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Polynuclear Metal Complexes Obtained from the Task-Specific Ionic Liquid Betainium Bistriflimide

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ABSTRACT: The task-specific ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], was used to dissolve metal oxides and hydroxides. The crystal structures of the resulting metal betaine bistriflimide complexes exhibit a rich structural variety. A trimeric structure was found for the cobalt(II) compound, [Co₃(bet)₈(Hbet)₂(H₂O)₂][Tf₂N]₉[Hbet], a tetrameric structure for the manganese(II) and zinc(II) compound, [Mn₄(bet)₁₀(H₂O)₄][Tf₂N]₈ and [Zn₄(bet)₁₀(H₂O)₂][Tf₂N]₈, respectively, a pentameric structure for the nickel(II) compound, [Ni₅(bet)₁₂(H₂O)₆][Tf₂N]₁₀, an oxo-hydroxo-cluster formation for the lead(II) compound, [(Pb₄O)Pb(OH)(bet)₈(Tf₂N)₃][Tf₂N]₄•MeOH, and a polymeric structure for the silver(I) compound, [Ag₂(bet)₂(Tf₂N)Ag₂(bet)₂][Tf₂N]₃. The zwitterionic nature of the betaine ligand and the weakly coordinating ability of the bis(trifluoromethylsulfonyl)imide [Tf₂N]⁻ anion facilitates the incorporation of metal ions into oligonuclear and polynuclear metal complexes.

Introduction

Ionic liquids have been receiving a lot of attention from both academia and industry.^{1–3} Ionic liquids are organic salts with low melting points that can exhibit intrinsically useful characteristics such as a wide liquid range (up to 400 °C), a negligible vapor pressure, a large electrochemical window, and a high electric conductivity.⁴ These compounds are being applied as solvents for organic reactions,^{5–7} for liquid-liquid extraction,⁸ for electrodeposition,^{9,10} for spectroscopic studies,^{9–15} but also as electrolyte in photovoltaic devices (solar cells)^{18,19} and as a component in hybrid materials.²⁰ One of the unique features of ionic liquids is the tunability of their chemical and physical properties by selection of an appropriate anion/cation combination.

Although most of the reports on ionic liquids focus on their use as reaction medium for organic reactions, recently, more and more applications of ionic liquids related to inorganic synthesis are being reported.^{21–23} For example, ionic liquids have been used as solvents and as templates to modify the morphology of inorganic nanomaterials.^{24–28} Furthermore, metal-containing ionic liquids are regarded as promising materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic, or catalytic properties that depend on the incorporated metal ion.^{29–33} Ionic liquids have also been used for the synthesis of coordination polymers,^{34,35} and for the crystallization and crystal engineering of coordination compounds.^{36–43} However, the great variety of available ionic liquids could offer a unique addition to the toolbox of inorganic chemists.

A problem that hampers the application of ionic liquids in the field of synthetic chemistry is the difficulty to separate the ionic liquid from the reaction product. Due to their low volatility, ionic liquids cannot be removed by evaporation. Furthermore, one is often faced with the low solubility of inorganic salts in ionic liquids. Especially for electrochemical applications and for applications in solvent extraction technology, a high solubilizing ability of the ionic liquids for metal salts and metal oxides is desirable. So-called task-specific ionic liquids (TSILs),

which are ionic liquids with a functional group covalently tethered to the cationic or anionic part, are being developed to increase the solubility of metal compounds in these solvents.^{44,45} A functional group that has the ability to coordinate to the metal ion, preferably as a bidentate or a polydentate ligand, facilitates the dissolution of metal oxides or metal salts in an ionic liquid.

Recently, we have reported on the selective solubilization of various metal oxides and metal salts by using the task-specific ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N] (in the following abbreviated as betainium bistriflimide).⁴⁶ We demonstrated a facile method to strip the metals from this ionic liquid by adding an acidic aqueous solution. After separation of the hydrophobic ionic liquid from the aqueous layer, the ionic liquid is ready for reuse. The deprotonated betaine is a zwitterionic ligand, Me₃N⁺CH₂COO⁻. Because of the inductive effect of the positive charge of the quaternary ammonium group, the protonated betaine (also called betainium) exhibits a higher acidity (*pKa* 1.83) than alkanoic acids like acetic acid (*pKa* 4.75) or propionic acid (*pKa* 4.87).⁴⁷ The higher acidity of the betainium ion results in an enhanced solubilizing ability for metal oxides. Betaine and its derivatives can be regarded as charge-neutral analogues of amino acids and have been used to prepare metal complexes in different metal–carboxylate molar ratios. Because of the neutrality of the zwitterionic ligand, it is possible to prepare metal carboxylate complexes with additional anionic ligands.

Mak and coworkers did pioneering work on the structure chemistry of zwitterionic betaine metal complexes.^{48,49} Since the discovery of the antiferroelectric phase transition in betaine phosphate, adducts of betaine with inorganic and organic acids, as well as in adducts with metal salts, have attracted much attention. Because of its delocalized π-system, the carboxylate group on one end of the betaine molecule can act as a bridging ligand providing super-exchange pathways between spin-bearing metal ions. The large trimethylammonio part on the other end behaves like a spacer that can separate adjacent chains of magnetic ions. The studies on the structural chemistry of betaine complexes indicate that the role of the anion is important. Although stronger coordinating anions like halides or nitrates

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Table 1. Comparison of Selected Infrared Absorption Bands of the Metal Complexes, the Ionic Liquid, and Anhydrous Betaine

complex	$\nu(\text{C=O})^{\text{a}}$ (cm ⁻¹)	$\nu(\text{C}-\text{O})^{\text{s}}$ (cm ⁻¹)	$\Delta^{\text{a}}(\nu(\text{C=O})^{\text{a}} - \nu(\text{C}-\text{O})^{\text{a}})$ (cm ⁻¹)
[Co ₃ (bet) ₁₀ [Hbet] ₂ (H ₂ O) ₂][Tf ₂ N] ₁₀ [Hbet] ₂	1742s(COOH), 1640s, 1625vs	1405s, 1350s	220/392
[Zn ₄ (bet) ₁₀ (H ₂ O) ₂][Tf ₂ N] ₈	1679vs, br 1668sh	1424s	255
[Mn ₄ (bet) ₁₀ (H ₂ O) ₄][Tf ₂ N] ₈	1616vs, br	1412s	203
[Ni ₅ (bet) ₁₂ (H ₂ O) ₆][Tf ₂ N] ₁₀	1686vs, br 1652sh	1412s	274
[Ag ₂ (bet) ₂ (Tf ₂ N)Ag ₂ (bet) ₂][Tf ₂ N] ₃	1630vs, br	1395s	235
[(Pb ₄ O)Pb(OH)(bet) ₈ (Tf ₂ N) ₂][Tf ₂ N] ₅ ·MeOH	1633vs, br	1398s	235
[Hbet][Tf ₂ N]	1743vs	1352s	391
Anhydrous betaine	1624vs	1388s	236

^a Δ, Difference; superscript a, asymmetrical; superscript s, symmetrical; v = very; s = strong; br = broad, m = medium, sh = shoulder.

often tend to form monomeric complexes, polynuclear species are obtained in combination with weakly coordinating anions like perchlorate or triflate.^{50,51}

In this paper, we describe the crystal structures of six metal complexes obtained after solubilizing metal oxides in the task-specific ionic liquid [Hbet][Tf₂N]. Crystals of the metal complexes were obtained from these solutions in the presence of water. The structural chemistry of these complexes is surprisingly rich. It will be shown that trimeric units are observed for the cobalt(II) compound, tetrameric units for the manganese(II) and zinc(II) compounds, pentameric units for the nickel(II), an oxohydroxo-cluster formation for the lead(II) compound, and polymeric units for the silver(I) compound. The zwitterionic nature of the betaine ligand in combination with the weakly coordinating ability of the [Tf₂N]⁻ anion actually facilitate the incorporation of the metal ions into oligonuclear and polynuclear metal complexes.

Experimental Section

General. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method (for the ionic liquid and metal complexes) or by making a mull with nujol (for the metal complexes). Elemental analyses (CHN) were obtained on a CE Instruments EA-1110 elemental analyzer. ¹H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer and ¹³C spectra on a Bruker 400 MHz NMR spectrometer. All commercially available reagents and starting materials were used without further purification unless otherwise stated. Metal oxides were purchased from ACROS (Belgium). Li(Tf₂N) was purchased from IoLiTec (Germany).

Synthetic Procedures. Synthesis of the Ionic Liquid [Hbet][Tf₂N]. The ionic liquid [Hbet][Tf₂N] was synthesized using a procedure described earlier.⁴⁶ An aqueous solution of betainium hydrochloride (1 mol, 153.61 g dissolved in 150 mL of water) was added to an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (1 mol, 287.08 g dissolved in 300 mL of water). The mixture was stirred for 1 h at room temperature. The ionic liquid phase immediately separated from the aqueous phase after combining the two aqueous solutions. After separation of the phases, the ionic liquid phase was washed with small amounts of cold water until no chloride impurities could be detected by the silver nitrate test. The ionic liquid was evaporated to dryness at 80 °C in vacuo on a rotary evaporator.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ 4.27 (s, 2H), 3.19 (s, 3 × CH₃). ¹³C-NMR (100.62 MHz [D₆]DMSO, TMS): δ 167.38 (COO), 125.99, 121.75, 117.52, 113.28 (2 × CF₃), 64.06 (N-CH₂), 54.16 (3 × CH₃). Elemental anal. Calcd (%) for C₇H₁₂N₂O₆F₆S₂ (M_r = 398.302): C, 21.10; H, 3.03; N, 7.03. Found: C, 20.78; H, 3.24; N, 6.85. IR (KBr-pellet, cm⁻¹): 1742s (COOH), 1640w (COO), 1475m (CH₂), 1135m (CH₃).

Solubility of Metal Oxides. As stated earlier, protonated betaine bis(trifluoromethyl sulfonyl)imide possesses the ability to dissolve metal oxides. The metal oxides react with the carboxylic acid group of the ionic liquid to form carboxylate complexes and water. The following oxides were solubilized in the ionic liquid [Hbet][Tf₂N] and the corresponding metal complexes were characterized: PbO, ZnO, Ag₂O, NiO, and MnO. The metal oxide powders were not activated (for instance by mechanical grinding) before the solubility studies. Also metal hydroxides dissolve in the ionic liquid [Hbet][Tf₂N]. Cobalt(II) hydroxide was dissolved and the resulting betaine complex was characterized. In a typical experiment, an excess of metal oxide / metal

hydroxide was mixed with [Hbet][Tf₂N] and water, and the mixture was stirred for several hours. The solution was filtered to remove the excess of metal oxide/metal hydroxide. After evaporation of water under reduced pressure, a solution of the metal betaine complex in [Hbet][Tf₂N] was obtained. The solubility of metal oxides in protonated betaine bis(trifluoromethylsulfonyl)imide is high because the ionic liquid can form stoichiometric compounds with the metals; i.e. so much metal oxide can be added to the [Hbet][Tf₂N] ionic liquid until all the ionic liquid is transformed into a metal complex.

Cobalt(II) Complex. Co(OH)₂ (1 g, 10.75 mmol) was mixed with [Hbet][Tf₂N] (8.57 g; 21.51 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 h. The excess metal hydroxide was removed by filtration. After filtration, water was evaporated under a vacuum. Purple crystals were obtained after recrystallization of the compound in a small amount of water. Elemental anal. Calcd (%) for C₁₀H₁₀CoF₁₂N₈O₈S₈ (M_r = 912.75): C, 13.15; H, 1.10; N, 12.27. Found: C, 13.36; H, 1.34; N, 12.43%.

Zinc(II) Complex. ZnO (1 g; 12.3 mmol) was mixed with [Hbet][Tf₂N] (9.788 g; 24.5 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 h. The excess metal oxide was removed by filtration. After filtration, water was evaporated under a vacuum. Colorless crystals were obtained and recrystallized from water. Elemental anal. Calcd (%) for C₆₆H₁₁₈F₄₈N₁₈O₅₆S₁₆Zn₄ (M_r = 3746.27): C, 21.15; H, 3.17; N, 6.72. Found: C, 20.47; H, 3.48; N, 6.42.

Manganese(II) Complex. MnO (1 g; 14.09 mmol) was mixed with [Hbet][Tf₂N] (11.2 g; 28.1 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 h. The excess metal oxide was removed by filtration. After filtration, water was evaporated under a vacuum. Purple crystals were obtained and recrystallized from water. Elemental anal. Calcd (%) for C₁₄H₂₄F₁₂MnN₄O₁₃S₄ (M_r = 3704.46): C, 19.38; H, 2.78; N, 6.45. Found: C, 19.49; H, 2.83; N, 6.28.

Nickel(II) Complex. NiO (1 g; 13.38 mmol) was mixed with [Hbet][Tf₂N] (1.733 g; 4.35 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 h. The excess metal oxide was removed by filtration. After filtration, water was evaporated under a vacuum. Green crystals were obtained and recrystallized from water. Elemental anal. Calcd (%) for C₁₄H₂₂F₁₂N₄NiO₁₂S₄ (M_r = 1895.77): C, 20.90; H, 3.35; N, 6.65. Found: C, 20.93; H, 3.23; N, 6.46.

Silver(I) Complex. Ag₂O (1 g; 4.35 mmol) was mixed with [Hbet][Tf₂N] (1.733 g; 4.35 mmol) and 10 mL of water. The mixture was stirred at room temperature and protected from light for 12 h. The excess metal oxide was removed by filtration. After filtration, water was evaporated under a vacuum. White crystals were obtained after recrystallization in water. Elemental anal. Calcd (%) for C₁₄H₂₂Ag₂F₁₂N₄O₁₂S₄ (M_r = 505.16): C, 16.64; H, 2.19; N, 5.54. Found: C, 16.79; H, 2.27; N, 5.31.

Lead(II) Complex. PbO (1 g; 4.46 mmol) was mixed with [Hbet][Tf₂N] (1.733 g; 4.35 mmol) and 10 mL of water. The mixture was stirred at room temperature and protected from light for 12 h. The excess metal oxide was removed by filtration. After filtration, water was evaporated under a vacuum. Colorless crystals were obtained and recrystallized from methanol. Elemental anal. Calcd (%) for C₁₀₉H₁₈₀F₈₄N₃₀O₉₄Pb₁₀S₂₈ (M_r = 7983.87): C, 16.38; H, 2.27; N, 5.26. Found: C, 16.53; H, 2.40; N, 5.31.

Crystallography. X-Ray intensity data were collected on a SMART 6000 diffractometer equipped with CCD detector using Cu-Kα radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker.⁵² All six structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.⁵³ Non-

Table 2. Summary of the Crystallographic Data of the Cobalt(II), Zinc(II), and Manganese(II) Complexes

	[Co ₃ (bet) ₈ (Hbet) ₂ (H ₂ O) ₂][Tf ₂ N] ₁₀ [Hbet] ₂	[Zn ₄ (bet) ₁₀ (H ₂ O) ₄][Tf ₂ N] ₈	[Mn ₄ (bet) ₁₀ (H ₂ O) ₄][Tf ₂ N] ₈
formula	C ₈₀ H ₁₄₀ Co ₃ F ₆₀ N ₂₂ O ₆₆ S ₂₀	C ₆₆ H ₁₁₀ F ₄₈ N ₁₈ O ₅₄ S ₁₆ Zn ₄	C ₆₆ H ₁₁₀ F ₄₈ Mn ₄ N ₁₈ O ₅₅ S ₁₆
mol wt	4424.60	3706.40	3680.61
dimensions (mm ³)	0.4 × 0.25 × 0.2	0.4 × 0.15 × 0.1	0.3 × 0.25 × 0.2
cryst syst	triclinic	triclinic	monoclinic
space group	P <bar{1}>(No. 2)</bar{1}>	P <bar{1}>(No. 2)</bar{1}>	C2/c (No. 15:b1)
a (Å)	15.283(5)	13.5478(10)	42.9460(18)
b (Å)	15.535(5)	14.4777(11)	13.4744(8)
c (Å)	19.275(5)	20.6903(17)	50.082(2)
α (deg)	107.573(19)	72.326(3)	90.00
β (deg)	101.12(2)	89.845(3)	106.700(2)
γ (deg)	91.82(2)	63.529(3)	90.00
V (Å ³)	4261(2)	3419.2(5)	27759(2)
Z	1	1	8
D _{calcd} (g cm ⁻³)	1.724	1.800	1.761
μ _{CuKα} (mm ⁻¹)	5.976	4.507	6.561
abs corr	multi-scan	multi-scan	refdelf
F(000)	2243	1872	14880
no. of measured reflns	40289	46853	139417
no. of unique reflns	14538	11833	26272
no. of obsd. reflns ($I_0 > 2\sigma(I_0)$)	7502	6723	17282
no. of params refined	1492	1359	2076
GOF on F^2	1.138	1.102	1.017
R ₁	0.0990	0.0977	0.0737
wR ₂	0.2112	0.1962	0.1582
R ₁ (all data)	0.1631	0.1404	0.1209
wR ₂ (all data)	0.2388	0.2131	0.1860

Table 3. Summary of the Crystallographic Data of the Nickel(II), Silver(I) and Lead(II) Complexes

	[Ni ₅ (bet) ₁₂ (H ₂ O) ₆][Tf ₂ N] ₁₀	[Ag ₄ (bet) ₄][Tf ₂ N] ₄	[(Pb ₄ O)Pb(OH)(bet) ₈][Tf ₂ N] ₇ · MeOH]
formula	C ₈₀ H ₁₃₂ F ₆₀ N ₂₂ Ni ₅ O ₇₃ S ₂₀	C ₄₂ H ₆₆ Ag ₆ F ₃₆ N ₁₂ O ₃₆ S ₁₂	C ₁₀₉ H ₁₈₀ F ₈₄ N ₃₀ O ₉₄ Pb ₁₀ S ₂₈
mol wt	4644.93	3031.13	7980.80
dimensions (mm ³)	0.4 × 0.3 × 0.2	0.35 × 0.2 × 0.15	0.25 × 0.15 × 0.15
cryst syst	monoclinic	monoclinic	triclinic
space group	P2 ₁ /c (14:b1)	P2 ₁ /n (14:b2)	P <bar{1}>(No. 2)</bar{1}>
a (Å)	20.789(3)	15.1684(4)	14.3771(14)
b (Å)	26.899(3)	28.3635(6)	14.6422(15)
c (Å)	16.243(2)	23.0544(6)	28.123(4)
α (deg)	90	90	88.758(6)
β (deg)	103.251(9)	106.297(2)	88.222(6)
γ (deg)	90	90	85.688(5)
V (Å ³)	8841.3(19)	9520.1(4)	5899.5(12)
Z	2	4	1
D _{calcd} (g cm ⁻³)	1.745	2.115	2.246
μ _{CuKα} (mm ⁻¹)	4.216	13.597	17.335
abs corr	multi-scan	refdelf	multi-scan
F(000)	4700	5952	3820
no. of measured reflns	29793	83891	48378
no. of unique reflns	15545	17690	18709
no. of obsd reflns ($I_0 > 2\sigma(I_0)$)	8040	11428	12726
Parameters refined	1406	1315	1633
GOF on F^2	1.009	0.920	1.014
R ₁	0.0789	0.0571	0.0775
wR ₂	0.1782	0.1288	0.1737
R ₁ (all data)	0.1574	0.0881	0.1243
wR ₂ (all data)	0.2235	0.1522	0.2009

hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times $U(\text{eq})$ of the parent atoms (1.5 times for methyl groups). CCDC 678114–678119 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: 44-1223-336033; or deposit@ccdc.cam.ac.uk). The crystallographic data of the complexes are summarized in Tables 2 and 3. Some of the bis(trifluoromethylsulfonyl)imide (or bistriflimide) ligands were found to be heavily disordered. Even though this positional disorder of the bistriflimide anions could be resolved and assigned to different parts, the residual factors of some structures, especially of the cobalt(II) and zinc(II) structure remained rather high. This was also the case when measuring several other crystals

of the same compounds. Of course, the low symmetry ($P\bar{1}$) and large unit cell of some of these compounds also contribute to that.

Results and Discussion

Betaine is a carboxylate ligand that is able to coordinate in different ratios to the metal ion as a result of its zwitterionic character. This has been observed, for example, for betaine complexes of the lanthanides, which were found as monomeric, dimeric, and polymeric complexes depending on the metal-to-ligand ratio. In this study, we reacted the task-specific ionic liquid [Hbet][Tf₂N] with an excess of the metal oxide or hydroxide, respectively. A table with the metal oxides indicating whether or not they are soluble in the ionic liquid is shown in

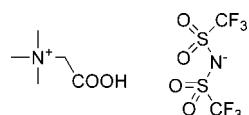


Figure 1. Structure of betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N].

Figure 2. The residual oxide or hydroxide was removed after the reaction by filtration. Also, water is formed during the reaction of the ionic liquid with the metal oxides. The presence of water accelerates the dissolution process. Many structures of metal complexes with betaine ligands have been discussed in the literature; however, most of these complexes exhibit monomeric or polymeric structures, which might also be influenced by the use of more coordinating anions like bromide, chloride, or nitrate.^{54–56}

Crystal Structure of [Co₃(bet)₈(Hbet)₂(H₂O)₂][Tf₂N]₁₀–[Hbet]₂. The crystal structure of the cobalt(II) compound [Co₃(bet)₈(Hbet)₂(H₂O)₂][Tf₂N]₁₀[Hbet]₂ consists of discrete trimeric [Co₃(bet)₈(Hbet)₂(H₂O)₂]⁸⁺ units, eight non-coordinating [Tf₂N][–] anions as counter ions and two additional [Hbet][Tf₂N] ion pairs as remaining ionic liquid “solvent” molecules in the crystal structure. An inversion center is located at the central Co₂. The three cobalt atoms of the trimeric [Co₃(bet)₈(Hbet)₂(H₂O)₂]⁸⁺ units are connected by four μ_2 -bridging carboxylate groups of the betaine ligands and two bridging water molecules; the linkage between the cobalt ions is shown in Figure 3.

The coordination polyhedra of the cobalt atoms Co1 and Co2 are slightly distorted octahedra. Co1 is coordinated by two monodentate coordinating terminal betaine ligands, one protonated monodentate betainium ligand and two bridging betaine ligands to Co2. A μ_2 -bridging water molecule completes the coordination sphere of Co1. The Co1–O bond lengths are ranging from 2.021(3) Å to 2.178(3) Å. Co2 is surrounded by the four bridging betaine ligands and in the apical position by the two bridging water molecules with Co2–O distances ranging from 2.059(3) Å to 2.100(3) Å. There is intramolecular hydrogen bonding observed from the bridging water molecules to the oxygens of the terminal monodentate coordinating carboxylate

groups (distance O11–H \cdots O6 = 2.572(5) Å; O11–H \cdots O6 = 2.592(5) Å) and from the protonated betainium ligand to a neighboring oxygen of μ_2 -bridging betaine ligand (distance O4–H \cdots O7 = 2.543(5) Å). These hydrogen atoms on the water molecules and on the protonated betainium ligands could be localized from a difference Fourier map and are being directed towards the betaine ligands. The crystal structure also contains the remaining co-crystallized ionic liquid betainium bistriflimide [Hbet][Tf₂N] with a characteristic anion-cation hydrogen bond (distance O13–H \cdots O29A = 2.595(2) Å) that is in the same range that has been reported for the pure ionic liquid. The co-crystallization of an ionic liquid has also been observed for crystallizations from ionic liquids before.^{36,43} The six bistriflimide counterions are not involved in any hydrogen bonding.

The only complex found in the literature with a related ligand, namely the zwitterionic pyridine betaine 1-(carboxymethyl)pyridinium consists of discrete octahedral [Co(pybet)₄(H₂O)]²⁺ cations and tetrahedral [Co(pybet)Cl₃][–] anions.⁵⁷

Crystal Structure of [Zn₄(bet)₁₀(H₂O)₂][Tf₂N]₈. The crystal structure of the zinc(II) complex [Zn₄(bet)₁₀(H₂O)₂][Tf₂N]₈ consists of discrete tetrameric [Zn₄(bet)₁₀(H₂O)₂]⁸⁺ units and eight non-coordinating [Tf₂N][–] anions as counter ions. An inversion center is located in the middle of the tetrameric unit. These zinc atoms are connected by bridging and chelating-bridging carboxylate groups of the betaine ligands.

The interlinkage of the zinc atoms to tetrameric units by the carboxylate groups of betaine is shown in Figure 4. The surroundings and labeling schemes of Zn1 and Zn2 are shown in Figure 5. In the coordination sphere of Zn2, there is one monodentate betaine ligand, three betaine ligands that are μ_2 -bridging to Zn1 and one water molecule. The Zn2–O bond lengths to the ligands are ranging from 1.939(5) to 2.100(4) Å; the Zn2–O distance to the coordinating water molecule is 2.091(5) Å. Zn1 is surrounded by five carboxylate groups bridging to the adjacent zinc atoms Zn2 and Zn1', respectively. The Zn1–O bond lengths to the ligands are ranging from 1.964(4) to 2.078(4) Å. The terminal coordinating water molecule on Zn2 exhibits intramolecular hydrogen bonding to a bistriflimide ligand with an O–O distance of 2.904 Å and forms an intramolecular hydrogen bond with O3 of the monodentate ligand (2.641(7) Å).

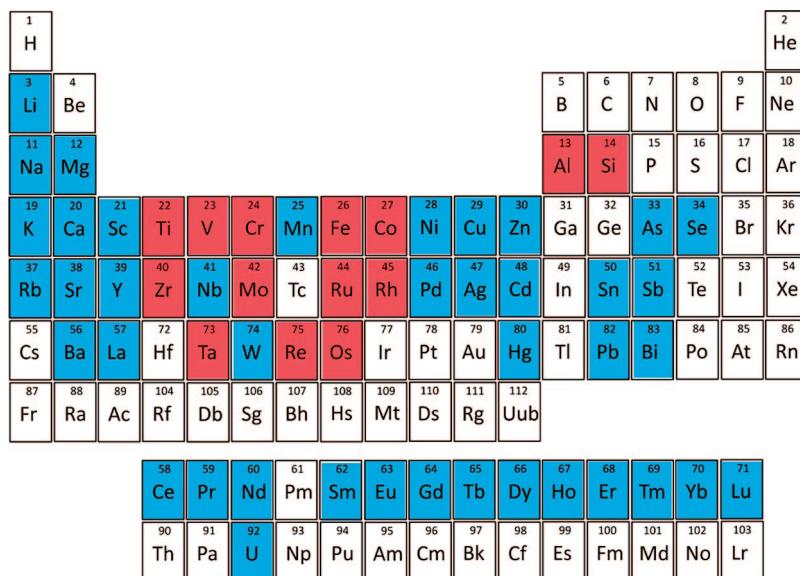


Figure 2. Periodic table indicating the solubility of metal oxides in the task-specific ionic liquid [Hbet][Tf₂N]. Color code: soluble in the task-specific ionic liquid [Hbet][Tf₂N] (blue), not soluble (red), not tested (white).

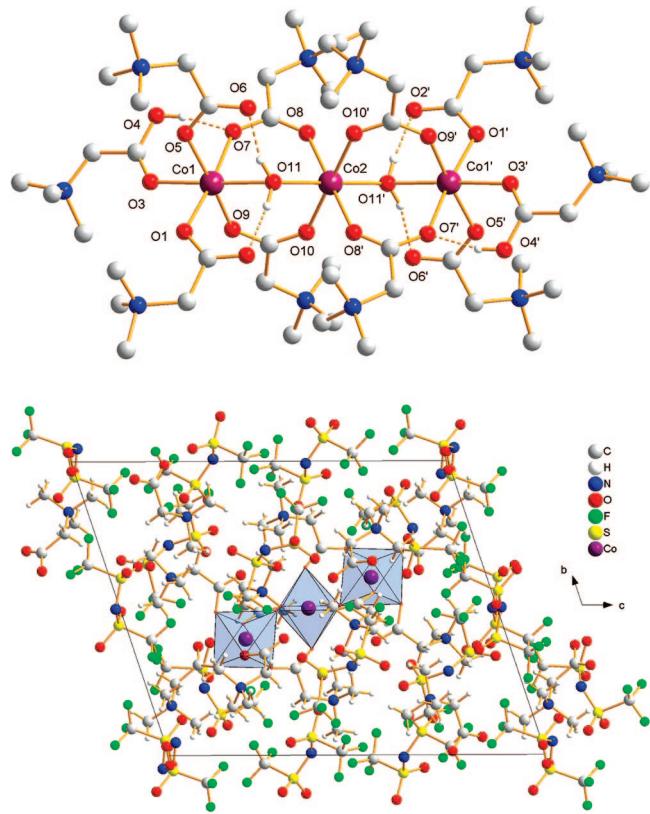


Figure 3. Trimeric cationic unit $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2]^{8+}$ in the crystal structure of $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2][\text{Tf}_2\text{N}]_{10}[\text{Hbet}]_2$ (upper part); packing of the molecules in the crystal structure viewed along the *a*-axis (lower part). Most of the hydrogen atoms are omitted for clarity.

Crystal Structure of $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4][\text{Tf}_2\text{N}]_8$. The crystal structure of the manganese(II) compound $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4]$ -

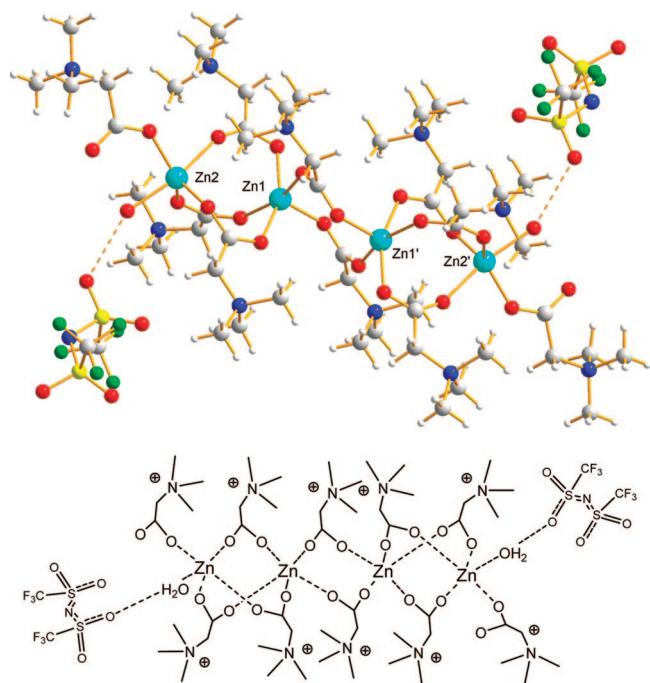


Figure 4. Tetrameric cationic unit $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2]^{8+}$ with two bistriflimide anions attached by hydrogen bonding (upper part); schematic presentation of the tetrameric unit of $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2]^{8+}$ (lower part).

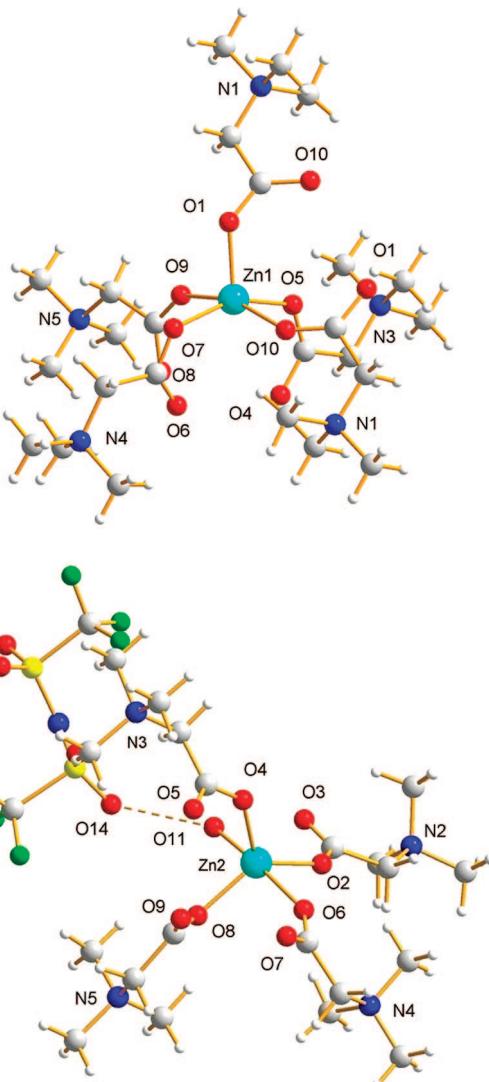


Figure 5. Surrounding and labeling scheme of Zn1 (upper part) and Zn2 (lower part) in the crystal structure of $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2][\text{Tf}_2\text{N}]_8$.

$[\text{Tf}_2\text{N}]_8$ consists of discrete tetrameric $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})]^{7+}$ units and seven noncoordinating $[\text{Tf}_2\text{N}]^-$ anions as counter ions. Four different manganese(II) atoms with different coordination spheres are linked together to form tetrameric units. These manganese atoms are connected by bridging and chelating-bridging carboxylate groups of the betaine ligands.

In Figure 6, the linkage of the carboxylate groups of betaine is shown. The surroundings and labeling schemes of Mn1 and Mn2 as well as for Mn3 and Mn4 are shown in Figures 7 and 8, respectively. The coordination polyhedra of the manganese atoms Mn2 and Mn4 can be described as strongly deformed octahedra. Mn1 and Mn3 are coordinated by five oxygen atoms and adopt a distorted square based pyramidal coordination. The Mn–Mn distances are quite different within the tetrameric unit and range from 3.976(1) Å for Mn4–Mn3 to a distance of 4.677(1) Å for Mn3–Mn2.

In the first coordination sphere of Mn1, there is one monodentate betaine ligand, three betaine ligands that are μ -bridging to Mn2 and one water molecule. The Mn1–O bond lengths to the ligands are ranging from 2.057(5) to 2.125(5) Å; the Mn1–O distance to the coordinating water molecule is 2.197(4) Å. Mn2 is surrounded by five carboxylate groups bridging to the adjacent manganese atoms Mn1 and Mn3,

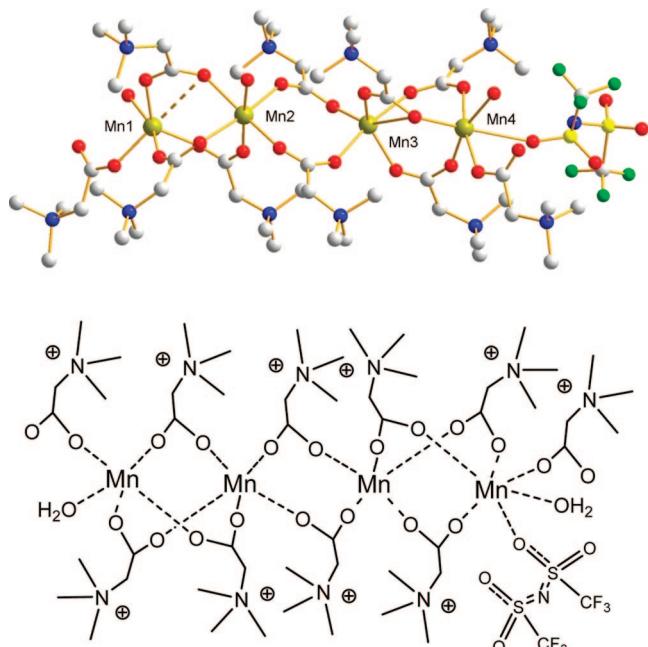


Figure 6. Tetrameric cationic unit $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})]^{7+}$ in the crystal structure of $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})][\text{Tf}_2\text{N}]_7$ (upper part); schematic presentation of the crystal structure of $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})][\text{Tf}_2\text{N}]_7$ (lower part).

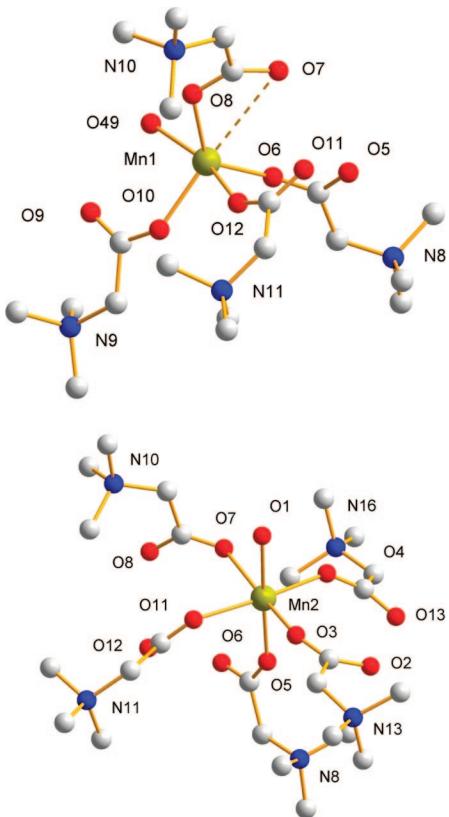


Figure 7. Surrounding and labeling scheme of Mn1 (upper part) and Mn2 (lower part) in the crystal structure of $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})][\text{Tf}_2\text{N}]_7$.

respectively. An additional water molecule completes the slightly distorted octahedral coordination sphere of Mn2. The Mn2–O bond lengths to the ligands are ranging from 2.127(5) Å to 2.210(5) Å; the Mn2–O distance to the coordinating water

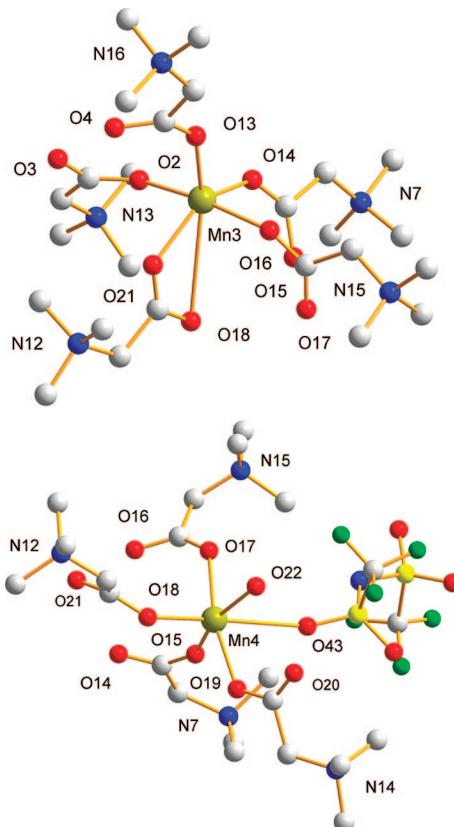


Figure 8. Surrounding and labeling scheme of Mn3 (upper part) and Mn4 (lower part) in the crystal structure of $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})][\text{Tf}_2\text{N}]_7$.

molecule is 2.236(4) Å. Mn3 is surrounded by four carboxylate groups bridging to the adjacent manganese atoms Mn2 and Mn4, respectively, and one chelating-bridging betaine ligand.

The coordination polyhedron of Mn3 can be described as a strongly distorted octahedron. The Mn3–O bond lengths to the ligands are ranging from 2.068(4) Å to 2.142(5) Å; the distorted octahedral surrounding of Mn3 is completed in apical position by a contact Mn3–O at 3.172 Å to a bridging-chelating oxygen atom. Mn4 is surrounded by three ligands bridging to the adjacent Mn3, one water molecule and one monodentate coordinating betaine and bis triflimide ligand in the terminal position of the tetrameric unit. The Mn4–O bond lengths to the ligands are ranging from 2.103(4) to 2.120(5) Å; the Mn4–O distance to the coordinating water molecule is 2.183(4) Å. The octahedral geometry of the coordination sphere is completed by an apical coordination to a bis triflimide ligand with a Mn4–O distance of 2.713(5) Å. One terminal coordinating water molecule exhibits an intramolecular hydrogen bond to O2 of a terminal monodentate betaine ligand (O–O distance of 2.689(7) Å) and an intermolecular hydrogen bond to a bis triflimide ligand (O–O distance of 2.894(7) Å). The other terminal water molecule also forms an intramolecular hydrogen bond to a monodentate betaine ligand (2.640(6) Å) and an intermolecular hydrogen bond to a bis triflimide anion (2.890(6) Å). The water molecule coordinating to Mn2 forms hydrogen bonds to two of the bis triflimide anions with O–O distances of 2.825(7) and 2.836(6) Å, respectively. The bis triflimide anions, which are attached by hydrogen bonding form additional hydrogen bonds to symmetry-equivalent tetrameric manganese unit.

Some structures of manganese complexes with betaine ligands have already been reported in the literature. Mak et al. described a linear polymeric catena-tris(betaine)manganese(II) tetrachloromanganate(II) bridged by skew-skew bridging carboxylato

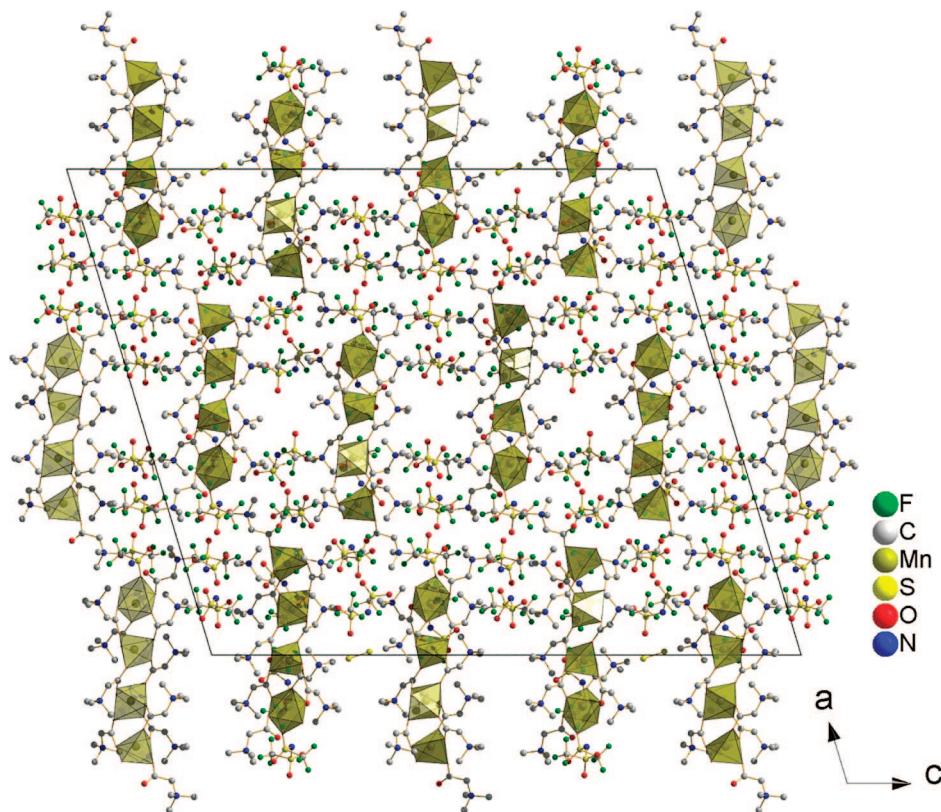


Figure 9. View of the packing of the molecules along the *b*-axis in the crystal structure of $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})][\text{Tf}_2\text{N}]_7$.

groups.⁵⁸ Haussühl et al. reported on a dimeric $[\text{Mn}(\text{bet})(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}_2(\text{H}_2\text{O})$ and a polymeric catena-betaine tetrachloro-aquadimanganese compound.⁵⁹ Another manganese(II) compound with a zwitterionic pyridine betaine ligand 1-(carboxymethyl)-pyridinium, pybet, has been reported by Mak et al. with the carboxylate groups of the betaine ligands exhibiting a common bidentate syn-anti bridging mode resulting in the polymeric $\{[\text{Mn}(\text{pybet})_2(\text{H}_2\text{O})_2]\text{Cl}_2\}_n$ compound.⁵⁷

Crystal Structure of $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6][\text{Tf}_2\text{N}]_{10}$. The crystal structure of the nickel(II) complex $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6][\text{Tf}_2\text{N}]_{10}$ consists of discrete pentameric $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6]$ units bridged by the betaine ligands and $[\text{Tf}_2\text{N}]^-$ anions as counter ions, which are not coordinating to the Ni₅-carboxylate core. In Figure 10, the interlinkage of the pentameric $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6]$ units and a view of the packing along the *a*-axis is shown.

An inversion center is located at the central Ni3. All Ni²⁺ ions are six-coordinated to four coordinating betaine ligands and two bridging water molecules to give a slightly distorted octahedral coordination polyhedron. The adjacent corner-shared $[\text{NiO}_6]$ octahedra are tilted toward each other along the bridging water molecules with an angle Ni1-O-Ni3 of 115.2(2) $^\circ$ and Ni2-O-Ni3 of 115.1(2) $^\circ$, respectively. The betaine ligands act as μ_2 -bridging ligands with typical Ni-O distances ranging from 1.984(4) Å to 2.055(3) Å. The axially coordinating water molecules are in the same range of distances from 2.067(4) to 2.115(4) Å. The terminal betaine ligands at Ni1 are monodentately coordinating. The Ni-Ni distances are Ni1-Ni2 = 3.527(1) Å and Ni2-Ni3 = 3.556(1) Å, respectively. The terminal water molecules of the pentameric Ni₅-carboxylate units form hydrogen bonds to one of the oxygen atoms of a $[\text{Tf}_2\text{N}]^-$ anion in a distance of 2.814(6) Å. Two lattice water molecules exhibit hydrogen bonding to the Ni2-O-Ni3 bridging water molecule in a distance of 2.617(9) Å and 2.648(11) Å, respectively. One of these lattice water molecules is further

attached by a hydrogen bond to an adjacent $[\text{Tf}_2\text{N}]^-$ anion (O—O distance of 2.940(9) Å). The remaining $[\text{Tf}_2\text{N}]^-$ anions show no hydrogen bonding; this results in a very strong disorder of these anions as it has been reported for bistriflimide anions before.⁴³ One way of positional disorder observed for the bistriflimide anion is illustrated in Figure 11.

Interestingly, a nickel(II) complex with the same betaine ligand has been reported before with nitrate as the counter anion. Its structure shows a *trans*-tetraquaabis(betaine)nickel(II) nitrate, which consists of discrete monomeric $[\text{Ni}(\text{bet})_2(\text{H}_2\text{O})_4]^{2+}$ cations and noncoordinating nitrate anions.⁵⁷ The formation of two polymeric nickel(II) complexes with the related double betaine ligands has also been reported by Mak et al.⁶⁰

Crystal Structure of $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3][\text{Tf}_2\text{N}]_4 \cdot \text{H}_2\text{O}$. The crystal structure of the lead(II) compound $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3][\text{Tf}_2\text{N}]_4 \cdot \text{H}_2\text{O}$ consists of discrete $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3]^{4+}$ oxo-hydroxo-clusters, five non-coordinating $[\text{Tf}_2\text{N}]^-$ counter ions and one molecule of crystal water. The $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3]^{4+}$ oxo-hydroxy-cluster, which is shown in Figure 12, is composed of an oxo-centered tetrahedral $\text{Pb}_4(\mu_4\text{-O})$ oxo-cluster which is connected by a μ_3 -bridging hydroxide and two chelating-bridging carboxylate groups of betaine ligands to an additional lead atom.

This $[\text{Pb}_4(\mu_4\text{-O})\text{Pb}(\mu_3\text{-OH})]^{7+}$ moiety is in total surrounded by eight betaine ligands and two coordinating $[\text{Tf}_2\text{N}]^-$ anions. The $\mu_4\text{-O}$ atom tetrahedrally bridges Pb2, Pb3, Pb4, and Pb5 with Pb—O distances ranging from 2.230(4) to 2.395(5) Å. The $(\mu_3\text{-OH})^-$ ligand that is bridging to the lead atom Pb1 is pyramidal positioned out of the Pb1-Pb2-Pb3 plane. The Pb-O distances range from 2.272(5) Å to 2.412(4) Å. Pb1 is surrounded by two betaine ligands bridging to the oxo-centered tetrahedral $\text{Pb}_4(\mu_4\text{-O})$ oxo-cluster, one monodentately coordinating betaine ligand, one coordinating methanol molecule and by the bridging hydroxide

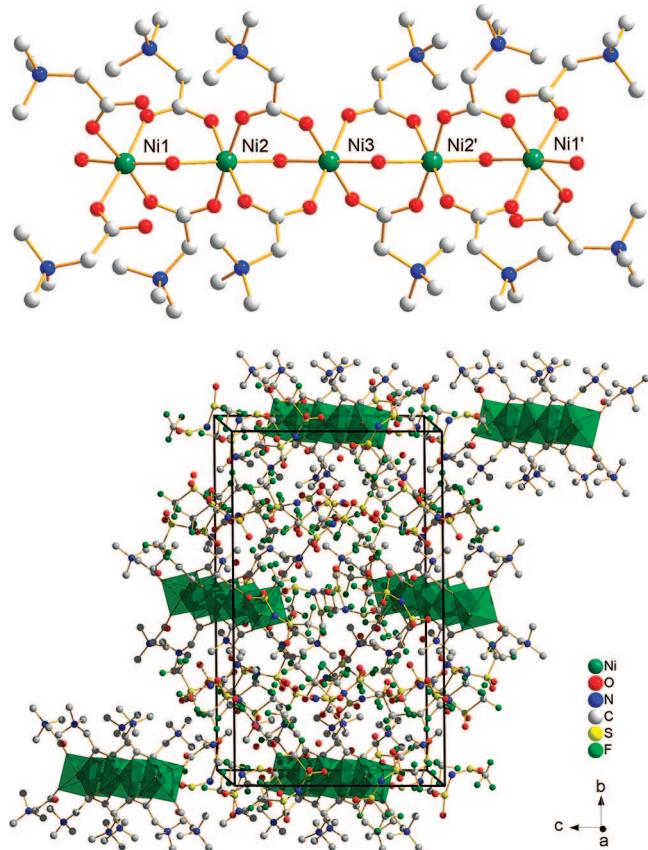


Figure 10. Pentameric cationic unit $[Ni_5(bet)_{10}(H_2O)_6]^{10+}$ in the crystal structure of $[Ni_5(bet)_{12}(H_2O)_6][Tf_2N]_{10}$ (upper part); view of the packing of the molecules along the *a*-axis in the crystal structure of $[Ni_5(bet)_{12}(H_2O)_6][Tf_2N]_{10}$ (lower part).

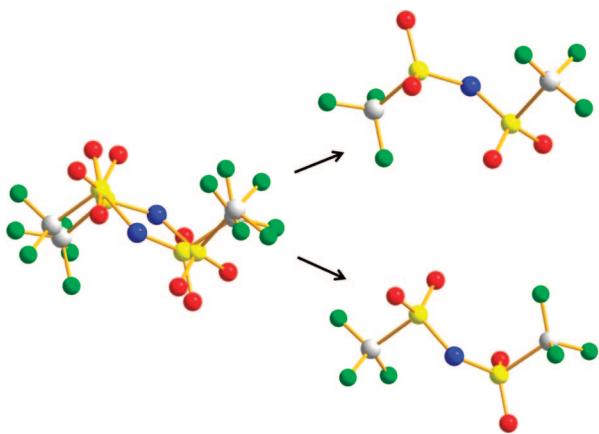


Figure 11. Exemplary illustration of the positional disorder of one of the bis(trifluoromethylsulfonyl)imide anions from the crystal structure of $[Ni_5(bet)_{12}(H_2O)_6][Tf_2N]_{10}$.

ligand. The Pb–O distances to the betaine ligands range from 2.330(4) to 2.916(4) Å. The monodentately coordinating carboxylate group of the betaine ligand forms a hydrogen bond with the O₃–OH with a distance O₁–O₄₆ = 2.752(6) Å.

The atom Pb4 is part of the tetrahedral Pb₄(μ_4 -O) oxo-cluster and is surrounded by eight oxygen atoms in the coordination sphere from one chelating and two bridging betaine ligands, the central μ_4 -O atom and a bidentate coordinating bis triflimide ligand. The Pb–O distances to the bis triflimide ligand are quite

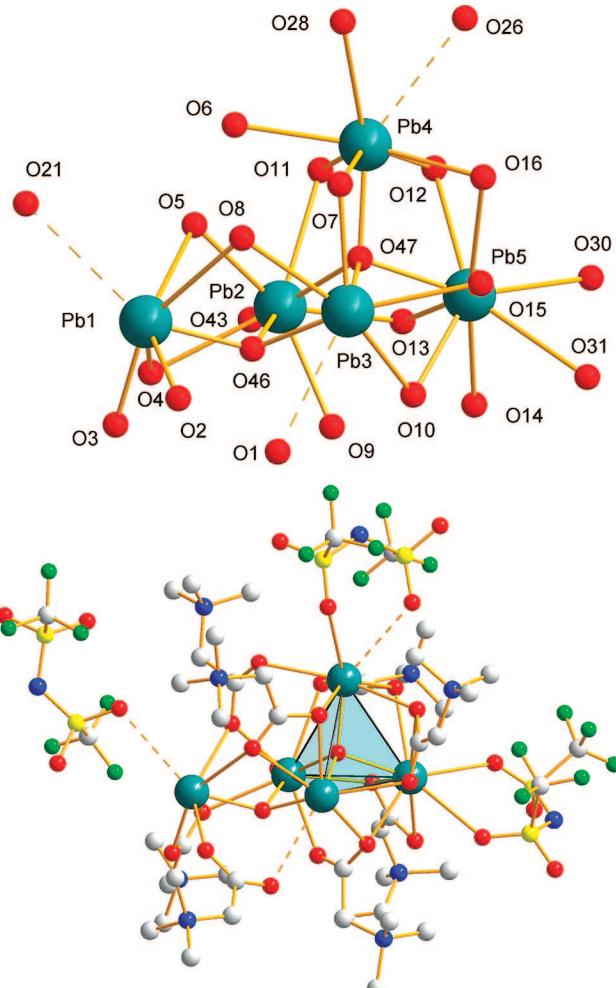


Figure 12. Surrounding, connection scheme, and labeling for the cationic cluster $[(Pb_4O)Pb(OH)(bet)_8(Tf_2N)_3]^{4+}$ (upper part). Cationic $[(Pb_4O)Pb(OH)(bet)_8(Tf_2N)_3]^{4+}$ cluster in the crystal structure of $[(Pb_4O)Pb(OH)(bet)_8(Tf_2N)_3][Tf_2N]_4 \cdot MeOH$ (lower part).

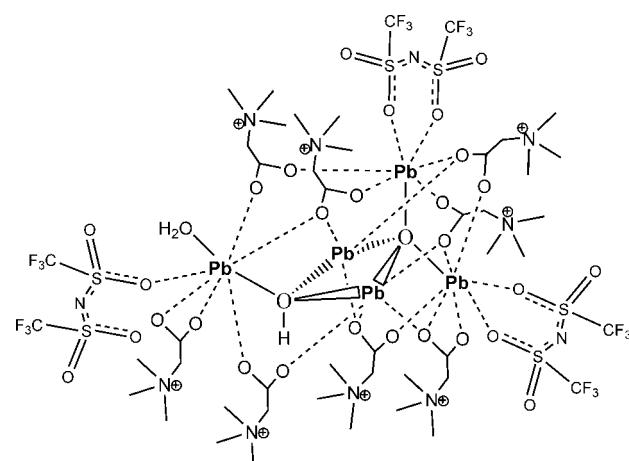


Figure 13. Schematic presentation of the cationic cluster $[(Pb_4O)Pb(OH)(bet)_8(Tf_2N)_3]^{5+}$.

long with 2.972(6) and 2.999(5) Å, respectively. The Pb–O distances to the betaine ligands are ranging from 2.591(5) to 2.653(5) Å. Pb2 is coordinating to four bridging betaine ligands and one monodentately coordinating bis triflimide ligands. The

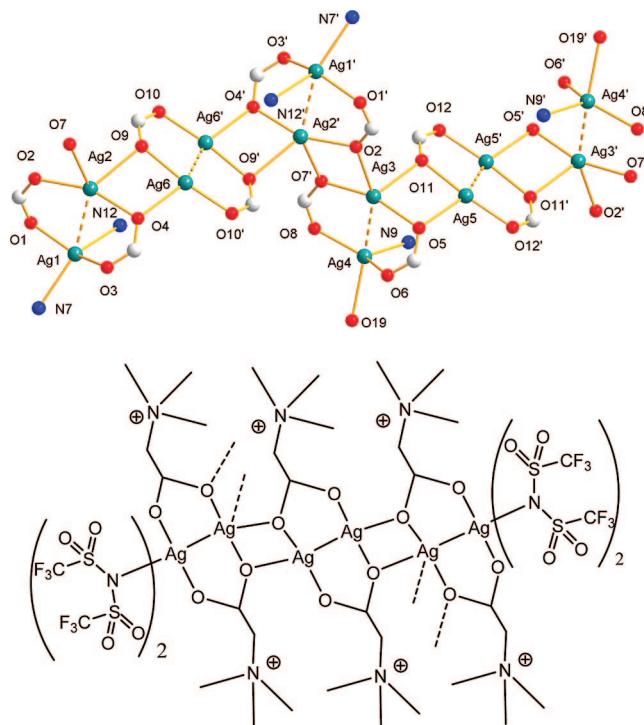


Figure 14. Surrounding, connection scheme, and labeling in the crystal structure of $[Ag_2(bet)_2(Tf_2N)Ag_2(bet)_2][Tf_2N]_3$ (upper part); schematic presentation of the interconnection along the helical strand (lower part).

Pb₂–O distances to the betaine ligands are ranging from 2.330(4) to 2.938(4) Å. The Pb₂–O contact to the coordinating bistriflimide ligand is quite long with 3.034(4) Å. Pb₃ is surrounded by one chelating and two bridging betaine ligands with Pb–O distances to the ligands ranging from 2.284(4) Å to quite long contacts at 2.965(7) Å. The atom Pb₅ is surrounded by nine oxygen atoms in the coordinating shell from one chelating and two bridging betaine ligands, the central μ_4 -O atom and a bidentately coordinating bistriflimide ligand. The coordination shell of atom Pb₅ is quite similar to Pb₄ with one chelating and two bridging betaine ligands, the central μ_4 -O atom and a bidentately coordinating bistriflimide ligand. The Pb₅–O distances to the bistriflimide ligand are quite long with 2.958(6) and 2.960(5) Å, respectively. The Pb₅–O distances to the betaine ligands are ranging from 2.395(5) Å to weak contacts at 2.950(4) Å.

The Pb–Pb distances in the tetrahedral Pb₄(μ_4 -O) oxo-cluster range from 3.678(1) to 3.892(1) Å and can therefore be considered as weak Pb–Pb interactions according to Bengtsson et al.⁶¹ In the crystal structure packing, the $[(Pb_4O)Pb(OH)(bet)_8(Tf_2N)_3]^{4+}$ oxo-hydroxy clusters exhibit no further hydrogen bonding contacts to the remaining bistriflimide counterions.

The coordination polyhedra of all five Pb atoms are strongly distorted as a result of the presence of the stereochemically active 6s² lone-pair electrons on the Pb²⁺ cations, as it is also reported for other oxo-lead clusters.⁶¹ Although a number of lead oxo-clusters has been reported and reviewed until now, this type of an $[Pb_4(\mu_4\text{-O})Pb(\mu_3\text{-OH})]^{7+}$ oxo-hydroxy cluster has, to the best of our knowledge, not been described before.^{62,63}

Crystal Structure of $[Ag_2(bet)_2(Tf_2N)Ag_2(bet)_2][Tf_2N]_3$. The crystal structure of the silver(I) complex $[Ag_2(bet)_2(Tf_2N)Ag_2(bet)_2][Tf_2N]_3$ consists of dimeric Ag–Ag units bridged by the betaine ligands to form a helix structure along the *c*-axis. In the asymmetric unit, there are six crystallographic unique

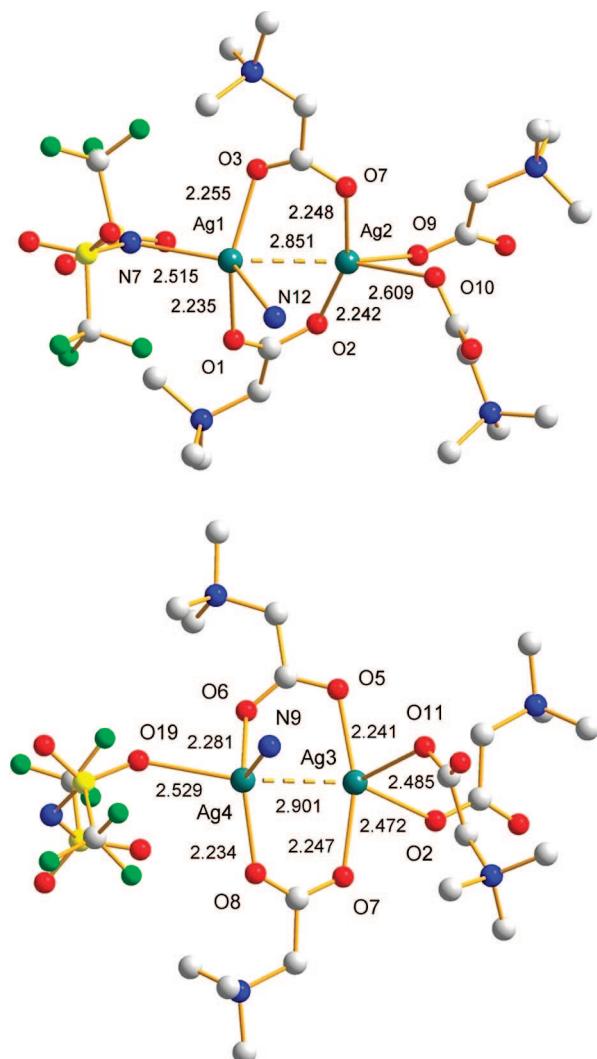


Figure 15. Surrounding and labeling for the Ag1/Ag2 dimer (upper part) and the Ag3/Ag4 dimer (lower part) in the crystal structure of $[Ag_2(bet)_2(Tf_2N)Ag_2(bet)_2][Tf_2N]_3$.

silver(I) atoms surrounded by six coordinating betaine ligands and six bistriflimide anions, from which three are coordinating to the silver(I) ions. In Figure 14, the interlinkage of the dimeric Ag–Ag units along the *c*-axis is shown.

The betaine ligands act as tridentate μ_3 bridges across the Ag–Ag dimeric units. Four different Ag–Ag dimeric units can be identified with different coordination spheres as shown in Figures 15 and 16. For the Ag1–Ag2 unit, the silver(I)–silver(I) interaction is with 2.851(6) Å significantly shorter than the van der Waals contact distance (3.40 Å), and even shorter than the Ag–Ag contact in metallic silver (2.89 Å), which points to a pronounced effect of argentophilicity.⁶⁴

Two betaine ligands act as μ_2 -bridging ligands with Ag–O distances in a range from 2.235(4) to 2.255(4) Å and are therefore comparable with other reported silver(I) carboxylate complexes.^{65,66} Additionally, Ag2 is connected to two coordinating carboxylates (Ag2–O, 2.345 Å; Ag2–O, 2.345 Å), which are on their part each linked with one adjacent Ag–Ag unit. Ag1 exhibits additional contacts to two weakly coordinating $[Tf_2N]^-$ anions (Ag1–N7, 2.515(4) Å; Ag1–N12, 2.851(6) Å).

The surrounding of the Ag3–Ag4 units is analogue to the Ag1–Ag2 units except for one of the contacts to the weakly coordinating $[Tf_2N]^-$ anions that coordinates via the oxygen

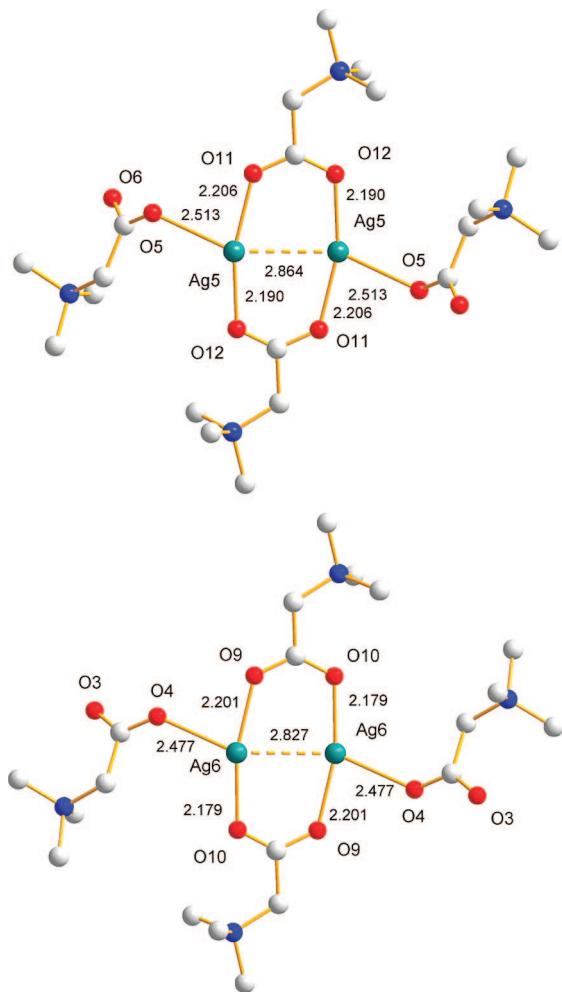


Figure 16. Surrounding and labeling for the Ag5/Ag5' dimer (upper part) and the Ag6/Ag6' dimer (lower part) in the crystal structure of $[\text{Ag}_2(\text{bet})_2(\text{Tf}_2\text{N})\text{Ag}_2(\text{bet})_2]\text{[Tf}_2\text{N}]_3$.

instead of the nitrogen ($\text{Ag4}-\text{O}19$, 2.529(4) Å; $\text{Ag4}-\text{N}9$, 2.430(5) Å). The Ag–Ag contact of this unit is slightly longer compared to the Ag1–Ag2 couple ($\text{Ag}-\text{Ag}$: 2.901(6)). The dimeric units Ag5–Ag5' and Ag6–Ag6' interconnect each two symmetry equivalent units of Ag3–Ag4 and Ag1–Ag2, respectively, via terminal coordination to the μ_2 -bridging betaine ligands. For these units, each two betaine ligands act as μ_2 -bridging ligands with Ag–O distances in a range from 2.235 to 2.255 Å. The Ag–Ag contacts of the units Ag5–Ag5' and Ag6–Ag6', respectively, are also rather short and indicate a strong argentophilicity ($\text{Ag5}-\text{Ag5}'$, 2.8644(6) Å; $\text{Ag6}-\text{Ag6}'$, 2.8269(6) Å).

The coordinating bis triflimide anions, together with the trimethylammonium parts of the betaine ligands, form a hydrophobic shell around the inner helix of dimeric Ag–Ag units. This is illustrated in a cross-sectional view along the *c* direction in Figure 17. A similar behavior has earlier been observed by Mak et al. for silver betaine compounds with trifluoroacetate ligands.⁶⁷ These silver(I) columns along the *c*-axis are positively charged. These charges are compensated by noncoordinating bis triflimide ligands that are situated in the cavities between the columns as is shown in the packing diagram, which can be found in the Supporting Information.

Infrared Spectra. A comparison of the $\nu(\text{C=O})^{\text{a}}$, $\nu(\text{C-O})^{\text{a}}$ and $\delta(\text{OCO})$ infrared absorption bands of the complexes, the

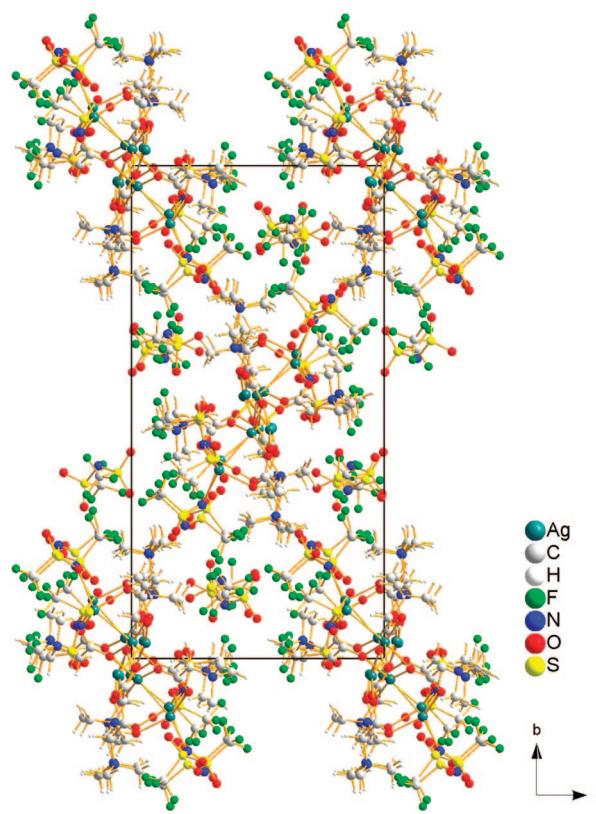


Figure 17. Packing in the crystal structure of $[\text{Ag}_2(\text{bet})_2(\text{Tf}_2\text{N})\text{Ag}_2(\text{bet})_2]\text{[Tf}_2\text{N}]_3$ viewed along the *c*-axis.

ionic liquid $[\text{Hbet}][\text{Tf}_2\text{N}]$ and anhydrous betaine is given in Table 1. The $\nu(\text{C=O})^{\text{a}}$ carboxylate frequencies of the 3d metal complexes shift according to the order in the Irving-Williams series with $\text{Mn}(\text{II}) < \text{Co}(\text{II}) < \text{Ni}(\text{II}) < \text{Zn}(\text{II})$.⁶⁸ The broad band of the $\nu(\text{C=O})^{\text{a}}$, which also exhibits a separate shoulder for the complexes of zinc(II) and nickel(II), may be attributed to the existence of up to three kinds of carboxylate groups that are bridging, chelating-bridging or monodentately coordinating. The complexes of manganese(II), silver(I), and lead(II) exhibit antisymmetric (C=O) stretching vibrations at 1616, 1630, and 1633 cm⁻¹, which is in the range of the anhydrous betaine ligand. The corresponding shift in the zinc(II) and nickel(II) complexes are significantly shifted to higher frequencies at 1679 and 1686 cm⁻¹, respectively, which points to a less covalent character of the latter complexes. In the spectrum of the cobalt(II) compound, additional vibrations of the protonated betaine, which is present as co-crystallized ionic liquid “solvent”, could be observed at 1742 and 1350 cm⁻¹.

Conclusions

The zwitterionic character of the betaine ligand and the weakly coordinating ability of the bis triflimide anion facilitate the isolation of oligonuclear or polynuclear complexes, presumably these structural features give rise to a highly favorable lattice energy. Similar considerations have been reported and observed for other complexes of zwitterionic ligands.⁶⁹ The betaine ligand supports a “shielding” of the charge around the metal core, so that oligomeric structures are favored. In the structures of silver(I), manganese(II), and lead(II), direct coordination of the bis triflimide anion to the metal ion could be observed. In a few cases, for cobalt(II) and nickel(II), hydrogen bond formation of the bis triflimide anions occurred with the coordi-

nated water molecules. In some of these structures, even no hydrogen bonding between the metal core complexes and the bistriflimide counter anions was found. In the silver(I) structure, the nitrogen of the bistriflimide anion coordinates directly to the silver(I) ion; in the lead(II) and manganese(II) structure, coordination was observed via the nitrogen of the bistriflimide. The pure ionic liquid co-crystallized in the cobalt(II) compound. The absence of any hydrogen bonding of a part of the bistriflimide counterions results often in a very strong disorder of these anions as it has been reported for bistriflimide anions before.⁴³ This is contrary to most of the reported bistriflimide containing ionic liquids.^{70–72} Some of the obtained oligomeric structures, e.g., with cobalt(II), nickel(II), or manganese(II), might be interesting for further investigations regarding their magnetic properties.

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Supporting Information Available: Crystallographic information files of the crystal structures (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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