

Synthesis, Structural and Spectroscopic Characterization of the α,ω -Diammonioalkane Hexabromorhodates(III) $[\text{H}_3\text{N}(\text{CH}_2)_x\text{NH}_3]_2[\text{H}_5\text{O}_2][\text{RhBr}_6]\text{Br}_2$ ($x = 3, 4$) – IR Spectra of $[\text{H}_5\text{O}_2]^+$ Ions with Weak Solid State Interactions

Maciej Bujak^b and Walter Frank^a

^a Lehrstuhl II für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany

^b Permanent address: Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

Reprint requests to Prof. Dr. W. Frank. Fax: (0049)-211-8114146.

E-mail: wfrank@uni-duesseldorf.de

Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

Z. Naturforsch. **57 b**, 1391–1400 (2002); received October 9, 2002

Hexabromorhodates(III), α,ω -Diammonioalkane Cations, Diaquahydrogen Cation

The reaction of rhodium(III) chloride trihydrate with 1,3-diaminopropane and 1,4-diaminobutane in concentrated hydrobromic acid results in the formation of the bis(α,ω -diammonioalkane) diaquahydrogen(1+) hexabromorhodate(III) dibromides $[\text{H}_3\text{N}(\text{CH}_2)_x\text{NH}_3]_2[\text{H}_5\text{O}_2][\text{RhBr}_6]\text{Br}_2$ ($x = 3, 4$). Dark red single crystals were obtained by diffusion-controlled crystallization at room temperature. Both compounds crystallize in space group type $P\bar{1}$ and their structures are closely related. In view of crystal engineering they are inorganic-organic hybrid materials built up from octahedral $[\text{RhBr}_6]^{3-}$, simple Br^- and flexible chain-like $[\text{H}_3\text{N}(\text{CH}_2)_x\text{NH}_3]^{2+}$ ions with the $[\text{H}_5\text{O}_2]^+$ and further Br^- ions incorporated and thus might be considered as addition compounds $[\text{H}_3\text{N}(\text{CH}_2)_x\text{NH}_3]_2[\text{RhBr}_6]\text{Br} \cdot [\text{H}_5\text{O}_2]\text{Br}$. Cationic and anionic moieties in the crystal are held together by a complex system of N-H...Br and O-H...Br hydrogen bonds. Geometric features of O-H...Br hydrogen bonding as well as the pronounced disorder of the $[\text{H}_5\text{O}_2]^+$ ions in the diammonioalkane salt indicate the weak association of these species in the solids. Weak association of the ions is also documented by difference ATR-FT-IR spectra of the compounds and related diammonioalkane dibromides that show the stretching modes of the terminal O-H bonds above 3300 cm^{-1} . Further characteristic bands are recognized at *ca.* 1635 (s), 985 (vs), and 670 (m) cm^{-1} .

1. Introduction

Hexahalogenorhodates with nitrogen-containing organic cations are known since the 19th century [1 - 7]. Nowadays selected members of this class of compounds play a crucial role in rhodium refining and recycling processes [8]. In the course of designing compounds with improved properties for the rhodium recycling process following the ideas of crystal engineering we synthesized and structurally characterized hexachlororhodates(III) with nitrogen-containing organic cations of various sizes and symmetries [9 - 14]. These compounds from a general point of view may be considered as inorganic-organic hybrid materials derived from simple starting materials: metal(III) halide, hydrohalic acid and oligofunctional organic amines. In view of crys-

tal engineering α,ω -diammonioalkane cations act as flexible and 'intelligent' building blocks, because their conformational flexibility enables them to act as cavity building elements with exactly the right lengths for the inclusion of guest ions like $[\text{H}_5\text{O}_2]^+$ [12]. Refining this idea to a concept of crystal and species engineering we succeeded in the synthesis of a compound with a framework that forces enclosed $[\text{H}_9\text{O}_4]^+$ ions into the unfavoured chain like topology [13].

Although various bromo complexes of Rh^{III} with simple 'inorganic' cations as well as complexes with substituted ammonium ions have been reported, such as $\text{Cs}_3[\text{RhBr}_6]$, $\text{K}_3[\text{RhBr}_6]$, $\text{K}_2[\text{RhBr}_5(\text{H}_2\text{O})]$, $\text{K}_5[\text{Rh}_2\text{Br}_{11}] \cdot 6\text{H}_2\text{O}$, $\text{RhBr}_3 \cdot 4\text{CH}_3\text{NH}_3\text{Cl}$, $\text{RhBr}_3 \cdot 2\text{C}_3\text{H}_6\text{N}_2\text{H}_6\text{Br}_2$ [15 - 18], until now to the best of our knowledge $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3][\text{RhBr}_6][\text{Br}] \cdot$

Table 1. Crystal data, X-ray measurements and structure determination summary for the diammoniopropane **1** and diammoniobutane salt **2**.

	1	2
Empirical formula	C ₆ H ₂₉ Br ₈ N ₄ O ₂ Rh	C ₈ H ₃₃ Br ₈ N ₄ O ₂ Rh
Formula weight	931.52	959.57
Crystal colour; habit	dark red; plate	dark red; plate
Crystal size (mm ³)	0.50 × 0.25 × 0.10	0.40 × 0.25 × 0.20
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)	<i>a</i> = 7.370(10) <i>b</i> = 9.150(2) <i>c</i> = 10.318(2) α = 64.79(3) β = 69.15(3) γ = 87.96(3)	<i>a</i> = 7.707(2) <i>b</i> = 9.423(2) <i>c</i> = 10.265(2) α = 112.15(3) β = 109.31(3) γ = 93.73(3)
Volume (Å ³)	583.29(19)	636.1(2)
Z	1	1
Density (calculated) (g·cm ⁻³)	2.652	2.505
Temperature (K)	295(2)	295(2)
Wavelength (Å)	Mo-K α , λ = 0.71073	Mo-K α , λ = 0.71073
Absorption coefficient (mm ⁻¹)	14.439	13.245
<i>F</i> (000)	434	450
θ Range (°)	3.0 - 35.3	2.9 - 35.4
Index ranges	-8 ≤ <i>h</i> ≤ 11; -14 ≤ <i>k</i> ≤ 13; -14 ≤ <i>l</i> ≤ 15	-12 ≤ <i>h</i> ≤ 9; -14 ≤ <i>k</i> ≤ 15; -15 ≤ <i>l</i> ≤ 14
Reflections collected/unique	12599/4005 (<i>R</i> _{int} = 0.054)	15353/4434 (<i>R</i> _{int} = 0.040)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2799	3037
Data/parameters	4005/136	4434/127
Goodness of fit on <i>F</i> ²	1.054	0.988
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.039, <i>wR</i> ₂ = 0.090	<i>R</i> ₁ = 0.035, <i>wR</i> ₂ = 0.075
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.064, <i>wR</i> ₂ = 0.102	<i>R</i> ₁ = 0.064, <i>wR</i> ₂ = 0.084
Largest diff. peak and hole (e·Å ⁻³)	1.38 and -1.73	1.45 and -1.41

H₂O is the only hexabromorhodate(III) with nitrogen containing organic cations, of which the structure was described [19].

Here we report a simple general procedure for the synthesis of hexabromorhodates(III) with nitrogen-containing organic cations and describe two acid containing compounds derived from short-chain α, ω -diaminoalkanes, focussing on the one hand on ideas of crystal engineering of inorganic-organic hybrid materials and on the spectroscopic properties of enclosed [H₅O₂]⁺ ions on the other hand.

2. Results and Discussion

2.1. Preparation and characterization

The reaction of 1,3-diaminopropane and 1,4-diaminobutane with rhodium(III) chloride trihydrate in concentrated hydrobromic acid after a few days yields almost quantitatively the ammonium

oxonium double salts bis(1,3-diammoniopropane) and bis(1,4-diammoniobutane) diaquahydrogen(1+) hexabromorhodate(III) dibromide (**1** and **2**), respectively. Simple halogen exchange procedures like this have proved to be generally applicable for the synthesis of hexabromorhodates(III) in further experiments with a great variety of nitrogen-containing organic compounds [20]. Due to the slow deterioration of **1** and **2** even at room temperature that proceeds under loss of hydrogen bromide and water, C, H, N analyses of the compounds are not satisfactory. Purity control with respect to the completeness of halogen exchange in the isolated product was done by energy dispersive X-ray fluorescence analysis investigating selected single crystals. Purity control with respect to the complex anions can easily be achieved by Raman spectroscopy showing the ν_1, ν_2, ν_5 -triple of bands for [RhBr₆]³⁻ near 187, 172 and 116 cm⁻¹ and indicating even small amounts of [RhCl₆]³⁻ by bands

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \cdot 10^3$) for non-hydrogen atoms of diammoniopropane **1** and diammoniobutane salt **2**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
[H ₃ N(CH ₂) ₃ NH ₃] ₂ [H ₅ O ₂][RhBr ₆]Br ₂ (1):				
Rh1	0	0	0	22(1)
Br1	3156(1)	-630(1)	-1465(1)	35(1)
Br2	1656(1)	796(1)	1374(1)	34(1)
Br3	816(1)	2866(1)	-2072(1)	35(1)
Br4	-2342(1)	2382(1)	-5338(1)	46(1)
N1	4116(6)	-2639(4)	1906(4)	38(1)
N2	2168(9)	-8575(5)	5117(5)	64(1)
C1	4194(8)	-4267(5)	1954(6)	47(1)
C2	3118(8)	-5605(5)	3548(5)	43(1)
C3	3208(7)	-7255(5)	3557(5)	38(1)
O11 ^b	-1421(7)	4046(5)	1028(5)	45(1)
O12 ^c	330(50)	3980(30)	1100(20)	54(11)
[H ₃ N(CH ₂) ₄ NH ₃] ₂ [H ₅ O ₂][RhBr ₆]Br ₂ (2):				
Rh1	0	0	0	22(1)
Br1	2799(1)	-812(1)	1352(1)	34(1)
Br2	1824(1)	725(1)	-1347(1)	32(1)
Br3	1175(1)	2739(1)	2046(1)	35(1)
Br4	-1506(1)	2630(1)	5578(1)	43(1)
N1	3931(6)	-2450(4)	-2062(4)	48(1)
N2	1964(4)	-8825(4)	-5371(4)	34(1)
C1	3856(7)	-3929(4)	-1878(5)	42(1)
C2	3853(6)	-5304(4)	-3229(4)	36(1)
C3	4056(6)	-6713(5)	-2855(5)	43(1)
C4	3866(6)	-8240(5)	-4166(5)	49(1)
O1	641(6)	4138(4)	-824(4)	51(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor; ^b occupation factor 0.87; ^c occupation factor 0.13;

near 291, 280 and 221 cm^{-1} , if present. Bands attributable to bromochlororhodates(III) have never been observed. Crystals of sufficient quality for X-ray structure determinations were grown by diffusion controlled crystallization using a triple layer procedure described in the Experimental Section.

2.2. Crystal structures

Both title compounds crystallize in the centrosymmetric space group type $P\bar{1}$. Crystal data and summaries of the structure determination details are listed in Table 1. The final atomic coordinates and equivalent isotropic displacement parameters for atoms heavier than hydrogen are shown in Table 2. The asymmetric units of the unit cells have been chosen thus that the close structural relationship of the compounds is documented by the

Table 3. Selected bond lengths (\AA) and angles ($^\circ$) for diammoniopropane **1** and diammoniobutane salt **2**.

[H ₃ N(CH ₂) ₃ NH ₃] ₂ [H ₅ O ₂][RhBr ₆]Br ₂ (1):			
Rh1-Br1	2.4862(9)	Br1-Rh1-Br2	89.84(2)
Rh1-Br2	2.4916(6)	Br1-Rh1-Br3	89.37(4)
Rh1-Br3	2.4958(13)	Br2-Rh1-Br3	89.66(3)
N1-C1	1.469(6)	N1-C1-C2	112.6(4)
N2-C3	1.472(6)	N2-C3-C2	111.8(4)
C1-C2	1.503(6)	C1-C2-C3	111.4(4)
C2-C3	1.504(6)		
[H ₃ N(CH ₂) ₄ NH ₃] ₂ [H ₅ O ₂][RhBr ₆]Br ₂ (2):			
Rh1-Br1	2.4899(9)	Br1-Rh1-Br2	88.63(2)
Rh1-Br2	2.4958(7)	Br1-Rh1-Br3	90.75(4)
Rh1-Br3	2.4985(13)	Br2-Rh1-Br3	89.10(3)
N1-C1	1.475(5)	N1-C1-C2	113.4(3)
N2-C4	1.471(5)	N2-C4-C3	113.0(3)
C1-C2	1.498(5)	C1-C2-C3	109.7(3)
C2-C3	1.519(6)	C2-C3-C4	115.7(4)
C3-C4	1.511(5)		

similarity of atomic coordinates. Opposite signs of the *z*-coordinates of corresponding atoms are obvious. They are essential because the standard type of reduced triclinic cell changes from one compound to the other. For **1** a Type-I standard cell with all angles acute, for **2** a Type-II cell with obtuse angles has to be chosen. The close relationship of the structures of **1** and **2** is also documented by the packing diagrams in Fig. 1 that show the principal arrangements of the [RhBr₆]³⁻ and [H₅O₂]⁺ ions that have crystallographically imposed $\bar{1}$ symmetry and of the α, ω -diammonioalkane and bromide ions which are in general positions.

Selected bond lengths and angles of the ionic building blocks are given in Table 3, geometric parameters of hydrogen bonds in Table 4.

The [RhBr₆]³⁻ ions in **1** and **2** are both surrounded by six NH₃ groups of different diammonioalkane and two H₂O fragments of different diaquahydrogen ions, the N and O atom positions of these groups defining a rather regular cube. Fig. 2 shows the rhodate ion of **2** with its environment. The arrangement of bromo ligands around the central rhodium(III) atoms slightly deviates from octahedral in both structures, reflecting the deforming influence of the environment. The lengths of the three crystallographically independent Rh-Br bonds of the [RhBr₆]³⁻ ions vary from 2.4862(9) to 2.4958(13) \AA for **1** and from 2.4899(9) to 2.4985(13) \AA for **2** (Table 3). The mean Rh-Br distances are 2.4912 and

Table 4. The hydrogen bond geometries (Å, °) for diammonio propane **1** (left) and diammonio butane salt **2** (right).

D-H...A	D-H	H...A	D...A	angle	D-H...A	D-H	H...A	D...A	angle
N1-H11...Br4 ^I	0.89	2.68	3.420(4)	141.1	N1-H11...Br4 ^I	0.89	2.56	3.403(4)	159.0
N1-H12...Br2	0.89	2.87	3.508(4)	129.8	N1-H12...Br1 ^{II}	0.89	2.85	3.524(4)	133.5
N1-H12...Br3 ^I	0.89	2.78	3.590(4)	152.5	N1-H12...Br3 ^{II}	0.89	2.99	3.795(4)	150.8
N1-H13...Br2 ^{II}	0.89	2.62	3.468(4)	160.0	N1-H13...Br1	0.89	2.88	3.680(4)	149.7
N2-H21...Br4 ^{III}	0.89	2.51	3.393(4)	169.4	N1-H13...Br2	0.89	2.82	3.449(4)	128.6
N2-H22...Br4 ^{IV}	0.89	2.82	3.550(6)	140.7	N2-H21...Br3 ^{VII}	0.89	2.53	3.400(3)	166.4
N2-H23...Br1 ^{IV}	0.89	2.80	3.548(5)	142.8	N2-H22...Br4 ^{VII}	0.89	2.47	3.343(3)	166.3
O11-H110...O11 ^V	1.193(10)	1.332(10)	2.426(8)	148(2)	N2-H23...Br4 ^{III}	0.89	2.69	3.499(3)	151.9
O11-H111...Br1 ^I	0.830(5)	2.49(3)	3.207(4)	145(4)	O1-H100...O1 ^V	1.18(15)	1.33(14)	2.392(7)	144(9)
O11-H112...Br4 ^{VI}	0.830(5)	2.44(3)	3.200(4)	152(5)	O1-H101...Br2	0.81(6)	2.63(6)	3.296(4)	141(5)
O12-H120...O12 ^V	1.19	1.33	2.45(5)	152.3	O1-H101...Br3	0.81(6)	2.91(6)	3.576(4)	141(5)
O12-H121...Br2	0.83	2.24	2.97(2)	147.4	O1-H102...Br4 ^{VIII}	0.80(5)	2.40(5)	3.177(4)	163(5)
O12-H122...Br4 ^{VI}	0.83	2.42	3.16(2)	149.5					

Symmetry codes: ^I $-x, -y, -z$; ^{II} $-x + 1, -y, -z$; ^{III} $-x, -y - 1, -z$; ^{IV} $x, y - 1, z + 1$; ^V $-x, -y + 1, -z$; ^{VI} $x, y, z + 1$; ^{VII} $x, y - 1, z - 1$; ^{VIII} $x, y, z - 1$.

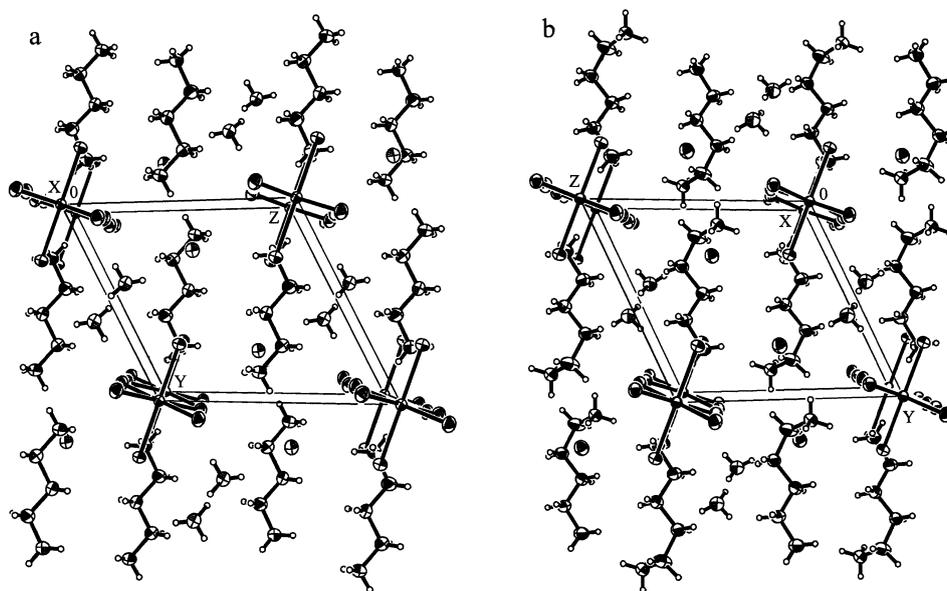


Fig. 1. Packing diagrams of the diammonio propane salt **1** (a: only one orientation (O11, H110, H111, H112) of the disordered $[\text{H}_5\text{O}_2]^+$ cation is shown for clarity) and the diammonio butane salt **2** (b) as seen along the a axes. Displacement ellipsoids are plotted at the 50% probability level; note the change of standard type of reduced triclinic cell from one compound to the other.

2.4947 Å. The Br-Rh-Br angles for Br atoms *cis* to one another range from 89.37(4) to 89.84(3)° and from 88.63(2) to 90.75(4)°, respectively. All these values and ranges are close to those found in $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3][\text{RhBr}_6][\text{Br}] \cdot \text{H}_2\text{O}$ [19]. It is also worth mentioning that the corresponding X-Rh-X angles in **2** and in the isotopic chlororhodate $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_2[\text{H}_5\text{O}_2][\text{RhCl}_6]\text{Cl}_2$ (**3**)

[12] are identical within three standard deviations.

Bond lengths and angles of the diammonioalkane ions in **1** and **2** are as expected (Table 3). The conformation of the $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]^{2+}$ ion in **1** is almost identical to the one found in 1,3-diammonio propane dibromide [21] and as will be shown in detail later vibrational spectra of these ions are

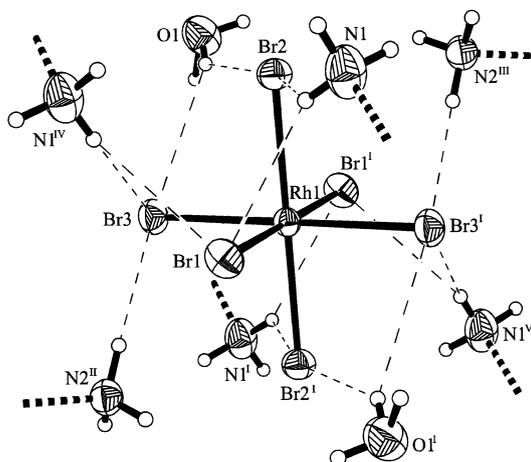


Fig. 2. The hydrogen bonding scheme (indicated by thin dashed lines) involving the $[\text{RhBr}_6]^{3-}$ octahedron in the structure of **2**. Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes: ^I $-x, -y, -z$; ^{II} $x, y + 1, z + 1$; ^{III} $-x, -y - 1, -z - 1$; ^{IV} $-x + 1, -y, -z$; ^V $x - 1, y, z$.

almost identical, too. All geometric parameters of the $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]^{2+}$ ion in **2** are in good agreement with those found in the isotopic chlororhodate **3**. With respect to the concept of crystal engineering with flexible building blocks closer inspection of the diammonio ions with their environments is fruitful (Fig. 3). The conformations of these ions are important features, because they determine the distances of the hydrophilic centers engaged in electrostatic as well as hydrogen bonding interactions. While the propane derivative in **1** adopts the all-transoid minimum conformation giving a $\text{N1}\cdots\text{N2}$ distance of 4.937(6) Å, the butane derivative in **2** is in an energy-unfavoured conformation mainly characterized by the torsion angle $\text{C2}-\text{C3}-\text{C4}-\text{N2}$ ($-65.8(5)^\circ$) and allowing for a $\text{N1}\cdots\text{N2}$ distance only 0.535 Å longer than in **1**. In conclusion it should be stated that crystallization of the title compounds neglecting to a great extent the different size of the flexible nitrogen-containing organic cations gives further confirmation for the validity of the crystal engineering concept of chain-like diammonioalkane cations acting as quasi-intelligent, flexible building blocks. Preliminary results show that even 1,5-diammonio-pentane is suitable for the synthesis of a hexahalo-genometallate that contains diaquahydrogen(1+) halide.

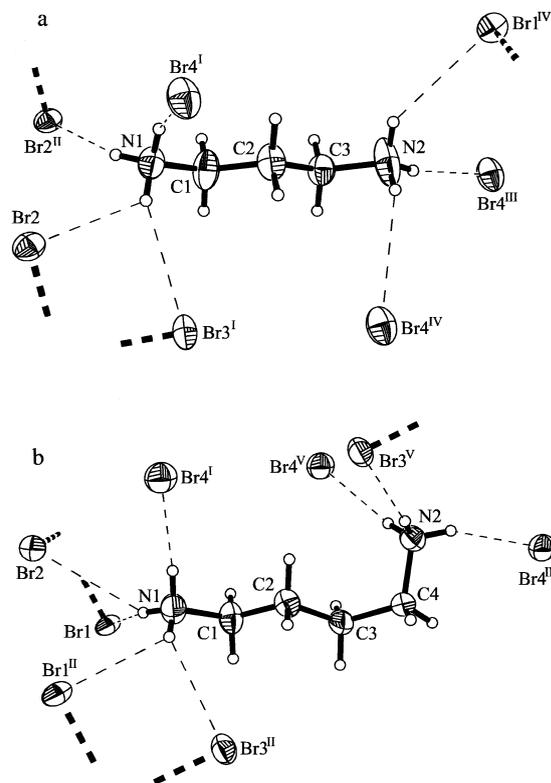


Fig. 3. Diagrams of the diammonioalkane ions in **1** (a) and **2** (b). The conformational flexibility of the butane derivative allows for acting as a building block similar to the propane derivative to give quasi-isotypic compounds. The thin dashed and dotted lines denote the $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds. Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes: ^I $-x, -y, -z$; ^{II} $-x + 1, -y, -z$; ^{III} $-x, -y - 1, -z$; ^{IV} $x, y - 1, z + 1$; ^V $x, y - 1, z - 1$.

The $[\text{H}_5\text{O}_2]^+$ ions in **1** and **2** are characterized by $\text{O}\cdots\text{O}$ separations of *ca.* 2.4 Å (Table 4) which are comparable to those previously reported [12, 13, 22 - 24]. In the course of refinement of the structure of **1** it became evident that there are two portions of this protonated water species occupying cavities in the surrounding inorganic-organic matrix according to two different orientations of the $\text{O}\cdots\text{O}$ direction, one populated to 87% the other to 13%. Furthermore for the major portion difference electron density maps clearly showed two different orientations of the terminal H atoms, *i. e.* in total there are three energetically different interaction modes of the $[\text{H}_5\text{O}_2]^+$ ion with its environment (Fig. 4). Finally, for both compounds in the regions of the central hydrogen atoms, split electron density was

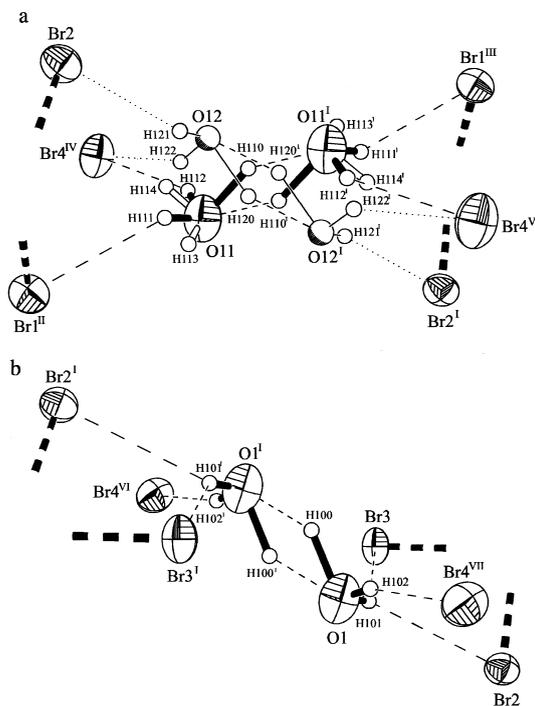


Fig. 4. The $[\text{H}_5\text{O}_2]^+$ cations with their neighboring $[\text{RhBr}_6]^{3-}$ and Br^- ions in **1** (a) and **2** (b). The thin dashed and dotted lines denote the O-H...Br hydrogen bonds. Note the similarities of the orientation of the O...O direction as well as of the hydrogen bonding pattern of the hydronium ion in **1** and of the minor fraction of the disordered ion in **2**. Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes: ^I $-x, -y + 1, -z$; ^{II} $-x, -y, -z$; ^{III} $x, y + 1, z$; ^{IV} $x, y, z + 1$; ^V $-x, -y + 1, -z - 1$; ^{VI} $-x, -y + 1, -z + 1$; ^{VII} $x, y, z - 1$.

found indicating the typical 1:1 disorder for strong O-H-O hydrogen bonds on a centrosymmetric site [12, 13, 23]. This observation is in accordance with the results of both theoretical and experimental investigations that show $[\text{H}_5\text{O}_2]^+$ to have a symmetric central hydrogen bond only in its C_2 symmetric minimum structure [25 - 30] and document that even very weak interactions give rise to a breakdown of the symmetric structure [31, 32]. Therefore it is most unlikely that any other than a $[\text{H}_5\text{O}_2]^+$ ion with crystallographically imposed C_2 symmetry and with weak solid state interactions should have a symmetrical, single minimum O-H-O hydrogen bond in a crystal. The torsion angles H101-O1...O1^I-H102^I and H113-O1...O11^I-H114^I are 63(6)° and 12(5)° in the $[\text{H}_5\text{O}_2]^+$ ion of **2** and in the major portion of the disordered $[\text{H}_5\text{O}_2]^+$ ion of **1**, respectively [^I $-x, -y - 1, -z$].

Looking at the similarity of the unit cell parameters and the positions of the ionic components, compounds **1** and **2** seem to be quasi-isotypic. However, a closer inspection of the structures shows a principal difference: as can be seen from the list of atomic coordinates or from Fig. 4, orientations of the O...O direction in the $[\text{H}_5\text{O}_2]^+$ ions of **2** and of the major fraction of the disordered species in **1** are completely different. As can be seen from Table 4 the strengths of the corresponding interionic O-H...Br hydrogen bonds are also significantly different for **1** and **2**. On the other hand it should be noted that the hydronium ion in **2** and the minor fraction of this ion in **1** are closely related with respect to O positions, O...O directions, and O-H...Br hydrogen bonding, a finding that explains the existence of the minor fraction of the disordered ion and that might be termed partial isotypism.

2.3. IR and Raman spectra

In the recorded regions (see experimental section) IR spectra of **1** and **2** present bands arising from internal modes of the diammonioalkane and the diaquahydrogen(1+) ions, while Raman spectra show strong bands of hexabromorhodate(III) vibrations, medium intensity bands of the diammonioalkane ions and some additional very weak and broad features that might be attributed to the $[\text{H}_5\text{O}_2]^+$ ions. The vibrational frequencies of the $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]^{2+}$ and $[\text{RhBr}_6]^{3-}$ ions are known from other compounds [12, 18, 33].

Strong lines in the 100 - 200 cm^{-1} region of the Raman spectra of **1** and **2** are associated with fundamental vibrational modes of the $[\text{RhBr}_6]^{3-}$ ion: the total symmetric stretching mode ν_1 (A_{1g}), the asymmetric stretching mode ν_2 (E_g) and the deformation mode ν_5 (F_{2g}). According to [18] the observed lines at 188 (**1**) and 186 cm^{-1} (**2**) are assigned to ν_1 , the slightly weaker lines at 173 (**1**) and 171 cm^{-1} (**2**) to ν_2 , and the lines at 120 (**1**) and 111 cm^{-1} (**2**), which are significantly weaker than the latter ones, to ν_5 . As can even better be shown by comparison with the value reported for ν_5 of $[\text{RhBr}_6]^{3-}$ in RhBr₃-doped AgBr (136 cm^{-1}) [18], this deformation mode to some extent is sensitive to the solid state interactions of the hexabromorhodate(III) ion. These seem to be stronger in **1** than in **2**.

Besides the oxonium ion $[\text{H}_3\text{O}]^+$, the $[\text{H}_5\text{O}_2]^+$ ion is the most important hydrated proton species

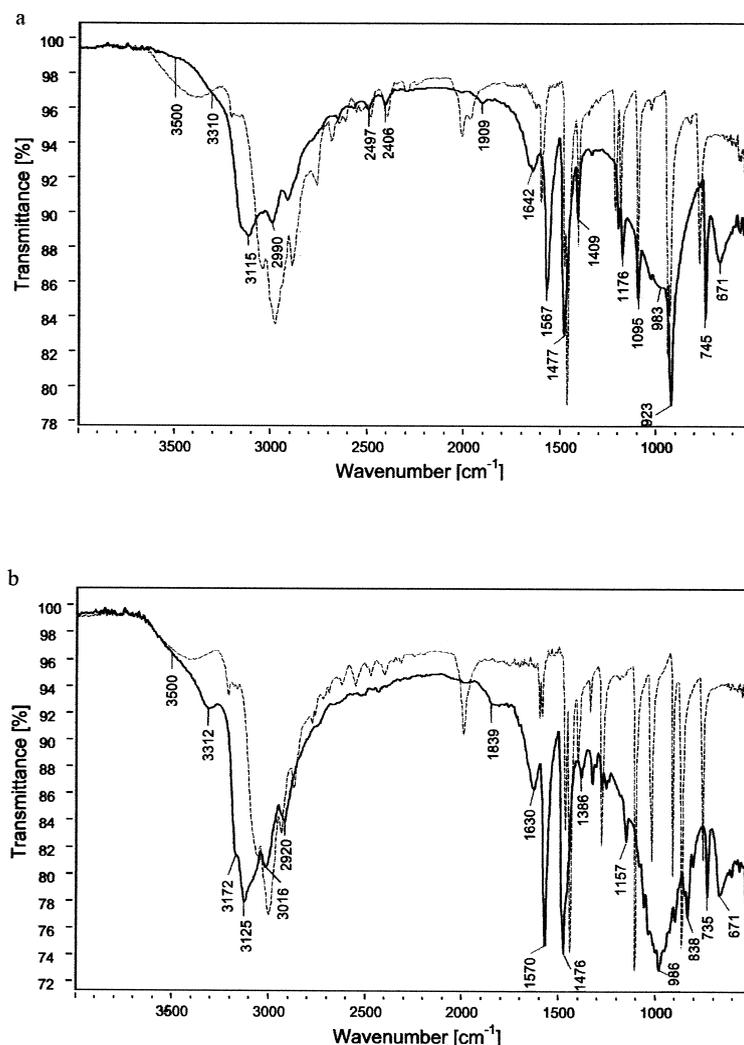


Fig. 5. a: Superimposed solid state IR spectra of the 1,3-diammoniopropane bromorhodate **1** (solid line) and 1,3-diammoniopropane dibromide (dashed). b: Spectra of the 1,4-diammoniobutane rhodate **2** (solid) and 1,4-diammoniobutane dibromide (dashed).

and as mentioned above it has been extensively investigated both experimentally and theoretically [25 - 32]. Results of many *ab initio* calculations have been published, of which the more recent ones characterize its minimum structure to be C_2 symmetric [26 - 29]. Although the theoretical studies have predicted frequencies of the internal vibration modes, it had to be stated that it is difficult to find good agreement among the theoretical results and the experimental spectra published so far [34].

In relation to the numerous spectroscopic studies of different compounds that revealed the presence of $[H_5O_2]^+$ cations there are only few examples of investigations of crystalline samples [35 - 40]. The $[H_5O_2]^+$ ion is characterized by a very short O-

H-O bond (*ca.* 2.4 Å), its symmetry depends on the arrangement of the two outer water molecules. In many publications the authors suggest that it is very difficult to unambiguously interpret the vibrational spectra of compounds containing this cation because the position of the proton is highly sensitive to the influence of environment. Therefore the spectra dramatically depend on the number of hydrogen bonds and electrostatic interactions in which the diquahydrogen(1+) cation takes part. Additionally the OH bands are always broad and either overlapped mutually or by the bands of other components present in the compounds.

Due to the very limited strength of O-H...Br hydrogen bonding in **1** and **2**, solid state IR spectra

of the discrete $[\text{H}_5\text{O}_2]^+$ ion under weak disturbing influence of anions can be presented in this work. IR spectra of the title compounds as well as the spectra of the related α, ω -diaminoalkane dihydrobromides are shown in Fig. 5. By comparison of these spectra, the bands of the diammonioalkanes are easily detected and additional features of the spectra clearly can be assigned to the $[\text{H}_5\text{O}_2]^+$ ions: the stretching modes of the terminal O-H bonds above 3300 cm^{-1} and further characteristic bands at *ca.* 1635 (s) , 985 (vs) and $670\text{ (m)}\text{ cm}^{-1}$. The first two of these further bands occur in frequency regions which have been reported as characteristic of the $[\text{H}_5\text{O}_2]^+$ ion in previous studies [35, 39, 40] and might be assigned in the usual way to $\delta(\text{OH}_2)$ and $\nu_{\text{as}}(\text{OHO})$. However, theoretical investigations showed that the origin of the bands is much more complicated due to the high anharmonicity of the O-H-O hydrogen bond potential and coupling of modes [28]. In a very recent *ab initio* investigation the vibrational spectrum of $[\text{H}_5\text{O}_2]^+$, calculated in the harmonic approximation at the DFT/B3LYP level of theory, shows the two strongest lines (intensity) at 1004 cm^{-1} (2596 km/mol) and at 1763 cm^{-1} (1395 km/mol) [29]. They are identified as mostly involving the proton transfer coordinate between the two oxygen atoms, this coordinate being strongly coupled to the HOH scissoring vibration of the OH_2 fragments. According to the same publication [29] complexation of $[\text{H}_5\text{O}_2]^+$ with a first solvation shell of four water molecules influences the IR lines associated with the proton transfer motion only marginally, giving 1033 cm^{-1} (2643 km/mol) and 1766 cm^{-1} , respectively. An additional intense lower-frequency line at 827 cm^{-1} also involves the proton transfer motion between the OH_2 fragments coupled to the out-of-plane bending of the latter. In the same study the OH stretching motions of the OH_2 fragments are found around 3800 cm^{-1} for the unsolvated and 3330 cm^{-1} for the solvated ion. Taking into account differences in the association of the $[\text{H}_5\text{O}_2]^+$ ion in the theoretical model and in the solids **1** and **2** on one and the harmonic approximation used in the theoretical treatment on the other hand, we suppose that the bands of $[\text{H}_5\text{O}_2]^+$ found in our IR spectra correspond to the theoretical modes of vibration described above.

In the Raman spectrum of **1** we found lines clearly assignable to the 1,4-diammoniobutane ion by comparison with the spectrum of the 1,4-diam-

moniobutane dibromide and some weak and broad additional features, that might be attributable to $[\text{H}_5\text{O}_2]^+$: clearly observable are broad bands with maxima at ~ 355 , ~ 760 , ~ 1050 ~ 1905 and $\sim 3300\text{ cm}^{-1}$. Further features that might be very weak and broad bands at ~ 1300 and $\sim 1500\text{ cm}^{-1}$ are uncertain because of superposition of several bands of the diammoniobutane ion.

3. Experimental Section

Elemental analyses were performed by the Institut für Pharmazeutische Chemie at the Heinrich-Heine-Universität Düsseldorf using a Perkin-Elmer 2400 elemental analyzer. IR spectra were recorded at room temperature with a Biorad Excalibur FTS 3500 FT-IR spectrometer in the range $4000\text{--}550\text{ cm}^{-1}$ using a DTGS detector (256 scans, resolution 4 cm^{-1}). The crystalline samples were placed on a MIRacle single refraction ATR sample plate (ZnSe). FT-Raman spectra in the range between 3450 and 50 cm^{-1} were recorded with the FT-Raman III subsystem attached to the spectrometer mentioned above at a resolution of 4 cm^{-1} (15000 scans) using the 1064 nm line of the Nd:YAG laser (power 1750 and 109 mW for **1** and **2**, respectively).

3.1. Synthesis and characterization

Rhodium(III) chloride trihydrate (6 M hydrochloric acid solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ containing 20% of RhCl_3 (Degussa AG, Germany)), concentrated hydrobromic acid (47%, Ferak, Germany), 1,3-diaminopropane (98%, Janssen Chimica, Belgium) and 1,4-diaminobutane (97%, Merck-Schuchardt, Germany) were the starting materials used for the synthesis of bis(1,3-diamminopropane) diaquahydrogen(1+) hexabromorhodate(III) dibromide (**1**) and bis(1,4-diamminobutane) diaquahydrogen(1+) hexabromorhodate(III) dibromide (**2**), respectively.

For the preparation of a macrocrystalline sample 0.10 ml (89 mg; 1.2 mmol) and 0.12 ml (106 mg; 1.2 mmol) of α, ω -diaminopropane and -butane, respectively, was dissolved in the minimum of hydrobromic acid (*ca.* 8 ml). This solution was carefully added to a test tube containing 0.1 ml of the acidic solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.15 mmol RhCl_3) covered by a layer of concentrated hydrobromic acid (1 ml). In the obtained triple-phase system at room temperature first dark red plates of suitable dimensions for characterization including single crystal X-ray structure analysis can be harvested after one or two days in the case of **1** and after two or three days in the case of **2**.

Compound **1**: Raman $\nu = \sim 3300\text{ (vwsh)}$, 3230 (sh) , 3143 (w) , 3087 (w) , 2993 (m) , 2963 (m) , 2941 (m) , 2918

(m), 2902 (w), 2865 (w), 2804 (w), 2789 (w), 2774 (w), 1903 (vw, br), 1605 (vw), 1567 (m), ~ 1500 (vw, br) 1481 (m), 1441 (m), 1408 (w), 1323 (m), ~ 1300 (vw, br), 1296 (w), 1201 (w), 1178 (m), 1094 (m), ~ 1050 (vw, br) 1028 (m), 931 (m), 818 (w), 781 (vw), 760 (w, br), 746 (w), 438 (m), 412 (w), 355 (w, br), 188 (vs), 173 (vs), 121 (s) cm^{-1} . – $\text{C}_6\text{H}_{29}\text{Br}_8\text{N}_4\text{O}_2\text{Rh}$ (931.52): calcd. C 7.74, H 3.14, N 6.02; found C 7.4, H 2.5, N 5.7.

Compound **2**: Raman $\nu = 3173$ (sh), 3083 (w), 3074 (w), 3064 (w), 2996 (m), 2972 (m), 2922 (w), 2884 (vw), 2860 (vw), 2763 (vw), 2735 (vw), 1870 (vw), 1580 (w), 1483 (w), 1466 (w), 1438 (w), 1446 (vw), 1390 (w), 1327 (m), 1311 (vw), 1281 (w), 1090 (w), 1064 (vw), 1043 (vw), 1018 (vw), 986 (w), 928 (w), 837 (vw), 781 (vw), 479 (vw), 415 (w), 186 (vs), 170 (vs), 111 (s) cm^{-1} . – $\text{C}_8\text{H}_{33}\text{Br}_8\text{N}_4\text{O}_2\text{Rh}$ (959.57): calcd. C 10.01, H 3.47, N 5.84; found C 10.3, H 3.3, N 6.0.

3.2. Crystal structure determination

Crystals of **1** and **2** suitable for X-ray structure determination were selected by means of a polarisation microscope and sealed in thin-walled glass capillaries. The intensity data were collected on a STADI4 CCD four circle, area detector single crystal diffractometer with graphite monochromatized Mo-K $_{\alpha}$ radiation. The ω -scan technique was used with $\Delta\omega = 1.0^\circ$ for one image. The lattice parameters were refined after data collection using 7809 and 7249 reflections for **1** and **2**, respectively. For all data Lp corrections and empirical absorption corrections based on symmetry-equivalent reflections [41] were performed including spherical contributions (**1**: $T_{\min} = 0.052$, $T_{\max} = 0.326$; **2**: $T_{\min} = 0.076$, $T_{\max} = 0.177$).

The structure of **1** was solved by the Patterson method. Atomic coordinates of the non-hydrogen atoms of **2** were taken from the isotypic hexachlororhodate chloride **3** [12]. ΔF maps of **1** clearly indicated some degree of disorder of the $[\text{H}_5\text{O}_2]^+$ ion. All hydrogen atoms of both structures were located in subsequent maps and quality of data even allowed to recognize partially occupied terminal hydrogen positions of the disordered $[\text{H}_5\text{O}_2]^+$ ion in **1** and split electron density in the regions of the central hydrogen atoms of this ion in both compounds.

For all atoms heavier than hydrogen anisotropic displacement parameters were refined. Idealized bonds lengths and angles were used for NH_3 and CH_2 groups. For the H atoms of the latter the riding model was applied. The hydrogen atoms of the ammonio groups were allowed to ride on the N atoms and to rotate around the neighbour-

ing C-N bonds. Free variables were used to constrain the isotropic displacement parameters of the hydrogen atoms of a single CH_2 or NH_3 group to be equal.

In the case of **2** atomic coordinates and isotropic displacement parameters were refined for the hydrogen atoms of the $[\text{H}_5\text{O}_2]^+$ cation. O-H bond lengths and H-O-H angles as well as U_{iso} values are very close to the ideal values for X-ray studies. The split electron density in the central region was treated by assigning two H atoms with occupation factor 0.5.

In the course of refinement of the structure of **1** two portions of the protonated water species were recognized that occupy the same centrosymmetric site according to two different orientations of the O \cdots O direction, one populated to 87% and the other to 13%. Furthermore, for the major portion difference electron density maps clearly showed two different orientations of the terminal H atoms (occupation 0.48 and 0.39, respectively). The asymmetric part of the major portion was treated using appropriate geometrical restraints. The asymmetric part of the minor portion of the disordered $[\text{H}_5\text{O}_2]^+$ ion (occupation 0.13) was treated as a rigid group using the same geometry at the O atom and the same H \cdots O † distance as refined for the diaquahydrogen ion in **2**. Plausible fixed U_{iso} values were used for the hydrogen atoms and allowance was made for translational and rotational movement of the fragment. Occupation factors for the three different components of the split model for the ion were refined using dependent free variables.

KUMA Diffraction Instruments software was used in the cell refinement, data collection [42] and data reduction processes [43]. SHELXS-97, SHELXL-97 [44] and SHELXTL [41] were used for the structure solutions, refinements and structure drawings. Crystallographic data (excluding structure factors) for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 195170 and CCDC 195171, respectively. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code+(1223) 336033 or e-mail: data_request@ccdc.cam.ac.uk).

Acknowledgements

We thank the Fonds der Chemischen Industrie and the Degussa AG for support, Ms E. Hammes for recording the vibrational spectra and Mr. P. Roloff for performing X-ray fluorescence analyses.

- [1] M. C. Vincent, M. Friedel, C. R. Acad. Sci. **101**, 322 (1886).
- [2] O. v. Fraenkel, Monatsh. Chem. **35**, 119 (1914).
- [3] A. Gutbier, Z. Anorg. Allg. Chem. **129**, 67 (1923).
- [4] A. Werner, Neuere Anschauungen auf dem Gebiet der Anorganischen Chemie, 3rd ed., p. 227, F. Enke Verlag (1923).
- [5] J. Meyer, M. Kawczyk, K. Hoehne, Z. Anorg. Allg. Chem. **232**, 410 (1937).
- [6] J. Meyer, H. Kienitz, Z. Anorg. Allg. Chem. **242**, 281 (1939).
- [7] F. A. Cotton, D. A. Ucko, Inorg. Chim. Acta **6**, 161 (1972).
- [8] W. D. Crozier, R. A. Grant (Johnson-Matthey Company), UK Patent Application GB 2 247 888 A (1990).
- [9] W. Frank, G. J. Reiß, I. Kleinwächter, Z. Anorg. Allg. Chem. **622**, 729 (1996).
- [10] W. Frank, G. J. Reiß, Z. Naturforsch. **51b**, 1459 (1996).
- [11] W. Frank, G. J. Reiß, Z. Naturforsch. **51b**, 1464 (1996).
- [12] W. Frank, G. J. Reiß, Chem. Ber. **129**, 1355 (1996).
- [13] W. Frank, G. J. Reiß, Inorg. Chem. **36**, 4593 (1997).
- [14] J. Graf, G. J. Reiß, W. Frank, Z. Krist. Suppl. **17**, 162 (2000).
- [15] P. Poulenc, Ann. Chim. **4** (11), 567 (1935).
- [16] J. Meyer, K. Hoehne, Z. Anorg. Allg. Chem. **231**, 372 (1937).
- [17] W. Robb, P. v. Z. Bekker, Inorg. Chim. Acta **7**, 626 (1973).
- [18] T. S. Kuan, Inorg. Chem. **13**, 1256 (1974).
- [19] R. D. Gillard, D. E. Hibbs, C. Holland, M. B. Hursthouse, K. M. A. Malik, G. Sykara, Polyhedron **15**, 225 (1996).
- [20] M. Bujak, W. Frank, to be published.
- [21] S.-q. Dou, H. Paulus, A. Weiss, J. Mol. Struct. **345**, 1 (1995).
- [22] J.-O. Lundgren, I. Olovsson, Acta Crystallogr. **23**, 966 (1967).
- [23] D. Mootz, E.-J. Oellers, M. Wiebecke, Z. Anorg. Allg. Chem. **564**, 17 (1988).
- [24] R. Minkwitz, C. Hirsch, Acta Crystallogr. **C55**, 703 (1999).
- [25] R. Janoschek, E. G. Weidemann, H. Pfeiffer, G. Zundel, J. Am. Chem. Soc. **94**, 2387 (1972).
- [26] M. J. Frisch, J. E. Del Bene, J. S. Binkley, H. F. Schaefer III, J. Chem. Phys. **84**, 2279 (1986).
- [27] F. F. Muguët, J. Mol. Struct. (Theochem) **368**, 173 (1996).
- [28] M. V. Vener, O. Kühn, J. Sauer, J. Chem. Phys. **114**, 240 (2001).
- [29] L. Sobolewski, W. Domcke, J. Phys. Chem. A **106**, 4158 (2002).
- [30] L. I. Yeh, Y. T. Lee, T. Hougen, J. Mol. Spectrosc. **164**, 473 (1994).
- [31] L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price, Y. T. Lee, J. Chem. Phys. **91**, 7319 (1989).
- [32] E. Bosch, M. Moreno, J. M. Liuch, J. Chem. Phys. **97**, 6469 (1992).
- [33] The Sadtler Handbook of Infrared Spectra (Ed.: W. Simons), p. 235, Heyden & Son Ltd., London (1978).
- [34] E. S. Stoyanov, J. Chem. Soc., Faraday Trans. **93**, 4165 (1997).
- [35] A. C. Pavia, P. A. Giguè, J. Chem. Phys. **52**, 3551 (1970).
- [36] A. S. Gilbert, N. Sheppard, Chem. Commun. 337 (1971).
- [37] G. Picotin, J. Roziere, J. Chim. Phys. **69**, 372 (1972).
- [38] J. Roziere, J. Potier, J. Mol. Struct. **13**, 91 (1972).
- [39] J. B. Bates, L. M. Toth, J. Chem. Phys. **61**, 129 (1974).
- [40] R. Ortwein, A. Schmidt, Z. Anorg. Allg. Chem. **425**, 10 (1976).
- [41] G. M. Sheldrick, SHELXTL Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1990).
- [42] KUMA Diffraction Instruments, UNIL IC and KUMA Diffraction Data collection GUI for CCD, version 1.166, KUMA Diffraction Instruments GmbH (2000).
- [43] KUMA Diffraction Instruments, UNIL IC and KUMA Diffraction CCD data reduction GUI, version 1.166, KUMA Diffraction Instruments GmbH (2000).
- [44] G. M. Sheldrick, SHELX-97. Program for the Solution and the Refinement of Crystal Structures. University of Göttingen, Germany (1997).