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On the structure of the N,N'-dimethylpropyleneurea and dimethylsulfoxide solvated gallium(III) and indium(III) ions and bromide complexes in solution and solid state, and the complex formation of the gallium(III) and indium(III) bromide systems in N,N'-dimethylpropyleneurea

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ABSTRACT

The structures of the *N*,*N*⁻dimethylpropyleneurea (DMPU) solvated gallium(III) and indium(III) ions have been determined in DMPU solution by means of EXAFS. The gallium(III) ion is five-coordinate with a mean Ga–O bond distance of 1.924(5) Å, while the larger indium(III) ion is octahedrally coordinated with a mean In–O bond distance of 2.146(3) Å. The complex formation equilibria in DMPU for the gallium(III) and indium(III) bromide systems have been studied calorimetrically at 298 K. Three relatively strong complexes are formed in the indium(III) bromide system in DMPU, whereas no stability constants could be established in the gallium(III) bromide system as the heats of complex formation were very close to zero. Gallium(III) bromide is present as DMPU solvated GaBr₃ complexes in solution with three equatorial Ga–Br bonds at 2.328(3) Å, and two Ga–O bonds at 1.92(3) Å in the apical positions of a distorted trigonal bipyramid. The DMPU solvated indium(III) bromide has the same configuration with a mean In–Br bond distance of 2.510(3) Å, and two In–O bonds at 2.201(6) Å. Indium(III) binds three bromides and three Me₂SO molecules through the oxygen atoms in octahedral *fac*-configuration with mean In–Br and In–O bond distances of 2.630(3) and 2.211(15) Å, respectively.

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1. Introduction

The hydrated gallium(III) and indium(III) ions have regular octahedral (O_h) configuration in both aqueous solution [1] and in solid compounds [2,3]. The mean Ga–O and In–O bond distances in the hydrates in aqueous solution, as determined by large angle X-ray scattering (LAXS) and EXAFS, are 1.959 and 2.131 Å, respectively [1], and in solid hydrates they are 1.946 and 2.125 Å, Table S1 [2,3]. The dimethylsulfoxide (Me₂SO) solvated gallium(III) [4] and indium(III) ions [4b,5], are also octahedral in solution as well as in solid compounds with mean Ga–O bond distances of 1.955 and 1.967 Å, and mean In–O bond distances of 2.135 and 2.142 Å, respectively. The *N*,*N*-dimethylformamide (DMF) solvated gallium(III) ion is octahedral with a mean Ga–O bond distance of 1.960 Å in the solid hexabromodigallate(III) salt [6]. No solvate structures of gallium(III) and indium(III) ions with neutral, monodentate *N*- and *S*-donor solvents have been reported so far [2,3].

It has been shown that space-demanding solvent molecules such as *N*,*N*'-dimethylpropyleneurea (DMPU, IUPAC name: 3,4,5,6-tetrahydro-1,3-dimethyl-2(1H)-pyrimidinone), 1.1.3.3tetramethylurea (TMU) and hexamethylphosphoric triamide (HMPA) force the coordination number of solvated metal ions to be lower than found in hydrates and solvates of small solvent molecules such as Me₂SO and DMF. Of the space-demanding solvents, we have chosen to work with DMPU, as both TMU and HMPA have been reported to be carcinogenic [7,8]. DMPU was developed as a less harmful substitute for TMU and HMPA, though one study has shown that also DMPU may act as a possible chemical mutagen in fruit flies [9]. DMPU is a polar, aprotic solvent with a wide range of uses including solvent for organic reactions and additive in paints and plastics [10]. The two methyl groups bordering the coordinating oxygen atom and the semi-rigid ring structure have been shown to obstruct the normal coordination, thereby forming solvates with lower coordination number [11–14], as previously also shown for TMU [15,16] and HMPA [17]. The nickel(II) and iron(III) ions have been shown to be five-coordinate in DMPU solution with square-pyramidal [11] and trigonal bipyramidal [12] configuration, respectively. The DMPU solvated zinc(II) and cadmium(II) ions are five- and six-coordinate in solution with mean Zn–O and Cd–O bond distances of 2.00 and 2.24 Å, respectively,



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while they are four-and six-coordinate in the solid state with mean bond distances of 1.925 and 2.26 Å, respectively [13]. The DMPU solvated lanthanoid(III) ions, except the lutetium(III) ion, are seven-coordinate in DMPU solution, while the solid solvates, as well as the lutetium(III) ion in solution, are octahedral [14].

Complex formation studies of the nickel(II) and iron(III) bromide systems in water, Me₂SO and DMPU have shown that only very weak complexes are formed in water and Me₂SO [18], where the metal solvates are octahedral, while much more stable complexes are formed in DMPU [11,19], where the metal solvates have lower symmetry. The stability of complexes increases in general with decreasing solvating ability of the solvent. However, DMPU is a significantly better electron-pair donor, $D_{\rm S} = 34$ [11], than water and dimethylsulfoxide, $D_{\rm S}$ = 18.0 and 27.5, respectively [20]. In protic solvents, the stability of metal complexes is affected by hydrogen bonding to the ligands. From this point of view, it is expected that complex formation is slightly stronger in aprotic solvents than protic ones [21]. The reason for the increased stability of the nickel(II) and iron(III) bromide complexes in DMPU is therefore most probably due to the significantly lower stability of the fivecoordinate solvate complexes in comparison to the octahedral ones [11, 19].

The complex formation in the gallium(III) and indium(III) bromide systems in aqueous media has been reported in several studies, Table 1 and Table S2 [18]. These systems form quite weak complexes with mean β_1 values of ca. 0.6 and 125 mol⁻¹ dm³, respectively [22,23]. For the indium(III) bromide system, some studies in aprotic solvents, i.e. Me₂SO [24], DMF [25] and formamide [26] have been reported as well, Table 1, while there are no such investigations reported for the gallium(III) bromide system. The complex formation in Me₂SO and DMF is significantly stronger than in water. Furthermore, formamide forms strong hydrogen bonds, and consequently, the indium(III) bromide complexes are weaker in formamide than in Me₂SO, DMF and water, cf. Table 1.

The aim of this study is to determine the structure of the DMPU solvated gallium(III) and indium(III) ions in solution, to study the

complex formation in the gallium(III) and indium(III) bromide systems in DMPU calorimetrically, and to determine the structures of the DMPU and Me₂SO solvated gallium(III) and indium(III) bromide systems in solution and solid state as a continuation on the studies of structure and reactivity of metal ions with forced low coordination numbers due to steric reasons [11,19].

2. Materials

2.1. Chemicals

N,N'-dimethylpropyleneurea, (CH₂)₃(CH₃)₂N₂CO (Aldrich), and dimethylsulfoxide, (CH₂)₃SO (Merck), were distilled over calcium hydride, CaH₂ (Fluka), under reduced pressure (~6 kPa), and stored in dark glass bottles over 3 Å molecular sieves. Tetrabutylammonium bromide, (*n*-C₄H₉)₄NBr (Merck), and tetrabutylammonium perchlorate, (n-C₄H₉)₄NClO₄ (Fluka), were used after being dried in a desiccator over phosphorous pentaoxide, P₄O₁₀, under vacuum at room temperature. Anhydrous gallium(III) and indium(III) bromide, GaBr₃ and InBr₃ (Aldrich, 99.9%), were used as purchased. Anhydrous gallium(III) and indium(III) trifluoromethanesulfonate, $M(CF_3SO_3)_3$, were prepared by adding an excess trifluoromethanesulfonic acid, CF₃SO₃H (Fluka), drop-wise to aqueous slurries of gallium(III) oxide, Ga₂O₃ (Fluka), and indium(III) hydroxide, In(OH)₃ (Fluka), respectively. The slurries were refluxed for 2 h until clear solutions were obtained. The solutions were filtered, and water and excess acid were boiled off at ca. 450 K. Anhydrous gallium(III) and indium(III) trifluoromethanesulfonate were stored in an oven at ca. 450 K to avoid uptake of water.

2.2. Solutions and crystals

The DMPU solutions of gallium(III) and indium(III) trifluoromethanesulfonate and gallium(III) bromide for EXAFS studies were prepared by dissolving respective salt in freshly distilled solvent.

Table 1

Overall stability constants, β_j , and thermodynamic functions for the individual steps in the complex formation of the indium(III)- and gallium(III) bromide systems in water, dimethylsulfoxide (Me₂SO), formamide (FA), *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylpropyleneurea (DMPU) at 25 °C.

In ³⁺ -Rr ⁻	
Water ^a 1 $9.5(5) \times 10^{1}$ $-11.3(2)$ $1.96(4)$	44.4(8)
2 $3.6(3) \times 10^2$ $-3.4(2)$ $5.64(4)$	30.5(3)
3	
Me ₂ SO ^b 1 6.92×10^3 -29.9	
$2 6.03 \times 10^6 -8.8$	
3 1×10^7 -1.3	
4 7.41×10^8 -10.7	
FA^{c} 1 2.8×10^{1} -8.3	
2 6.5×10^1 -2.1	
3 3.1×10^2 -3.9	
DMF ^d 1 3.24×10^3 -20.0	
2 6.3×10^5 -13.1	
$3 2.0 \times 10^8 -14.2$	
4 3.2×10^{10} -16.2	
DMPU ^e 1 $7.18(7) \times 10^2$ $-16.3(1)$ $8.1(1)$	81.8(4)
2 $2.08(3) \times 10^5$ $-14.1(4)$ 19.1(3)	111(2)
3 $5.64(18) \times 10^7$ $-13.9(4)$ $3.3(4)$ 5	58(1)
$Ga^{3+}-Br^-$	
Water ^f 1 0.58 -1.37	
2 0.32 -2.85	

^a Ref. [23].

^b Ref. [24].

^c Ref. [25].

^d Ref. [26].

^e This work.

^f Ref. [22].

Solid tris(dimethylsulfoxide)trisbromoindium(III) and bis(*N*,*N*'-dimethylpropyleneurea)trisbromoindium(III) were prepared by dissolving anhydrous indium(III) bromide in freshly distilled solvent to saturation in vials under nitrogen atmosphere while carefully heating them in an oil bath to maximum 323 K. The vials were left in the oil bath, which were allowed to slowly cool to room temperature, and single crystals suitable for crystallographic studies were obtained.

3. Methods

3.1. Calorimetric measurements

Calorimetric titrations were performed on a ThermoMetric 2277 TAM microcalorimeter to determine the heat of complex formation of gallium(III) and indium(III) with bromide in DMPU solution at 298.15 ± 0.01 K. The titrations were carried out in a titration vessel rhodium-plated for chemical inertness, $V = 4.0 \text{ cm}^3$. The stirrer was a gold propeller. The start volume in the titrations was 3.00 cm³ of 2.0 mmol dm⁻³ metal(III) trifluoromethanesulfonate in DMPU containing 0.100 mol dm⁻³ tetrabutylammonium perchlorate as a supporting electrolyte. These solutions were titrated portionwise with 0.100 mol dm⁻³ tetrabutylammonium bromide in DMPU. In every titration point 5 mm³ ligand solution was added by a computer-controlled pump driving a microliter syringe through a very thin gold capillary. In total, 111 portions were added in the indium(III) bromide system in each titration series, while totally 74 portions per series were added in the gallium(III) bromide system. At least three titration series were carried out for each system. Two titration series to determine the heats of dilution of metal(III) and bromide ions in DMPU were performed. All heats of dilution were very small, and used to correct the experimental heats of complex formation. The stability constants and the corresponding enthalpy changes were calculated by means of the least-squares program KALORI [27]. The calorimeter system was calibrated with the barium-18-crown-6 system in water. The values of $K_1 = 6.0 \times 10^3$ dm³ mol⁻¹ and $\Delta H = -30.6$ kJ mol⁻¹ were obtained for the system. The corresponding literature data is: $K_1 = 7.41 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and $\Delta H = -31.7 \text{ k} \text{ mol}^{-1}$ [28].

3.2. Extended X-ray absorption fine structure measurements

Gallium and indium K edge X-ray absorption data were recorded at the wiggler beam-lines I811 at MAX-lab, Lund University, Sweden, and 4-1 at Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA, respectively. The beam-lines were equipped with Si[1 1 1] and Si[2 2 0] double crystal monochromators, respectively. The storage ring at MAX-lab operated at 1.5 GeV and a maximum current of 220 mA, and at SSRL it operated at 3.0 GeV and a maximum current of 100 mA. Data collection at the gallium K edge was carried out in transmission and fluorescence mode simultaneously, using ion chambers with a stationary gas mixture of helium and nitrogen, and a Lytle detector [29] filled with argon gas. Higher order harmonics were rejected by detuning the second monochromator crystal to 50% of maximum intensity at the end of the scan. Data collection at the indium K edge was only carried out in transmission mode, using ion chambers with a flow of a gas mixture of nitrogen and argon. The second monochromator crystal was detuned to 80% of maximum intensity to reject higher order harmonics. The gallium solutions were kept in cells with Mylar tape windows and an 1-2 mm thick Teflon spacer, while for the indium solution a 5 mm Teflon spacer was used. The solids were ground to homogeneous mixture with an appropriate amount of boron nitride (BN) to achieve an edge step of unity and placed in a 1.5 mm aluminum frame with Mylar tape windows. Energy calibration of the X-ray absorption spectra was performed by simultaneously recording the edge spectrum of a metallic gallium or indium foil during the data collection, and assigning the first Kedge inflection point to 10368.2 and 27940.0 eV, respectively [30]. The EXAFS program package was used for the data treatment [31]. The EXAFS oscillations were extracted using standard procedures for pre-edge subtraction, spline removal and data normalization. Model fitting, including both single and multiple backscattering pathways, was performed with theoretical phase and amplitude functions calculated *ab initio* by means of the computer code FEFF7 [32]. The k^3 weighted EXAFS oscillation was analyzed by a non-linear least-squares fitting procedure of the model parameters.

The standard deviations given for the refined parameters in Table 2 are obtained from k^3 weighted least-squares refinements of the EXAFS function (k), and do not include systematic errors of the measurements. These statistical error values provide a measure of the precision of the results and allow reasonable comparisons e.g. of the significance of relative shifts in the distances. However, the variations in the refined parameters, including the shift in the E_0 value (for which k = 0), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.005 to 0.02 Å for well-defined interactions. The "standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

3.3. Single crystal X-ray diffraction

Data collection were performed on a Bruker SMART platform equipped with a CCD area detector [33] and a graphite monochromator using Mo K α (λ = 0.7107 Å) radiation at room temperature. A hemisphere data with 1271 frames was collected for each structure using the omega scan method. The crystal to detector distance was 5.0 cm. The first 50 frames were re-measured at the end of the data collection to check crystal and instrument stability. No correction was necessary for the crystals studied. Both structures were solved by direct methods in SHELXTL [34], and refined using full-matrix least-squares on F^2 . Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were calculated in ideal positions riding on their respective carbon atom.

4. Results and discussion

4.1. The N,N'-dimethylpropyleneurea solvated gallium(III) and indium(III) ions

The EXAFS data of the DMPU solvated gallium(III) ion in solution give a mean Ga–O bond distance of 1.924(2) Å, with no multiple scattering (MS) within the first coordination shell, but strong MS within the Ga–O–C entity. According to the ionic radii given by Shannon for the gallium(III) ion in four-, five- and six-coordination [35], the expected Ga-O bond distances should be 1.81, 1.89, and 1.96 Å, respectively, assuming that the oxygen radius is 1.34 Å, as in coordinated water [2e]. However, Shannon's value for five-coordination is listed as the most uncertain one albeit without any comment. A literature search of five-coordinated gallium(III) complexes, mainly polymeric phosphate-gallium complexes, show that the mean Ga–O bond distance is 1.905 Å (range 1.876–1.928 Å), Table S3. This shows that the Ga–O bond distance in the DMPU solvated gallium(III) ion is within the expected range for five-coordination. This is in full agreement with the results from previous studies on the DMPU solvated nickel(II), zinc(II) and iron(III) ions which all have a slightly larger ionic radius than gallium(III). The Ga–O–C angle, 146(2)°, is significantly larger than

Table 2

Bond distances, d/Å, Debye–Waller factors, $\sigma^2/Å^2$, and number of distances, n, for the DMPU solvated gallium(III) and indium(III) ions in solution, and DMPU and dimethylsulfoxide solvated gallium(III) bromide in solution determined by EXAFS at room temperature; E_0 is the refined threshold energy and S_0^2 is refined amplitude reduction factor.

	n	d	σ^2	Eo	S_{0}^{2}
N,N'-dimethyl propyleneurea	1				
Ga=0	5	1 924(2)	0.0069(2)	-117	1.00(2)
Gauc	5	3 058(4)	0.0025(3)	11.7	1.00(2)
Ga-O-C	10	3 136(11)	0.017(4)		
Ga-0-C-0	5	3.19(2)	0.004(2)		
Gallium(III) Bromide					
Ga–Br	3	2.328(1)	0.0054(1)	-15.6(5)	0.99(4)
Ga–O	2	1.915(14)	0.029(3)		
Indium(III) Ion					
In-O	6	2.146(1)	0.0048(2)	-17.4	1.00(2)
In…C	6	3.16(2)	0.019(3)		
In-O-C	12	3.29(1)	0.019(2)		
Dimethyl sulfoxide					
Gallium(III) Bromide					
Ga-O	6	1.958(1)	0.0047(2)	-14.9	0.93(3)
Ga···S	6	3.114(2)	0.0067(2)		
Ga-O-S	12	3.303(9)	0.013(2)		
MS	3 imes 6	3.98(1)	0.011(2)		

observed in DMPU solvated metal ions and complexes without steric restrictions, $125-130^{\circ}$ [11]. The large Ga–O–C bond angle, and the relatively long Ga–O bond distance being five-coordinate, supports the view that the bound DMPU molecules are affected by steric restrictions. The structure parameters are summarized in Table 2, and the fit of the EXAFS data and the Fourier transform are shown in Figs. 1 and 2.

The EXAFS data of the DMPU solvated indium(III) ion in solution gives a mean In–O bond distance of 2.146(1) Å, which is in the expected range for six-coordination of oxygen donor solvents, see Introduction. The larger indium(III) ion is able to accommodate six *N*,*N*-dimethylpropyleneurea ligands, and the packing around indium(III) ion is less crowded than around gallium(III), seen by a significantly smaller In–O–C angle, $134(2)^\circ$. The contribution from the multiple scattering within the InO₆ core is strongly



Fig. 1. Fit of the EXAFS data of (a) gallium(III) trifluoromethanesulfonate in DMPU, (b) gallium(III) bromide in DMPU, (c) gallium(III) bromide in dimethylsulfoxide, and (d) indium(III) trifluoromethanesulfonate in DMPU.



Fig. 2. Fourier transforms of (a) gallium(III) trifluoromethanesulfonate in DMPU, (b) gallium(III) bromide in DMPU, (c) gallium(III) bromide in dimethylsulfoxide, and (d) indium(III) trifluoromethanesulfonate in DMPU.

damped due to the short core hole life time at the indium *K* edge [36].

4.2. Indium(III) bromide in N,N'-dimethylpropyleneurea

Calorimetric measurements on the indium(III) bromide system in DMPU showed that three complexes with $\beta_1 = 7.2(2) \cdot 10^2$ (mol dm⁻³)⁻¹, $\beta_2 = 2.1(1) \cdot 10^5$ (mol dm⁻³)⁻² and $\beta_3 = 5.6(2) \cdot 10^7$ (mol dm⁻³)⁻³, respectively, are formed. The obtained values in this study, and literature data in oxygen donor solvents, are summarized in Table 1 for comparison. The total molar enthalpy changes and the complex distribution functions are shown in Figs. 3 and 4. The complex formation is endothermic in all three steps, and thereby entropy-driven. The large endothermic value of ΔH_2^0 , and the large entropy gain at the formation of the second bromide complex, ΔS_2^{0} , are strong indicators of substantial desolvation and a coordination switch at this step [37]. In general, as long as the complex formation is considered only as substitution of a solvent molecule in the first solvation shell, a monotonous decrease of the ΔS_i^0 values is expected at each step. However, when a coordination change at any step takes place, ΔH_i^0 becomes more positive due to increase of required energy for desolvation and the liberation of more solvent molecules results in a large increment of ΔS_i^0 . By increasing the free ligand concentration, the third complex becomes more dominant. It is important to stress that the complex formation of the indium(III) bromide system in DMPU is slightly weaker than the corresponding one in Me₂SO. This is expected as DMPU is a stronger electron-pair donor than Me₂SO, and indium(III) a fairly soft electron-pair acceptor. This shows that the complex formation of indium(III) in DMPU behaves as expected as the starting solvate has an octahedral configuration. Furthermore, the complex formation in DMPU is stronger than in water due to significantly weaker solvation of the bromide ion [38].

The crystal structure of bis(N,N'-dimethylpropyleneurea)trisbromoindium(III) was solved in the orthorhombic space group Fdd2 (No. 43). The crystallographic data show that the structure is five-coordinate with three bromides in a plane and two oxygens from DMPU in the apical positions of a slightly distorted trigonal bipyramid, Fig. 5. The indium(III) ion is in the same plane as the three bromide atoms. The oxygen atoms in the apical positions are equidistant, 2.201 Å, and with an O-In-O angle of 172.2°. One In–Br bond distance, 2.495 Å, is slightly shorter than the other two, 2.518 Å. The angle between the longer In-Br bonds is unexpectedly larger, 134.0°, than the other two Br-In-Br angles, 113.0°. This unexpected behavior with the largest angle between the longest M-Br bonds is also seen in the crystal structure of bis(*N*,*N*'-dimethylpropyleneurea)trisbromoiron(III) [19]. The DMPU molecules are oriented according to the bisector at the angle between the longer In–Br bonds. The mean In–O distance, 2.201 Å. is somewhat longer than in the DMPU solvated indium(III) ion. 2.146 Å. This shows that indium(III) binds bromide more strongly than DMPU as expected. Crystallographic data and selected bond distances and angles are given in Table 3 and Table S4, respectively.

4.3. Gallium(III) bromide system in N,N'-dimethylpropyleneurea

The EXAFS data on the gallium(III) bromide solution in DMPU shows that the shape of oscillations is obviously different from that of DMPU solvated gallium(III), Fig. 1. The maximum in the EXAFS function envelope is at about 9–10 Å⁻¹ showing that bromide is



Fig. 3. The total molar enthalpy change Δh_{v} , as a function of ligand number \bar{n} for the indium(III) bromide system in DMPU. The symbols show different titration series and the solid line is calculated from the corresponding β_j and ΔH_j^0 values in Table 1.



Fig. 4. Complex distribution function for the indium(III) bromide system in DMPU.



Fig. 5. Molecular structure of bis(N,N'-dimethylpropyleneurea)trisbromoindium (III).

the main back-scatterer. Data analysis reveals three Ga–Br bonds at 2.328(1)Å in a triangular configuration. The shoulder at ca. 1.9Å has been assigned to two Ga–O bonds, refined to 1.92(3)Å, completing a trigonal bipyramidal configuration. The Debye– Waller parameter indicates a large distribution in the Ga–O distance, but the value is in agreement with Ga–O distance in the

Table 3

Crystallographic data on the solid bis(*N*,*N*'-dimethylpropyleneurea)trisbromoindium(III) and bis(dimethylsulfoxide)trisbromoindium(III) complexes at room temperature.

	[InBr ₃ (dmpu) ₂]	[InBr ₃ (OSMe ₂) ₃]
Formula	C ₁₂ H ₂₄ N ₄ O ₂ Br ₃ In	C ₆ H ₁₈ S ₃ O ₃ Br ₃ In
Molecular weight	610.90	588.93
Crystal system	orthorhombic	triclinic
Space group	Fdd2 (No. 43)	P1 (No. 2)
a (Å)	17.698(14)	8.138(3)
b (Å)	27.72(3)	9.141(3)
<i>c</i> (Å)	8.1520(16)	13.884(4)
α (°)	90	89.780(6)
β(°)	90	77.513(6)
γ (°)	90	66.120(5)
V (Å ³)	3999(5)	918.0(5)
T (K)	298(2)	298(2)
Ζ	8	2
Density(calculated) (g cm ⁻³)	2.030	2.131
$\mu (\mathrm{mm}^{-1})$	7.188	8.149
Crystal size (mm)	$0.45 \times 0.25 \times 0.15$	$\textbf{0.48} \times \textbf{0.26} \times \textbf{0.10}$
θ Range (°)	2.735-23.984	2.45-28.37
Index ranges	$-20 \leqslant h \leqslant 19$	$-9 \leqslant h \leqslant 8$
	$-28 \leqslant k \leqslant 32$	$-10 \leqslant k \leqslant 10$
	$-9 \leqslant l \leqslant 9$	$-16 \leqslant l \leqslant 12$
Measured reflections	4416	4501
Unique reflections (R _{int})	1732 (0.0854)	3155 (0.029)
Refinement method	full-matrix least- squares on F ²	
Final R_1 , $wR_2 [I > 2s(I)]^a$	0.0522, 0.1240	0.0636, 0.1933
	0.0684, 0.1302 (all	0.0748, 0.2018
	data)	(all data)
Largest difference in peak (e Å ⁻³)	1.267	1.373
Largest difference in hole (e Å ⁻³)	-0.927	-1.840

^a *R* values are defined as $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$, $wR_2 = [\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)^2]^{0.5}$.

five-coordinate DMPU solvated gallium(III) ion, see above. The structure parameters from the EXAFS studies are summarized in Table 2. The fit of EXAFS oscillations and the corresponding Fourier transform are given in Figs. 1 and 2.

The EXAFS data have shown that the DMPU solvated gallium(III) ion and gallium(III) bromide complex are both five-coordinate most probably in slightly distorted trigonal bipyramidal fashion in solution. This also strongly indicates that the stabilities of the gallium(III) bromide complexes in DMPU solution are relatively strong. Furthermore, the heats of complex formation are endothermic, but very small. This shows that the complex formation takes place in substitution reactions and that the bond strength of the Ga–O_{dmpu} and Ga–Br bonds is similar, and that the complex formation is entropy-driven due to release of bound solvent molecules at the complex formation. Unfortunately, the very small and similar heats of complex formation do not allow determination of the β_n and $\Delta H_{\beta n}$ values from the calorimetric data.

4.4. Dimethylsulfoxide solvated gallium(III) and indium(III) bromide in the solid state

The EXAFS oscillations on Me₂SO solvated gallium(III) bromide in the solid state show that gallium is present as Me₂SO solvated gallium(III) ions. The bond distances were modeled with the main contributions from the Ga–O and Ga \cdots S single back-scattering paths, a three-leg Ga–O–S back-scattering path, and multiple scattering within the GaO₆ core. The shape of the EXAFS oscillations and the fitted parameters are in agreement with those reported for the Me₂SO solvated gallium(III) ion [4b]. No Ga–Br scattering path was found to improve the fit of the experimental data. The structure parameters from the refined EXAFS data are given Table 2. The fit of EXAFS data and the corresponding Fourier transform are given in Figs. 1 and 2.



Fig. 6. Molecular structure of tris(dimethylsulfoxide)trisbromoindium(III).

The crystallographic data on tris(dimethylsulfoxide)trisbromoindium(III) show six-coordinate complexes with distorted octahedral configuration. The crystal structure was solved in the triclinic space group P1 (No. 2). Crystallographic data, selected bond distances and angles are given in Table 3 and Table S4, respectively. The complex has octahedral fac-configuration with mean In-Br and In–O bond distances of 2.630(3) and 2.211(15) Å, respectively, Fig. 6. The mean In–Br bond distance, 2.630(3) Å is significantly longer than in bis(N,N'-dimethylpropyleneurea)trisbromoindium(III), 2.510(3) Å, while the mean In–O bond distances in the two complexes are almost the same, 2.211(15) and 2.201(6) Å, respectively, Table S4.

5. Conclusions

The coordination chemistry of the gallium(III) and indium(III) ions is quite different in the two oxygen donor solvents DMPU and Me₂SO. This is mainly due to the space-demanding properties of the former, and the significantly more soft electron-pair acceptor abilities of indium(III). The DMPU solvated gallium(III) and indium(III) ions are five- and six-coordinate in solution, respectively, with mean Ga-O and In-O bond distances of 1.924(5) and 2.146(3) Å, respectively. Indium(III) forms three medium strong complexes with bromide in DMPU, and the structural studies show that also gallium(III) forms the third bromide complex in DMPU, GaBr₃(DMPU)₂. This indicates that that at least three bromide complexes are formed in this system. The DMPU solvated GaBr₃ and InBr₃ complexes are trigonal bipyramidal with the bromides in a trigonal plane, and with DMPU oxygens in the apical positions. Solid Me₂SO solvated gallium(III) bromide consists of hexakis(dimethylsulfoxide)gallium(III) and bromide ions, while the corresponding indium compound consists of fac-octahedral tris(dimethylsulfoxide)trisbromoindium(III) complexes. The complex formation of the indium(III) bromide system in DMPU is of the same magnitude as in other aprotic oxygen donor solvents as expected as the DMPU solvated indium(III) ion is octahedral as the other oxygen donor solvent solvates, Table 1. On the other hand, gallium(III) form significantly stronger complexes with bromide in DMPU than in water in line with previous observations where the metal ion solvate is five-coordinate [11–13].

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Appendix A. Supplementary material

CCDC 739827 and 739729 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.12.024.

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