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Dedicated to Professor Vladimir Fedorov
on the occasion of his 75th birthday

Low-Melting Salts with the $[Cr^{III}(NCS)_4(1,10\text{-Phenanthroline})]^-$ Complex Anion: Syntheses, Properties, and Structures[1]

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Abstract—Four new low melting salts, "Ionic Liquids" consisting of the $[Cr^{III}(NCS)_4(Phen)]^-$ complex monoanion and imidazolium based cations *A*, with *A* = 1-ethyl-3-methylimidazolium (EMIm), 1-butyl-3-methylimidazolium (BMIm), 1,3-dimethyl-2,4,5-triphenylimidazolium (DML), and 1,2,3,4,5-pentamethylimidazolium (PMIm), were investigated. Single-crystal X-ray investigations established the structures of the four compounds. $(EMIm)[Cr(NCS)_4(Phen)]$ (**I**): triclinic, $P\bar{1}$, $a = 8.1382(6)$, $b = 10.4760(8)$, $c = 16.003(1)$ Å, $\alpha = 90.330(4)°$, $\beta = 94.759(4)°$, $\gamma = 107.305(4)°$, $Z = 2$, $R_1(F)/wR_2(F^2) = 0.0650/0.1770$; $(BMIm)[Cr(NCS)_4(Phen)]$ (**II**): triclinic, $P\bar{1}$, $a = 8.5545(4)$, $b = 9.8620(4)$, $c = 16.6762(6)$ Å, $\alpha = 92.503(2)°$, $\beta = 97.517(2)°$, $\gamma = 91.249(2)°$, $Z = 2$, $R_1(F)/wR_2(F^2) = 0.0393/0.0848$; $(DML)[Cr(NCS)_4(Phen)] \cdot C_3H_6O$ (**III**): triclinic, $P\bar{1}$, $a = 11.0475(9)$, $b = 13.589(1)$, $c = 14.582(1)$ Å, $\alpha = 83.013(4)°$, $\beta = 87.116(4)°$, $\gamma = 70.333(5)°$, $Z = 2$, $R_1(F)/wR_2(F^2) = 0.0407/0.1023$; $(PMIm)[Cr(NCS)_4(Phen)] \cdot C_3H_6O$ (**IV**): orthorhombic, *Pbca*, $a = 17.379(1)$, $b = 16.514(1)$, $c = 22.304(1)$ Å, $Z = 8$, $R_1(F)/wR_2(F^2) = 0.0460/0.1107$ (in addition **III** and **IV** contain co-crystallized acetone molecules). Each compound was characterized by elemental analysis, NMR, IR, und UV–Vis spectroscopy. Magnetic properties were derived from NMR investigations (EVANS method). All four compounds are paramagnetic with effective magnetic moments of spin-only Cr^{III}. Melting points were obtained from DSC measurements. All melting points are higher than required for "Ionic Liquids", but nevertheless "low" for molten salts.

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INTRODUCTION

The various intriguing properties of salts with melting points below 100°C have become an intensively explored research field under the term "Ionic Liquids" (ILs) for about the last decade. The properties of attention of this class of materials include wide liquid ranges, high electrical conductivities, large electrochemical windows, and low vapor pressures (to name a few) [1–8]. The number of possible anion-cation combinations forming Ionic Liquids is extremely large. By no surprise also transition metal complex anions belong to the candidate anions of this group of materials. Besides the other unique properties, Ionic Liquids with paramagnetic complex anions, called "Magnetic Ionic Liquids", exhibit interesting magnetic behaviors [9–21].

One appealing transition metal complex anion with respect to ILs is the Reineckate anion, diammine-tetra(isothiocyanato) chromate(III), $[Cr(NCS)_4(NH_3)_2]^-$. Salts of the Reineckate anion are known for more than 150 years [22–26]. Reineckates and derived compounds have been used for a variety of applications, like chemical actinometers, as substances for quantum yield determinations, as compounds in charge transfer photochemistry, and in the analysis of medicinal products [27–35].

Recently, we have reported about the syntheses, structure determinations, and property determinations of a series of imidazolium-based Reineckates [36].

In this contribution, we report on the synthesis, properties, and structures of a series of imidazolium-based salts with the Reineckate-analogue anion $[Cr(NCS)_4(Phen)]^-$ (Phen = 1,10-phenanthroline). The following four new Reineckate-analogue compounds were synthesized and investigated: $(EMIm)[Cr(NCS)_4(Phen)]$ (EMIm = 1-ethyl-3-methylimidazolium) (**I**), $(BMIm)[Cr(NCS)_4(Phen)]$ (BMIm = 1-butyl-3-methylimidazolium) (**II**), $(DML)[Cr(NCS)_4(Phen)] \cdot C_3H_6O$ (DML = 1,3-dimethyllophinium = 1,3-dimethyl-2,4,5-triphenylimidazolium) (**III**), and $(PMIm)[Cr(NCS)_4(Phen)] \cdot C_3H_6O$ (PMIm = 1,2,3,4,5-pentamethylimidazolium) (**IV**). Results of crystal structure determinations by means

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of single crystal X-ray diffraction, of temperature independent magnetic measurements using NMR techniques, as well as results of elemental analyses, and NMR measurements are reported.

EXPERIMENTAL

Materials. All commercially available starting materials were purchased from Sigma-Aldrich (>99%) and were used as received. EMImBr and BMImBr were synthesized according to known procedures [37].

For EMImBr ($C_6H_{11}N_2Br$)

calcd., %:	C, 37.85;	H, 6.04;	N, 14.48.
Found, %:	C, 37.72;	H, 5.80;	N, 14.66.

Mp. 77°C (77°C [38]). ^1H NMR ($CDCl_3$); δ, ppm): 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 ($CDCl_3$): δ = 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).

For BMImBr ($C_8H_{15}N_2Br$)

calcd., %:	C, 43.98;	H, 7.01;	N, 12.98.
Found, %:	C, 43.85;	H, 6.90;	N, 12.78.

Mp. 78°C (78°C [38]). ^1H NMR ($CDCl_3$); δ, ppm): 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 ($CDCl_3$): δ = 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). 1,2,3,4,5-Pentamethylimidazolium iodide (PMImI) and 1,3-dimethyl-2,4,5,-triphenylimidazolium iodide (1,3-dimethyllophinium iodide, DMLI), respectively, were synthesized according to [21, 39].

Synthesis of $K_3[Cr(NCS)_6]$ [40]. A 100 mL aqueous solution of 5.00 g (0.01 mol) chrome alum (chromium(III) potassium sulfate) and 5.83 g (0.06 mol) potassium thiocyanate is evaporated to dryness. The residue is extracted exhaustively with ethyl acetate and the resulting solution is evaporated to dryness again. The red-violet solid is finally dried at 140°C in vacuum to liberate water of crystallization. The yield is 4.66 g (90%) of a hygroscopic solid.

For $C_6CrK_3N_6S_6 \cdot 0.5H_2O$

calcd., %:	C, 13.68;	H, 0.19;	N, 15.95.
Found, %:	C, 13.71;	H, 0.17;	N, 15.98.

(The water content results from the hygroscopic nature and the necessity to handle the compound in air for a short time prior to the analysis.)

IR (ν_{max}, cm^{-1}): 2098 ν(CN), 1698, 823 ν(CS), 479. UV–Vis (($CH_3)_2CO$; λ_{max}, nm; 23°C): 418, 553. μ_{eff}/μ_B = 3.97 (T = 25°C, $c = 0.75 \times 10^{-2}$ mol/L, ν_0 = 300 MHz, $\chi_{mol} = 6.61 \times 10^{-3}$).

Synthesis of $K[Cr(NCS)_4(Phen)]$ [41]. About 1.00 g (5.55 mmol) Phen and 3.78 g (7.30 mmol) carefully dried $K_3[Cr(NCS)_6]$ are heated under reflux in 150 mL of absolute ethanol overnight and then cooled to room temperature. The precipitate of $K[Cr(NCS)_4(Phen)]$ is filtered off, washed thoroughly with ethanol and finally with diethyl ether. The resulting pink solid is dried overnight in a drying oven at 60°C. The yield is 2.43 g (87%).

For $C_{16}H_8N_6CrKS_4$

calcd., %:	C, 38.16;	H, 1.60;	N, 16.69.
Found, %:	C, 38.67;	H, 1.54;	N, 16.23.

IR (ν_{max}, cm^{-1}): 3092, 2085 ν(CN); 1609, 1600, 1467, 1446, 1037, 820 ν(CS); 767, 666, 486, 451. UV–Vis (($CH_3)_2CO$; λ_{max}, nm; 23°C): 390, 442 sh, 551. μ_{eff}/μ_B = 3.91 (T = 25°C, $c = 0.53 \times 10^{-2}$ mol/L, ν_0 = 300 MHz, $\chi_{mol} = 6.41 \times 10^{-3}$).

General synthesis of (AlkMIm)-, (PMIm)-, and (DML)$[Cr(NCS)_4(Phen)]$. 2.0 mmol of the appropriate Ionic Liquid precursor halide are added to 100 mL of an acetonic solution of 2.0 mmol $K[Cr(NCS)_4L]$ (L = Phen). The resulting solution is refluxed for 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 a ruby red solid. The yield is >90%.

(EMIm)$[Cr(NCS)_4(Phen)]$ (I). From EMImBr. Yield 99%; mp. 210°C.

For $C_{22}H_{19}N_8CrS_4 \cdot 0.5H_2O$

calcd., %:	C, 45.19;	H, 3.45;	N, 19.16;	S, 21.94.
Found, %:	C, 45.21;	H, 3.14;	N, 18.62;	S, 20.10.

(The water content results from the hygroscopic nature and the necessity to handle the compound in air for a short time prior to the analysis.)

IR (ν_{max}, cm^{-1}): 3138, 3106, 3072, 3051, 2981, 2929, 2871, 2092, 2051 ν(CN), 1627, 1604, 1581, 1564, 1517, 1494, 1423, 1342, 1310, 1224, 1209, 1166, 1145, 1108, 1052, 1033, 959, 913, 875, 843, 831 ν(CS), 771, 747, 739, 718, 647, 619, 594, 560. UV–Vis (($CH_3)_2CO$; λ_{max}, nm; 23°C): 440 sh, 543. μ_{eff}/μ_B = 3.85 (T = 25°C, $c = 0.57 \times 10^{-2}$ mol/L, ν_0 = 300 MHz, $\chi_{mol} = 6.21 \times 10^{-3}$).

(BMIm)$[Cr(NCS)_4(Phen)]$ (II). From BMImBr. Yield 98%; mp. 181°C.

For $C_{24}H_{23}N_8CrS_4$

calcd., %:	C, 47.74;	H, 3.84;	N, 18.56;	S, 21.24.
Found, %:	C, 47.81;	H, 3.63;	N, 17.87;	S, 22.10.

IR (ν_{max}, cm^{-1}): 3137, 3104, 3078, 3050, 2948, 2928, 2867, 2097, 2055 ν(CN), 1682, 1629, 1603, 1581, 1557, 1518, 1493, 1463, 1455, 1423, 1344, 1309, 1224, 1207, 1156, 1141, 1106, 1021, 951, 877, 839 ν(CS), 772, 736, 727, 716, 652, 622. UV–Vis ($(CH_3)_2CO$; λ_{max}, nm; 23°C): 440 sh, 543. $\mu_{eff}/\mu_B = 3.78$ ($T = 25$°C, $c = 1.04 \times 10^{-2}$ mol/L, $\nu_0 = 300$ MHz, $\chi_{mol} = 5.97 \times 10^{-3}$).

(PMIm)[Cr(NCS)$_4$(Phen)] (IV). From PMImI. Yield 98%; mp. 290°C.

For $C_{24}H_{23}N_8CrS_4$

calcd., %:	C, 47.74;	H, 3.84;	N, 18.56;	S, 21.24.
Found, %:	C, 47.34;	H, 3.80;	N, 17.67;	S, 21.82.

IR (ν_{max}, cm^{-1}): 3171, 3105, 3044, 2953, 2281, 2098 ν(CN), 2048, 1643, 1581, 1538, 1517, 1494, 1439, 1424, 1347, 1331, 1181, 1136, 1105, 1052, 960, 875, 851, 827 ν(CS), 787, 762, 738, 719, 652, 614, 569. UV–Vis ($(CH_3)_2CO$; λ_{max}, nm): 440 sh, 543. $\mu_{eff}/\mu_B = 3.78$ ($T = 25$°C, $c = 1.27 \times 10^{-2}$ mol/L, $\nu_0 = 300$ MHz, $\chi_{mol} = 6.00 \times 10^{-3}$).

(DML)[Cr(NCS)$_4$(Phen)] (III). From DMLI. Yield 94%. mp. 236°C.

For $C_{39}H_{29}N_8CrS_4 \cdot H_2O$

calcd., %:	C, 57.97;	H, 3.87;	N, 13.87;	S, 15.87.
Found, %:	C, 57.99;	H, 3.59;	N, 13.49;	S, 15.92.

(The water content results from the hygroscopic nature and the necessity to handle the compound in air for a short time prior to the analysis.)

IR (ν_{max}, cm^{-1}): 3046, 2912, 2417, 2349, 2285, 2094 ν(CN), 2044, 1581, 1514, 1486, 1442, 1413, 1343, 1277, 1147, 1110, 1023, 966, 931, 876, 856, 842 ν(CS), 769, 760, 718, 698, 652, 560, 527. UV–Vis ($(CH_3)_2CO$; λ_{max}, nm): 440 sh, 543. $\mu_{eff}/\mu_B = 3.76$ ($T = 25$°C, $c = 0.97 \times 10^{-2}$ mol/L, $\nu_0 = 300$ MHz, $\chi_{mol} = 5.91 \times 10^{-3}$).

Analysis and spectroscopic measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX 300 spectrometer. Spectra were calibrated with respect to the solvent signal (DMSO-d$_6$: ^{1}H δ = 2.50; ^{13}C δ = 39.5 ppm). MIR spectra (500–4000 cm^{-1}) were recorded by using ATR technique on 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 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 (N_2 atmosphere, Al crucible). All melting points are peak temperatures. Magnetic data were determined by means of ^{1}H NMR techniques (EVANS method) [42, 43]. Molar susceptibilities were corrected by applying PASCAL constants [44, 45]. Effective magnetic moments μ_{eff}/μ_B are given by applying the Langevin equation [46, 47].

X-ray structure analysis. Suitable single crystals for X-ray measurements were obtained within a few days by slow evaporation of the solvent off acetonic solutions of the salts at ambient temperature and pressure. Ruby-red crystals of A[Cr(NCS)$_4$(Phen)] · nC_3H_6O, where A = EMIm ($n = 0$; **I**), BMIm ($n = 0$; **II**), DML ($n = 1$; **III**), or PMIm ($n = 1$; **IV**) 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 MoK_α radiation ($\lambda = 0.71073$ 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 [48]. The structure solutions and refinements were done with the aid of the SHELX-97 program package [49]. 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, atom distances are given in Table 2, and selected bond angles are listed in Table 3. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 840095 (**I**), 840093 (**II**), 840094 (**III**), and 840096 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The synthesis of imidazolium-based salts containing the Reineckate-analogue anion [Cr(NCS)$_4$(Phen)]$^-$ is facile and can be achieved easily by metathesis reactions between the corresponding potassium salt K[Cr(NCS)$_4$(Phen)] and alkylated imidazolium halides in high yields (>90%). The precursor potassium salt is accessible from $K_3[Cr(NCS)_6]$ [40] and Phen, respectively, in ethanolic solution. All compounds are distinguished by a deep ruby-red color in the solid state. They are insoluble in water, but soluble in organic solvents, especially in acetone and acetonitrile.

All four compounds consist of isolated [Cr(NCS)$_4$(Phen)]$^-$ anions, imidazolium-based cations, and, in the case of **III** and **IV**, co-crystallized acetone solvent molecules. Thermal ellipsoid plots of the ion pairs for complexes **I**–**IV** are shown in Fig. 1. All four compounds contain the same Reineckate-derived [Cr(NCS)$_4$(Phen)]$^-$ anion, with the Cr^{3+} ion being

Table 1. Crystallographic data and structure refinement for **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Formula	$C_{22}H_{19}CrN_8S_4$	$C_{24}H_{23}CrN_8S_4$	$C_{42}H_{35}CrN_8OS_4$	$C_{27}H_{29}CrN_8OS_4$
Fw	575.69	603.7404	848.02	661.82
T, K	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*
a, Å	8.1382(6)	8.5545(4)	11.0475(9)	17.379(1)
b, Å	10.4760(8)	9.8620(4)	13.589(1)	16.514(1)
c, Å	16.003(1)	16.6762(6)	14.582(1)	22.304(1)
α, deg	90.330(4)	92.503(2)	83.013(4)	
β, deg	94.759(4)	97.517(2)	87.116(4)	
γ, deg	107.305(4)	91.249(2)	70.333(5)	
V, Å^3; Z	1297.5(2); 2	1392.9(1); 2	2046.0(3); 2	6400.9(8); 8
ρ, g cm^{-3}	1.474	1.439	1.377	1.374
μ, mm^{-1}	0.791	0.740	0.528	0.653
θ Range, deg	7.56–56.74	4.72–46.40	4.78–59.34	7.06–56.06
Collected reflections	16490	14784	47716	48144
Unique reflections (R_{int})	6196 (0.051)	4216 (0.045)	1159 (0.025)	12175 (0.058)
Variables	316	334	524	407
GOOF on F^2	1.058	1.018	1.024	0.995
R_1, wR_2 ($I > 2\sigma(I)$)$^{a, b}$	0.0650, 0.1770	0.0393, 0.0848	0.0407, 0.1023	0.0460, 0.1107
R_1, wR_2 (all data)$^{a, b}$	0.0836, 0.1933	0.0637, 0.0946	0.0618, 0.1129	0.1068, 0.1357
A, B^b	0.1258, 0.3934	0.0384, 0.8772	0.0538, 0.8653	0.0655, 0.3042
Largest diff. peak and hole, e A^{-3}	1.314, –0.752	0.364, –0.286	0.478, –0.392	0.442, –0.425

$^{a}R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $^{b}wR_2 = \sqrt{\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}}$; $w = 1/[(\sigma^2(F_o^2) + (AP)^2 + BP]$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) for complex anion in **I–IV** and S···H contacts around the complex anion

Bond	*d*, Å			
	I	**II**	**III**	**IV**
Cr(1)–NCS: Cr(1)–N(1)	1.985(3)	2.000(3)	1.999(2)	1.986(2)
Cr(1)–N(2)	1.974(3)	1.985(3)	2.009(2)	1.980(2)
Cr(1)–N(3)	1.990(3)	1.982(3)	1.999(2)	2.015(2)
Cr(1)–N(4)	1.977(3)	1.980(3)	1.991(2)	1.979(2)
Average Cr(1)–N(NCS)	1.982	1.987	2.000	1.990
Cr(1)–N(Phen): Cr(1)–N(5)	2.069(3)	2.065(2)	2.086(1)	2.067(2)
Cr(1)–N(6)	2.077(3)	2.077(3)	2.087(1)	2.068(2)
Average Cr(1)–N(Phen)	2.073	2.071	2.087	2.068
Average N–C	1.150	1.160	1.152	1.142
Average C–S	1.619	1.625	1.629	1.622
S···H contacts up to 3 Å				
Number of S···H contacts	4	6	3	6
Shortest S···H contact	2.769	2.824	2.711	2.757

Table 3. Selected bond angles (deg) for the complex anion in **I–IV**

Angle	ω, deg			
	I	**II**	**III**	**IV**
N(5)Cr(1)N(6)	79.4(1)	79.9(1)	79.19(5)	79.89(6)
NCr(1)N(NCS)*	177.8(1)	177.1(1)	178.67(6)	175.68(6)
Average NCS	178.8	178.4	179.0	179.1
Average Cr(1)NC	166.6	174.2	165.7	174.1
Range	158.3–171.2	169.7–178.7	159.0–176.6	172.4–176.9
Average N(Phen)CrN(NCS) (*trans*)	172.6	172.5	171.3	172.7

* The NCr(1)N angle of the *trans* arranged NCS groups with the NCr(1)N vector perpendicular to the mean plane of the phenanthroline moiety.

distorted octahedrally coordinated by 6N atoms. The 2N atoms of the neutral Phen ligand coordinate necessarily in a *cis* manner to the metal ion. The other four coordination sites are occupied by the N atoms of the *iso*-thiocyanate ligands. Because of the fixed bite angle of the two donor atoms of the Phen ligand, which range from 79.19(5)° (**III**) to 79.9(1)° (**II**) (Table 3), the coordination geometry around the Cr^{3+} ion deviates from ideal octahedral. Because it is significantly smaller than 90°, also the N(Phen)CrN(NCS) (*trans*) are smaller than the ideal 180°. Unaffected from this ligand induced constrain the N(NCS)CrN(NCS) (*trans*) angle, with the N–Cr–N vector being perpendicular oriented to the mean plane of the atoms of the Phen ligand, deviates much less from the ideal 180° (in the range of 175.68(6)° (**IV**) to 178.67(6)° (**III**)). The Cr(1)NCS angles are found in the range from 158.3° to 178.7°. The NCS units are almost linear, as expect-

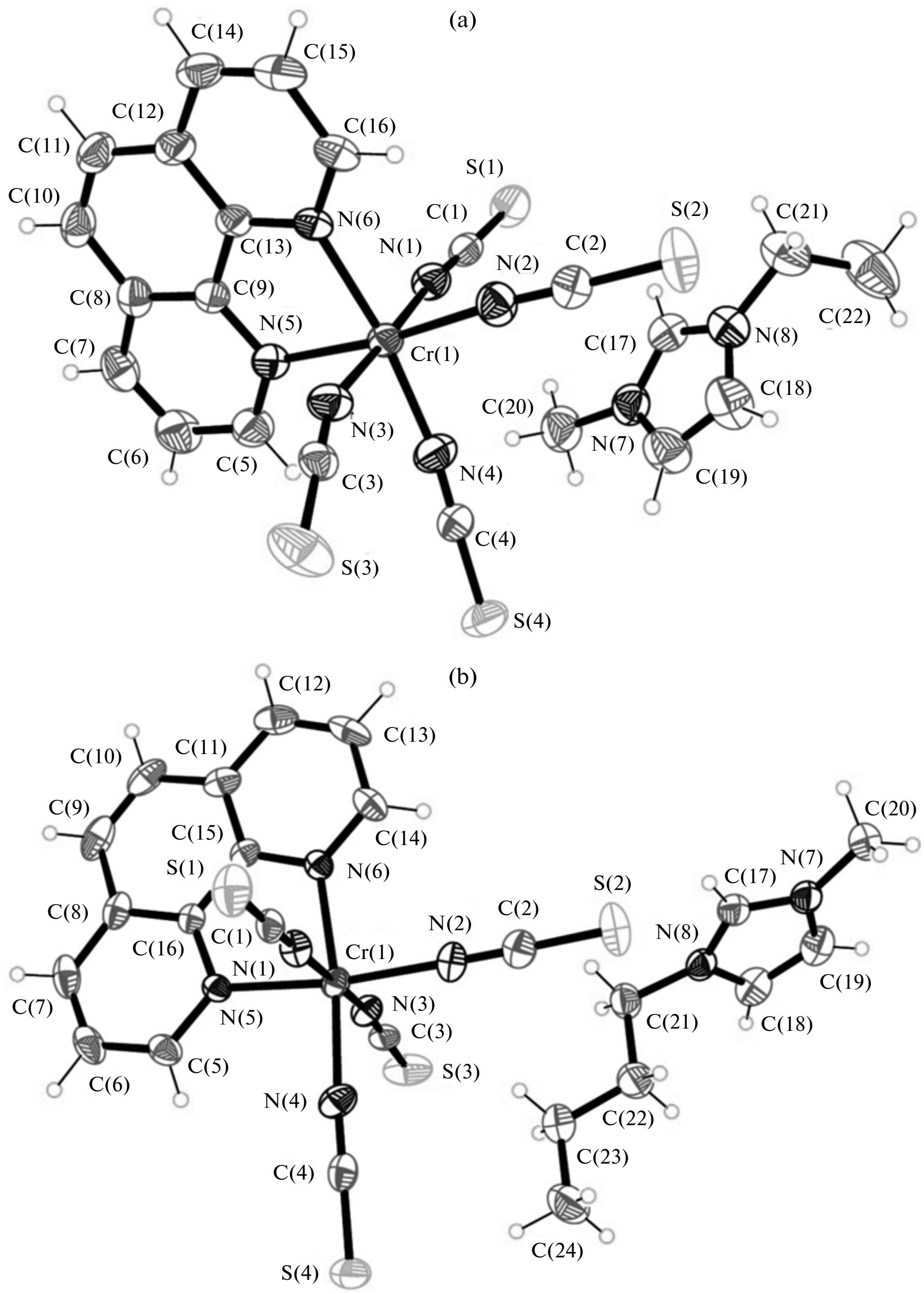

Fig. 1. Molecular structure of the cation-anion pair in crystals of **I** (a), **II** (b), **III** (c), and **IV** (d) with atom labeling scheme (thermal ellipsoids at the 50% probability level).

ed (Table 3). All these structural parameters compare well with those found in compounds of the $[Cr(NCS)_4(Phen)]^-$ complex anion with other cations [50–55]. In the crystals of the Reineckate derived anion with the EMIm, BMIm, and the DML cation, the anions are arranged such that all the planar phenanthroline ligands are parallel to each other. Packing plots in crystals of **I** and **II**–**IV** are shown in Figs. 2 and 3, respectively. In crystals of the EMIm salt, the Phen rings are separated by a distance of 4.069 Å, indicating π–π interactions. In **I** and **II**, every next anion on both sides of each Phen ligand is switched around by 180°. Thereby, double layers of anions are formed extending in the *xy*-planes of the lattice. The mean planes

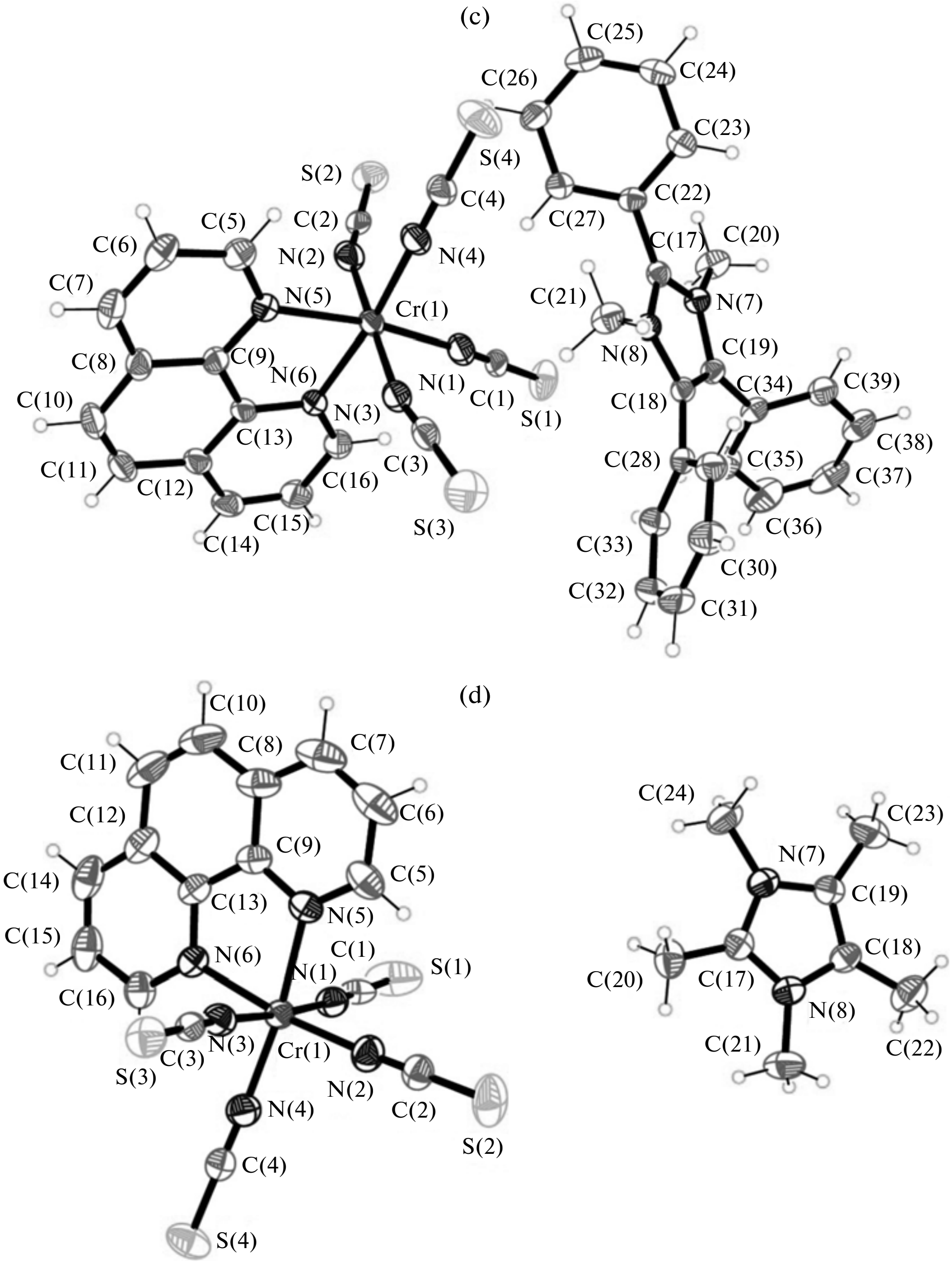

Fig. 1. (Contd.).

through the atoms of the phenanthroline molecules extend in the [110] direction. Out of both sides of the anionic double layers NCS units stick out (Fig. 2). Between the anionic layers the cations are located (not shown in Fig. 2). The arrangement of ions in **IV** is different from that in **I**, **II**, and **III** with respect to the assembly of the phenanthroline ligands; here two different, non-parallel orientations are found (Fig. 3c).

Another structural aspect worth mentioning are the shortest anion–cation contacts with respect to the interaction strength influencing necessarily macroscopic properties like the melting points of the compounds. The number and distances up to 3 Å of the S(anion)···H(cation) contacts are listed in Table 2. Whereas **I** and **II** contain acidic protons on the imidazolium based cations, these are absent in **III** and **IV**. Figure 4 shows the molecular environment of one complex anion of **I** with the S···H contacts shorter than 3 Å sketched. Both compounds, **I** and **II**, have the shortest hydrogen contacts between the sulfur atoms of the anion and the acidic H atoms of the neighboring cations.

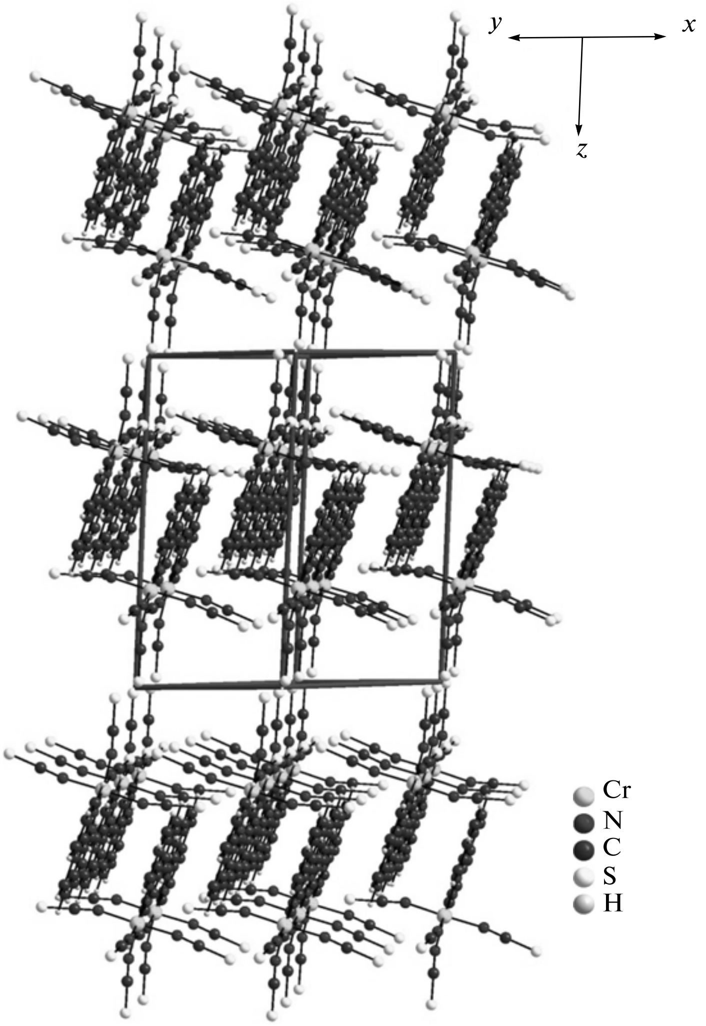

Fig. 2. Arrangement of the complex anions with the parallel orientation of the planar phenanthroline moieties in crystals of **I**.

The MIR data in the region of 4000–500 cm^{-1} of all four compounds are listed in the Experimental Section. IR spectra of imidazolium-based compounds have been discussed extensively in the literature [56–59]. As expected, they all show aliphatic C–H stretching frequencies in the region of 3100–3000 cm^{-1}. Many other ILs with imidazolium cations, which carry an acidic hydrogen atom on the C atom between the two nitrogen atoms of the imidazolium ring, show a strong, broad peak in the same IR region, which has been assigned to hydrogen bonding [56–59]. With this H atom being absent in the compounds **III** and **IV**, the respective hydrogen bonding and the corresponding band in the IR spectra 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 compounds containing the Reineckate-analogue anions $[Cr(NCS)_4(Phen)]^-$ are reported in detail in the literature [41, 60–62]. The CN stretching frequencies ν(CN) are located between 2080–2100 cm^{-1}, the CS stretching frequencies ν(CS) between 820–850 cm^{-1}, respectively, and are in accordance with published values [41, 60–65].

The positions of the absorption maxima in the electronic spectra in the region from 190 to 1000 nm for all four compounds in acetonic solution at room temperature are given in the Experimental Section. Octahedrally coordinated Cr(III) complexes exhibit two spin allowed transitions, $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$, in the Vis region. In addition, there is a third transition, $^4T_{1g}(P) \leftarrow {}^4A_{2g}$, which is often interfered by charge transfer bands. UV–Vis investigations on compounds containing the Reineckate-analogue anions $[Cr(NCS)_4L]^-$ (L = Bipy, Phen) have been reported in the literature [41, 60–62, 66–68]. The charge transfer band (e.g. 388 nm for $K[Cr(NCS)_4(Bipy)]$) and the lo-

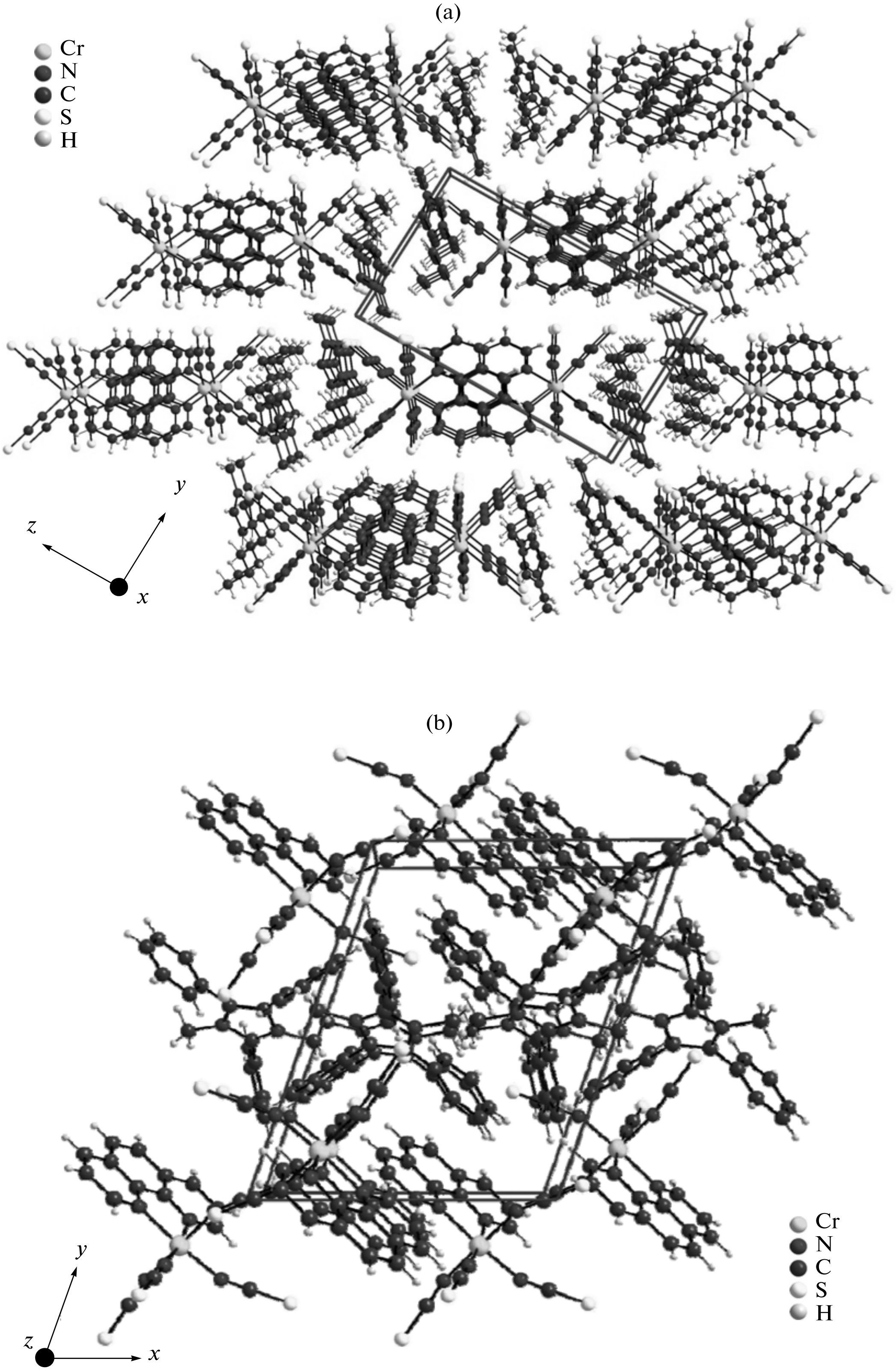

Fig. 3. Packing of the isolated cations and anions in crystals of **II** (a), **III** (b), and **IV** (c).

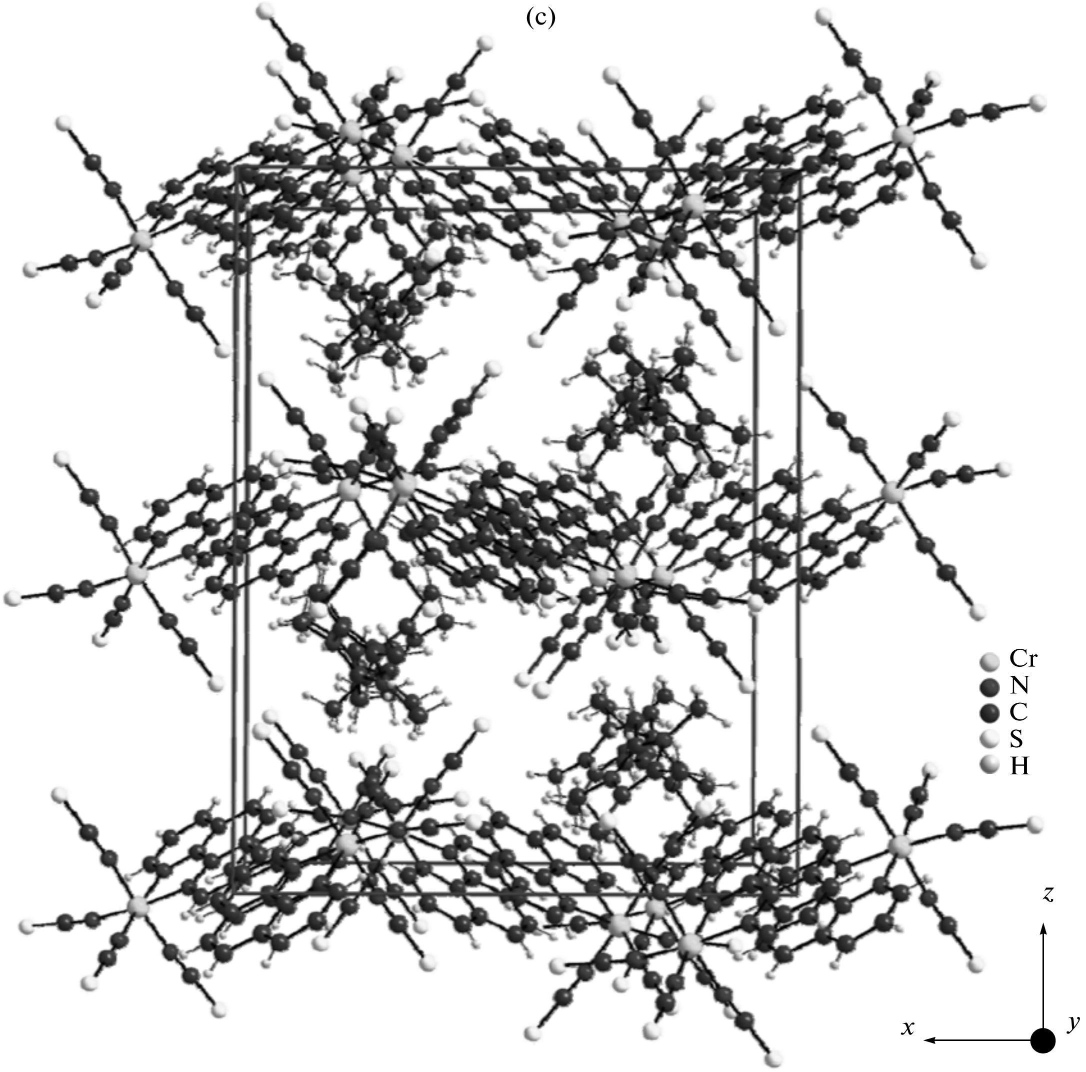

Fig. 3. (Contd.).

cation of the two $^4T_{2g} \leftarrow {}^4A_{2g}$ (540–550 nm) and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ (440–445 nm) transitions, respectively, are nearly independent of the choice of the cation in acetonic solution and are in accordance with values found for the four title compounds.

In order to see if the title compounds can be considered to belong to the chemical subclass of “Ionic Liquids”, thermal data have been measured using DSC techniques in the temperature range from 0–400°C. 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 the melting points in the corresponding imidazolium-based Reineckates A[$Cr(NCS)_4(NH_3)_2$] (A = EMIm, BMIm, PMIm, DML) [36]. The melting point is slightly decreasing with increasing alkyl chain length from ethyl to butyl in the imidazolium-based cation from 210°C in (EMIm)[$Cr(NCS)_4$(Phen)] to 181°C in (BMIm)[$Cr(NCS)_4$(Phen)]. It is obvious that these compounds have high melting points, which lie far above the limit for “Ionic Liquids”. It is interesting to note, that in the case when the most acidic hydrogen atom in the imidazolium ring between the two nitrogen atoms is exchanged by either methyl or phenyl substituents in the compounds (PMIm)- or (DML)[$Cr(NCS)_4$(Phen)], the melting points are not decreasing. This behavior supports the finding, that often directed hydrogen contacts disturb the otherwise more symmetrical coulomb system and leads to lower melting points [39, 69]. The highest melting point can be found for the compound (PMIm)[$Cr(NCS)_4$(Phen)] due to the high symmetry of the 1,2,3,4,5-pentamethylimidazolium cation. This behavior can be also found in other known PMIm-containing systems [39, 69].

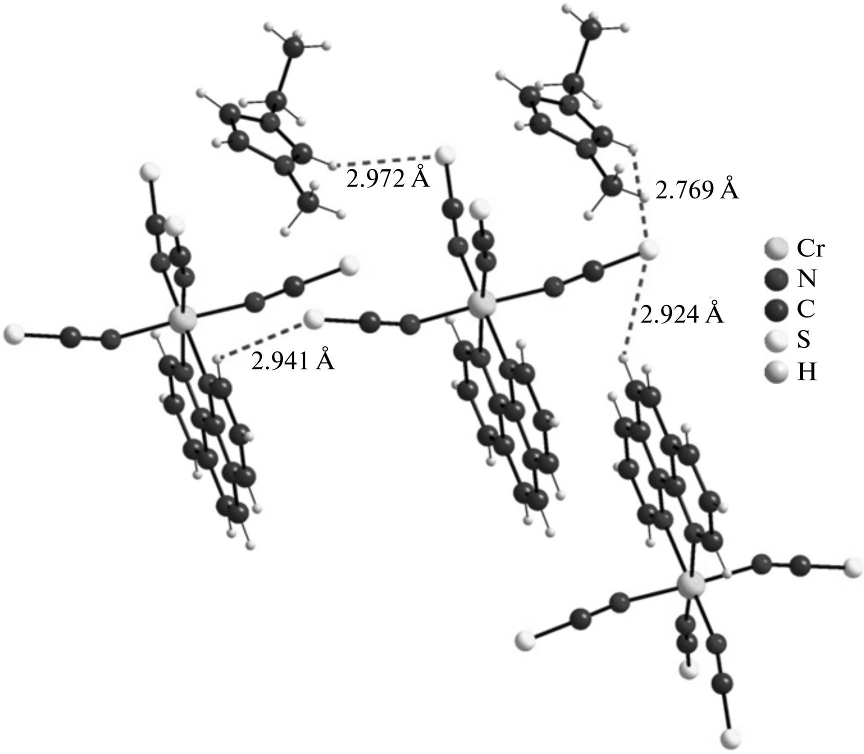

Fig. 4. Molecular environment of each complex anion in crystals of $(EMIm)[Cr(NCS)_4(Phen)]$ with the S···H contacts shorter than 3 Å shown as dashed lines.

The magnetic properties at room temperature of all investigated complex salts were determined in solution using NMR techniques applying the Evans method [42, 43]. 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 Cr^{3+}: $\mu_{eff} = 3.87\ \mu_B$). These values resemble closely those of related compounds, for example $K[Cr(NCS)_4(Phen)]$ ($\mu_{eff} = 4.10\ \mu_B$) [70], $[Ce(Phen)_4][Cr(NCS)_4(Phen)]$ ($\mu_{eff} = 3.77\ \mu_B$) [60–62], or $(Ph_3Ge)[Cr(NCS)_4(Phen)]$ ($\mu_{eff} = 3.73\ \mu_B$, 300 K) [66–68].

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