

Crystal Structures and Thermal Behavior of Isostructural Bis(dibenzyltrimethylammonium) Tetrachlorometallate [$M = \text{Mn(II)}$, Co(II) , Ni(II) and Zn(II)] Solvates Crystallized from Acetonitrile and/or Methanol Solutions

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Five isostructural bis(dibenzyltrimethylammonium) tetrachlorometallate solvate complexes [$M = \text{Mn(II)}$, Co(II) , Ni(II) or Zn(II)] were crystallized from acetonitrile and/or methanol solutions. The crystal structures are compared to those of the analogous, isostructural copper compounds ($X = \text{Cl}$ or Br) reported earlier. The complexes crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$, and unit cell dimensions of $a \approx 14.1$, $b \approx 16.1$, $c \approx 15.7$ Å and $\beta \approx 108–109^\circ$. The asymmetric unit of these compounds contains one MCl_4^{2-} anion, two $\text{Bz}_2\text{Me}_2\text{N}^+$ cations in the W-conformation and one half of a disordered solvent molecule (acetonitrile or methanol). The geometry of the MCl_4^{2-} anion is close to tetrahedral, whereas the analogous copper anions appeared in distorted tetrahedral geometries with *trans* angles of 124.4° for $X = \text{Cl}$ and 123.6° for $X = \text{Br}$. In addition to the ionic interactions between the cations and the anions, the components are connected by weak $\text{C-H}\cdots\text{Cl}^-$ bonds. As a distinction between the two crystallographically independent cations in the asymmetric unit, one type of independent cations form long chains *via* weak edge to face π – π interactions along the crystallographic b axis, whereas the other type of cations are not tied together by such weak π – π interactions. The coordination around the N atoms is also nearly tetrahedral, and neither static nor dynamic disorder of the $\text{Bz}_2\text{Me}_2\text{N}^+$ cations can be observed. The complexes are thermally stable and melt close to the decomposition temperatures in the range $170–205^\circ\text{C}$.

Key words: Quaternary Ammonium Compound, Tetrachlorometallate, Tetrahalometallate, X-Ray Single Crystal Diffraction, Thermal Studies

Introduction

The A_2MX_4 structures, where A is an organic cation (usually an ammonium [1–8], phosphonium [9–11] or pyridinium cation [12–14]), M is a transition metal ion(II) and X is a halide (Cl^- or Br^-), have been of interest for a long time because of their structural properties [7–8, 10, 15–19], phase transitions [7–8, 11, 18–23] and thermochromic behavior [24–26] in the solid state. Among these compounds a large number of structural phase transitions and modulated phases, both incommensurate and commensurate, induced by pressure or temperature has been found [23, 27–29]. The thermochromic behavior of A_2MX_4 structures, which includes the change in color when heating/cooling the sample, can be divided into two classes [30, 31]. In one class the material shows a phase transition at a certain

temperature, which is associated with a change in the coordination geometry or in the effective ligand field strength. The other class includes a gradual change in band position and/or absorption edge by increasing the temperature.

Tetrahalometallate complexes with different counterions have been investigated because of their wide structural variabilities. The first-row transition metals have an ability to form several coordination complexes with mainly octahedral, tetrahedral and square planar stereochemistry [32]. The isolated tetrahalometallate(II) anions with $M = \text{Mn(II)}$, Co(II) , Ni(II) or Zn(II) quite often show the tetrahedral geometry [33–35]. When $M(\text{II})$ is a copper ion Cu^{2+} , additional flexibility is brought into the system, because the Cu^{2+} ion can cause a Jahn-Teller distortion [32]. In addition to the Jahn-Teller effect, the geometry of the CuX_4^{2-} anion

Table 1. Crystallographic data for compounds **1**–**5**.

Compound	1	2*	3	4	5
Formula	(C ₁₆ H ₂₀ N) ₂ MnCl ₄ ·0.5CH ₃ CN	(C ₁₆ H ₂₀ N) ₂ CoCl ₄ ·0.5CH ₃ CN	(C ₁₆ H ₂₀ N) ₂ CoCl ₄ ·0.5CH ₃ OH	(C ₁₆ H ₂₀ N) ₂ NiCl ₄ ·0.5CH ₃ CN	(C ₁₆ H ₂₀ N) ₂ ZnCl ₄ ·0.5CH ₃ OH
M _r [g mol ^{−1}]	669.93	673.92	669.41	673.70	675.85
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	14.085(3)	14.001(4)	14.147(3)	14.070(3)	14.144(3)
<i>b</i> [Å]	16.201(3)	16.058(20)	16.119(3)	16.162(3)	16.127(3)
<i>c</i> [Å]	15.818(3)	15.722(30)	15.752(3)	15.686(3)	15.762(3)
α [°]	90	90	90	90	90
β [°]	108.55(3)	108.83(11)	108.76(3)	108.96(3)	108.75(3)
γ [°]	90	90	90	90	90
<i>V</i> [Å ³]	3422(2)	3346(6)	3401(2)	3374(2)	3404(2)
<i>Z</i>	4	4	4	4	4
ρ_{calcd} [g cm ^{−3}]	1.300	1.338	1.307	1.326	1.319
μ [mm ^{−1}]	0.723	0.858	0.844	0.917	1.061
<i>F</i> (000)	1400	1408	1400	1412	1412
Crystal size [mm]	0.15 × 0.10 × 0.05	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.05	0.15 × 0.10 × 0.05	0.15 × 0.20 × 0.10
Temperature [K]	173(2)	173(2)	173(2)	173(2)	173(2)
θ range [°]	2.34–25.00	3.02–22.50	2.11–25.00	2.11–28.30	2.35–25.00
Reflections collected	10249	45876	11298	15920	11514
Independent reflections	6021	4356	5992	8304	5997
Data/Restraints/Param.	6021 / 2 / 368	4356 / 0 / 385	5992 / 1 / 363	8304 / 0 / 384	5997 / 1 / 364
GooF	1.141	1.017	1.057	1.088	1.063
<i>R</i> (int)	0.1074	0.2088	0.0672	0.0935	0.0949
Final <i>R</i> indices	0.0865 / 0.1343	0.0489 / 0.0701	0.0660 / 0.1356	0.0728 / 0.1058	0.0790 / 0.1979
[<i>I</i> ≥ 2 σ (<i>I</i>)], <i>R</i> 1/ <i>wR</i> 2					
<i>R</i> indices (all data), <i>R</i> 1/ <i>wR</i> 2	0.1458 / 0.1576	0.1152 / 0.0858	0.1024 / 0.1579	0.1481 / 0.1282	0.1160 / 0.2272
Largest diff. peak / hole [e Å ^{−3}]	0.568 / −0.428	0.336 / −0.311	1.270 / −0.344	0.337 / −0.333	1.375 / −0.683

* The crystal quality of **2** and thus the data of **2** were not fully satisfactory.

in the solid state is influenced by many other factors, such as the electrostatic repulsion between the halogen atoms, the packing forces as well as the hydrogen bonding between the cations and anions [36]. Hydrogen bonding removes the charge from the halogen atoms and reduces the electrostatic repulsion between the halogen atoms, which allows the anions to flatten toward the square planar geometry [30, 37].

The aim of our studies was to synthesize different types of tetrachlorometallate complexes and investigate the structural properties of the MX_4^{2-} anion in the crystal structure. Furthermore, interactions between the cations and anions were in the focus of our research. To examine only the effect of the metal atom on the packing within the crystal structure, the investigations have been carried out varying the first-row transition metal atom and/or the ligands ($X = \text{Br}$ and/or Cl) of the anion and using the same counter ion, the dibenzyltrimethylammonium cation [38, 39], in all experiments. In this paper, we present the crystal structures and thermal behavior of five isomorphous $(\text{Bz}_2\text{Me}_2\text{N})_2\text{MCl}_4$ solvate compounds [$M = \text{Mn(II)}$, Co(II) , Ni(II) , Zn(II)] and compare the crystal structures to the previously re-

ported isostructural $(\text{Bz}_2\text{Me}_2\text{N})_2\text{CuX}_4$ ($X = \text{Cl}$ or Br) solvate structures [40], in which the anions have a distorted tetrahedral geometry. Finally, the thermal behavior of the compounds has been examined by TG and DSC methods.

Results and Discussion

X-ray structure analysis

Crystallographic data and selected bond lengths and angles of compounds **1**–**5** are presented in Tables 1 and 2. The bond lengths are typical for this kind of compounds. The molecular structure and the labeling scheme of compound **5** is presented in Fig. 1 as an example of the isostructural compounds **1**–**5**, which crystallize as solvates in the monoclinic space group *P*2₁/*n* having unit cell dimensions of about $a \approx 14.1$ Å, $b \approx 16.1$ Å and $c \approx 15.7$ Å, and an angle $\beta \approx 108$ – 109° . Compounds **1**, **2** and **4** contain two acetonitrile molecules and compounds **3** and **5** two methanol molecules as co-crystallized solvent molecules in the unit cell. The acetonitrile molecules show no hydrogen bonds ($\text{Cl}^- \cdots \text{H}-\text{C}$) toward the tetrahalometallate

Compound	1	2	3	4	5
N(1)–C(11)	1.537(8)	1.522(5)	1.532(7)	1.535(5)	1.528(8)
N(1)–C(21)	1.546(7)	1.529(5)	1.524(6)	1.533(5)	1.534(8)
N(1)–C(31)	1.482(8)	1.493(5)	1.482(7)	1.484(5)	1.490(8)
N(1)–C(41)	1.491(7)	1.484(5)	1.487(7)	1.482(6)	1.491(8)
N(2)–C(51)	1.535(7)	1.526(6)	1.534(7)	1.531(5)	1.531(8)
N(2)–C(61)	1.538(7)	1.527(5)	1.534(7)	1.527(5)	1.531(8)
N(2)–C(71)	1.493(8)	1.475(6)	1.497(7)	1.494(5)	1.485(8)
N(2)–C(81)	1.488(7)	1.488(5)	1.486(7)	1.495(5)	1.502(8)
<i>M</i> (1)–Cl(1)	2.384(2)	2.287(3)	2.254(2)	2.263(2)	2.280(2)
<i>M</i> (1)–Cl(2)	2.359(2)	2.268(2)	2.273(2)	2.259(2)	2.268(2)
<i>M</i> (1)–Cl(3)	2.368(2)	2.261(3)	2.281(2)	2.279(2)	2.296(2)
<i>M</i> (1)–Cl(4)	2.338(2)	2.248(2)	2.297(2)	2.242(2)	2.248(2)
Average of <i>M</i> –Cl	2.362	2.266	2.276	2.261	2.273
Cl(1)– <i>M</i> –Cl(2)	106.28(7)	106.63(11)	113.95(6)	108.07(5)	109.07(7)
Cl(1)– <i>M</i> –Cl(3)	109.66(7)	110.23(8)	108.76(6)	110.20(5)	109.27(7)
Cl(1)– <i>M</i> –Cl(4)	107.84(7)	108.46(10)	108.70(6)	107.76(5)	109.02(7)
Cl(2)– <i>M</i> –Cl(3)	108.96(7)	109.09(6)	109.15(6)	105.04(5)	106.52(7)
Cl(2)– <i>M</i> –Cl(4)	114.78(7)	113.80(8)	106.61(6)	118.18(5)	114.00(7)
Cl(3)– <i>M</i> –Cl(4)	109.21(7)	108.60(8)	109.61(6)	107.47(5)	108.85(7)
Average of two large Cl– <i>M</i> –Cl	112.22	112.02	111.78	114.19	111.64
Solvents:					
N(1A)–C(1A)–C(2A)	165(3)	175(3)		176(2)	
H(1AA)–O(1A)–H(1AB)			109.5		109.5
C(1A)–O(1A)–H(1A)					
C(100)–O(100)–H(100)					

Table 2. Selected bond lengths (Å) and bond angles (°) of compounds **1–5**, where *M* = Mn(II) (**1**), Co(II) (**2–3**), Ni(II) (**4**) or Zn(II) (**5**).

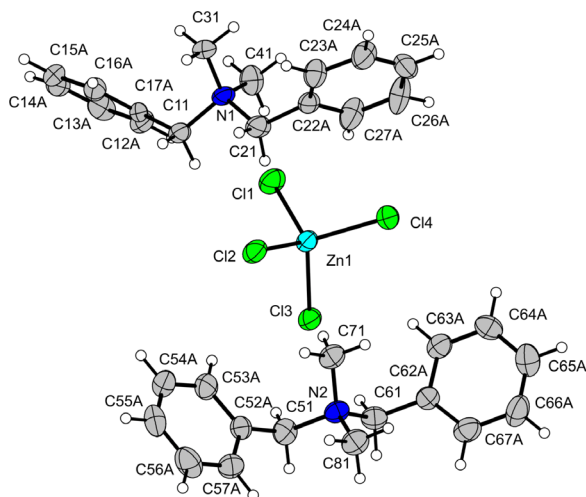


Fig. 1. The molecular structure and labelling scheme of compound **5** as an example of the isostructural compounds **1–5**. Displacement ellipsoids are at the 50 % probability level. The disordered solvent molecules are omitted for clarity.

anion, whereas $\text{Cl}^- \cdots \text{H}-\text{O}$ hydrogen bonds between the disordered methanol molecules and the tetrachlorozincate anions are observed in the crystal structure of **5**. However, the $\text{Cl}^- \cdots \text{H}-\text{O}$ hydrogen bonds are not found in the crystal structure of the isostructural compound **3**. Because the disordered solvent molecules

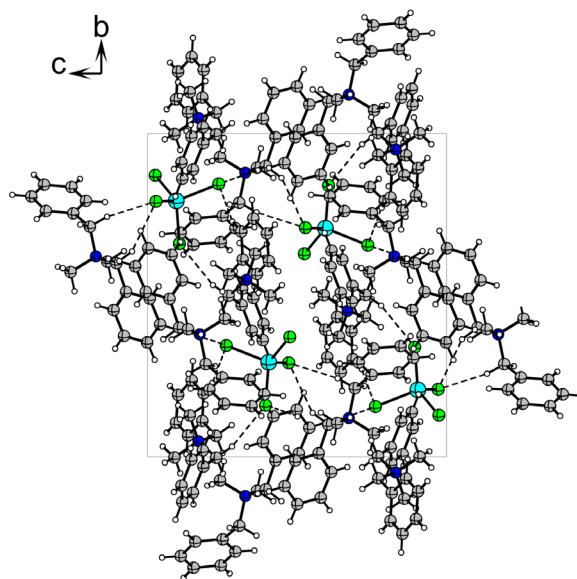


Fig. 2. Packing of the molecules in the isostructural compounds **1–5** (compound **5** shown as an example) viewed along the crystallographic *a* axis with hydrogen bonding ($\text{C}-\text{H} \cdots \text{Cl}^- < 2.8 \text{ Å}$) shown as dashed lines. The disordered solvent molecules are omitted for clarity.

in all isostructural crystal structures (except for compound **5**) form no hydrogen bonds ($\text{Cl}^- \cdots \text{H}-\text{O}$,

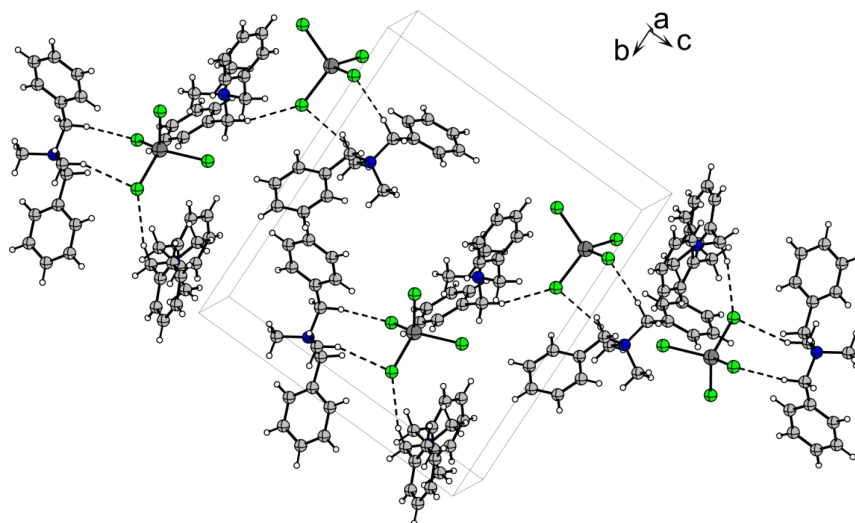


Fig. 3. The hydrogen bonding between the components in the isostructural compounds **1–5** ($\text{C-H}\cdots\text{Cl}^- < 2.8 \text{ \AA}$). Compound **5** is presented as an example. The solvent molecules have been omitted for clarity.

$\text{Cl}^- \cdots \text{H-C}$) toward the tetrahalometallate anions, the solvent molecules can be said to fill only the empty space of the crystal structures not affecting substantially the packing of the components.

Compounds **1–5** are isostructural and the atoms are distributed in the same way in all crystal structures despite of the different nature of the co-crystallized solvent molecules. The lattice dimensions and interatomic distances as well as the atomic coordinates vary only slightly. Because the nature of the solvent molecules differs for **1**, **2** and **4** as compared to **3** and **5**, the concept of isomorphism should not be used in this context.

The asymmetric unit of **1–5** consists of one MCl_4^{2-} anion, two $\text{Bz}_2\text{Me}_2\text{N}^+$ cations and one half of a disordered solvent molecule (acetonitrile or methanol). A typical packing diagram is presented in Fig. 2. In addition to the ionic interactions, the components are connected by weak $\text{C-H}\cdots\text{Cl}^-$ bonds ($\text{C-H}\cdots\text{Cl}^- < 2.8 \text{ \AA}$) as indicated in Fig. 3. Both cations are in the W-conformation. One type of the two crystallographically independent cations forms long chains along the crystallographic *b* axis and these cations are connected by weak intermolecular edge to face π – π interactions. Instead, the other type of independent cations does not interact in this way.

The compounds presented here are also isostructural with previously reported copper(II) complexes [40] $(\text{Bz}_2\text{Me}_2\text{N})_2\text{CuX}_4 \cdot 0.5\text{CH}_3\text{CN}$ ($\text{X} = \text{Br}$ or Cl), which crystallize in the same space group with similar unit cell dimensions. In both cases ($\text{X} = \text{Br}$ or Cl), the CuX_4^{2-} anions have a distorted tetrahedral geom-

etry with an average of the two largest X-Cu-X angles of 123.6° for Br and of 124.4° for Cl. This kind of flattening of CuX_4^{2-} anions from tetrahedral geometry (T_d symmetry) toward D_{2d} symmetry is typical for copper(II) ions, which have the d^9 coordination and thus a tendency to form non-regular stereochemistry due to the Jahn-Teller effect. In the present case, where $\text{N-H}\cdots\text{Cl}^-$ hydrogen bonds are not possible, the distortion is smaller (*trans* X-Cu-X angle $< 129^\circ$) than in cases where hydrogen bonds exist (*trans* X-Cu-X angle $> 129^\circ$). The packing in the crystals of compounds **1–5** is similar. However, the coordination geometry of the MCl_4^{2-} anions with $\text{M} = \text{Mn(II)}$, Co(II) , Ni(II) and Zn(II) is nearly tetrahedral (Table 2).

The coordination around the N atom in the $\text{Bz}_2\text{Me}_2\text{N}^+$ cations of all compounds is close to tetrahedral. The displacement ellipsoids of the atoms and the uncertainties in the positions of the atoms are small (except for compound **2**, see Table 2) in both cations and anions. Thus, neither static nor dynamic disorder of the $\text{Bz}_2\text{Me}_2\text{N}^+$ cations can be observed among these crystal structures. $\text{C-H}\cdots\text{Cl}^-$ interactions are likely to affect the packing of **1–5** as it is the case with bis(4-dimethylaminopyridinium)tetrachlorocuprate(II) as reported by Haddad and Willett [37].

Thermal properties

The TG diagrams for compounds **1–5** are presented in Fig. 4. The DSC and TG data have been included in Table 3 as melting points, enthalpy changes and decomposition ranges.

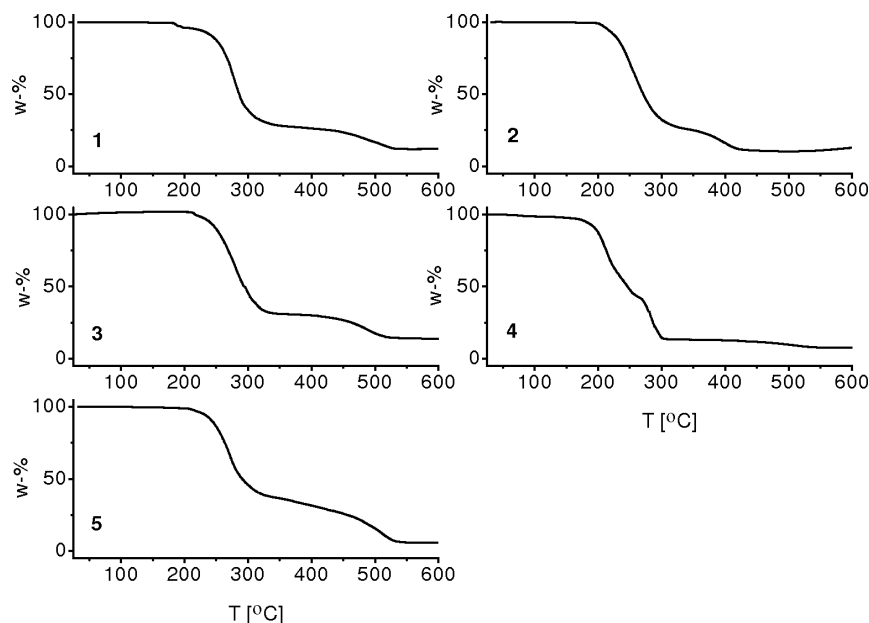


Fig. 4. TG diagrams for compounds **1–5**.

Table 3. Melting temperatures (DSC onsets), enthalpy changes and decomposition ranges (the starting value was taken from the initial mass loss in the decomposition) for compounds **1–5**.

Compound	T_m and Enthalpy change (°C, (Jg ⁻¹))	Decomposition range (°C)
1	177.4	205–540
2	201.6 (90.4)	190–460
3	201.5 (86.4)	195–515
4	201.4 (65.9)	170–525
5	201.6 (67.5)	195–545

Except for the tetrachloromanganate salt all the compounds showed only a narrow melting range very close to 200 °C. In contrast, the tetrachloromanganate salt showed a melting-crystallization-melting-crystallization-melting cycle starting from 177 °C and ending (final melting) close to 200 °C. A two-step loss of acetonitrile molecules was also observed in a TG curve of the tetrachloromanganate salt at 177–198 °C. According to the DSC and TG measurements, the complex first melted and about half of the acetonitrile molecules evaporated (Δw_{exp} 1.8%, Δw_{calc} 1.8%) after which the complex crystallized to a new structural form. Next the new form melted releasing the rest of the acetonitrile molecules, followed by the crystallization of the solvent free form, which finally melted close to 200 °C. The analyzed compounds started to decompose approx. at 200 °C. The decomposition occurred mainly in two stages.

No phase transitions were observed for any of the compounds between –50 °C and the melting point, which indicates the high thermal stability of these structures. Regardless of the transition metal atom [$M = \text{Mn(II)}$, Co(II) , Ni(II) , Zn(II)] in the anion, the thermal behavior of the compounds is very similar when the same organic cation is used. Therefore, the altering of the transition metal atom in the MX_4^{2-} anion appears to have no significant effect on the melting points and the decomposition temperatures of these isostructural complexes.

Conclusions

Bis(dibenzyltrimethylammonium) tetrachlorometallates [$M(\text{II}) = \text{Mn(II)}$, Co(II) , Ni(II) or Zn(II)] crystallize as isostructural monoclinic acetonitrile/methanol solvates. The solvent molecules do not affect significantly the packing of the components but fill the voids of the crystal structure. The packing is affected by $\text{C–H} \cdots \text{Cl}^-$ bonds between the anions and cations. In addition, edge to face π – π interactions are observed between one type of the crystallographically independent cations, whereas the other type of cations have no such contacts.

The geometry of the MCl_4^{2-} anions [$M = \text{Mn(II)}$, Co(II) , Ni(II) and Zn(II)] is close to tetrahedral, which is common for cases where no $\text{N–H} \cdots \text{Cl}^-$ hydrogen bonds can be established. In the present crystal structures, weak hydrogen bonds ($\text{C–H} \cdots \text{Cl}^-$ bonds) to-

gether with the π – π interactions appear to stabilize the packing of the compounds. No static or dynamic disorder is observed for the cations and no phase transitions are found in a temperature range from -50 °C to the melting point of the complexes. Usually, multiple phase transitions are observed for A_2CuX_4 salts when A is a small and non-hydrogen-bonding cation, and the phase transitions are associated with disorder of the cations and the CuX_4^{2-} anions.

Experimental Section

Preparation and elemental analyses of the complexes

General procedure

Compounds **1**–**5** were obtained from acetonitrile and/or methanol solution by slow evaporation after a few days. The solutions contained stoichiometric amounts (2:1) of dibenzyltrimethylammonium chloride and MCl_2 . Bz_2Me_2NCl was synthesized and characterized as described in recent publications [38, 39]. Commercial MCl_2 salts were used as received from manufacturers.

$[Bz_2Me_2N]_2MnCl_4 \cdot 0.5CH_3CN$ (**1**)

Reagents: Bz_2Me_2NCl and $MnCl_2 \cdot 4H_2O$ in acetonitrile solution. White single crystals. Calcd. C 59.16, H 6.24, N 5.23; found C 58.23, H 6.08, N 4.87.

$[Bz_2Me_2N]_2CoCl_4 \cdot 0.5CH_3CN$ (**2**)

Reagents: Bz_2Me_2NCl and $CoCl_2 \cdot 6H_2O$ in acetonitrile solution. Light blue single crystals. Calcd. C 58.81, H 6.21, N 5.20; found C 58.31, H 6.14, N 5.21.

$[Bz_2Me_2N]_2CoCl_4 \cdot 0.5CH_3OH$ (**3**)

Reagents: Bz_2Me_2NCl and $CoCl_2 \cdot 6H_2O$ in methanol solution. Light blue single crystals. Calcd. C 58.31, H 6.32, N 4.18; found C 57.26, H 6.13, N 4.22.

$[Bz_2Me_2N]_2NiCl_4 \cdot 0.5CH_3CN$ (**4**)

Reagents: Bz_2Me_2NCl and $NiCl_2 \cdot 6H_2O$ in acetonitrile solution. Light blue single crystals. Calcd. C 60.28, H 6.31, N 4.60; found C 58.23, H 6.08, N 4.87.

$[Bz_2Me_2N]_2ZnCl_4 \cdot 0.5CH_3OH$ (**5**)

Reagents: Bz_2Me_2NCl and $ZnCl_2$ in methanol solution. White single crystals. Calcd. C 57.76, H 6.26, N 4.14; found C 56.39, H 5.90, N 3.86.

Structure analysis

The crystal structures for compounds **1**–**5** were determined with a Kappa APEX II diffractometer at -100 °C

using graphite monochromatized MoK_α ($\lambda = 0.71069$ Å) radiation. The data were processed with Denzo-SMN v0.95.373 [41] or with the EvalCCD [42] software package and the absorption correction was performed using Denzo or SADABS (included in the EvalCCD software package). All crystal structures were solved with Direct Methods (SIR97 [43]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-97 [44]). The thermal motion of all non-hydrogen atoms was treated using anisotropic displacement parameters. All hydrogen atoms were calculated in idealized positions as riding atoms by using isotropic displacement parameters. The restraints appearing in Table 1 for compounds **1**, **3** and **5** were applied to fix the disordered solvent molecules. Figs. 1–3 were made using the Diamond program [45]. Crystallographic data for the crystal structures **1**–**5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 612674 – 612678. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Thermal properties

Melting points of the compounds **1**–**5** were determined on a PerkinElmer PYRIS 1 DSC instrument and with a Mettler Toledo FP62 melting point instrument. DSC measurements were carried out using 50 μ L sealed aluminum sample pans with pinholes. The temperature calibration was carried out using three standard materials (*n*-decane, In, Zn) and an energy calibration by an indium standard. The samples were heated in a nitrogen atmosphere (flow rate of 50 mL min⁻¹) at a rate of 10 °C min⁻¹ from -50 °C up to the temperature close to the predetermined (DSC, TG/DTA) decomposition temperature and then cooled at a rate of 10 °C min⁻¹ back to the temperature of -50 °C. The heating-cooling cycle was repeated twice. The sample weights were about 2–6 mg.

The thermal decomposition diagrams were obtained with Perkin Elmer TGA7 thermogravimetric analyzer. The measurements were carried out in platinum pans in a synthetic air atmosphere (flow rate 50 mL min⁻¹) with a heating rate of 10 °C min⁻¹ in the temperature range from 25–700 °C. The temperature calibration of the TGA equipment was carried out using the Curie-point calibration technique (Alumel, Ni, Perkalloy, Fe). The weight balance was calibrated by measuring the standard weight of 50 mg at r. t.. The sample weights were 2–4 mg.

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