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# Low-Melting Imidazolium-Based Salts with the Paramagnetic Reineckate-Analogue Anion $[Cr(NCS)_4(bipy)]^-$ (bipy = 2,2′-Bipyridine): Syntheses, Properties, and Structures

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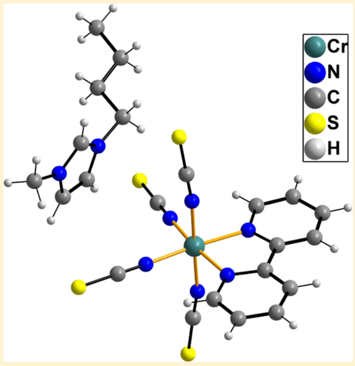
**ABSTRACT:** In order to investigate the potential ionic liquid properties of Reineckate-analogue materials, four new salts, consisting of the heteroleptic $[Cr(NCS)_4(bipy)]^-$ complex anion and imidazolium-based cations $A^+$ = 1-ethyl-3-methylimidazolium, 1-*n*-butyl-3-methylimidazolium, pentamethylimidazolium, and 1,3-dimethyl-2,4,5-triphenylimidazolium, were investigated. Their structures were established by single-crystal X-ray diffraction. The compounds are paramagnetic with effective magnetic moments in the range of those expected by the number of unpaired spins of the chromium(III) ion. All melting points are above 100 °C, which prevents us from calling these compounds "ionic liquids". Nevertheless, they are low for salts of this constitution and may be useful for molten salt reactions. Cyclic voltammetry measurements show no reversible electron-transfer steps.



## INTRODUCTION

Salts containing the diamminetetra(isothiocyanato)chromate(III) anion $[Cr(NCS)_4(NH_3)_2]^-$ (Reineckate anion) are among the earliest known chromium(III) complexes and have been known for more than 150 years.[1−5] Since then, Reineckates and related compounds have been developed as useful chemical actinometers, substances for quantum yield determinations, and compounds in charge-transfer photochemistry.[6−13] Reineckates have also been used in the analysis of medical products.[14] In addition, Reineckate-analogue complexes bearing $[Cr(NCS)_4L]^-$ anions [L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] have shown their ability in the analytical determination of alkaloids[15] and chloroquine (drug for malaria prevention and treatment),[16] in the analytical determination of bismuth,[17] and as promising magnetic charge-transfer salts.[18] Recently, we have reported on a series of imidazolium-based Reineckates in order to investigate their properties with respect to ionic liquids (ILs).[19]

ILs, salts 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 conductivities.[20−22] Some transition-metal-based ILs (magnetic ILs) exhibit interesting magnetic properties in addition.[23−25]

In this contribution, we report on the syntheses, properties, and structures of a series of imidazolium-based salts with Reineckate-analogue anions $[Cr(NCS)_4(bipy)]^-$. Four new Reineckate-analogue compounds with the $[Cr(NCS)_4(bipy)]^-$ anion and the imidazolium-based cations EMIm (1-ethyl-3-methylimidazolium; **1**), $^n$BMIm (1-*n*-butyl-3-methylimidazolium; **2**), PeMIm (pentamethylimidazolium; **3**), and DML (1,3-dimethyllophinium or 1,3-dimethyl-2,4,5-triphenylimidazolium; **4**) were synthesized and investigated. The crystal and molecular structures were determined by single-crystal X-ray diffraction (XRD). Magnetic data at room temperature of all substances were obtained using NMR techniques. The temperature dependence of the magnetism was measured for (EMIm)$[Cr(NCS)_4(bipy)]$ by means of a Physical Property Measurement System (PPMS) magnetometer in the temperature range of 10−300 K. Furthermore, cyclic voltammetry (CV) measurements and differential scanning calorimetry (DSC) measurements were performed.

## EXPERIMENTAL SECTION

**Materials.** All commercially available starting materials were obtained from Sigma-Aldrich. Their stated purity was at least 99%. They were used without further purification or drying. 1-Ethyl-3-methylimidazolium bromide (EMImBr) and 1-*n*-butyl-3-methylimidazolium bromide ($^n$BMImBr) were synthesized according to known procedures.[26]

Elem anal. Found (calcd) for EMImBr ($C_6H_{11}N_2Br$): C, 37.85 (37.72); H, 6.04 (5.80); N, 14.48 (14.66). Mp: 77 °C (lit.[27] 77 °C). $^1$H NMR (DMSO-$d_6$): $\delta$ 1.48 (t, 3H, Me), 4.00 (s, 3H, N−Me), 4.29 (q, 2H, N−$CH_2$−), 7.56 (s, 2H, N−CH−CH−N), 10.17 (s, 1H, N−CH−N). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 15.8 (Me), 36.7 (N-Me), 45.3 (N−$CH_2$−), 122.1 (N−CH−CH−N), 123.8 (N−CH−CH−N), 136.9 (N−CH−N).

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Table 1. Crystal Data and Structure Refinement Parameters for A[Cr(NCS)$_4$(bipy)]·$x$CH$_3$COCH$_3$ [A = EMIm, $x$ = 0 (1); $^n$BMIm, $x$ = 0 (2); PeMIm, $x$ = 1 (3); DML, $x$ = 1.5 (4)]

| | A group | | | |
|---|---|---|---|---|
| | EMIm | $^n$BMIm | PeMIm | DML |
| formula | $C_{20}H_{19}N_8CrS_4$ | $C_{22}H_{23}N_8CrS_4$ | $C_{25}H_{29}N_8OCrS_4$ | $C_{41.5}H_{38}N_8O_{1.5}CrS_4$ |
| fw (g/mol) | 551.67 | 579.72 | 637.80 | 853.04 |
| cryst syst | triclinic | triclinic | orthorhombic | monoclinic |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $Pbca$ (No. 61) | $C2/c$ (No. 15) |
| $Z$ | 2 | 2 | 8 | 8 |
| $a$ (Å) | 8.1787(1) | 8.6614(2) | 16.6243(3) | 26.6517(9) |
| $b$ (Å) | 10.5510(2) | 9.1172(2) | 16.7415(2) | 10.8706(3) |
| $c$ (Å) | 15.7910(3) | 17.1404(4) | 22.2693(3) | 29.0065(8) |
| $\alpha$ (deg) | 96.333(1) | 89.610(1) | 90 | 90 |
| $\beta$ (deg) | 91.635(1) | 83.295(1) | 90 | 97.947(2) |
| $\gamma$ (deg) | 106.288(1) | 86.654(2) | 90 | 90 |
| $V$ (Å$^3$) | 1297.46(4) | 1341.99(5) | 6197.9(2) | 8323.1(4) |
| $\rho_{calc}$ (g/cm$^3$) | 1.412 | 1.435 | 1.367 | 1.361 |
| $\mu$ (mm$^{-1}$) | 0.787 | 0.765 | 0.672 | 0.520 |
| reflns colld | 17287 | 20937 | 39851 | 82181 |
| reflns indep | 6802 | 6051 | 8909 | 12191 |
| no. of param | 298 | 316 | 352 | 506 |
| GOF on $F^2$ | 1.010 | 0.998 | 1.013 | 1.034 |
| R1/wR2$^{a,b}$ [$I \geq 2\sigma(I)$] | 0.0478/0.1115 | 0.0513/0.1121 | 0.0359/0.0944 | 0.0505/0.1130 |
| R1/wR2$^{a,b}$ (all data) | 0.1001/0.1347 | 0.1062/0.1280 | 0.0521/0.1052 | 0.0904/0.1285 |
| weighting A/B$^b$ | 0.0521/0.3419 | 0.0596/0.0 | 0.0544/2.9838 | 0.0496/10.8795 |

$^a$R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $(\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)])^{1/2}$. $^b$$w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$; $P = (F_o^2 + 2F_c^2)/3$.

Elem anal. Found (calcd) for $^n$BMImBr ($C_8H_{15}N_2Br$): C, 43.98 (43.85); H, 7.01 (6.90); N, 12.98 (12.78). Mp: 78 °C (lit.[27] 78 °C). $^1$H NMR (DMSO-$d_6$): $\delta$ 0.85 (t, 3H, Me), 1.25 (m, 2H, −CH$_2$−Me), 1.81 (m, 2H, −CH$_2$−), 4.02 (s, 3H, N−Me), 4.24 (t, 2H, N−CH$_2$−), 7.48 (s, 1H, N−CH−CH−N), 7.60 (s, 1H, N−CH−CH−N), 10.24 (s, 1H, N−CH−N). $^{13}$C NMR (CDCl$_3$): $\delta$ 13.5 (Me), 19.5 (CH$_2$−Me), 32.2 (−CH$_2$−), 36.8 (N−Me), 49.9 (N−CH$_2$−), 122.3 (N−CH−CH−N), 123.9 (N−CH−CH−N), 137.3 (N−CH−N).

Pentamethylimidazolium iodide (PeMImI) and 1,3-dimethyl-2,4,5,-triphenylimidazolium iodide (1,3-dimethyllophinium iodide, DMLI) were synthesized according to published procedures.[19,28]

K$_3$[Cr(NCS)$_6$], which was used as the starting material for the synthesis of the title compounds, was prepared according to ref 29. It is a hygroscopic solid. Elem anal. Found (calcd) for K$_3$[Cr(NCS)$_6$]·0.5H$_2$O): C, 13.71 (13.68); H, 0.17 (0.19); N, 15.98 (15.95). IR (cm$^{-1}$, $\nu_{max}$): 2098 ($\nu_{CN}$), 1698, 823 ($\nu_{CS}$), 479. UV/vis ($\lambda_{max}$/nm in acetone, 23 °C): 418, 553. $\mu_{eff}/\mu_B$ = 3.97 ($T$ = 25 °C, $c$ = 0.75 × 10$^{-2}$ mol/L, $\nu_0$ = 300 MHz, and $\chi_{mol}$ = 6.61 × 10$^{-3}$).

K[Cr(NCS)$_4$(bipy)] was prepared from K$_3$[Cr(NCS)$_6$] according to ref 30.

Elem anal. Found (calcd) for K[Cr(NCS)$_4$(bipy)] ($C_{14}H_8N_6CrKS_4$): C, 35.23 (35.06); H, 1.69 (1.68); N, 16.95 (17.52); S, 26.92 (26.74). IR (cm$^{-1}$, $\nu_{max}$): 3091, 2083 ($\nu_{CN}$), 1609, 1600, 1468, 1444, 1037, 822 ($\nu_{CS}$), 767, 729, 666, 486, 451, 420. UV/vis ($\lambda_{max}$/nm in acetone, 23 °C): 388, 443 (shoulder), 550. $\mu_{eff}/\mu_B$ = 3.95 ($T$ = 25 °C, $c$ = 0.76 × 10$^{-2}$ mol/L, $\nu_0$ = 300 MHz, and $\chi_{mol}$ = 6.54 × 10$^{-3}$).

**General Synthesis of the (Imidazolium)[Cr(NCS)$_4$(bipy)] Compounds.** A total of 2.0 mmol of the appropriate IL precursor halide is added to 100 mL of an acetonic solution of 2.0 mmol of K[Cr(NCS)$_4$(bipy)]. The resulting solution is refluxed for an additional 2 h in order to complete cation exchange and potassium halide precipitation. The red solution is filtered, the solvent is evaporated, and the resulting residue is thoroughly washed with a mixture of ethyl acetate/diethyl ether (1:1). Final drying in a drying oven at 60 °C leads to ruby-red solids. Yield: >90%.

*(EMIm)[Cr(NCS)$_4$(bipy)].* From EMImBr. Yield: 96%. Mp: 196 °C. Elem anal. Found (calcd) for $C_{20}H_{19}N_8CrS_4$: C, 43.30 (43.54); H, 3.46 (3.47); N, 20.38 (20.31); S, 24.23 (23.25). IR (cm$^{-1}$, $\nu_{max}$): 3108, 3078, 2075 ($\nu_{CN}$), 1608, 1600, 1565, 1445, 1167, 1034, 819 ($\nu_{CS}$), 765, 730, 481, 420. UV/vis ($\lambda_{max}$/nm in acetone, 23 °C): 440 (shoulder), 543. $\mu_{eff}/\mu_B$ = 3.93 ($T$ = 25 °C, $c$ = 1.13 × 10$^{-2}$ mol/L, $\nu_0$ = 300 MHz, and $\chi_{mol}$ = 5.99 × 10$^{-3}$).

*($^n$BMIm)[Cr(NCS)$_4$(bipy)].* From $^n$BMImBr. Yield: 98%. Mp: 172 °C. Elem anal. Found (calcd) for $C_{22}H_{23}N_8CrS_4$: C, 45.75 (45.58); H, 3.92 (4.00); N, 18.86 (19.33); S, 21.86 (22.12). IR (cm$^{-1}$, $\nu_{max}$): 3106, 3079, 2069 ($\nu_{CN}$), 1608, 1599, 1563, 1442, 1169, 1032, 823 ($\nu_{CS}$), 768, 483, 423. UV/vis ($\lambda_{max}$/nm in acetone, 23 °C): 440 (shoulder), 544. $\mu_{eff}/\mu_B$ = 3.89 ($T$ = 25 °C, $c$ = 0.60 × 10$^{-2}$ mol/L, $\nu_0$ = 300 MHz, and $\chi_{mol}$ = 6.33 × 10$^{-3}$).

*(PeMIm)[Cr(NCS)$_4$(bipy)].* From PeMImI. Yield: 91%. Mp: 293 °C. Elem anal. Found (calcd) for $C_{22}H_{23}N_8CrS_4$·0.5H$_2$O: C, 44.85 (44.88); H, 3.85 (4.11); N, 18.57 (19.03); S, 21.60 (21.79). IR (cm$^{-1}$, $\nu_{max}$): 3108, 3075, 2951, 2917, 2418, 2350, 2294, 2095 ($\nu_{CN}$), 2047, 1650, 1600, 1563, 1537, 1494, 1468, 1441, 1370, 1318, 1307, 1271, 1237, 1222, 1168, 1105, 1060, 1046, 1033, 969, 829 ($\nu_{CS}$), 772, 729, 664, 650, 578, 561. UV/vis ($\lambda_{max}$/nm in acetone, 23 °C): 440 (shoulder), 543. $\mu_{eff}/\mu_B$ = 3.87 ($T$ = 25 °C, $c$ = 0.36 × 10$^{-2}$ mol/L, $\nu_0$ = 300 MHz, and $\chi_{mol}$ = 6.27 × 10$^{-3}$).

*(DML)[Cr(NCS)$_4$(bipy)].* From DMLI. Yield: 99%. Mp: 198 °C. Elem anal. Found (calcd) for $C_{37}H_{29}N_8CrS_4$·H$_2$O: C, 56.67 (56.69); H, 3.73 (3.99); N, 14.15 (14.29); S, 16.46 (16.36). IR (cm$^{-1}$, $\nu_{max}$): 3114, 3054, 2952, 2913, 2093 ($\nu_{CN}$), 2052, 1601, 1572, 1564, 1557, 1538, 1505, 1494, 1444, 1413, 1353, 1314, 1276, 1244, 1174, 1161, 1122, 1108, 1060, 1033, 1023, 999, 968, 927, 856 ($\nu_{CS}$), 803, 786, 759, 728, 698, 663, 650,646, 620. UV/vis ($\lambda_{max}$/nm in acetone, 23 °C): 440 (shoulder), 543. $\mu_{eff}/\mu_B$ = 3.88 ($T$ = 25 °C, $c$ = 0.34 × 10$^{-2}$ mol/L, $\nu_0$ = 300 MHz, and $\chi_{mol}$ = 6.32 × 10$^{-3}$).

**Physicochemical Characterization and Spectra.** $^1$H and $^{13}$C NMR spectra were recorded using a Bruker ARX 300 spectrometer. Spectra were calibrated with respect to the solvent signal (DMSO-$d_6$: $^1$H, $\delta$ 2.50; $^{13}$C, $\delta$ 39.5).

MIR spectra (500−4000 cm$^{-1}$) were recorded by using the ATR technique attached to 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.

UV/vis spectra were recorded using a PerkinElmer Lambda 2 spectrometer with sample holders of 10 mm thickness made from quartz (Suprasil).

Melting points were determined by DSC measurements using a Mettler Toledo DSC823$^e$ instrument in the range of 0−400 °C with a heating rate of 10 K/min (under a nitrogen atmosphere, aluminum crucible). All melting points are peak temperatures.

Thermogravimetric (TG) measurements were performed on a Netzsch STA 449 F3 Jupiter device in the temperature ranges of 30−1000 °C (dynamic) and 30−200/250 °C (isothermal) with heating rates of 20 K/min (dynamic) and 5 K/min (isothermal), respectively, in a compressed-air atmosphere.

Magnetic data at room temperature were determined by means of $^1$H NMR techniques (Evans method).[31] Molar susceptibilities were corrected by applying Pascal constants.[32] Effective magnetic moments $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ are obtained by applying the Langevin equation.[33]

Temperature-dependent magnetic data of **1** were measured using a PPMS (Quantum Design Inc.) in a magnetic field of 500 Oe. The measuring temperature range was 300−10 K. The weight of the sample was 78.99 mg.

For the electrochemical, CV experiments, a three-electrode cell design (Gamry) was used. Platinum was used as the working and counter electrodes and a saturated calomel electrode (SCE) as the reference electrode. The scan rate was set at 100 mV/s. One scan included three cycles. The samples were dissolved in a 0.1 mol/L dried acetonitrile/tetrabutylammonium tetrafluoroborate solution. The concentration of the samples used for the measurements was 5 mmol/L. Prior to each measurement, the solutions were degassed for about 15 min with argon. Ferrocene was used as an internal reference.

**X-ray Structure Analysis.** Crystals of A[Cr(NCS)$_4$(bipy)]·$x$C$_3$H$_6$O (A = EMIm, $x$ = 0; $^n$BMIm, $x$ = 0; PeMIm, $x$ = 1; DML, $x$ = 1.5) with a intense ruby-red color were mounted on the tips of thin glass fibers for single-crystal XRD measurements. Data were collected using a Bruker-Nonius Apex X8 diffractometer equipped with a CCD detector. Monochromatic Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) was used. For all data collections, preliminary data of the unit cell dimensions were obtained from the reflex positions of 36 frames, measured in three different directions of reciprocal space. After completion of the data measurements, the measured reflex intensities were corrected for Lorentz, polarization, and absorption effects using the Bruker-Nonius software.[34] The structure solutions and refinements were done with the aid of the *SHELX-97* program package.[35] 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): 854028 for ($^n$BMIm)[Cr(NCS)$_4$(bipy)], 854029 for (DML)[Cr(NCS)$_4$(bipy)]·1.5C$_3$H$_6$O, 854030 for (EMIm)[Cr(NCS)$_4$(bipy)], and 854031 for (PeMIm)[Cr(NCS)$_4$(bipy)]·C$_3$H$_6$O.

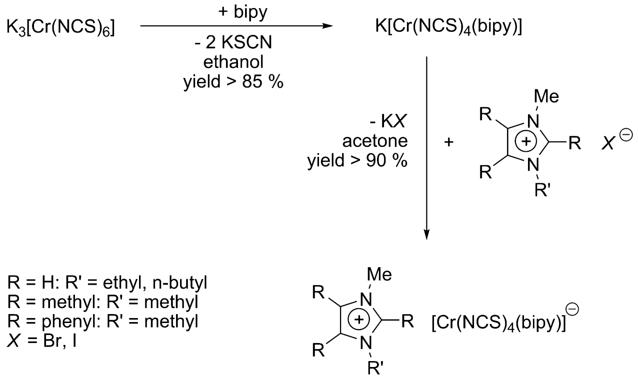
These data can be obtained free of charge via http://www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K. [fax (+44)-1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

## ■ RESULTS AND DISCUSSION

**Synthesis.** The synthesis of imidazolium-based salts containing the Reineckate-analogue anion [Cr(NCS)$_4$(bipy)]$^-$ can be achieved easily by metathesis reactions between the potassium salt K[Cr(NCS)$_4$(bipy)] and alkylated imidazolium halides in high yields (>90%) according to Scheme 1.

In order to obtain the products in high yield, it is important to choose a solvent that dissolves the title compounds well and precipitates the side products completely. The precursor potassium salts are accessible from K$_3$[Cr(NCS)$_6$] and bipy in ethanolic solutions.[29] All compounds are distinguished by a deep-red color in crystalline form. They are insoluble in water but soluble in organic solvents, especially in acetone and acetonitrile. Suitable single crystals for X-ray measurements were obtained within a few days by slow evaporation of the solvent from an acetonic solutions of the salts at ambient temperature and pressure.

**Scheme 1. Reaction Sequence for the Synthesis of the Imidazolium-Based Salts Containing the Reineckate-Analogue Anion [Cr(NCS)$_4$(bipy)]$^-$**



**Crystal Structures.** Single crystals of all four title compounds were grown and subjected to XRD experiments in order to get detailed structural information. Crystallographic data are given in Table 1. Selected atom distances and bond angles are listed in Tables 2 and 3.

All four compounds contain isolated [Cr(NCS)$_4$(bipy)]$^-$ anions, imidazolium-based cations, and, in the case of **3** and **4**, cocrystallized solvent molecules (acetone). Thermal ellipsoid plots of the ion pairs of each compound are shown in Figures 1−4.

The complex anions of all four compounds derive from the Reineckate anion, [Cr(NCS)$_4$(NH$_3$)$_2$]$^-$, by replacement of the NH$_3$ ligands by bipy. As in the parent Reineckate anion, the chromium(III) ion is octahedrally coordinated by six nitrogen-donor functions, of which four belong to the NCS groups and the remaining to the bipy ligand. All NCS$^-$ ligands are bonded to the chromium(III) ion through the nitrogen atom. Therefore, the title compounds are isothiocyanato complexes.

The Cr−N(NCS) bond lengths are within the anion range from 1.977 Å (**1**) to 2.004 Å (**3**). They are shorter than the Cr−N(bipy) bond lenghts in all four compounds, which have been investigated by means of X-ray techniques in this study and are found to be between 2.064 and 2.071 Å; see Table 2. A similar observation has been made for compounds with imidazolium-based cations and the parent [Cr(NCS)$_4$(NH$_3$)$_2$]$^-$ or the [Cr(NCS)$_4$(phen)]$^-$ anion[19,36] and others; see, for example, ref 37 and references cited therein.

The average N−C bond lengths in the thiocyanato ligand range from 1.147 Å (**3**) to 1.166 Å (**2**). These values are within the expected range.

Contrary to the parent Reineckate anion, where the two NH$_3$ ligands are arranged trans, in **1**−**4**, as well as in the comparable [Cr(NCS)$_4$(phen)]$^-$ anion,[36] the nitrogen-donor functions of the organic chelate ligand are necessarily coordinated cis to the metal ion. Because of the relatively constrained bite angle of the organic ligand, the (bipy)N···Cr···N(bipy) angle is significantly smaller than 90° (around ~78°; see Table 3) and, consequently, the (bipy)N−Cr−(NCS) trans to each other smaller than 180° (around ~178°). Therefore, the coordination environment around the chromium(III) ions deviates from the ideal $O_h$. Nevertheless, the NCS groups are very close to linear,

**Table 2. Selected Atom Distances (Å) for the Complex Anions in A[Cr(NCS)$_4$(bipy)] (A = EMIm, $^n$BMIm, PeMIm, and DML)**

| bond | | *d*, Å | | | |
|---|---|---|---|---|---|
| | | EMIm | $^n$BMIm | PeMIm | DML |
| Cr1−NCS: | Cr1−N1 | 1.972(3) | 1.978(3) | 2.007(2) | 2.001(2) |
| | Cr1−N2 | 1.984(3) | 1.984(3) | 1.996(2) | 1.980(2) |
| | Cr1−N3 | 1.973(2) | 1.984(3) | 2.020(2) | 1.990(2) |
| | Cr1−N4 | 1.980(3) | 1.978(3) | 1.992(2) | 1.999(2) |
| average Cr1−N(NCS) | | 1.977 | 1.981 | 2.004 | 1.993 |
| Cr1−N(bipy): | Cr1−N5 | 2.065(2) | 2.066(2) | 2.069(2) | 2.073(2) |
| | Cr1−N6 | 2.063(2) | 2.062(3) | 2.063(2) | 2.068(2) |
| average Cr1−N(bipy) | | 2.064 | 2.064 | 2.066 | 2.071 |
| average N−C | | 1.153 | 1.166 | 1.147 | 1.154 |
| average C−S | | 1.609 | 1.618 | 1.629 | 1.620 |

**Table 3. Selected Bond Angles (deg) for the Complex Anions in A[Cr(NCS)$_4$(bipy)] (A = EMIm, $^n$BMIm, PeMIm, and DML)**

| angle | *ω*, deg | | | |
|---|---|---|---|---|
| | EMIm | $^n$BMIm | PeMIm | DML |
| N5−Cr1−N6 | 78.19(9) | 78.2(1) | 78.57(5) | 78.12(7) |
| average (bipy)N−Cr−(NCS) (trans) | 172.4 | 171.5 | 172.2 | 171.3 |
| (SCN)N−Cr1−N(NCS) (trans) | 177.1(1) | 179.0(1) | 177.12(6) | 178.78(8) |
| average N−C−S | 179.1 | 178.5 | 179.5 | 178.9 |
| range Cr1−N−C | 88.5−94.5 | 87.7−94.6 | 87.7−95.1 | 88.6−95.2 |
| average Cr1−N−C | 91.0 | 91.1 | 91.8 | 91.1 |

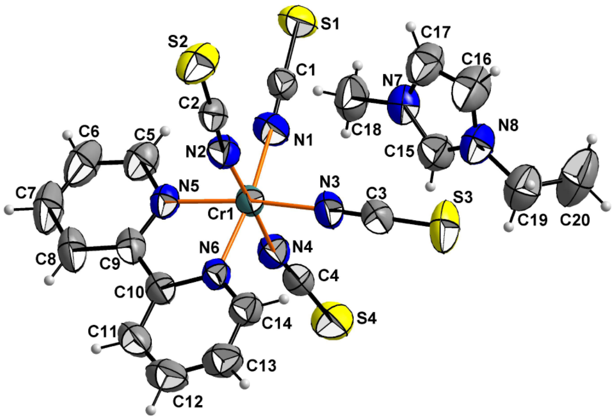


**Figure 1.** Structure of the cation−anion pair in crystals of **1** with an atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

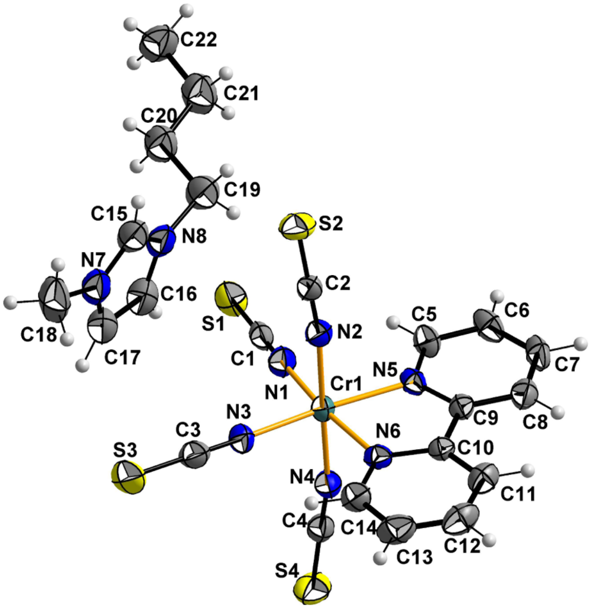


**Figure 2.** Structure of the cation−anion pair in crystals of **2** with an atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

as expected, and are oriented close to perpendicular to the rectangular of nitrogen atoms, which are arranged cis to each NCS group. The bond lengths and angles between atoms of the cations are within the expected ranges.

Because the hydrogen atom attached to the carbon atom between the two nitrogen atoms of the EMIm and $^n$BMIm cations is more acidic than all of the other hydrogen atoms within the compounds, it is eligible for hydrogen bonding. Possible donor atoms are the sulfur atoms of the complex anions. The shortest H···S distances are 2.921 Å in **1** and 2.955 Å in **2**, which indicate weak hydrogen bonding. For packing of the ions, a parallel arrangement of the biyridine as well as the phenyl rings of the DML units in **4** seems to be important. Exemplarily, packing plots of **2** and **4** are shown in Figures 5 and 6.

**Physicochemical Properties and Spectra.** *IR Spectra.* The IR data in the region from 4000 to 500 cm$^{-1}$ of all compounds are listed in the Experimental Section. IR spectra of imidazolium-based compounds have been discussed in the literature in detail.[38] 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 band in this region, which has been assigned to hydrogen bonding.[38] With this hydrogen atom being absent in the compounds A[Cr(NCS)$_4$(bipy)] (A = PeMIm and DML), the respective hydrogen bonding and corresponding band in the IR spectra are absent. The region 2000−500 cm$^{-1}$ is dominated by internal vibrations of the imidazolium ring and is employed as

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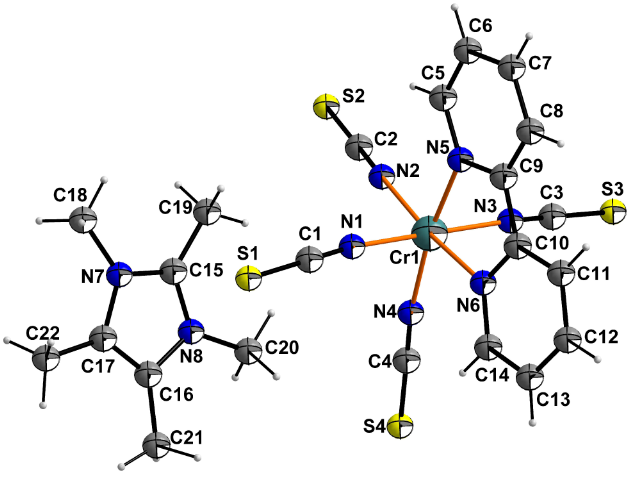

**Figure 3.** Structure of the cation−anion pair in crystals of **3** with an atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

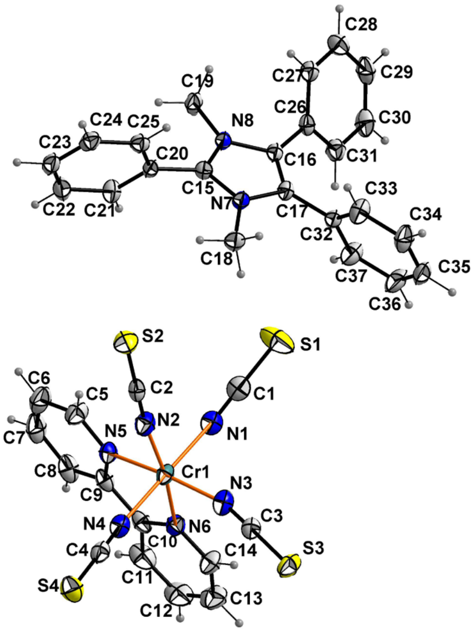

**Figure 4.** Structure of the cation−anion pair in crystals of **4** with an atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

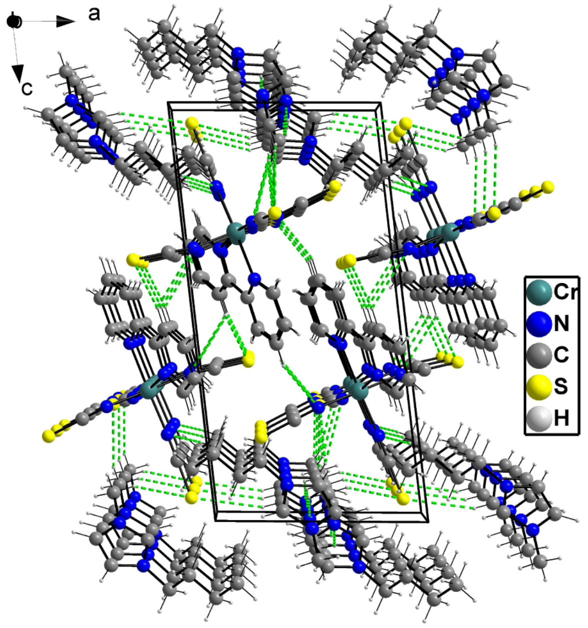

**Figure 5.** View of an extended part of the unit cell of **2** along the crystallographic *b* direction with hydrogen bonds drawn as dotted lines.

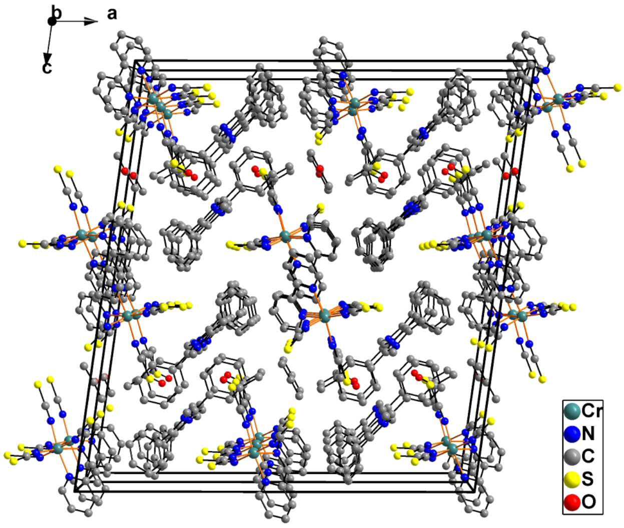

**Figure 6.** View of an extended part of the unit cell of **4** along the crystallographic *b* direction.

the fingerprint domain for the presence of the planar imidazolium ring. IR spectra of compounds containing the Reineckate-analogue anion $[Cr(NCS)_4(bipy)]^-$ are reported in the literature.[30,39] The CN stretching frequencies ($\nu_{CN}$) are located between 2080 and 2100 $cm^{-1}$ and the CS stretching frequencies ($\nu_{CS}$) between 820 and 850 $cm^{-1}$ and are in accordance with published values.[7,30,39]

*Electronic Spectra.* Data of the electronic spectra in the region from 190 to 1000 nm for all compounds in an acetonic solution at room temperature are given in the Experimental Section. Octahedrally coordinated chromium(III) complexes exhibit two spin-allowed transitions in the visible region, which are characterized by $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$. In addition, there is a third transition at shorter wavelength, which is often interfered by charge-transfer bands and characterized by $^4T_{1g}(P) \leftarrow {}^4A_{2g}$. Investigations of electronic spectra of compounds containing the Reineckate-analogue anion $[Cr(NCS)_4(bipy)]^-$ are reported in the literature.[30,39,40] The charge-transfer band at 388 nm for $K[Cr(NCS)_4(bipy)]$ and the wavelengths of the $^4T_{2g} \leftarrow {}^4A_{2g}$ (540−550 nm) and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ (440−445 nm) transitions are nearly independent of the choice of the cation in an acetonic solution and in accordance with reported values.[30,39,40]

*Thermal Properties.* In order to investigate the ability of counting the title compounds to the chemical subclass of ILs, thermal data have been measured using TG and DSC techniques. Melting points were detected as endothermic peaks in the DSC experiments above 100 °C. All melting points are listed in the Experimental Section.

All detected melting points are higher than those in the corresponding imidazolium-based Reineckates with ammonia ligands, $[Cr(NCS)_4(NH_3)_2]^-$, and the same imidazolium-based cations.[19] The melting points decrease slightly with increasing alkyl chain length from ethyl to *n*-butyl in the imidazolium-based cation from 196 °C in (EMIm)$[Cr(NCS)_4(bipy)]$ to 172 °C in ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$.

The melting points of the four compounds are above the arbitrarily chosen limit for ILs. Therefore, they can be described as low melting salts. It is interesting to note that those compounds in which the most acidic hydrogen atom in the imidazolium ring between the two nitrogen atoms is exchanged by either a methyl or a phenyl substituent in the compounds (PeMIm)- or (DML)$[Cr(NCS)_4(bipy]$ do not have lower but higher melting points. The highest melting point is found for (PeMIm)$[Cr(NCS)_4(bipy)]$ because of the high symmetry of the pentamethylimidazolium cation. This behavior is also found in other known PeMIm-containing systems.[28,41]

Additional TG analyses were done to obtain further thermal stability values. The decomposition curves of A$[Cr(NCS)_4(bipy)]$ (A = EMIm, $^{n}$BMIm, PeMIm, and DML) in air and exemplarily in a nitrogen atmosphere for ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$ in the temperature range of 30−1000 °C are depicted in Figure 7.

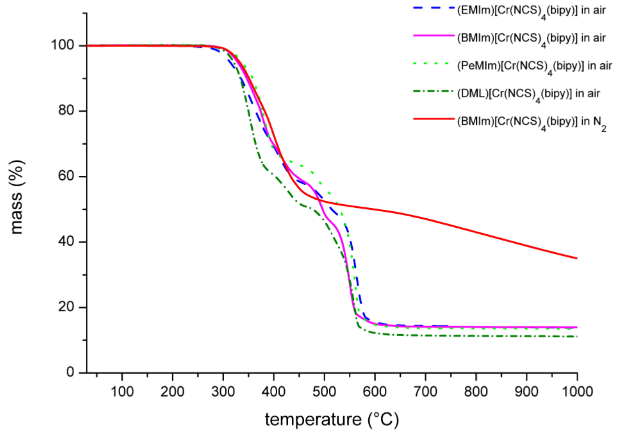

**Figure 7.** TG curves of A$[Cr(NCS)_4(bipy)]$ (A = EMIm, $^{n}$BMIm, PeMIm, and DML) in the temperature range of 30−1000 °C in compressed-air and nitrogen atmospheres exemplarily for ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$.

From Figure 7, it can be seen that decomposition of all four compounds in air starts at 300 °C and follows complex pathways, leaving $Cr_2O_3$ as a green residual powder starting from 600 °C (residual masses for A$[Cr(NCS)_4(bipy)]$ in air [theoretical]: A = EMIm, 13.8% [13.8%]; A = $^{n}$BMIm, 13.8% [13.1%]; A = PeMIm, 13.3% [13.1%]; A = DML, 11.0% [9.9%]). Decomposition of ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$ in a nitrogen atmosphere starts at 300 °C, which closely resembles the values obtained in air, leaving a residual mass of 35.0% at 1000 °C. This value does not result from a straight horizontal, so it cannot be attributed to a final residual product, e.g., $Cr_2S_3$ (17.3%) or probable CrN (11.4%).

Figure 8 shows additional isothermal TG curves exemplarily for the lowest melting substance ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$ (mp 172 °C) in a compressed-air atmosphere over a longer period of time at 200 °C (6 h) and 250 °C (12 h).

At 200 °C even after 6 h of heating, no considerable mass loss can be detected, leaving a residual mass of 99.5%. At 250 °C, a residual mass of approximately 80.5% after a thermal treatment of 12 h can be detected, even though the decomposition rate at 250 °C can be considered as low to moderate with 1.3%/h in the first 6 h and 1.8%/h in the last 6 h of measurement. The mass loss of 19.5% can be attributed to partial loss of the bipy ligand from the complex anion (theoretical mass loss 27.0%). From Figure 8, it is obvious that the rate of decomposition of ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$ is highly dependent on the chosen temperature, and it can be concluded that ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$ could be a suitable candidate for molten salt reactions below 250 °C, at least for reaction time periods up to 6 h, not only under inert gas but also in air.

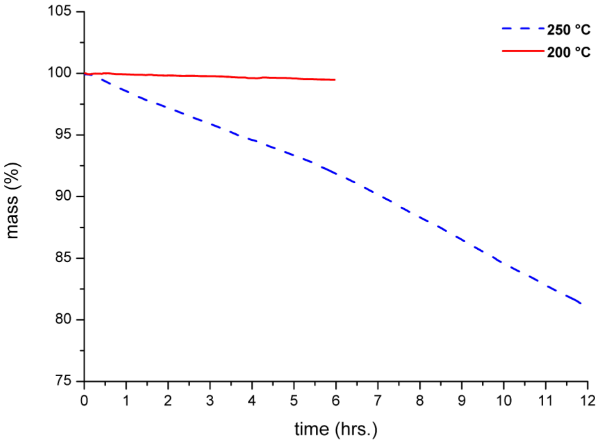

**Figure 8.** Isothermal TG curves of ($^{n}$BMIm)$[Cr(NCS)_4(bipy)]$ at 200 and 250 °C in a compressed-air atmosphere.

*Magnetic Properties.* The magnetic properties at room temperature of all complex salts have been determined in solution using NMR techniques by applying the Evans method.[31] All complexes display similar magnetic properties. They are paramagnetic with effective magnetic moments in the range of $\mu_{eff}$ = 3.76−3.93 $\mu_B$ at 25 °C (spin-only high-spin chromium(III): $\mu_{eff}$ = 3.87 $\mu_B$). These values resemble closely those of related compounds with the $[Cr(NCS)_4(bipy)]^-$ anion, for example, K$[Cr(NCS)_4(bipy)]$ ($\mu_{eff}$ = 3.82 $\mu_B$)[30] or $[Ce(phen)_4][Cr(NCS)_4(bipy)]$ ($\mu_{eff}$ = 3.82 $\mu_B$).[42] In addition, temperature-dependent magnetic investigations were made with a PPMS magnetometer in the temperature range of 10−300 K of (EMIm)$[Cr(NCS)_4(bipy)]$ in order to answer the question of whether there is any cooperative magnetic interaction within the sample besides the observed paramagnetism. The temperature dependence of the molar magnetic susceptibility $\chi_m$ and the reciprocal molar magnetic susceptibility $\chi_m^{-1}$ of (EMIm)$[Cr(NCS)_4(bipy)]$ shows Curie−Weiss paramagnetic behavior over the full measured temperature range. The Weiss constant $\Theta$ was determined in the temperature range of 10−50 K and equals $\Theta$ = −2.9 K. Therefore, there is no indication for any stronger cooperative magnetic interaction between the isolated spin-only systems. The magnetic moment of (EMIm)$[Cr(NCS)_4(bipy)]$ equals $\mu_{eff}$ = 4.05 $\mu_B$ at 298 K and $\mu_{eff}$ = 3.84 $\mu_B$ at 10 K. The value at 298 K is in good agreement with the measured value obtained using the NMR technique ($\mu_{eff}$ = 3.93 $\mu_B$ at 298 K).

*Electrochemical Properties.* In order to obtain information about the electrochmical properties of the title compounds, i.e., to check for a possible reversible reduction to chromium(II), cyclic voltammogramms were measured in acetonitrile solutions and show no reversible electron transfer. At +105 mV (vs SCE), an irreversible oxidation peak is visible.

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### Notes

The authors declare no competing financial interest.

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## DEDICATION

Dedicated to the memory of Prof. J. D. Corbett.

## REFERENCES

(1) Morland, J. Q. *J. Chem. Soc.* **1861**, *13*, 252−254.

(2) Werner, A.; Richter, G. *Z. Anorg. Chem.* **1897**, *15*, 243−277.

(3) Nordenskjöld, O. *Z. Anorg. Chem.* **1892**, *1*, 126−143.

(4) Reinecke, A. *J. Liebigs Ann. Chem.* **1863**, *126*, 113−118.

(5) Christensen, O. T. *J. Prakt. Chem.* **1892**, *45*, 213−222.

(6) Mainusch, B.; Karocki, A.; Guldi, D. M.; Stasicka, Z.; Wasgestian, F. *Inorg. Chim. Acta* **1997**, *255*, 87−93.

(7) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394−404.

(8) Balzani, V.; Carassisi, V. *Photochemistry of Coordination Compounds*; Academic Press: London, 1970.

(9) Adamson, A. W., Fleischhauer, P. D., Eds. *Concepts of Inorganic Photochemistry*; Wiley: New York, 1975.

(10) Mainusch, B.; Wasegestian, F.; Stasicka, Z.; Karocki, A. *J. Inf. Rec. Mats.* **1994**, *21*, 687−689.

(11) Al-Ghannam, S. M.; Sheikha, M. *Spectrochim. Acta* **2007**, *A69*, 1188−1194.

(12) Uivarosi, V.; Monciu, C. *Rev. Chim.* **2009**, *60*, 132−136.

(13) Bratulescu, G.; Ganescu, I. *Braz. J. Chem.* **2007**, *15*, 49−57.

(14) Ganescu, I.; Preda, M. *Pharmazie* **1990**, *45*, 438−439.

(15) Ganescu, I.; Varhelyi, C.; Brinzan, G. *Arch. Pharm.* **1976**, *309*, 887−892.

(16) Ganescu, I.; Papa, I.; Verhelyi, C. *Pharmazie* **1983**, *38*, 563−564.

(17) Ganescu, I.; und, G.; Brinzan, C. V. *Microchim. Acta* **1977**, *67*, 139−144.

(18) Turner, S. S.; Pevelen, D. L.; Day, P.; Prout, K. *J. Chem. Soc., Dalton Trans.* **2000**, 2739−2744.

(19) Peppel, T.; Schmidt, C.; Köckerling, M. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1314−1321.

(20) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083.

(21) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.

(22) Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(23) Hayashi, S.; Hamaguchi, H. *Chem. Lett.* **2004**, *33*, 1590−1591.

(24) Kozlova, S. A.; Verevkin, S. P.; Heintz, A.; Peppel, T.; Köckerling, M. *J. Chem. Eng. Data* **2009**, *54*, 1524−1528.

(25) Peppel, T.; Köckerling, M.; Geppert-Rybczynska, M.; Ralys, R. V.; Lehmann, J. K.; Verevkin, S. P.; Heintz, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 7116−7119.

(26) Namboodiri, V.; Varma, R. *Org. Lett.* **2002**, *4*, 3161−3163.

(27) Paulechka, Y.; Kabo, G.; Blokhin, A.; Shaplov, A.; Lozinskaya, E.; Vygodskii, Y. *J. Chem. Thermodyn.* **2007**, *39*, 158−166.

(28) Peppel, T.; Roth, C.; Fumino, K.; Paschek, D.; Köckerling, M.; Ludwig, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 10221−10224.

(29) Roesler, J. *J. Liebigs Ann. Chem.* **1867**, *141*, 185−197.

(30) Bennett, M. A.; Clark, R. J. H.; Goodwin, A. D. J. *Inorg. Chem.* **1967**, *6*, 1625−1631.

(31) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005.

(32) Pacault, A.; Hoarau, J.; Marchand, A. *Adv. Chem. Phys.* **1960**, *3*, 171−238.

(33) Langevin, P. *J. Phys. Theor. Appl.* **1905**, *4*, 678−693.

(34) *SADABS—Software for the CCD detector System*; Bruker-Nonius: Madison, WI, 2003.

(35) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(36) Peppel, T.; Thiele, P.; Köckerling, M. *Russ. J. Coord. Chem.* **2012**, *38*, 207−218.

(37) Nikitina, V. M.; Nesterova, O. V.; Kokozay, V. N.; Dyakonenko, V. V.; Shishkin, O. V.; Jezierska, J. *Polyhedron* **2009**, *28*, 1265−1272.

(38) Tait, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4352−4360.

(39) Ganescu, I.; Varhelyi, C.; Oprescu, D. *Rev. Chim. Miner.* **1969**, *6*, 765−774.

(40) Cioica, M.; Ganescu, I.; Lepadatu, C. I. *Z. Phys. Chem.* **1975**, *97*, 41−45.

(41) Peppel, T.; Roth, C.; Fumino, K.; Paschek, D.; Köckerling, M.; Ludwig, R. *Angew. Chem.* **2011**, *123*, 6791−6795.

(42) Pandey, Y. N.; Mathur, P. K.; Kapoor, S. N. *J. Indian Chem. Soc.* **1985**, *62*, 153−154.

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