal investigation of compounds **1–3** was performed using an Imaging Plate Diffraction System (IPDS) [29] with monochromated Mo-K α -radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS-97 [30] and the refinement was done against *F*² using SHELXL-97 [31]. The data were corrected for Lorentz, polarisation and absorption effects. The crystal of compound **1** was racemically twinned, and a TWIN refinement was performed using SHELXL-97 (BASF parameter:

Table 3. Selected geometric parameters (Å, °) of ((Et)₄N)₂[WS₄] (**2**).

W(1)-S(1)	2.2030(12)	W(1)-S(3)	2.1933(12)
W(1)-S(2)	2.1867(12)	W(1)-S(4)	2.1846(12)
S(2)-W(1)-S(1)	109.40(5)	S(3)-W(1)-S(1)	110.59(5)
S(2)-W(1)-S(3)	108.12(5)	S(4)-W(1)-S(1)	109.00(5)
S(4)-W(1)-S(2)	110.21(6)	S(4)-W(1)-S(3)	109.52(6)

Table 4. Selected geometric parameters (Å, °) of ((nPr)₄N)₂[WS₄] (**3**).

W(1)-S(1)	2.1978(11)	W(1)-S(3)	2.1834(11)
W(1)-S(2)	2.2009(14)	W(1)-S(4)	2.1919(12)
S(1)-W(1)-S(2)	110.24(4)	S(4)-W(1)-S(1)	109.78(5)
S(3)-W(1)-S(4)	109.16(5)	S(3)-W(1)-S(2)	108.30(5)
S(3)-W(1)-S(1)	109.49(5)	S(4)-W(1)-S(2)	109.84(6)

0.43(4)). All non-hydrogen atoms were refined anisotropically except most of the C and N atoms in compound **1** in which three of the six crystallographically independent cations were disordered. All hydrogen atoms were placed in ideal geometry and were refined using a riding model. In compounds **2** and **3** also some of the cations were disordered and were refined using a split model.

Technical details of the data acquisitions and some refinement results are summarised in Table 1. Lists of selected bond lengths are given in Tables 2, 3 and 4. 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 608050 (**1**), CCDC 608051 (**2**) and CCDC 608052 (**3**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

Results and Discussion

For compound **1** some crystallographic data can be found in literature [32]. It was reported that this compound crystallises in the orthorhombic space group *Pnam* with $a = 12.48(1)$, $b = 15.37(2)$ and $c = 8.94(1)$ Å. However, no atomic coordinates and no R-values can be found in the CCDC data base [33]. In addition, the similarity of the unit cell parameters indicates that the authors have overlooked reflections which are leading to a triplication of one unit cell axis.

Complex **1** crystallises in the orthorhombic chiral space group *P2₁2₁2₁*. There are three crystallographically independent anions per asymmetric unit with no imposed symmetry (Table 2). The W(1)-S distances in the first anion range from 2.162(8) to 2.196(8) Å

with an average of 2.184(2) Å. The coordination environment around W(1) is nearly a perfect tetrahedron with minimum and maximum S-W(1)-S angles of 108.0(4) and 112.5(4)° and an average of 109.5(7)°. The W(2)-S bonds are different with values ranging from 2.079(7) to 2.176(7) Å with a mean value of 2.143(7) Å and S-W(2)-S angles between 108.5(4) and 110.7(4)° (average: 109.48(4)°). In the third anion, W(3)-S distances range from 2.182(8) to 2.219(10) Å (average: 2.20(5) Å) and the S-W(3)-S angles are between 108.1(3) and 111.0(3)° (average: 109.46(7)°). At a first glance the W-S bond lengths seem to scatter over a wide range which is unusual for thiotungstates where no S...H bonding interactions can be formed. For instance, the W-S distances with such H bonding interactions range from 2.1856(11) to 2.2090(10) Å in (NH₄)₂WS₄ [20]. The difference between the longest and shortest W-S bond distance Δ is a good measure for the distortion of the WS₄ tetrahedron, and the values are 0.034, 0.097, and 0.037 Å for the three independent tetrahedra. Analysing the anisotropic displacement parameters of the S atoms it is obvious that there is some positional disorder in the W(2)S₄ tetrahedron which is not pronounced enough to refine the S positions with a split model. Hence it can be assumed that the very short W-S bonds are due to an artefact. A libration correction was also performed but without a significant effect onto the W(2)-S bond lengths. One should keep in mind that libration only shortens the bond lengths if the vibration of the atom is perpendicular to the bond axis. In the present tetrahedron this is not the case, explaining the very small difference of the bond lengths with and without the correction. The spectroscopic results (see below) support the assumption that the true W(2)S₄ tetrahedron must be more regular. An appreciable contamination with oxygen can be excluded because no bands are seen in the IR or Raman spectra accounting for W-O stretching vibrations. Furthermore, some of the displacement parameters of the S atoms of W(1)S₄ and W(3)S₄ are larger than those for the S atoms in compounds **2** and **3**. This may be the reason that the values for Δ of these two tetrahedra are larger than in the other two compounds.

Three methyl groups of the cations show a positional disorder with 50% occupancies for two positions in cations N(1) and N(6), while for cation N(2) the three CH₃ groups exhibit occupancies 60% : 40%. Fig. 1 shows two different views of the arrangement of the cations and anions.

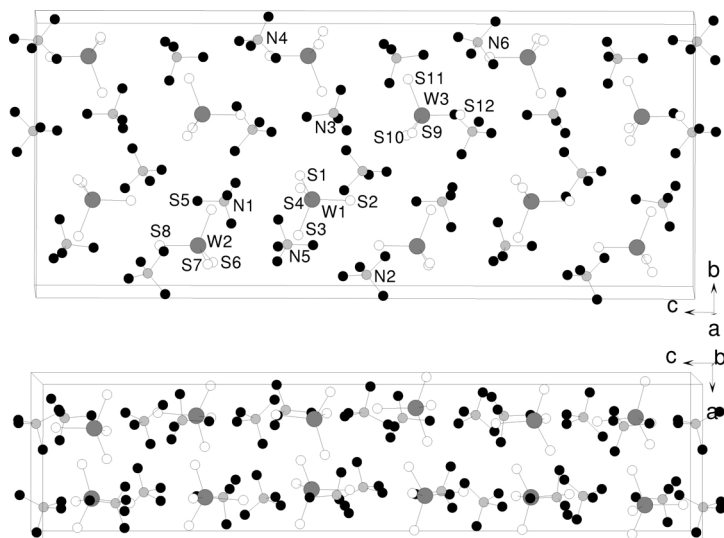


Fig. 1. View of the arrangement of cations and anions in compound **1** along [100] with labelling (top) and along [010] (bottom). Note: H atoms and disordered C atoms are not displayed for clarity.

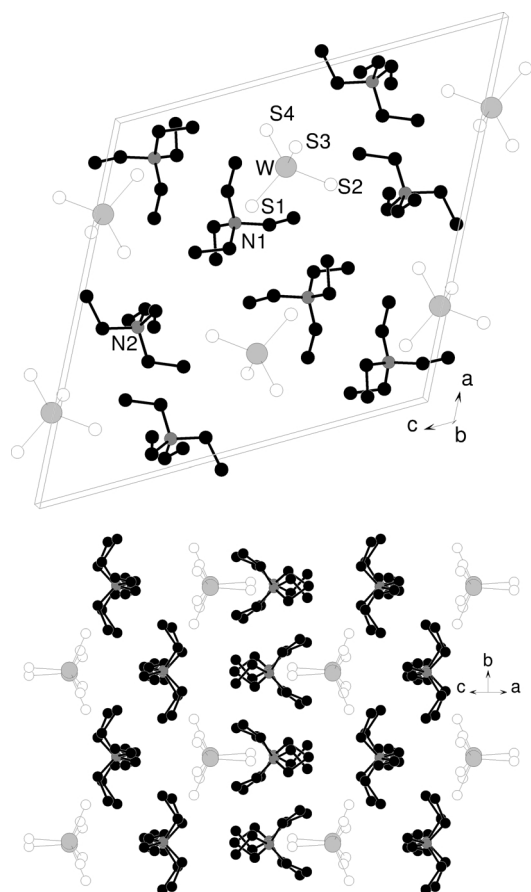


Fig. 2. View of the crystal structure of compound **2** along [010] with labelling (top) and onto the (101) plane (bottom). H atoms and disordered C atoms are not displayed for clarity.

Along [001] there are different types of rods. One is composed only of NMe_4^+ cations (I) and the other contains cations and anions in an alternating fashion (II). These rods show the order (I)-(II)-(II)-(I)-(I)··· along [010] leading to a layer-like arrangement in the (010) plane.

Compound **2** crystallises in the monoclinic space group $P2_1/n$ and is different compared to the analogous Mo compound which crystallises in the triclinic space group $P-1$ [34]. The crystal structure consists of a discrete tetrathiotungstate anion and two independent tetraethylammonium cations with all atoms located on general positions. The tetrahedral geometry of the WS_4^{2-} anion is only slightly distorted with S-W-S angles between $108.12(5)$ and $110.59(5)^\circ$ (Table 2). The W-S bond lengths are between $2.1846(12)$ and $2.2030(12)$ Å giving a Δ value of 0.0184 Å. In one of the two cations a positional disorder occurs for the CH_2 group of one C_2H_5 unit (occupancies: 80 : 20). In Fig. 2 the arrangement of the constituents of **2** are displayed. Along [010] the anions and cations form individual rods, and a view onto the (101) plane reveals that within adjacent stacks the cations are arranged in a different way.

Compound **3** crystallises in the monoclinic space group $C2/c$ with all atoms except two N atoms being located on general positions. The structure contains an unique anion and three independent cations with two of them located in special positions. The WS_4 tetrahedron shows only a moderate distortion (S-W-S angles: $108.30(5)$ – $110.24(4)^\circ$, Table 3) and W-S bond

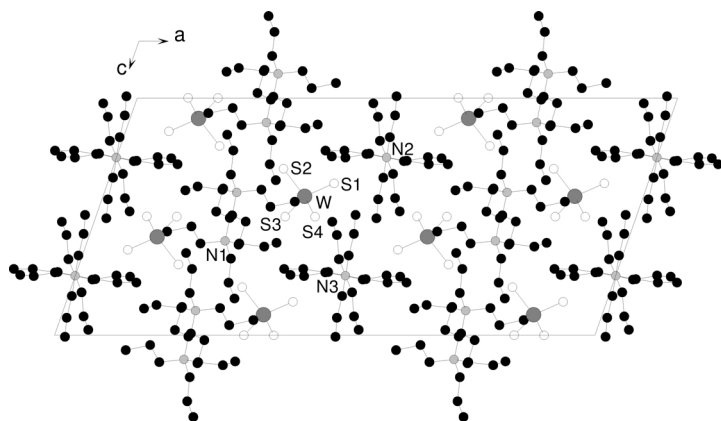


Fig. 3. Packing diagram of the constituents in compound **3** with view along [010] and labelling. Note that H atoms and disordered C atoms are not shown for clarity.

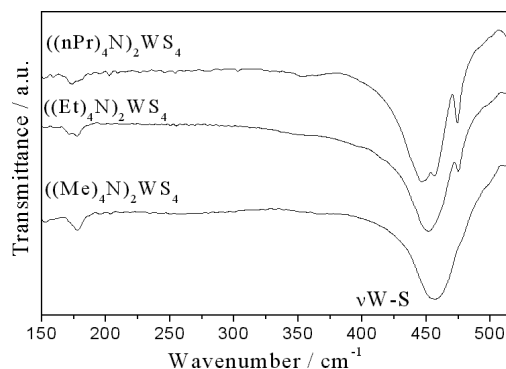


Fig. 4. IR spectra of compounds **1–3**.

lengths from 2.1834(11) to 2.2009(14) Å with a corresponding value for Δ of 0.0174 Å. In one of the three cations (N(3)) a positional disorder is observed with the C atoms involved showing a 50:50 occupancy. A packing diagram of the anions and cations in $((n\text{Pr})_4\text{N})_2\text{WS}_4$ is displayed in Fig. 3.

The cations with the N(1) atom are arranged in columns along [001] whereas the remaining two cations alternate along this direction and the WS_4 tetrahedra are located between the rods of cations.

The compounds have been further characterised by IR and Raman spectroscopy. In the middle of the IR spectra several bands are observed which are caused by the organic cation vibrations. The absorptions around 3000 cm^{-1} are assigned to the C-H stretching vibrations with a shift to lower wave numbers with increasing chain length. Between 900 and 1500 cm^{-1} further vibrations of the aliphatic chains and the C-N vibrations are seen [35, 36]. For a free tetrahedral WS_4 anion one can expect four characteristic bands $\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$, $\nu_4(\text{F}_2)$. The bands are Raman active and

only ν_3 and ν_4 are IR active [37]. The strong band observed in the $458\text{--}478\text{ cm}^{-1}$ region of the IR spectra (Fig. 4) is assigned to the triply degenerated asymmetric vibration ν_3 of the WS_4 tetrahedron [24, 26, 38]. A slight shift of the maximum of the absorption is observed with increasing alkyl chain length. A similar observation was reported earlier for $\text{R} = \text{Me}$ and $n\text{Bu}$ [28] and was explained on the basis of decreasing electropositivity with increasing chain length. But such an effect was not found when R was pentyl or hexyl [39]. Note that the sharp bands at about 480 cm^{-1} in the spectra of the ethyl and propyl compound are due to the organic part of the compounds. The weak absorption at around 175 cm^{-1} can be explained with the ν_4 vibration of the anion. This assignment is supported by strong lines in the Raman spectra located at the same energy [24, 26].

The difference between the longest and shortest W-S distances is an important factor which may be considered as a measure for the distortion of the $[\text{WS}_4]^{2-}$ tetrahedron. In a recent report [24] we analysed the structural and spectroscopic properties of 14 tetrathiotungstate complexes. One interesting result of the analysis is that a critical value for Δ of about 0.03 Å is required to see a splitting of the bands of the W-S vibrations in the IR spectra. In many tetrathiotungstates the large Δ values are caused by N-H...S interactions and the number as well as the strengths of these determine the distortion of the tetrahedron. In the present compounds no such hydrogen bonding interactions are possible and consequently the values for Δ are small and below the above mentioned limit. The large Δ values for the anions in compound **1** are caused by structural disorder and consequently no splitting of the W-S vibrations occurs in the spectra. For the other two com-

pounds Δ is less than 0.03 Å and as expected only broad absorptions are seen in the IR spectra.

The methyl compound shows the strongest structural disorder of all three samples. The calculation of the space available for a non-hydrogen atom yields 28.8 Å³ for compound **1** and about 25.7 Å³ for the other two compounds. The larger space for the atoms

in **1** suggests a less dense packing of the constituents and consequently less strong interactions.

Acknowledgements

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- [1] K. G. Knudsen, B. H. Cooper, H. Topsøe, *Appl. Catal. A*, **189**, 205 (1999).
- [2] J. W. Gosselink, *CaTTech*, **4**, 127 (1998).
- [3] J. C. Duchet, E. M. van Oers, V. H. J. de Beer, R. Prins, *J. Catal.*, **80**, 386 (1983).
- [4] J. P. R. Vissers, B. Scheffer, V. H. J. de Beer, J. A. Mouljin, R. Prins, *J. Catal.*, **105**, 277 (1987).
- [5] B. Scheffer, P. Arnoldy, J. A. Mouljin, *J. Catal.*, **112**, 516 (1988).
- [6] H. Farag, I. Mochida, K. Sakanishi, *Appl. Catal. A*, **194**, 147 (2000).
- [7] E. Hillerova, Z. Vit, M. Zdrzil, *Appl. Catal.*, **67**, 231 (1991).
- [8] H. Farag, D. D. Whitehurst, K. Sakanishi, I. Mochida, *Catal. Today*, **50**, 9 (1999).
- [9] G. Kishan, L. Coulier, V. H. J. de Beer, J. A. R. van Veen, J. W. Niemantsverdriet, *J. Catal.*, **19**, 180 (2000).
- [10] G. Kishan, L. Coulier, J. A. R. van Veen, J. W. Niemantsverdriet, *J. Catal.*, **200**, 194 (2001).
- [11] G. Alonso, M. del Valle, J. Cruz, V. Petranovskii, A. Licea-Claverie, S. Fuentes, *Catal. Lett.*, **52**, 55 (1998).
- [12] M. Poisot, W. Bensch, S. Fuentes, G. Alonso, *Thermochim. Acta*, **444**, 35 (2006).
- [13] G. Berhault, A. Mehta, A. C. Pavel, J. Yang, L. Rendon, M. J. Yacaman, L. C. Araiza, A. D. Moller, R. R. Chianelli, *J. Catal.*, **198**, 9 (2001).
- [14] M. Nath, A. Govindaraj, C. N. R. Rao, *Adv. Mater.*, **13**, 283 (2001).
- [15] J. Chen, S. L. Li, F. Gao, Z. L. Tao, *Chem. Mater.*, **15**, 1012 (2003).
- [16] Y. D. Li, X. L. Li, R. R. He, J. Zhu, Z. X. Deng, *J. Am. Chem. Soc.*, **124**, 1411 (2002).
- [17] J. Ellermeier, R. Stähler, W. Bensch, *Acta Crystallogr.*, **C58**, m70 (2002).
- [18] J. Ellermeier, Ph. D. thesis, University of Kiel, Germany (2002).
- [19] J. Yao, J. A. Ibers, *Acta Crystallogr.*, **E60**, i10 (2004).
- [20] B. R. Srinivasan, M. Poisot, C. Näther, W. Bensch, *Acta Crystallogr.*, **E60**, i136 (2004).
- [21] B. R. Srinivasan, S. N. Dhuri, C. Näther, W. Bensch, *Acta Crystallogr.*, **E58**, m622 (2002).
- [22] B. R. Srinivasan, S. N. Dhuri, C. Näther, W. Bensch, *Acta Crystallogr.*, **C59**, m124 (2003).
- [23] B. R. Srinivasan, S. N. Dhuri, M. Poisot, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.*, **631**, 1087 (2005).
- [24] B. R. Srinivasan, C. Näther, S. N. Dhuri, W. Bensch, *Monatsh. Chem.*, **137**, 397 (2006).
- [25] B. R. Srinivasan, S. N. Dhuri, C. Näther, W. Bensch, *Acta Crystallogr.*, **E59**, m681 (2003).
- [26] B. R. Srinivasan, C. Näther, S. N. Dhuri, W. Bensch, *Polyhedron*, 2006, in press.
- [27] J. W. McDonald, G. D. Friesen, L. D. Rosenhein, W. E. Newton, *Inorg. Chim. Acta*, **72**, 205 (1983).
- [28] G. Alonso, A. Aguirre, I. A. Rivero, S. Fuentes, *Inorg. Chim. Acta*, **274**, 108 (1998).
- [29] Stoe & Cie, IPDS (Version 2.89), X-SHAPE (Version 1.03) and REDU4 (Version 7.03), Stoe & Cie, Darmstadt, Germany (1998).
- [30] G. M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, University of Göttingen, Germany (1994).
- [31] G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, University of Göttingen (1997).
- [32] V. N. Serezhkin, *Zh. Neorg. Khim. (Russ) Russ. J. Inorg. Chem.*, **22**, 1554 (1977).
- [33] ConQuest Version 1.8; Refcode ZZZBNS (2006).
- [34] M. G. Kanatzidis, D. Coucouvanis, *Acta Crystallogr.*, **C39**, 835 (1983).
- [35] G. Berhault, L. C. Araiza, A. D. Moller, A. Mehta, R. R. Chianelli, *Catal. Lett.*, **78**, 81 (2002).
- [36] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 5th Edition, G. Thieme, Würzburg (1995).
- [37] A. Müller, N. Weinstock, H. Schulze, *Spectrochim. Acta*, **28A**, 1075 (1972).
- [38] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edition, John Wiley, New York (1997).
- [39] G. Alonso, J. Yang, M. H. Siadat, R. R. Chianelli, *Inorg. Chim. Acta*, **325**, 193 (2001).