DALTON
FULL PAPER

Investigations of the polyiodides $H_3O{\cdot}I_x$ (x = 3, 5 or 7) as dibenzo-18-crown-6 complexes

Lars Kloo,[a] **Per H. Svensson**[b] **and Michael J. Taylor**[c]

[a] *Inorganic Chemistry, Department of Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden*
[b] *Dipartimento di Chimica Fisica ed Inorganica, University of Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy*
[c] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

Received 6th October 1999, Accepted 4th February 2000

The compounds $[H_3O(\text{dibenzo-18-crown-6})][I_x]$ (x = 3,5,7) have been synthesised and investigated by X-ray diffraction as well as Raman and far-IR spectroscopy. The structure of the triiodide contains two independent, slightly asymmetric and bent I_3^- ions with I–I distances in the range 2.92–2.94 Å. The pentaiodide can be described as composed of $(I_3^-){\cdot}I_2$, where the I–I distances in the asymmetric and slightly bent I_3 unit are 2.894(2) and 2.942(2) Å and in the I_2 unit 2.763(2) Å. The L-shaped I_5^- ions are linked together forming a chain of I_{10} rectangles through van der Waals interactions in the range 3.7–3.8 Å. The structure determination supports a pyramidal geometry of the H_3O^+ ion in the dibenzo-18-crown-6 moiety of both structures. Because of severe crystal twinning the crystal structure of the heptaiodide could not be determined. However, the results from the spectroscopic investigation are consistent with a heptaiodide of composition $(I_3^-){\cdot}2I_2$.

Introduction

Polyiodides are of interest on account of their wide variety of geometric arrangements and different degrees of catenation. Presently, polyiodides in the formal range from I_2^- to I_{29}^{3-} are known and of these the most common are the I_3^- and I_5^- ions.[1–5] The higher polyiodides are usually extended networks and they have a very different three-dimensional arrangement creating linear and zigzag chains as well as layers. However, in common for all of the polyiodides is that with very few exceptions they can be described as being constructed from three building blocks; I^-, I_2 and I_3^-. An exception to this rule is a new type of compound in which metal iodides are incorporated as guest molecules in the polyiodide networks.[6–9]

Polyiodides have found applications in many different areas, *e.g.* electronics, batteries, conducting organic polymers, *etc.* and as a consequence of this, numerous spectroscopic and theoretical investigations have been performed.[10–13] The spectroscopic investigations have been concentrated on the identification of the nature of the iodine species in the polyiodides, while the theoretical investigations have mainly been devoted to the understanding of ambiguities of spectral features and the rationalization of the geometry of the structures.

In the literature, there are a few crown-ether polyiodides known.[14–18] In this work we present the crystal structures of $[H_3O(\text{dibenzo-18-crown-6})][I_x]$ (x = 3,5), and the Raman/far-IR spectra of the compounds with x = 3,5,7 together with an interpretation of the spectral features.

Results and discussion

The compound $[H_3O(\text{dibenzo-18-crown-6})][I_3]$ **1** was encountered during an attempt to synthesise indium complexes, such as $[In(\text{dibenzo-18-crown-6})][InI_4]$ by electrochemical means.[19] Acetonitrile containing dibenzo-18-crown-6 and a small amount of aqueous hydriodic acid was being employed in a cell with an indium metal anode and platinum cathode. Electrolysis had proceeded smoothly, with a weight loss from the anode which indicated oxidation to the In(III) state, but without the separation of any crystalline indium-containing product, in contrast to the behavior of related gallium systems.[20] Having been set aside, the pale yellow solvent phase turned dark brown after an hour, owing to atmospheric oxidation of HI to I_2, and deposited orange crystals. This same product was obtained in a blank test where a solution of the dibenzo-crown ether in acetonitrile with HI present was left exposed to air.

The Experimental section describes a typical preparation of **1** which was identified by chemical analysis, X-ray study and its vibrational spectra as a dibenzo-crown ether complex of the acid HI_3. Subsequently the dibenzo-crown ether complexes of two further polyiodides, HI_5 and HI_7 were prepared by the addition of iodine to **1**.

$[H_3O(\text{dibenzo-18-crown-6})][I_3]$

Crystals of **1** were shown by X-ray diffraction to consist of two independent $[H_3O(\text{dibenzo-18-crown-6})]^+$ moieties, H_3O^+ ions in the cavity of the crown-ethers and I_3^- ions (Fig. 1). The triiodide ions are distributed as layers which are separated by $[H_3O(\text{dibenzo-18-crown-6})]^+$ cations. Within the layers the anions are oriented as rows of parallel, discrete anions (weak $I_3^- \cdots I_3^-$ interactions, >4 Å, are present in the structure). The I_3^- ions [I(1)–I(2)–I(3) and I(4)–I(5)–I(6)] are slightly asymmetric and they have I–I distances of I(1)–I(2) 2.926(1) Å, I(2)–I(3) 2.940(1) and I(4)–I(5) 2.940(1) Å, I(5)–I(6) 2.915(1) Å. The I–I–I angles are 174.32(4)° [I(1)–I(2)–I(3)] and 174.75(4)° [I(4)–I(5)–I(6)], respectively. Both the bond distances and angles agree well with those found in the literature.[3] The H_3O^+ cation is situated in the cavity of the dibenzo-18-crown-6 macrocycle and it is coordinated by the six oxygen atoms with distances in the range 2.69–2.81 Å. This is within the range reported for hydrogen bonding in similar compounds.[15,21,22] The oxygen atom of the H_3O^+ cation is displaced from the mean plane formed by the six crown-ether oxygen atoms by 0.061 Å [O(13)] and 0.78 Å [O(14)] in the two different crown-ether moieties. This might suggest the presence of one planar and one pyram-

DOI: 10.1039/a908053h

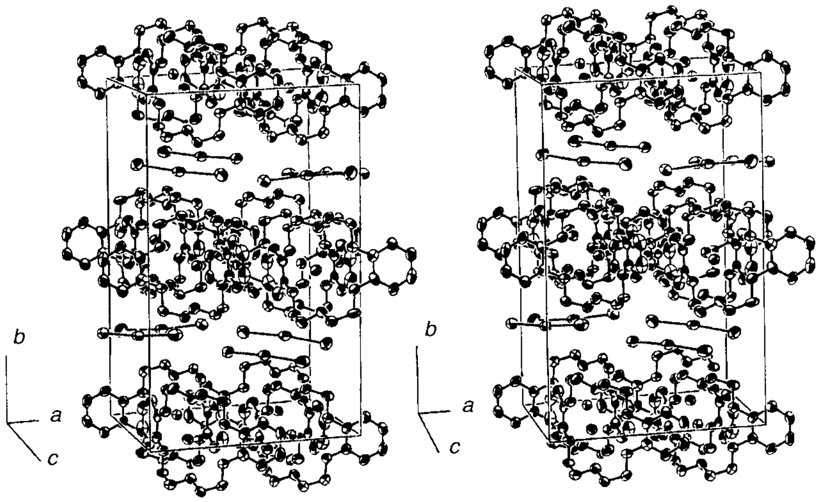

Fig. 1 Stereoscopic view of the crystal structure of [H_3O(dibenzo-18-crown-6)][I_3].

Table 1 Vibrational spectra of [H_3O(dibenzo-18-crown-6)][I_3] (cm^{-1})

Raman			
λ_{ex} = 514 nm	1064 nm	Far-infrared	Assignment
		232m	dibenzo-crown
219w	219vw		$2\nu_1$
		203m	?
180w	175w	178w	?
		125vs	ν_1 (asym. str.)
110vs	110vs	116m	ν_1 (sym. str.)
72w			?
		56w	ν_2 (bending)
		42w	ν_2 (bending)
35w			Lattice mode
21w			Lattice mode

idal H_3O^+ cation. However, the displacement from the plane of the three closest oxygen atoms of the H_3O^+ oxygen atoms O(13) and O(14) (0.78–1.31 Å) indicate that both cations are pyramidal.[15,22–25] The O–C, C–C aliphatic and O–C, C–C aromatic bond distances are in agreement with the corresponding distances in similar compounds.[16,26]

The vibrational spectra of a $D_{\infty h}$ triiodide ion is expected to have one Raman-active symmetric stretch ν_1 at 110 cm^{-1}, one infrared-active bending mode ν_2 (degenerate) at 75 cm^{-1} and one asymmetric stretch ν_3 at 145 cm^{-1}.[12,27–29] If the symmetry is lower than $D_{\infty h}$, all modes are expected to be Raman and infrared active. The peaks and assignment of the low-frequency part of the Raman and far-IR spectra are shown in Table 1. The IR data of **1** consist of a series of absorptions from dibenzo-18-crown-6 in association with the H_3O^+ cation, plus a weak band at 56 cm^{-1} and a very strong band at 125 cm^{-1} due to the ν_2 and ν_3 modes of the I_3^- anion, respectively (Fig. 2). The ν_3 mode is quite low in frequency but there are several spectroscopic investigations of triiodides which have reported ν_3 around 130 cm^{-1}.[28,30–32] There is also a peak at 116 cm^{-1} which agrees well with the symmetric ν_1 mode. In the Raman spectrum, the bands of dibenzo-18-crown-6 are very weak compared with the scattering from the triiodide ion, in particular that of the symmetric stretching mode which is seen at 110 cm^{-1}. Since the triiodide in **1** is asymmetric, the ν_3 band would also be expected to appear in the Raman spectrum. However, it is not seen, most likely because of the low intensity of the band. This type of anomaly for the triiodide ion has been observed before.[30–32]

[H_3O(dibenzo-18-crown-6)][I_5]

Compound **2** is produced from **1** as red-brown crystals by the addition of one mole of I_2. The structure shown in Fig. 3 reveals the presence of sheets of L-shaped pentaiodides separated by [H_3O(dibenzo-18-crown-6)]$^+$ moieties. The I_5^- anion can be regarded as an I_2 unit [I(4)–I(5), 2.763(2) Å] coordinating to an asymmetric I_3^- ion [I(1)–I(2)–I(3) with I(1)–I(2) 2.894(2) and I(2)–I(3) 2.942(2) Å; I(1)–I(2)–I(3) 175.23(4)°] at a distance of 3.291(2) Å [I(3)–I(4)]. Pure iodine has a significantly shorter intramolecular distance [2.715(6) Å in the solid state and in the gas phase 2.667(2) Å] compared with the I_2 unit in the I_5^- anion thus indicating a substantial charge-transfer interaction between I_3^- and I_2.[33,34] The top angle of the I_5^- ion [I(2)–I(3)–I(4)] is 102.16(5)°, while the angle between I(3) · · · I(4)–I(5), formed by the terminal iodide atom of the I_3^- unit and I_2, is 170.49(5)°. The structurally characterised pentaiodides of the $(I_3^-)\cdot I_2$ type in the literature correspond well to our results.[3,35] Intermolecular I · · · I distances in the range 3.5–3.7 Å have been regarded as secondary bonds [van der Waals (vdW) diameter of iodine 4.30 Å] and in the structure of **2** the I_5^- ions are linked together forming a chain of I_{10} rectangles through strong vdW interactions (3.7–3.8 Å).[36,37] The O · · · O distances between the crown-ether oxygen atoms and the oxonium ion (2.52–2.87 Å) indicate H-bonding (*vide supra*). The H_3O^+ cation is displaced from the mean plane formed by the six crown-ether oxygen atoms by 0.35 Å and from the plane of the three closest oxygen atoms by 0.42 Å. This indicates a pyramidal geometry of the H_3O^+ cation. The O–C, C–C aliphatic and O–C, C–C aromatic bond distances are as expected.

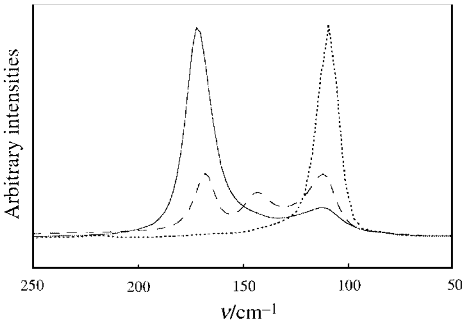

Fig. 2 The Raman spectra of **1** (– – –), **2** (— —) and **3** (———).

The peaks and assignment of the low-frequency part of the IR and Raman spectra of **2** are shown in Table 2. The Raman spectra of a pentaiodide of the $(I_3^-)\cdot I_2$ type is expected to have a strong peak (ν_1 of the I_3^-) close to 110 cm^{-1} and one at approximately 180 cm^{-1} corresponding to a coordinated I_2 molecule (ν_1 of I_2).[27,28–41] This is in good agreement with our results and the peak at 168 cm^{-1} thus indicates a significant interaction between the donor and acceptor. The peak at 143

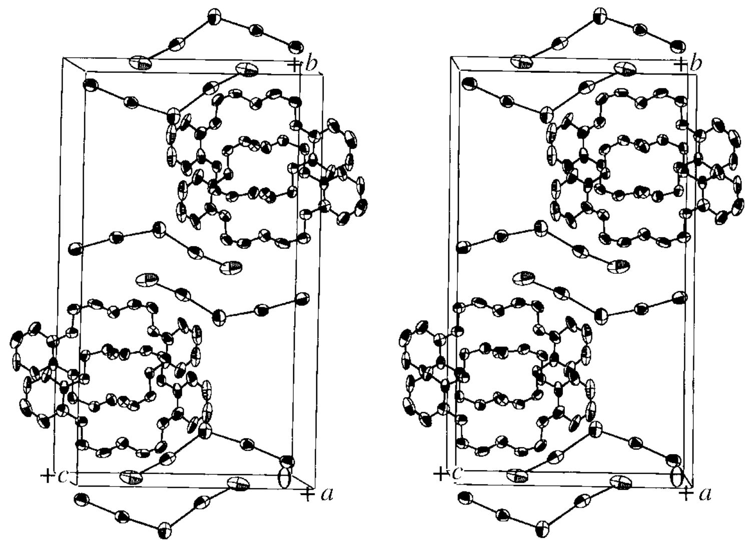

Fig. 3 Stereoscopic view of the crystal structure of [H_3O(dibenzo-18-crown-6)][I_5].

Table 2 Vibrational spectra of [H_3O(dibenzo-18-crown-6)][I_5] (cm^{-1})

Raman	Far-infrared	Assignment
232vw	232m	dibenzo-crown
220vw	220m	$2\nu_1$ (I–I–I^-)
	203vw	?
168s	172w	ν_1 (I–I str)
143m	132vs	ν_3 (I–I–I^- asym. str.)
112s	106m	ν_1 (I–I–I^- sym. str.)
	66w	ν_2 (I–I–I^- bending)
	43w	ν_2 (I–I–I^- bending)

Table 3 Vibrational spectra of [H_3O(dibenzo-18-crown-6)][I_7] (cm^{-1})

Raman	Far-infrared	Assignment
230vw	232m	dibenzo-crown
	220w	$2\nu_1$ (I–I–I^-)
	203vw	?
171vs	172w	ν_1 (I–I sym. str.)
140vw	138vs	ν_3 (I_3^- asym. str.)
113m	104w	ν_1 (I_3^- sym. str.)
	68w	ν_2 (I–I–I^- bending)
	54w	ν_2 (I–I–I^- bending)
	44w	Lattice mode

cm^{-1} can be assigned to the normally Raman-forbidden ν_3 mode of the I_3^- ion, which has become Raman active because of the lower symmetry. Estimates of the depolarisation ratios of these bands were obtained from the spectrum of an acetonitrile/aqueous HI solution in which I_5^- was present. Intense bands at 110 cm^{-1} (ν_1 of I_3^-) and 168 cm^{-1} (I–I stretch) are strongly polarised. However, the medium intensity band at 143 cm^{-1} appears to be depolarised, which is consistent with its assignment to asymmetric stretching of the I–I–I component of the $I_3^- \cdots I_2$ species.

The far-IR spectra have a peak at 172 cm^{-1} which can be assigned to the ν_1 mode of I_2 which normally is infrared forbidden and the peaks at 106 cm^{-1} and 132 cm^{-1} can be assigned to the ν_1 and ν_3 modes respectively of the I_3^- ion. The peaks at 66 cm^{-1} and 43 cm^{-1} seem to be consistent with the bending mode ν_2 of the I_3^- ion. It is important to point out that the assumption made when assigning the spectra from the separate units I_2 and I_3^- is that the coupling between the different vibrational modes of the two units is small. This assumption gains support from the results of quantum chemical calculations.[10]

[H_3O(dibenzo-18-crown-6)][I_7]

Compound **3** results when the triiodide **1** combines with I_2 which is present in excess. X-Ray examination of the brown needles was prevented by severe crystal twinning. The formulation of **3** as a heptaiodide is supported by the peaks in the Raman and IR spectra (Table 3). Heptaiodides can have three types of composition: $(I_3^-)\cdot 2I_2$, $(I^-)\cdot 3I_2$ and $(I_5^-)\cdot I_2$. The Raman spectra of $(I_3^-)\cdot 2I_2$ heptaiodides are expected, making the same approximation as for the pentaiodide, to have a strong ν_1 I_3^- vibration at about 110 cm^{-1} and also a strong ν_1 I_2 vibration at about 180 cm^{-1}.[39,42] A vibration mode at about 145 cm^{-1}, corresponding to the ν_3 mode of I_3^- should also be present if the I_3^- unit deviates from $D_{\infty h}$ symmetry. Both the Raman and far-infrared spectra of **3** fit well with this description (Table 3), thus supporting the $(I_3^-)\cdot 2I_2$ model for the heptaiodide in **3**. In the far-infrared spectra there are also peaks below 70 cm^{-1}, which originate from the ν_2 mode of I_3^- and lattice modes. These results were first published in the Ph.D. Thesis of Svensson in September 1998.[43] In early 1999, the crystal structure of a near analogue of **3** was published by Tebbe and coworkers.[44] The I_7^- unit in this compound is part of an extended chain of I_5^- units $[(I^-)\cdot 2I_2]$ bridged by I_2 molecules *via* the iodide ion. Unfortunately, no vibrational spectrocopic data are available for this compound. However, a more separated structure is expected for compound **3** because of the dibenzo spacers of the crown-ether.

Experimental

Dibenzo-18-crown-6 was obtained from Acros Organics. Iodine and hydriodic acid were analytical grade materials. Organic solvents were used as received. Vibrational spectroscopy of crystalline solid samples were obtained with a Bio-Rad FT Raman spectrometer which gave data from 70 to 4000 cm^{-1}, and supplemented by scanning the range 10–400 cm^{-1} using a Jobin-Yvert U1000 Raman system with a Spectra Physics 2016 argon-ion laser tuned to the green line of wavelength 514 nm at a power of <1 mW. Infrared spectra were recorded as pressed discs in Polythene or Nujol mulls using Bio-Rad FTS60V or FTS6000 spectrometers. Metal-grid and Mylar beam-splitters of 6.25, 12.5 and 50 mm were used to cover the far-IR range 500–30 cm^{-1}. Melting points were determined with Reichart apparatus.

Preparations

[H_3O(dibenzo-18-crown-6)][I_3] 1. In an open beaker, dibenzo-18-crown-6 (0.40 g, 1.1 mmol) was dissolved in acetonitrile (12 mL) to which hydriodic acid (55% aq., 1 mL) was added to give a yellow solution. After two hours the solution was dark colored due to atmospheric oxidation and orange crystals had formed. The solution was decanted to another beaker and the crystals were collected on filter paper and allowed to dry in air. Two further crops of crystals were collected in the next 24 hours. Yield 0.62 g (73% related to dibenzo-18-crown-6) of orange crystals, mp 157–158 °C. Anal. Calc. for $C_{20}H_{27}I_3O_7$ (760.1 g mol^{-1}): C, 31.6; H, 3.58. Found: C, 31.7; H, 3.44%.

[H_3O(dibenzo-18-crown-6)][I_5] 2. Iodine (0.032 g, 0.125 mmol) in acetonitrile (2 mL) was added to a solution of **1** (0.092 g, 0.12 mmol) in hot acetonitrile (6 mL). On cooling, the mixture deposited crystals differing in shape from those of **1** which may be obtained by recrystallisation from this solvent. The solution phase was withdrawn and the product was rinsed with diethyl ether until the washings were colorless. Yield: 0.070 g (57%) of red-brown crystals, mp 150 °C (decomp.). Anal. Calc. for $C_{20}H_{27}I_5O_7$ (1013.9 g mol^{-1}): C, 23.7; H, 2.68. Found: C, 24.0; H, 2.53%. The product may contain a trace of **1**.

[H_3O(dibenzo-18-crown-6)][I_7] 3. Iodine (0.096 g, 0.375 mmol) in acetonitrile (4 mL) was added to a solution of **1** (0.092 g, 0.12 mmol) in hot acetonitrile (6 mL). After cooling, the mixture comprised a dark brown solution containing a mass of needles. The solution was decanted off and the solid product was rinsed with diethyl ether and allowed to dry in air. Yield: 0.109 g (71%) of brown crystals which decompose on heating before reaching the melting point of **1** and slowly evolve iodine on standing. Anal. Calc. for $C_{20}H_{27}I_7O_7$ (1267.7 g mol^{-1}): C, 18.9; H, 2.15. Found: C, 22.6; H. 2.39%. The results are consistent with loss of I_2 from the product which is formulated as the heptaiodide **3** on the basis of spectroscopic data from freshly prepared samples. An attempt to identify the product by X-ray diffraction was prevented by severe twinning of the crystals.

Other combinations of 1 with I_2. Iodine was combined with **1** in acetonitrile in other proportions. A 2 : 1 mixture of I_2 with **1** yielded a solid product which was shown by its Raman spectrum to comprise **2** and **3** in approximately equal amounts. A 6 : 1 mixture of I_2 with **1** yielded crystals of **3** with no sign that higher polyiodides might be produced. Admixture of I_2 with **1** in acetone (3 : 1) yielded crystals of **3**, as above. Attempts to conduct similar reactions in $CHCl_3$, CH_2Cl_2, benzene or toluene were restricted by the low solubility of **1** in these solvents.

Solution studies

The products **1**, **2** and **3** were not sufficiently soluble to be investigated in solution by spectroscopic methods. Some Raman spectra were obtained from the dark-colored liquid (a mixture of acetonitrile and aqueous HI, containing I_2) from which the crystals of **1** had been collected. These spectra confirmed the presence of the triiodide and pentaiodide ions. Depolarisation ratio measurements were made which were employed in the discussion of assignments.

Residual solids

Several aliquots of the aqueous acetonitrile solution decanted during preparations of **1** were allowed to evaporate to dryness. Small quantities of dark-colored crystals were obtained. Raman investigation showed these to be mixtures which included various amounts of the products **1**, **2** and **3**. One sample also gave a strong Raman band at 157 cm^{-1} with a weak shoulder at 175 cm^{-1}. These features suggest the presence of another polyiodide solid, being similar to the spectrum of the heptaiodide reported by Poli *et al.*, but we were unable to identify this solid any further.[45]

Raman spectrum of I_2

The spectrum of solid iodine observed by FT Raman spectroscopy consisted of a very strong band at 181 cm^{-1} with a weak shoulder at 190 cm^{-1} as previously reported.[46]

Table 4 Crystallographic data for **1** and **2**[a]

	1	**2**
Formula	$C_{20}H_{27}I_3O_7$	$C_{20}H_{27}I_5O_7$
M	760.14	1013.95
a/Å	14.460(4)	8.2508(8)
b/Å	22.065(10)	24.949(5)
c/Å	16.364(5)	14.224(6)
β/°	101.81(1)	97.59(2)
V/Å^3	5110(2)	2902(1)
Space group	$P2_1/n$	$P2_1/a$
Z	8	4
D_c/g cm^{-3}	1.976	2.320
μ/cm^{-1}	37.06	53.94
Total data collected	11071	6583
Unique data	10657	6158
R_{int}	3.71	4.44
Final difference map	−1.18, 1.25	−1.34, 1.15
R, R'	0.0415, 0.0432	0.0390, 0.0374

[a] Details in common: monoclinic, Mo-Kα radiation (λ=0.71069 Å), T/K = 293, CAD4 diffractometer, ω–2θ scans.

Crystallography

A summary of the crystallographic data is provided in Table 4. All data were corrected for Lorentz and polarisation effects and empirical absorption correction was applied using the ψ-scan method.[47] All the structures were solved by direct methods (SIR 92).[48] The final cycle of full-matrix, least-squares refinement, $\Sigma w(|F_o| - |F_c|)$, was based on the observed reflections [$I \geq 3\sigma(I)$] and the number of variable parameters, using neutral atom scattering factors and anomalous dispersion corrections. All calculations were performed with the TEXSAN crystallographic software package.[49] Hydrogen atoms were included at calculated positions for the crown-ether molecules, while the hydrogen atoms of the oxonium ion were excluded.

CCDC reference number 186/1857.

See http://www.rsc.org/suppdata/dt/a9/a908053h/ for crystallographic files in .cif format.

Acknowledgements

The Swedish Natural Science Research Council and Human Capital & Mobility (contract no. CHRX CT93 0277) are gratefully acknowledged for their financial support.

References

1 P. Coppens, in *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum Press, New York, 1982, vol. 1, p. 333.
2 T. J. Marks and D. W. Kalina, in *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum Press, New York, 1982, vol. 1, p. 197.
3 K.-F. Tebbe, in *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*, ed. A. L. Rheingold, Elsevier, Amsterdam, 1977, p. 551.
4 K.-F. Tebbe and R. Buchem, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1345.
5 K.-F. Tebbe and M. Bittner, *Z. Anorg. Allg. Chem.*, 1995, **621**, 218.
6 H. Stegemann, K.-F. Tebbe and L. A. Bengtsson, *Z. Anorg. Allg. Chem.*, 1995, **621**, 165.
7 E. S. Lang and J. Strähle, *Z. Anorg. Allg. Chem.*, 1996, **622**, 981.
8 P. H. Svensson, L. Bengtsson-Kloo and P. Persson, *J. Chem. Soc., Dalton Trans.*, 1998, 1425.
9 P. H. Svensson, J. Rosdahl and L. Bengtsson-Kloo, *Chem. Eur. J.*, 1999, **5**, 305.
10 S. B. Sharp and G. I. Gellene, *J. Phys. Chem. A*, 1997, **101**, 2192.
11 G. A. Landrum, N. Goldberg and R. Hoffman, *J. Chem. Soc., Dalton Trans.*, 1997, 3605.
12 J. Milne, *Spectrochim. Acta, Part A*, 1992, **48**, 553.
13 M. Kertész and F. Vonderviszt, *J. Am. Chem. Soc.*, 1982, **104**, 5889.
14 G. S. Heo and R. A. Bartsch, *J. Org. Chem.*, 1982, **47**, 3557.

15 P. C. Junk, L. R. MacGillivray, M. T. May, K. D. Robinson and J. L. Atwood, *Inorg. Chem.*, 1995, **34**, 5395.
16 A. J. Blake, R. O. Gould, S. Parsons, C. Radek and M. Schröder, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 24.
17 M. Sievert, V. Krenzel and H. Bock, *Z. Kristallogr.*, 1996, **211**, 794.
18 K.-F. Tebbe and A. Kavoosian, *Acta Crystallogr.*, *Sect. C*, 1995, **51**, 562.
19 M. J. Taylor, D. G. Tuck and L. Victoriano *J. Chem. Soc.*, *Dalton Trans.*, 1981, 928.
20 M. J. Taylor and D. G. Tuck, *Inorg. Synth.*, 1983, **22**, 135.
21 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, Benjamin Press, New York, 1968, p. 12.
22 J.-P. Behr, P. Dumas and D. Moras, *J. Am. Chem. Soc.*, 1982, **104**, 4540.
23 J. L. Atwood, S. G. Abott, A. W. Coleman, K. D. Robinson, S. B. Whetstone and C. M. Means, *J. Am. Chem. Soc.*, 1987, **109**, 8100.
24 D. Chenervert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, 1989, **67**, 32.
25 W. R. Rodwell and L. Radom, *J. Am. Chem. Soc.*, 1981, **103**, 2865.
26 K. F. Mok and V. McKee, *Acta Crystallogr.*, *Sect. C*, 1990, **46**, 2078.
27 P. Deplano, F. A. Devillanova, J. A. Ferraro, F. Isaia, V. Lippolis and M. L. Mercuri, *Appl. Spectrosc.*, 1992, **46**, 1625.
28 J. S. Zambounis, E. I. Kamitsos, A. P. Patsis and G. C. Papavassiliou, *J. Raman Spectrosc.*, 1992, **23**, 81.
29 L. A. Bengtsson, H. Stegemann, B. Holmberg and H. Füllbier, *Mol. Phys.*, 1991, **73**, 283.
30 W. Gabes and H. Gerding, *J. Mol. Struct.*, 1972, **14**, 267.
31 P. W. Parrett and N. J. Taylor, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2458.
32 W. Gabes, D. J. Stufkens and H. Gerding, *J. Mol. Struct.*, 1973, **17**, 329.
33 F. van Bolhuis, P. B. Koster and T. Migchelsen, *Acta Crystallogr.*, 1967, **23**, 90.
34 I. L. Karle, *J. Chem. Phys.*, 1955, **23**, 1739.
35 K.-F. Tebbe and K. Nagel, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1323.
36 M. Bittner, Ph.D. Thesis, University of Köln,1994.
37 J. Blake, F. A. Devillanova, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *Chem. Soc. Rev.*, 1998, **27**, 195.
38 J. R. Ferraro, K. Martin, A. Furlani and M. V. Russo, *Appl. Spectrosc.*, 1984, **38**, 267.
39 P. Deplano, F. A. Devillanova, J. R. Ferraro, M. L. Mecuri, V. Lippolis and E. F. Trogu, *Appl. Spectrosc.*, 1994, **48**, 1236.
40 R. C. Teitelbaum, S. L. Ruby and T. J. Marks, *J. Am. Chem. Soc.*, 1980, **102**, 3322.
41 E. M. Nour, L. H. Chen and J. Laane, *J. Phys. Chem.*, 1986, **90**, 2841.
42 H. Mittag, H. Stegemann, H. Füllbier and G. Irmer, *J. Raman Spectrosc.*, 1989, **20**, 251.
43 P. H. Svensson, Ph.D. Thesis, University of Lund, 1998.
44 S. El Khalik, M. El Essawi, I. Dombrowski and K.-F. Tebbe, *Z. Naturforsch.*, *Teil B*, 1999, **54**, 136.
45 R. Poli, J. C. Gordon, R. K. Khanna and P. E Fanwick, *Inorg. Chem.*, 1992, **31**, 3165.
46 A. Anderson and T. S. Sun, *Chem. Phys. Lett.*, 1970, **6**, 611.
47 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.
48 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
49 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985, 1992.

Paper a908053h