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Synthesis, Properties, and Structures of Salts with the Reineckate Anion, $[Cr^{III}(NCS)_4(NH_3)_2]^-$, and Large Organic Cations

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Keywords: Chromium; Crystal structure; Reinecke's salt; Imidazolium

Abstract. A series of 9 new Reineckate salts, $A[Cr^{III}(NCS)_4(NH_3)_2]$ with various large organic cations A = tetraalkylammonium, $[R_4N]^+$, R = *n*-butyl, *n*-dodecyl; 1-alkyl-3-methylimidazolium, $(R\mathrm{MIm})^+$: R = methyl, ethyl, *iso*-propyl, *n*-butyl, and *n*-hexyl; A = 1,3-dimethyl-2,4,5-triphenylimidazolium and A = 1,2,3,4,5-pentamethylimidazolium was synthesized. The melting point of each compound was measured to see if any belongs to the group of metal-containing Ionic Liquids with low melting points. Each compound was further characterized by elemental analysis, NMR, IR, and UV/Vis spectroscopy. From NMR investigations information about the magnetic behavior was derived using the *Evans* method. It has been found that every compound is paramagnetic with effective magnetic moments of spin-only Cr^{III}. The structures of the Reineckates with A = tetra-*n*-butyl-ammonium, tetra-*n*-dodecyl-ammonium, 1-ethyl-3-methylimidazolium, and 1,2,3,4,5-pentamethylimidazolium were determined by single-crystal X-ray diffraction measurements: $(n\mathrm{Bu}_4\mathrm{N})[\mathrm{Cr(NCS)_4(NH_3)_2}]$: monoclinic, $C2/c$ (no. 15), a = 12.0818(8), b = 10.2425(8), c = 24.222(2) Å, β = 98.324(3)°, Z = 4, $R1(F)/wR2(F^2)$ = 0.0332/0.0871; $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$: triclinic, $P\bar{1}$ (no. 2), a = 8.4049(1), b = 20.1525(4), c = 20.7908(4) Å, α = 67.487(1)°, β = 81.328(1)°, γ = 78.040(1)°, Z = 2, $R1(F)/wR2(F^2)$ = 0.0533/0.1343; $(\mathrm{EMIm})[\mathrm{Cr(NCS)_4(NH_3)_2}]$: orthorhombic, $Pbcm$ (no. 57), a = 8.765(2), b = 15.888(3), c = 14.191(3) Å, Z = 4, $R1(F)/wR2(F^2)$ = 0.0466/0.1271; $(\mathrm{PeMIm})[\mathrm{Cr(NCS)_4(NH_3)_2}]$: monoclinic, $P2_1/n$ (no. 14), a = 6.0817(2), b =13.9811(5), c = 25.2902(9) Å, β = 90.075(2)°, Z = 4, $R1(F)/wR2(F^2)$ = 0.0405/0.1111.

Introduction

The first compounds based on the Reineckate anion $[Cr^{III}(NCS)_4(NH_3)_2]^-$ were reported by *Morland* and *Reinecke* 150 years ago, without any knowledge of the constitution of their obtained salts.[1] Later, *Christensen*, *Nordenskjöld*, and *Werner*, respectively, elaborated the correct constitution by means of chemical analyses of follow reactions and decomposition products.[2] The correct constitution of Reinecke's salt (ammonium Reineckate, $(NH_4)[Cr(NCS)_4(NH_3)]\cdot 0.66H_2O$) was finally established by single-crystal X-ray diffraction techniques by *Takéuchi* and *Saito* 55 years ago.[3] Since then, only a few crystal structure determinations of compounds containing the Reineckate anion have been reported,[4] although the chemistry of Reineckates and related substances has emerged great interests not only in the last decades. Reineckates have been used as chemical actinometers,[5] substances for quantum yield determinations,[6] and as compounds in charge transfer photochemistry.[7] Reineckates have also been used in the gravimetric, volumetric as well as spectrophotometric analysis of medicinal products.[8] Although, *Łodzińska* and *Ali* have reported about the influence of organic cations on the properties of Reineckates,[9] until today there has been no information about imidazolium-based Reineckates in the literature, which could be tested as suitable candidates for Magnetic Ionic Liquids. In general Ionic Liquids (ILs) with melting points below 100 °C have attracted great interest because of their special and useful properties, such as wide liquid ranges, negligible vapor pressures, large electrochemical windows, or high electric conductivity.[10–13] Some transition metal based Ionic Liquids (Magnetic Ionic Liquids) exhibit interesting magnetic properties in addition to those mentioned above. It has turned out, that ILs containing $[FeCl_4]^-$ or $[CoX_4]^{2-}$ (X = Br, NCS) anions are paramagnetic liquids, which show a distinct response to magnetic fields.[14–16] In this contribution we report on the synthesis, properties and structures of imidazolium- and tetraalkylammonium-based Reineckates. In order to investigate the dependence of the melting points with the length and nature of the substituents in the imidazolium cations, three different types of cations were tested: 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, *iso*-propyl, *n*-butyl, *n*-hexyl), 1,3-dimethyl-2,4,5-triphenylimidazolium, and 1,2,3,4,5-pentamethylimidazolium. Furthermore, for the reason of comparison, two tetraalkylammonium Reineckates were synthesized as well: tetra-*n*-butylammonium and tetra-*n*-dodecylammonium Reineckate. In total 9 new Reineckates were synthesized and investigated of which 4 were characterized by means of single-crystal X-ray diffraction.

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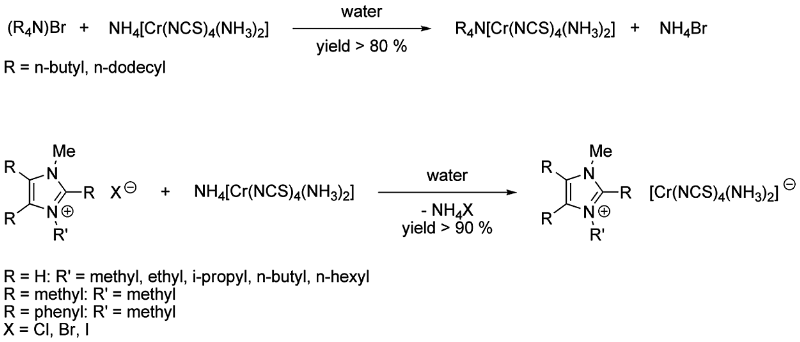

Scheme 1. Reaction sequence for the synthesis of the tetraalkylammonium- and imidazolium-based salts containing the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$.

Results and Discussion

Synthesis

The synthesis of salts with large organic cations containing the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$ can be easily achieved by metathesis reactions between the Reinecke salt $(NH_4)[Cr(NCS)_4(NH_3)_2]{\cdot}0.66H_2O$) and alkylimidazolium or tetraalkylammonium halides in high yields (>80 %) according to Scheme 1. All compounds have a deep ruby-red color in crystalline form. They are insoluble in water, but highly soluble in organic solvents, especially in acetone and acetonitrile.

Infrared Spectra

The IR data in the region 4000–500 cm^{-1} of the imidazolium-, and tetraalkylammonium-based Reineckates are listed in the Experimental Section. IR spectra of imidazolium-based compounds are discussed in the literature in detail.[17] The IR spectra show aliphatic C–H stretching frequencies in the region of 3100–3000 cm^{-1}, as expected. Many other ILs with imidazolium cations, which carry an acidic hydrogen atom at the carbon atom between the two nitrogen atoms of the imidazolium ring, show a strong, broad peak in this region, which was assigned to hydrogen bonding.[17] With this hydrogen atom being absent in the two compounds $(PeMIm)[Cr(NCS)_4(NH_3)_2]$ and $(DML)[Cr(NCS)_4(NH_3)_2]$ (PeMIm = 1,2,3,4,5-pentamethylimidazolium; DML = 1,3-dimethyl-2,4,5-triphenylimidazolium = 1,3-dimethyllophium), the respective hydrogen bonding and the corresponding peak in the IR spectrum is absent. The region 2000–500 cm^{-1} is dominated by internal vibrations of the imidazolium ring and is employed as the fingerprint domain for the presence of planar imidazolium rings. The IR spectra of the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$ is interpreted in detail in the literature,[9] and references cited therein. The CN stretching frequencies (ν_{CN}) are located between 2080–2090 cm^{-1}, the CS stretching frequencies (ν_{CS}) between 820–850 cm^{-1}, respectively, and are in accordance with reported values for N-bonded thiocyanato complexes of 3d metals such as Cr^{III}.[9,18]

Electronic Spectra

Octahedrally coordinated Cr^{III} complexes exhibit two transitions in the Vis region, which are characterized by $^4T_{2g} \leftarrow {}^4A_{2g}$ (lower energy) and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ (higher energy). In addition, there is a third short-waved transition, which is often interfered by charge-transfer bands and characterized by $^4T_{1g}(P) \leftarrow {}^4A_{2g}$. Intensive UV/Vis investigations with compounds containing the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$ are reported in the literature.[9,18] The location of the two $^4T_{2g} \leftarrow {}^4A_{2g}$ (526 nm) and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ (396 nm) transitions is independent of the choice of the cation in acetone solution and in accordance with reported values.[9,18]

Melting Points

Thermal data of the title compounds were measured using DSC (differential scanning calorimetry) in the temperature range from 0–400 °C. Melting points were detected as endothermic peaks in the DSC experiments above 100 °C, except for $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]{\cdot}0.85H_2O$ ($C_{12}H_{25}$ = *n*-dodecyl, mp. 48 °C). All melting points can be found in the Experimental Section. The melting points decrease with increasing alkyl chain length in the imidazolium-based cation from 201 °C in $(DMIm)[Cr(NCS)_4(NH_3)_2]$ to 122 °C in $(BMIm)[Cr(NCS)_4(NH_3)_2]$, see Figure 1. $(HexMIm)[Cr(NCS)_4(NH_3)_2]$ melts at 126 °C. This value is slightly higher than the melting point of $(BMIm)[Cr(NCS)_4(NH_3)_2]$, although the alkyl chain in the cation is longer than in $(BMIm)[Cr(NCS)_4(NH_3)_2]$. This behavior is possibly due to the energetic improved conformation of the *n*-hexyl alkyl chain (fully staggered) in the cation of $(HexMIm)[Cr(NCS)_4(NH_3)_2]$. Unfortunately, we have not been successful in proving this assumption by means of single-crystal X-ray diffraction methods, yet. The melting point of compounds with higher alkylated imidazolium cations like $(PeMIm)[Cr(NCS)_4(NH_3)_2]$ (mp. 198 °C) and $(DML)[Cr(NCS)_4(NH_3)_2]$ (mp. 172 °C) are in the range between 150–200 °C. None of these synthesized salts can be assigned as Ionic Liquids (ILs) nor Room

Temperature Ionic Liquids (RTILs), except $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$. All compounds show excellent stabilities at least up to 250 °C in inert atmosphere (N_2) and neither endothermic nor exothermic decomposition effects.

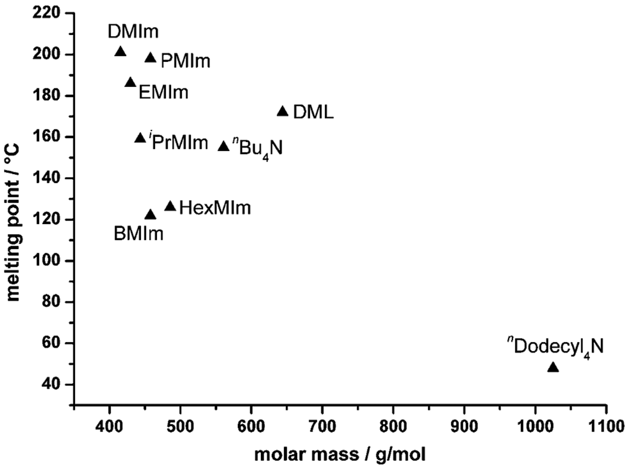

Figure 1. Molar mass dependence of the melting point of the investigated Reineckates.

Magnetic Properties

The magnetic properties of all complex salts, which contain the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$ were determined using ^1H NMR shifts by applying the *Evans* method.[19, 20] All complexes display similar magnetic properties. They are paramagnetic with effective magnetic moments in the range of μ_{eff} = 3.83–3.90 μ_B at 25 °C (spin only high-spin Cr^{III}: μ_{eff} = 3.87 μ_B). These values resemble closely those of other Reineckate compounds with isolated octahedrally coordinated Cr^{III} atoms, for example $K[Cr(NCS)_4(NH_3)_2]$ (μ_{eff} = 3.80 μ_B),[21a] $(NH_4)[Cr(NCS)_4(NH_3)_2]$ (μ_{eff} = 3.86 μ_B),[21b,21c] or $(NH_4)[Cr(NCS)_4(NH_3)_2]\cdot 0.66H_2O$ (μ_{eff} = 3.91 μ_B).[21d] There is no indication for any cooperative magnetic interaction between the isolated spin-only systems.

Crystal Structures

The single crystal structures of $(nBu_4N)[Cr(NCS)_4(NH_3)_2]$, $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$, $(EMIm)[Cr(NCS)_4(NH_3)_2]$, and $(PeMIm)[Cr(NCS)_4(NH_3)_2]$ were established by X-ray diffraction analysis. Crystal data and parameters of the structure determinations are given in Table 1, and selected bond lengths as well as bond angles in Table 2 and Table 3, respectively. Suitable crystals were obtained by slow evaporation of the solvent (acetone) of saturated solutions at room temperature over one week. All compounds consist of isolated tetraalkylammonium or imidazolium-based cations, the corresponding Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$, and in the case of $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$ with 0.85 co-crystallized water molecules.

$(nBu_4N)[Cr(NCS)_4(NH_3)_2]$ crystallizes in the monoclinic space group *C*2/*c* (no. 15) with four formula units in the unit cell. Figure 2 shows the molecular structures of the tetrabutyl-

Table 1. Crystal, X-ray diffraction data, data collection and refinement parameters for $(n\text{-}Bu_4N)[Cr(NCS)_4(NH_3)_2]$, $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$, $(EMIm)[Cr(NCS)_4(NH_3)_2]$, and $(PeMIm)[Cr(NCS)_4(NH_3)_2]$.

Compound	$(n\text{-}Bu_4N)$-$[Cr(NCS)_4(NH_3)_2]$	$\{(C_{12}H_{25})_4N\}$-$[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$	(EMIm)-$[Cr(NCS)_4(NH_3)_2]$	(PeMIm)-$[Cr(NCS)_4(NH_3)_2]$
Formula	$C_{20}H_{42}CrN_7S_4$	$C_{52}H_{107.7}CrN_7O_{0.85}S_4$	$C_{10}H_{17}CrN_8S_4$	$C_{12}H_{21}CrN_8S_4$
Fw /g·mol^{-1}	560.85	1025.00	429.56	457.61
T /K	173(2)	173(2)	293(2)	173(2)
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	*C*2/*c*, no. 15	$P\bar{1}$, no. 2	*Pbcm*, no. 57	$P2_1/n$, no. 14
a /Å	12.0818(8)	8.4049(1)	8.765(2)	6.0817(2)
b /Å	10.2425(8)	20.1525(4)	15.888(3)	13.9811(5)
c /Å	24.222(2)	20.7908(4)	14.191(3)	25.2902(9)
α /°		67.487(1)		
β /°	98.324(3)	81.328(1)		90.075(2)
γ /°		78.040(1)		
V /Å^3, Z	2965.8(4), 4	3172.6(1), 2	1976.2(7), 4	2150.4(1), 4
ρ /g·cm^{-3}	1.256	1.073	1.444	1.413
μ /mm^{-1}	0.688	0.349	1.010	0.933
2θ range /°	5.24 to 57.20	4.02 to 70.44	5.12 to 56.96	4.34 to 60.00
Collected refl.	13351	103210	21805	26938
Unique refl., R_{int}	3781, 0.0263	27884, 0.0259	2500, 0.0286	6262, 0.0287
Variables	159	581	149	250
Goof on F^2	1.063	1.018	1.043	1.069
$R1$, $wR2$ $[I > 2\sigma(I)]^{a,b)}$	0.0333, 0.0862	0.0580, 0.1494	0.0466, 0.1271	0.0405, 0.1112
$R1$, $wR2$ (all data)$^{a,b)}$	0.0423, 0.0898	0.1020, 0.1846	0.0622, 0.1396	0.0571, 0.1248
A, B$^{a,b)}$	0.0447, 1.9473	0.0824, 1.4485	0.0716, 1.5541	0.0606, 1.0550
Res. dens. /e·Å^{-3}	0.606, –0.447	1.443, –0.993	0.834, –0.608	0.806, –0.452

a) $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $wR2 = \sqrt{\Sigma\{w(F_o^2-F_c^2)^2\}}$; $w = 1/[(\sigma^2(F_o^2) + (A\cdot P)^2 + B\cdot P]$; $P = (F_o^2+2\,F_c^2)/3$.

Table 2. Selected bond lengths /Å and angles /° for the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$ in $(n\text{-}Bu_4N)[Cr(NCS)_4(NH_3)_2]$ and $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$.

$(^nBu_4N)[Cr(NCS)_4(NH_3)_2]$		$\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$			
atoms	bond length	atoms	bond length	atoms	bond length
Cr1–N1	1.989(1)	Cr1–N1	1.983(2)	Cr2–N3	1.989(2)
Cr1–N2	1.986(1)	Cr1–N2	1.999(1)	Cr2–N4	1.989(2)
Cr1–N3	2.072(2)	Cr1–N5	2.072(2)	Cr2–N6	2.056(4)
N1–C1	1.159(2)	N1–C1	1.164(2)	N3–C3	1.154(4)
N2–C2	1.164(2)	N2–C2	1.160(2)	N4–C4	1.146(3)
C1–S1	1.622(2)	C1–S1	1.614(2)	C3–S3	1.619(3)
C2–S2	1.621(2)	C2–S2	1.624(2)	C4–S4	1.614(3)
atoms	bond angle	atoms	bond angle	atoms	bond angle
N1–Cr1–N2	90.21(6)	N1–Cr1–N2	90.18(6)	N3–Cr2–N4	90.20(9)
N1–Cr1–N3	91.40(6)	N1–Cr1–N5	89.86(6)	N3–Cr2–N6	89.9(1)
N2–Cr1–N3	88.48(6)	N2–Cr1–N5	91.64(6)	N4–Cr2–N6	91.9(1)
Cr1–N1–C1	173.3(1)	Cr1–N1–C1	171.9(2)	Cr2–N3–C3	172.6(3)
Cr1–N2–C2	177.3(1)	Cr1–N2–C2	176.4(2)	Cr2–N4–C4	165.0(3)

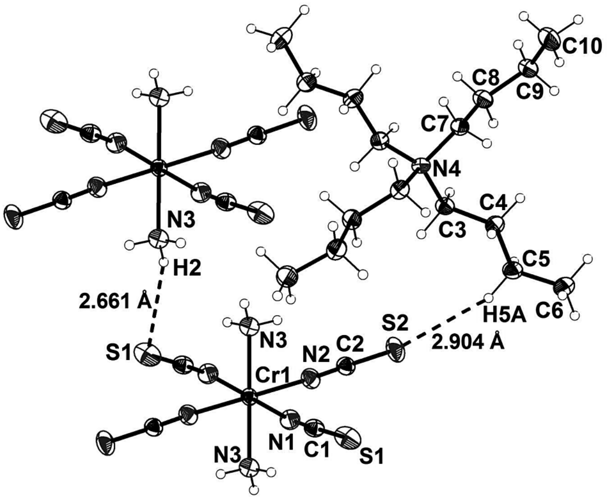

Figure 2. View of the molecular structures of the $(n\text{-}Bu_4N)^+$ cation and of the Reineckate anion $[Cr(NCS)_4(NH_3)_2]^-$ in crystals of $(n\text{-}Bu_4N)[Cr(NCS)_4(NH_3)_2]$ with atom numbering scheme. Atomic displacement ellipsoids are shown at the 50 % probability level. C–H···S hydrogen contacts, which are shorter than 2.95 Å, are shown as dashed lines.

ammonium cation and the Reineckate anion as well as hydrogen bond contacts. Selected bond lengths and bond angles of the anion can be found in Table 2. The Cr–N bonds within the anion range from 1.986(1) to 2.072(2) Å. The latter is the distance between the Cr^{III} atom and the nitrogen atom of the NH_3 ligand. In all four compounds, which have been investigated by means of X-ray techniques, the Cr–N(*H₃*) bond is slightly longer than the Cr–N(*CS*) bond. This can be also found in comparable Reineckates known from the literature.[4] The N–C bond lengths in the thiocyanate ligands are 1.159(2) for N1–C1 and 1.164(2) Å for N2–C2, the corresponding C–S bond lengths are 1.621(2) for C2–S2 and 1.622(2) Å for C1–S1, respectively. The averaged Cr–N–C bond angle is 175.3° and slightly lower than 180° for an expected end-on coordination of the thiocyanate ligand. This behavior is in accordance with published data.[4] Hydrogen bonding interactions are commonly found in Ionic Liquids as well as in known transition metal-based ILs.[14–17] The shortest H···S contact is formed in between two different Reineckate anions: N–H2···S1 with 2.661 Å. The longer H···S contact is formed between a methylene group and the Reineckate anion: C5–H5B···S2 with 2.904 Å. Bond lengths between atoms of the cation are within expected ranges.

Table 3. Selected bond lengths /Å and angles /° for $(EMIm)[Cr(NCS)_4(NH_3)_2]$ and $(PeMIm)[Cr(NCS)_4(NH_3)_2]$.

$(EMIm)[Cr(NCS)_4(NH_3)_2]$				$(PeMIm)[Cr(NCS)_4(NH_3)_2]$			
Anion atoms	bond length	*Cation* atoms	bond length	*Anion* atoms	bond length	*Cation* atoms	bond length
averaged Cr–N(*NCS*)	1.99	C4–N6	1.358(6)	*averaged* Cr–N(*NCS*)	2.00	C5–N7	1.359(3)
		C5–C6	1.282(8)			C5–N8	1.351(3)
averaged Cr–N(*NH₃*)	2.08	C4–N7	1.303(8)	*averaged* Cr–N(*NH₃*)	2.07	N7–C6	1.370(3)
		N6–C5	1.358(6)			N8–C7	1.366(3)
averaged N–C	1.15	N7–C6	1.35(1)	*averaged* N–C	1.16	C6–C7	1.356(3)
averaged C–S	1.62			*averaged* C–S	1.62		
atoms	bond angle	atoms	bond angle	atoms	bond angle	atoms	bond angle
Cr1–N1–C1	177.4(3)	N6–C4–N7	104.6(5)	Cr–N1–C1	170.8(2)	N7–C5–N8	107.7(2)
Cr1–N2–C2	167.7(2)	C4–N6–C5	108.0(3)	Cr–N2–C2	172.3(2)	C5–N7–C6	108.6(2)
Cr1–N3–C3	175.0(4)	C4–N7–C6	111.1(5)	Cr–N3–C3	172.9(2)	C5–N8–C7	108.4(2)
		N6–C5–C6	108.5(4)	Cr–N4–C4	174.8(2)	N7–C6–C7	107.1(2)
		N7–C6–C5	106.8(5)			N8–C7–C6	108.2(2)

$\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$ crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two formula units in the unit cell. Figure 3 shows the molecular structures of both the cation and Reineckate anion. Selected bond lengths and bond angles of the anion are given in Table 2. The averaged Cr–N(*CS*) bond length is 1.99 Å, the averaged Cr–N(*H_3*) bond length 2.06 Å. This is similar to the values found in $(n\mathrm{Bu}_4N)[Cr(NCS)_4(NH_3)_2]$. Interestingly, only one of the four dodecyl chains in the cation shows the most favorable staggered conformation for all carbon atoms within the alkyl chain (C29 to C40). This could be an important hint towards the question, why no liquid crystalline behavior is present in $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$.

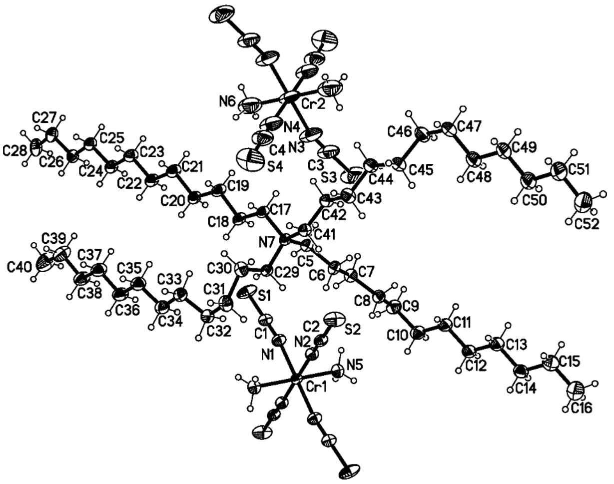

Figure 3. View of the molecular structures of the $\{(C_{12}H_{25})_4N\}^+$ cation and of the two symmetry independent $[Cr(NCS)_4(NH_3)_2]^-$ anions in crystals of $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$ with atom numbering scheme. Atomic displacement ellipsoids are shown at the 50 % probability level.

Figure 4 shows the molecular structures of the cation and the anion in the imidazolium-based Reineckate $(\mathrm{EMIm})[Cr(NCS)_4(NH_3)_2]$. Selected bond lengths and bond angles can be found in Table 3, which also has the values for $(\mathrm{PeMIm})[Cr(NCS)_4(NH_3)_2]$. The correct assignment of the orientation with respect to the allocation of the nitrogen atoms in the 1,2,3,4,5-pentamethylimidazolium cation in crystals of $(\mathrm{PeMIm})[Cr(NCS)_4(NH_3)_2]$ can be difficult due to possible disorder. Such disorder is known for example with the isoelectronic fragment $C_5Me_5^-$.[22] The correct assignment was established by applying known models from the literature.[23,24] Bond lengths and bond angles for the EMIm^+ cation and the PeMIm^+ cation are in accordance with published values for similar ILs. Figure 5 shows the arrangement of the molecular ions in $(\mathrm{PeMIm})[Cr(NCS)_4(NH_3)_2]$ with all H···S contacts, which are shorter than 2.90 Å. The shortest H···S contact is formed between N6–H5···S2 with 2.661 Å. From Figure 5 it can be seen that H···S contacts are not only present between the $(\mathrm{PeMIm})^+$ cation and the Reineckate anion, but also between different Reineckate anions themselves (e.g. N5–H3···S2···H5–N). This can be found also in the other three compounds.

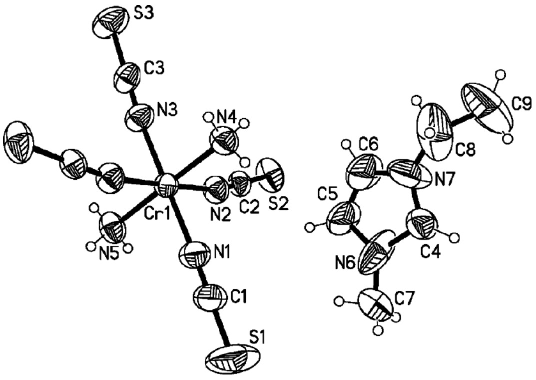

Figure 4. View of the molecular structures of the $(\mathrm{EMIm})^+$ cation and the $[Cr(NCS)_4(NH_3)_2]^-$ anion in crystals of $(\mathrm{EMIm})[Cr(NCS)_4(NH_3)_2]$ with atom numbering scheme. Atomic displacement ellipsoids are shown at the 50 % probability level.

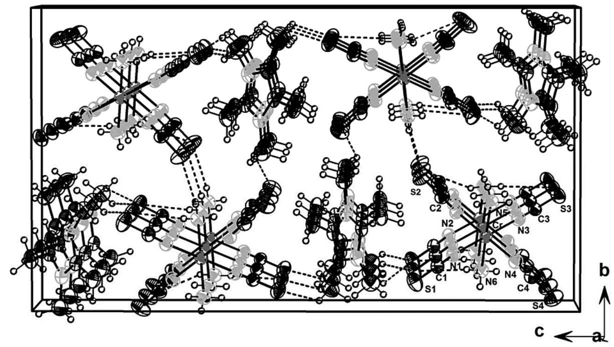

Figure 5. View of the unit cell content of $(\mathrm{PeMIm})[Cr(NCS)_4(NH_3)_2]$ with all C–H···S contacts, which are shorter than 2.90 Å in a view along the crystallographic *a* direction. Atomic displacement ellipsoids are shown at the 50 % probability level.

Experimental Section

Analysis and Spectroscopic Measurements

^{1}H NMR, and ^{13}C NMR spectra were recorded with a Bruker ARX 300 spectrometer. Spectra were calibrated with respect to the solvent signal ([D$_6$]DMSO: ^{1}H δ = 2.50; ^{13}C δ = 39.5 ppm). MIR spectra (500–4000 cm^{-1}) were recorded by using ATR technique with a Thermo Nicolet 380 FT-IR spectrometer. Elemental analyses for C, H, N, and S were obtained with a Flash EA 1112 NC Analyzer from CE Instruments (error ±0.5). UV/Vis spectra were recorded using a Perkin–Elmer Lambda 2 spectrometer with quartz cuvettes (Suprasil®, d = 10 mm). Melting points were determined by DSC measurements using a Mettler Toledo DSC823^e in the range of 0–400 °C with a heating rate of 10 K·min^{-1} (Ar atmosphere, Al crucible). All melting points are peak temperatures. Magnetic data were determined by means of ^{1}H NMR techniques (*Evans* method).[19,20] Molar susceptibilities were corrected by applying *Pascal* constants.[25] Effective magnetic moments μ_{eff}/μ_B are given by applying the *Langevin* equation.[26]

X-ray Structure Analysis

Ruby-red crystals of $(n\mathrm{Bu}_4N)[Cr(NCS)_4(NH_3)_2]$ (nBu = n-butyl), $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot H_2O$ ($C_{12}H_{25}$ = n-dodecyl), (EMIm)$[Cr(NCS)_4(NH_3)_2]$ (EMIm = 1-ethyl-3-methylimidazolium), and (PeMIm)$[Cr(NCS)_4(NH_3)_2]$ (PeMIm = 1,2,3,4,5-pentamethylimidazolium) were mounted on the tips of thin glass fibers for the single-crystal X-ray diffraction measurements. Data were collected on a Bruker–Nonius Apex X8 diffractometer equipped with a CCD detector. Measurements were done using monochromatic Mo-K_α radiation (λ = 0.71073 Å). Preliminary data of the unit cell were obtained from the reflex positions of 36 frames, measured in different directions of the reciprocal space. After completion of the data measurements the intensities were corrected for Lorentz, polarization, and absorption effects using the Bruker–Nonius software.[27] The structure solutions and refinements were done with the aid of the SHELX-97 program package.[28] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added on idealized positions and refined using riding models. Crystal data, data collection, and refinement parameters are collected in Table 1. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC-790229 for (n-Bu_4N)$[Cr(NCS)_4(NH_3)_2]$, CCDC-790230 for $\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$, CCDC-790231 for (EMIm)$[Cr(NCS)_4(NH_3)_2]$, and CCDC-809956 for (PeMIm)$[Cr(NCS)_4(NH_3)_2]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk.

Materials

Reinecke's salt, $(NH_4)[Cr(NCS)_4(NH_3)_2\cdot H_2O]$, was synthesized according to known procedures.[1,29] The Ionic Liquid precursors RMImX (RMIm = 1-alkyl-3-methylimidazolium, X = Cl, Br, I) were also prepared by applying published procedures.[32–34] 1,2,3,4,5-pentamethylimidazolium iodide (PeMImI) was synthesized according to ref.[23] Tetra-n-butylammonium bromide ($n$$Bu_4$NBr, Fluka, >99 %), tetra-n-dodecylammonium bromide ($(C_{12}H_{25})_4$NBr, Aldrich, >99 %), benzil (Aldrich, >98 %), benzaldehyde (Aldrich, >99.5 %), NH_4OAc (Aldrich, >98 %), KOH (VWR, >86 %), K_2CO_3 (Aldrich >99 %), and iodomethane (Aldrich, >99 %) were used as received without any further purification.

Synthesis of Lophine (2,4,5-Triphenyl-1H-imidazole)

Benzil (4.2 g, 20.0 mmol), NH_4OAc (5.4 g, 70.0 mmol) and freshly distilled benzaldehyde (2.2 g, 20.0 mmol) were mixed in a PTFE vessel and heated in a microwave oven over a period of 5 min at 800 W (T_{max} = 120 °C). The resulting solid was suspended in methanol, transferred to a mortar and well ground. The powder was finally recrystallized from methanol/acetone (2:1, 150 mL), yielding a slightly yellow solid. Yield: 5.4 g (87 %), mp. 273–275 °C (lit.[30] 276–277 °C). $C_{21}H_{16}N_2$ % (calcd.): C 85.1 (85.1); H 5.6 (5.4); N 9.3 (9.5). **^{1}H NMR** ([D$_6$]DMSO): δ = 7.27–8.06 (m, 15 H, phenyl), 12.48 (s, 1 H, N*H*). **^{13}C NMR** ([D$_6$]DMSO): δ = 125.0–131.0 (C_{phenyl}), 135.0, 137.0 (NH–*C*=*C*–N), 145.4 (NH–*C*=N). **IR:** $\tilde{\nu}_{max}$ = 3164, 3079, 3059, 3040, 2988, 2966, 2869, 2866, 2810, 2784, 2731, 1602, 1588, 1504, 1489, 1462, 1446, 1442, 1412, 1397, 1129, 1071, 966, 917, 843, 777, 766, 736, 713, 706, 698, 691, 674, 606 cm^{-1}.

Synthesis of DMLI (DML = 1,3-Dimethyllophinium = 1,3-Dimethyl-2,4,5-triphenylimidazolium)

Lophine (1.0 g, 3.4 mmol), K_2CO_3 (1.4 g, 10.1 mmol) and 50 mL iodomethane were heated to reflux in actonitrile (150 mL) overnight. The suspension was filtered, and the resulting filtrate was evaporated in vacuo, yielding an off-white powder. Yield 1.4 g (92 %), mp. 272 °C (lit.[31] 266 °C). $C_{23}H_{21}N_2I$ % (calcd.): C 60.9 (61.1); H 4.6 (4.7); N 6.0 (6.2). **^{1}H NMR** ([D$_6$]DMSO): δ = 7.48–7.94 (m, 15 H, phenyl), 3.53 (s, 6 H, N–*Me*). **^{13}C NMR** ([D$_6$]DMSO): δ = 121.9–132.4 (C_{phenyl}, Me–N–*C*=*C*–N), 144.1 (Me–N–*C*=N), 34.5 (N–*Me*). **IR:** $\tilde{\nu}_{max}$ = 3053, 3021, 2992, 2947, 1651, 1644, 1604, 1592, 1512, 1485, 1443, 1415, 1392, 1365, 1280, 1179, 1167, 1153, 1074, 1057, 1023, 995, 983, 940, 931, 859, 768, 753, 698, 668, 653 cm^{-1}.

Synthesis of $(R_4N)[Cr(NCS)_4(NH_3)_2]$ (R = n-Butylammonium, n-Dodecylammonium)

An aqueous solution of $(NH_4)[Cr(NCS)_4(NH_3)_2]\cdot H_2O$ (Reinecke's salt, 8 mmol in 100 mL water) was given to a stirred aqueous solution of the corresponding tetraalkylammonium precursor (8 mmol in 100 mL water). A pink solid precipitated immediately, which was filtered off, washed with water, diethyl ether and finally dried in air. Yield >80 %.

(n-Bu_4N)$[Cr(NCS)_4(NH_3)_2]$: Yield 84 %. mp. 155 °C. $C_{20}H_{42}CrN_7S_4$ (calcd.): C 42.9 (42.8); H 7.8 (7.6); N 17.0 (17.5). **IR:** $\tilde{\nu}_{max}$ = 3382, 3342, 3254, 3168, 2963, 2871, 2064 (ν_{CN}), 1603, 1487, 1464, 1377, 1243, 1179, 1151, 1107, 1029, 881, 848 (ν_{CS}), 804, 741, 649 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. μ_{eff}/μ_B = 3.89 (lit. μ_{eff}/μ_B = 3.80–3.95,[21] spin only: μ_{eff}/μ_B = 3.88, T = 25 °C, c = 3.21·10^{-2} mol·l^{-1}, ν_0 = 300 MHz, χ_{mol} = 6.35·10^{-3})

$\{(C_{12}H_{25})_4N\}[Cr(NCS)_4(NH_3)_2]\cdot 0.85H_2O$: Yield 88 %. mp. 48 °C. $C_{52}H_{106}CrN_7S_4\cdot H_2O$ (calcd.): C 60.6 (60.8); H 10.8 (10.6); N 9.0 (9.5). **IR:** $\tilde{\nu}_{max}$ = 3289, 3150, 2953, 2920, 2851, 2119, 2069 (ν_{CN}), 1600, 1482, 1465, 1402, 1377, 1259, 1235, 1184, 1092, 1026, 961, 915, 869, 836 (ν_{CS}), 802, 720, 674 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. μ_{eff}/μ_B = 3.85 (T = 25 °C, c = 0.13·10^{-2} mol·l^{-1}, ν_0 = 300 MHz, χ_{mol} = 6.22·10^{-3})

General Synthesis of (AlkMIm)-, (PeMIm)-, and (DML)$[Cr(NCS)_4(NH_3)_2]$ (AlkMIm = 1-Alkyl-3-methylimidazolium, PeMIm = 1,2,3,4,5-Pentamethylimidazolium, DML = 1,3-Dimethyllophinium)

An aqueous solution of $(NH_4)[Cr(NCS)_4(NH_3)_2]\cdot H_2O$ (Reinecke's salt, 8 mmol in 100 mL water) was given to a stirred aqueous solution of the corresponding IL precursor (8 mmol in 100 mL water). A pink solid precipitated immediately, which was filtered off, washed with water and finally dried in air. Yield >90 %.

(DMIm)$[Cr(NCS)_4(NH_3)_2]$ (DMIm = 1,3-Dimethylimidazolium): From DMImI.[32] Yield 93 %. mp. 201 °C. $C_9H_{15}N_8CrS_4$ (calcd.): C 25.8 (26.0); H 3.5 (3.6); N 26.6 (27.0) %. **IR:** $\tilde{\nu}_{max}$ = 3312, 3230, 3153, 2082 (ν_{CN}), 1602, 1572, 1260, 1170, 822 (ν_{CS}), 699, 620, 491 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. μ_{eff}/μ_B = 3.88 (T = 25 °C, c = 2.17·10^{-2} mol·l^{-1}, ν_0 = 300 MHz, χ_{mol} = 6.26·10^{-3})

(EMIm)$[Cr(NCS)_4(NH_3)_2]$ (EMIm = 1-Ethyl-3-methylimidazolium): From EMImBr.[33] Yield 91 %. mp. 186 °C. $C_{10}H_{17}N_8CrS_4$ (calcd.): C 27.6 (28.0); H 4.0 (4.0); N 25.9 (26.1) %. **IR:** $\tilde{\nu}_{max}$ = 3313, 3229, 3150, 2090 (ν_{CN}), 1602, 1567, 1260, 1166, 825 (ν_{CS}), 701, 493 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. μ_{eff}/μ_B = 3.84 (T = 25 °C, c = 3.23·10^{-2} mol·l^{-1}, ν_0 = 300 MHz, χ_{mol} = 6.41·10^{-3})

(i-PMIm)$[Cr(NCS)_4(NH_3)_2]$ (i-PMIm = 1-Methyl-3-isopropylimidazolium): From i-PMImI.[33] Yield 91 %. mp. 159 °C. $C_{11}H_{19}N_8CrS_4$

(calcd.): C 29.7 (29.8); H 4.2 (4.3); N 25.0 (25.3) %. **IR:** $\tilde{\nu}_{max}$ = 3303, 3226, 3151, 2083 (ν_{CN}), 1553, 1266, 1151, 828 (ν_{CS}), 764, 698, 492 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. $\mu_{eff}/\mu_B = 3.85$ (T = 25 °C, $c = 4.21 \cdot 10^{-2}$ mol·l^{-1}, ν_0 = 300 MHz, $\chi_{mol} = 6.22 \cdot 10^{-3}$)

(BMIm)[Cr(NCS)$_4$(NH$_3$)$_2$] (BMIm = 1-Butyl-3-methylimidazolium): From BMImCl.[34] Yield 91 %. mp. 122 °C. $C_{12}H_{21}N_8CrS_4$ (calcd.): C 31.3 (31.5); H 4.6 (4.6); N 24.1 (24.5) %. **IR:** $\tilde{\nu}_{max}$ = 3309, 3227, 3150, 2926, 2082 (ν_{CN}), 1560, 1262, 1158, 822 (ν_{CS}), 743, 693, 488 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. $\mu_{eff}/\mu_B = 3.83$ (T = 25 °C, $c = 2.75 \cdot 10^{-2}$ mol·l^{-1}, ν_0 = 300 MHz, $\chi_{mol} = 6.14 \cdot 10^{-3}$)

(HexMIm)[Cr(NCS)$_4$(NH$_3$)$_2$] (HexMIm = 1-Hexyl-3-methylimidazolium): From HexMImBr.[33] Yield 93 %. mp. 126 °C. $C_{14}H_{25}N_8CrS_4$ (calcd.): C 34.4 (34.6); H 5.1 (5.2); N 23.0 (23.1) %. **IR:** $\tilde{\nu}_{max}$ = 3372, 3302, 3231, 3154, 2928, 2080 (ν_{CN}), 1259, 1164, 823 (ν_{CS}), 690, 489 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. $\mu_{eff}/\mu_B = 3.90$ (T = 25 °C, $c = 0.79 \cdot 10^{-2}$ mol·l^{-1}, ν_0 = 250 MHz, $\chi_{mol} = 6.36 \cdot 10^{-3}$)

(PeMIm)[Cr(NCS)$_4$(NH$_3$)$_2$] (PeMIm = 1,2,3,4,5-Pentamethylimidazolium): From PeMImI.[23] Yield 95 %. mp. 198 °C. $C_{12}H_{21}N_8CrS_4$ (calcd.): C 31.3 (31.5); H 4.6 (4.6); N 24.5 (24.5) %. **IR:** $\tilde{\nu}_{max}$ = 3305, 3280, 3228, 3193, 3152, 2956, 2924, 2469, 2424, 2298, 2071 (ν_{CN}), 1650, 1601, 1544, 1439, 1390, 1369, 1252, 1073, 1033, 972, 830 (ν_{CS}), 704, 650, 578, 562 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. $\mu_{eff}/\mu_B = 3.85$ (T = 25 °C, $c = 2.99 \cdot 10^{-2}$ mol·l^{-1}, ν_0 = 300 MHz, $\chi_{mol} = 6.22 \cdot 10^{-3}$)

(DML)[Cr(NCS)$_4$(NH$_3$)$_2$] (DML = 1,3-Dimethyllophinium): From DMLI. Yield 95 %. mp. 172 °C. $C_{27}H_{27}N_8CrS_4$ (calcd.): C 50.2 (50.4); H 4.2 (4.2); N 17.5 (17.4); S 19.9 (19.9) %. **IR:** $\tilde{\nu}_{max}$ = 3368, 3350, 3320, 3232, 3219, 3187, 3139, 3054, 3029, 2951, 2912, 2056 (ν_{CN}), 1500, 1591, 1509, 1485, 1441, 1409, 1392, 1350, 1273, 1237, 1179, 1158, 1076, 1052, 1021, 963, 937, 926, 855 (ν_{CS}), 786, 770, 759, 697, 671 cm^{-1}. **UV/Vis** (acetone): λ_{max} = 396, 526 nm. $\mu_{eff}/\mu_B = 3.85$ (T = 25 °C, $c = 1.47 \cdot 10^{-2}$ mol·l^{-1}, ν_0 = 300 MHz, $\chi_{mol} = 6.21 \cdot 10^{-3}$)

Conclusions

A series of 9 different complex compounds with the $[Cr(NCS)_4(NH_3)_2]^-$ Reineckate anion and large organic cations was synthesized. Looking for the possibility to use such compounds as metal-containing Ionic Liquids the melting points were measured using the DSC technique. It turned out that all Reineckates with imidazolium based cations have melting points higher than 100 °C. Only the tetra-*n*-dodecylammonium Reineckate melts below 100 °C at 48 °C and can be considered an "Ionic Liquid". Single crystal X-ray structures of 4 selected compounds show that most likely H···S and H···N hydrogen bonds contribute to the relative high melting points of the imidazolium based Reineckates.

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