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Preparation and Crystal Structures of *trans*-K[Cr(NCS)$_4$py$_2$] · 4py and *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic)

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trans-K[Cr(NCS)$_4$py$_2$] · 4py (**1**) (py = pyridine) was prepared by refluxing K$_3$[Cr(NCS)$_6$] in pyridine, where the substitution of two isothiocyanate ligands with two pyridine molecules was taking place. By a similar synthesis procedure in γ-picoline (γ-pic), neutral *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic) (**2**) was obtained. The crystal structure of compound **1** consists of polymeric chains in which *trans*-octahedrally coordinated Cr^{III} in [Cr(NCS)$_4$py$_2$]$^-$ anions and *trans*-octahedrally coordinated K$^+$ are connected via nonlinear K···SCN–Cr–NCS···K contacts. In the structure of compound **2**, isolated *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] molecules together with free γ-pic lattice molecules were identified. The results of IR spectroscopy are in agreement with Cr–NCS bonding of the NCS ligand for both compounds.

INTRODUCTION

A series of pseudohalideamine complexes of types [Cr^{III}X$_4$L$_2$]$^-$ and [Cr^{III}X$_3$L$_3$] (X = NCO,[1] NCS,[2,3] N$_3$[4–6]; L = py, α-, β-, and γ-pic) have already been prepared and characterized by ^{1}H NMR,[7] IR,[1–3,6] and electronic[1–3,6] spectra, TG analysis,[3] and X-ray crystallography.[4,5] Reaction of K$_3$[Cr(NCS)$_6$] with pyridine,[1,2] picolines[3] or amines[8,9] seemed to be a reliable and selective synthetic route for preparing bis(amine)tetra(pseudohalide)chromium(III) complexes. Patel's method gives exclusively [Cr(NCS)$_3$py$_3$] via reaction of Cr(NCS)$_3$ · xH$_2$O with pyridine.[10] In contrast, both types of related azide compounds can be obtained from the reaction mixture of CrCl$_3$ · 6H$_2$O, KN$_3$ and pyridine.[6] Although the synthesis of compounds with [Cr(NCS)$_4$L$_2$]$^-$ and [Cr(NCS)$_3$L$_3$] (L = py, pic) has already been reported, the single crystal X-ray structure analysis has not been presented to date. There are only thirteen structures of related compounds reported in the literature: *trans*-[MX$_4$L$_2$]$^{z-}$ (z = 1, M^{III} = Cr,[5] Mo[11,12] and z = 2, M^{II} = Co,[13] Fe,[14] Mn;[14] X = NCO,[11] NCS,[12–14] N$_3$;[5] L = py,[5,11–13] γ-pic[14]) and *mer*-[M^{III}(N$_3$)$_3$L$_3$] (M = Cr,[4] Mo,[11] Os,[15] Co,[16–18]; X = NCO,[11] NCS,[15] N$_3$;[4,16–18] L = py,[4,11,15,16] γ-pic,[16,17] 3,4-Me-py,[18] 3,5-Me-py[18]).

In this paper, we present the preparation, characterization and crystal structures of *trans*-K[Cr(NCS)$_4$py$_2$] · 4py (**1**) and *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic) (**2**). In the present work, the analogy between the related chromium isothiocyanate and azide complexes has been established with regard to the coordination tendency of pyridine rings and isothiocyanate/azide groups.[4,5]

EXPERIMENTAL

All starting compounds and solvents were of analytical grade quality. K$_3$[Cr(NCS)$_6$] · 4H$_2$O was prepared by the reaction of KCr(SO$_4$)$_2$ · 12H$_2$O with KNCS.[19] The purity of

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TABLE I. Crystal data, data collection and refinement parameters for compounds **1** and **2**

Compound	**1**	**2**
Chemical formula	$C_{34}H_{30}CrKN_{10}S_4$	$C_{29}H_{91/3}CrN_{22/3}S_3$
M_r	798.04	629.80
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a / Å	8.734(1)	16.035(2)
b / Å	9.207(1)	16.847(3)
c / Å	13.623(1)	19.122(3)
α / °	71.54(1)	91.08(1)
β / °	89.00(1)	106.26(1)
γ / °	88.75(1)	95.32(1)
Z	1	6
V / Å^3	1038.8(2)	4932(1)
D_{calc} / g cm^{-3}	1.276	1.272
μ(MoK_α) / cm^{-1}	0.613	0.568
Crystal shape	prism	prism
Crystal color	red	red
Crystal size / mm	0.72 × 0.32 × 0.24	0.56 × 0.32 × 0.28
λ(MoK_α) / Å	0.71069	0.71069
Temperature / K	293(2)	293(2)
Scan type	ω–2θ	ω–2θ
Intensity change / %	–0.57	–21.54
θ (min/max) / °	1.58/28.0	1.11/26.5
Index range ($h/k/l$)	–11,11/–12,9/–17,17	–21,20/–22,22/0,25
No. of refl. measured	10876	24477
No. of indep. refl.	5018	20432
Observed reflections	3412 ($I > 2.5\sigma(I)$)	7423 ($I > 2.5\sigma(I)$)
No. of contributing reflections	4269	14144
No. of parameters	266	1090
Final R indices: R, R_w	0.040, 0.038	0.061, 0.062
Largest peak and hole ($\Delta\rho_{max}/\Delta\rho_{min}$) / e Å^{-3}	0.334, –0.366	1.14, –0.903
R_{int}	0.0293	0.0115

$K_3[Cr(NCS)_6] \cdot 4H_2O$ was checked by elemental (C, H, N) analysis, powder diffraction technique and vibrational spectroscopy.

Synthesis

trans-*K[Cr(NCS)$_4$py$_2$] · 4py (**1**).* – 10.4 g (0.0200 mol) of $K_3[Cr(NCS)_6]$ was placed in a 100 ml round bottom flask and refluxed with 35 ml of pyridine for 4–5 hours at 115–120 °C. The deep red solution was left at room temperature overnight and the resulting unstable prismatic red crystals of **1** on the surface of the pink-coloured precipitate were removed (6.4 g, 40 %). IR(nujol) $\bar{\nu}_{max}$ / cm^{-1}: 2076 ν(NC), 484 δ(NCS), 450 py, 383, 363, 340 ν(Cr–N(NCS)), 212 ν(Cr–N(py)); $\Lambda(CH_3CN)$/(S cm^2 mol^{-1}): 131.

Anal. Calcd. for $C_{34}H_{30}CrKN_{10}S_4$ (M_r = 798.0): C 51.17, H 3.79, N 17.55; found: C 50.40, H 3.64, N 17.24.

mer-*[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic) (**2**).* – A suspension of 4.50 g (8.70 mmol) of $K_3[Cr(NCS)_6]$ and 15 mL of γ-picoline was refluxed and stirred for about 5–6 hours at 140–145 °C. The deep purple solution was allowed to stand at room temperature for 50 hours, and the red-violet precipitate was removed by filtration. The resulting filtrate was slowly cooled down to 3 °C, and the unstable red crystals of **2** were obtained after 4 days (1.75 g, 32 %). IR(nujol) $\bar{\nu}_{max}$ / cm^{-1}: 2085 ν(NC), 2043 ν(NC), 498, 488 (sh) δ(NCS), 396, 371, 349, 332 ν(Cr–N(NCS)), 272, 261, 207 ν(Cr–N(γ-pic)); $\Lambda(CH_3CN)$/(S cm^2 mol^{-1}): 3.

Anal. Calcd. for $C_{29}H_{91/3}CrN_{22/3}S_3$ (M_r = 629.8): C 55.31, H 4.85, N 16.30; found: C 55.26, H 4.63, N 16.60.

Measurements

Elemental CHN analyses were obtained on a Perkin-Elmer Elemental Analyzer 2400 CHN.

Conductivity measurements were performed on an Iskra conductometer MA 5964 (with Iskra HEK 1213 electrode). Samples were prepared as 1.0×10^{-3} M solutions in acetonitrile and were measured at room temperature.

Infrared spectra were recorded as nujol suspension by a Perkin-Elmer 1720 X FT-IR instrument within the range 4000–400 cm^{-1} (with KBr plates) and a Perkin-Elmer 2000 FT-IR instrument within the range 700–30 cm^{-1}.

Thermogravimetric curves were recorded in air on a Perkin-Elmer Thermogravimetric Analyzer TGA 7; the temperature range was 25–900 °C and the heating rate of 5 K min^{-1} was applied.

X-ray powder diffraction measurements were obtained using a Guinier camera Enraf Nonius FR 552 with Cu-*K*α radiation.

The X-ray data were collected by an Enraf Nonius CAD-4 diffractometer using graphite monochromatized Mo-*K*α radiation (λ = 0.71069 Å) at 20 °C. The crystal was mounted in a thin-walled glass capillary together with some mother liquor to prevent the release of pyridine (**1**) and picoline (**2**) molecules. In both cases, cell dimensions were determined from setting angles of 75 reflections. Changes of –0.57 % (**1**) and –21.54 % (**2**) in the intensities of check reflections were observed and corrections were applied. An analytical absorption correction and Lp corrections were applied for both compounds. Both structures were solved by direct methods using SIR92.[20] In both structures, most of the H-atom positions were found in the intermediate difference Fourier map. The remaining H-atom positions were calculated in ideal geometrical positions. Full-matrix least-squares refinement on *F* magnitudes with anisotropic temperature factors for all non-hydrogen atoms was employed. For **1,** also the positions of the H-atoms (with the exception of three) were refined. For correlation and reduction of data, structure refinement and interpretation, the XTAL 3.4 system of crystallographic programs was used.[21] Details of the refinement and other crystal data for both compounds are listed in Table I. Selected bond lengths and angles between atoms are given in Table II (**1**), and Tables III and IV (**2**). Planes through atoms and angles between planes for **2** (labelled in Figure 3) are presented in Table V. The asymmetric units of both compounds with the atom-numbering scheme are shown in Figures 2 and 3 (**1** and **2**). Both drawings were produced using ORTEPII.[22]

RESULTS AND DISCUSSION

Crystal Structures

In **1,** the chromium atom is six-coordinated with two pyridine molecules in *trans* position and four square-planar N-bound NCS groups. There are four pyridine molecules and two *trans* S-coordinated NCS groups round the potassium ion. The [$Cr(NCS)_4py_2$]$^-$ and K^+ share isothiocyanate ligands to form a chain, the arrangements around Cr^{III} and K^+ are octahedral (Figure 1). Both the chromium and the potassium atoms occupy special positions at inversion centres, (0, 1/2, 1/2) and (0, 1/2, 0), respectively. The Cr–N bond lengths involving the isothiocyanate groups are shorter than those involving the pyridine molecules (Table II), but they are still close to the average Cr–NCS terminal bond lengths in **2** (Table III) and to those reported elsewhere.[23–25] All the angles at the Cr atom (N–Cr–N) and those in the isothiocyanate groups (N–C–S) are close to 90° and 180°, respectively. The K···S(2)–C(2) angle is 110.88(11)° and is much lower compared to N–N–Na/K/Rb angles observed in the related azide complexes (120–165°).[4,5]

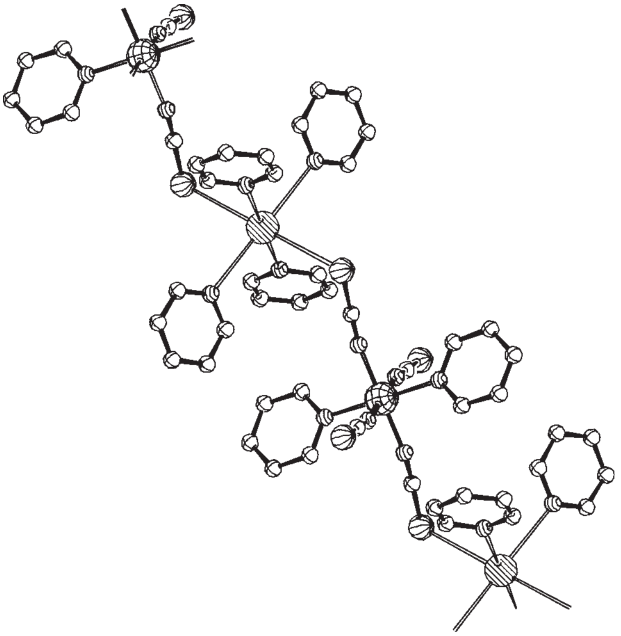

Figure 1. PLATON drawing of the chains in compound **1**. Hydrogen atoms are omitted for clarity.

In **2**, there are three independent *mer* coordinated [$Cr(NCS)_3(\gamma\text{-pic})_3$] molecules together with four free γ-pic molecules in the asymmetrical unit. The Cr–N bond distances are close to those found in **1**. Cr to isothiocyanate-N distances are slightly shorter than 2.00 Å whereas those between Cr and picoline N atoms are close to 2.10 Å. In

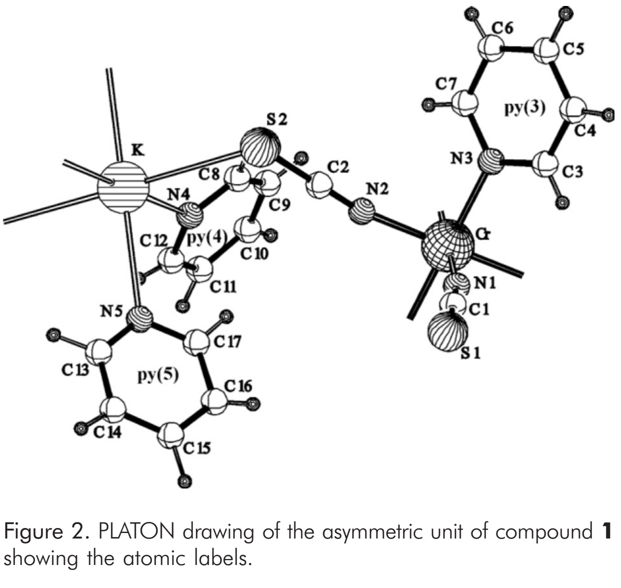

Figure 2. PLATON drawing of the asymmetric unit of compound **1** showing the atomic labels.

TABLE II. Selected bond distances and angles in [Cr^{III}(NCS)$_4$py$_2$]$^-$ and (Kpy$_4$)$^+$ of **1**

		Bond distances / Å			
Cr–N1	1.990(2)	Cr–N2	1.990(3)	Cr–N3	2.078(2)
K–N4	2.784(3)	K–N5	2.825(5)	K···S2	3.2048(11)
N1–C1	1.151(3)	N2–C2	1.149(4)	C1–S1	1.619(3)
C2–S2	1.613(3)				
		Bond angles / °			
N1–Cr–N2	88.68(10)	N1–Cr–N3	90.04(8)	N2–Cr–N3	89.28(9)
N4–K–N5	85.67(12)	N4–K···S2	87.92(8)	N5–K···S2	93.41(11)
Cr–N1–C1	170.0(3)	Cr–N2–C2	166.6(2)	K···S2–C2	110.88(11)
N1–C1–S1	179.4(2)	N2–C2–S2	178.6(3)		

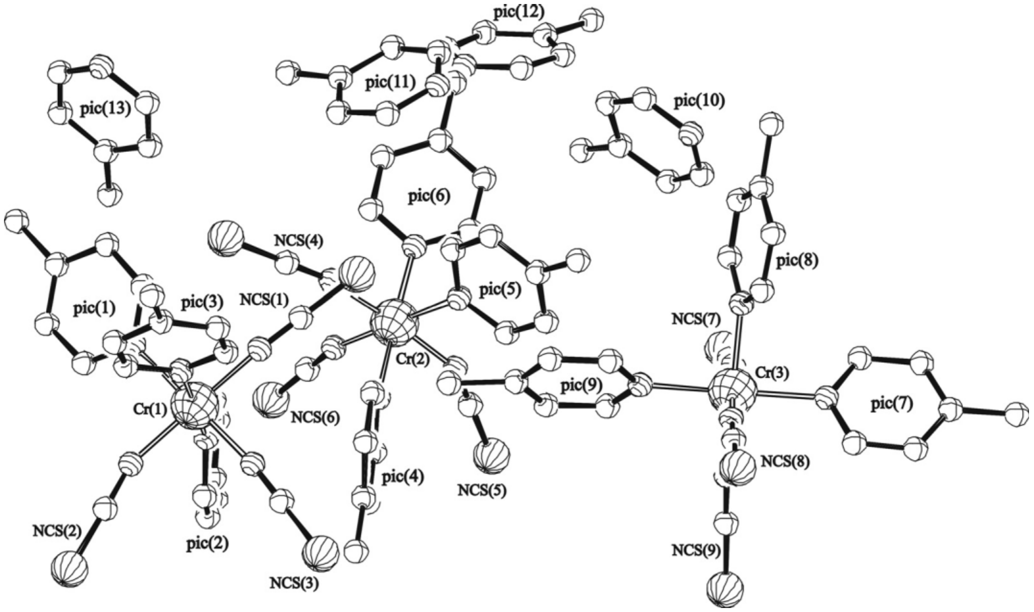

Figure 3. PLATON plot of the asymmetric unit of compound **2**. Hydrogen atoms are omitted for clarity.

TABLE III. Selected contact bond distances in [Cr^{III}(NCS)$_3$(γ-pic)$_3$] of **2**

		Bond distances / Å			
Cr1–N1	2.090(6)	Cr1–N2	2.109(6)	Cr1–N3	2.083(6)
Cr1–N1'	1.965(7)	Cr1–N2'	1.970(7)	Cr1–N3'	1.979(8)
N1'–C1	1.175(10)	N2'–C2	1.169(11)	N3'–C3	1.160(12)
C1–S1	1.599(8)	C2–S2	1.600(9)	C3–S3	1.602(10)
Cr2–N4	2.090(7)	Cr2–N5	2.104(6)	Cr2–N6	2.073(7)
Cr2–N4'	1.995(7)	Cr2–N5'	1.992(7)	Cr2–N6'	1.993(6)
N4'–C4	1.162(9)	N5'–C5	1.153(10)	N6'–C6	1.146(9)
C4–S4	1.596(7)	C5–S5	1.604(9)	C6–S6	1.603(8)
Cr3–N7	2.106(6)	Cr3–N8	2.109(7)	Cr3–N9	2.088(6)
Cr3–N7'	1.968(7)	Cr3–N8'	1.991(7)	Cr3–N9'	1.995(8)
N7'–C7	1.169(10)	N8'–C8	1.162(11)	N9'–C9	1.148(13)
C7–S7	1.596(8)	C8–S8	1.591(9)	C9–S9	1.593(11)

TABLE IV. Selected angles in [Cr^{III}(NCS)$_3$(γ-pic)$_3$] of **2**

Bond angels / °					
N1–Cr1–N2	87.8(2)	N1–Cr1–N3	89.1(3)	N1–Cr1–N1'	89.6(3)
N1–Cr1–N2'	90.8(3)	N1–Cr1–N3'	179.6(3)	N2–Cr1–N3	176.8(3)
N2–Cr1–N1'	89.6(3)	N2–Cr1–N2'	89.2(3)	N2–Cr1–N3'	91.8(3)
N3–Cr1–N1'	90.1(3)	N3–Cr1–N2'	91.2(3)	N3–Cr1–N3'	91.4(3)
N1'–Cr1–N2'	178.7(3)	N1'–Cr1–N3'	90.6(3)	N2'–Cr1–N3'	89.1(3)
Cr1–N1'–C1	175.4(6)	Cr1–N2'–C2	162.2(7)	Cr1–N3'–C3	173.0(7)
N1'–C1–S1	179.3(8)	N2'–C2–S2	178.4(8)	N3'–C3–S3	179.6(10)
N4–Cr2–N5	87.8(2)	N4–Cr2–N6	176.3(2)	N4–Cr2–N4'	88.5(3)
N4–Cr2–N5'	89.9(3)	N4–Cr2–N6'	91.5(3)	N5–Cr2–N6	88.6(2)
N5–Cr2–N4'	91.3(2)	N5–Cr2–N5'	91.1(2)	N5–Cr2–N6'	179.0(3)
N6–Cr2–N4'	90.6(3)	N6–Cr2–N5'	91.2(3)	N6–Cr2–N6'	92.2(3)
N4'–Cr2–N5'	177.1(2)	N4'–Cr2–N6'	89.5(3)	N5'–Cr2–N6'	88.1(3)
Cr2–N4'–C4	166.3(6)	Cr2–N5'–C5	154.3(6)	Cr2–N6'–C6	166.8(8)
N4'–C4–S4	179.1 (7)	N5'–C5–S5	179.5(12)	N6'–C6–S6	178.9(7)
N7–Cr3–N8	88.3(2)	N7–Cr3–N9	179.2(3)	N7–Cr3–N7'	89.8(3)
N7–Cr3–N8'	90.6(3)	N7–Cr3–N9'	90.4(3)	N8–Cr3–N9	90.9(3)
N8–Cr3–N7'	90.2(3)	N8–Cr3–N8'	90.7(3)	N8–Cr3–N9'	178.7(3)
N9–Cr3–N7'	90.1(3)	N9–Cr3–N8'	89.6(3)	N9–Cr3–N9'	90.4(3)
N7'–Cr3–N8'	179.0(3)	N7'–Cr3–N9'	90.0(3)	N8'–Cr3–N9'	89.1(3)
Cr3–N7'–C7	169.4(6)	Cr3–N8'–C8	172.9(8)	Cr3–N9'–C9	175.4(8)
N7'–C7–S7	179.3(8)	N8'–C8–S8	178.9(8)	N9'–C9–S9	179.1(8)

all three symmetrically independent coordinated molecules, the perfect staggered configurations of the *trans* positioned γ-pic rings are closely approached (80–84°, Table V-A). The planes through *trans* positioned γ-pic rings approximately bisect the N–Cr–N angles in the plane perpendicular to them (37–44°, Table V-C). In all three independent units, the plane of the middle ring of the *trans*-coordinated picoline molecules is turned with regard to the plane described by N-atomes of isothiocyanate groups and the related N-atom of the γ-pic ring (20–30°, Table V-B). In all the three molecules, the *trans* N–Cr–N angles are smaller than 180° (176.3(2)–179.6(3)°) (Table IV). The Cr–N–C angles in both compounds are between 154.3(6) and 175.4(8)° (Tables II and IV).

Thermal Analyses

For compound **1** (Figure 4), the first mass-loss step, completed at 105 °C, can be attributed to the weight loss of four molecules of pyridine. The theoretical value is slightly higher than that obtained from the TG curve (calcd. 39.6 %, found 36.5 %). Further decomposition/oxidation begins at about 175 °C and is completed at *ca.* 760 °C, resulting in a mixture of K_2SO_4 and Cr_2O_3 (calcd. 20.4 %, found 23.3 %).

The weight loss of the first step in the case of **2** (Figure 4), ascribed to the loss of 4/3 γ-picoline molecules, is close to the theoretical value (calcd. 19.7 %, found 18.1 %). Further decomposition begins at about 215 °C and is completed at about 660 °C, resulting in Cr_2O_3 (calcd. 12.1 %, found 12.6 %).

For both compounds, the identity of products (K[Cr(NCS)$_4$py$_2$] and Cr(NCS)$_3$(γ-pic)$_3$]), obtained by decomposition of **1** and **2** at about 100 °C, was confirmed by CHN analyses, and by comparison of their IR and electronic spectra. The identity of oxidation products was verified by IR spectra and powder X-ray measurements.

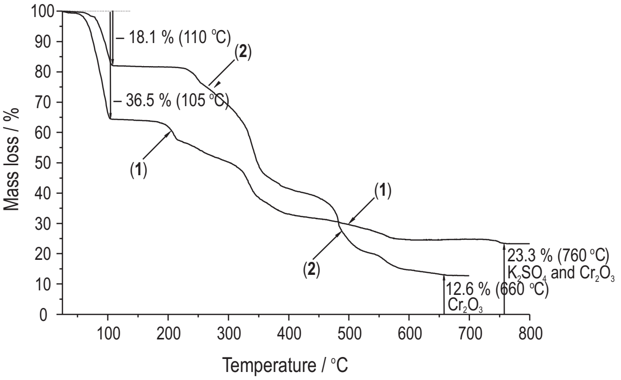

Figure 4. Thermogravimetric curves of compound **1** and compound **2**, within the range 25–800 °C (**1**) and 25–700 °C (**2**).

TABLE V. Planes through atoms (**2**, shown in Figure 3)[(a),(b)]

Plane	Individual atoms	*Atom	Deviation / Å
1	N1, C11–C16	C16	–0.021(13)
2	N2, C21–C26	C26	–0.044(16)
3	N3, C31–C36	C33	0.017(12)
10	N1, N1', N2', N3'	N3'	0.010(9)
11	N2, N1', N2', N3	N2'	0.033(9)
4	N4, C41–C46	C46	0.013(17)
5	N5, C51–C56	C56	–0.043(13)
6	N6, C61–C66	C65	–0.016(11)
12	N4, N4', N5', N6	N5'	–0.058(9)
13	N5, N4', N5', N6’	N6'	0.009(9)
7	N7, C71–C76	C76	–0.008(14)
8	N8, C81–C86	C85	–0.018(12)
9	N9, C91–C96	C96	–0.052(16)
14	N7, N7', N8', N9	N8'	–0.016(9)
15	N8, N7', N8', N9'	N9'	0.016(9)
Planes	**Angle / °**	**Planes**	**Angle / °**
Section A		Section B	
2.3	79.8(3)	1.10	29.7(3)
4.6	84.1(3)	5.13	28.3(3)
7.9	83.3(3)	8.15	19.9(3)
Section C			
2.11	42.8(3)	3.11	37.1(3)
4.12	44.0(3)	6.12	40.1(3)
7.14	39.3(3)	9.14	44.0(3)

(a) *Atoms with the largest deviations from that planes and angles between planes in [Cr^{III}(NCS)$_3$(γ-pic)$_3$] of **2**.

(b) N'-labeled atoms are from isothiocianate groups

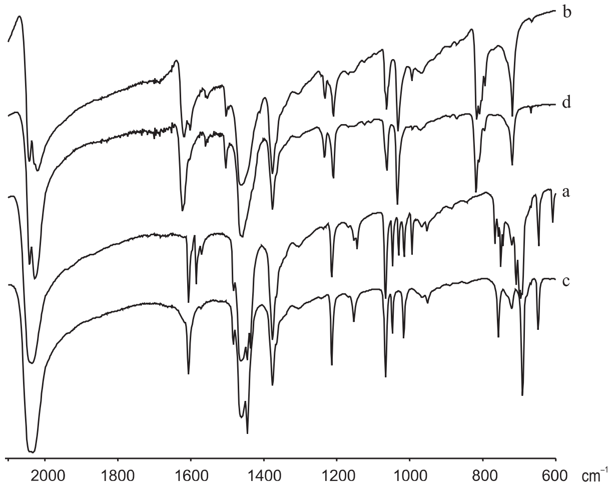

Figure 5. Vibrational spectra of compound **1** and compound **2**, within the range 2200–600 cm^{-1}; immediately after filtration: **1** (a), **2** (b); after drying **1** at 110 °C (c), **2** at 115 °C (d).

Spectroscopy

The bonding mode of the NCS group can be predicted from IR spectra, since the shift in the frequencies of the three vibration modes (C–N stretching, C–S stretching and N–C–S bending) in the NCS moiety depends upon complexation.[12] The position and the width of *ν*(CN) (2076 cm^{-1} for **1**, and 2085 and 2043 cm^{-1} for **2**), as well as the position of *γ*(NCS) band (484 cm^{-1} (**1**); 498, 488 (sh) cm^{-1} (**2**)) indicate that NCS ligands are bonded through N in both compounds.[26–30] For the *trans*-(cat)[Mo(NCS)$_4$L$_2$] (cat = pyH$^+$, py$_2$H$^+$), the corresponding bands at *ca.* 2050 *ν*(CN) and 485 *δ*(NCS) cm^{-1} are observed.[12] The *δ*(CH) absorption bands of aromatic N-donor ligand (py, γ-pic) mask the weak *ν*(CS) band, so its position cannot be determined.[28–31] The band at 450 cm^{-1} present in the spectrum of **1** can be assigned as a shift of the 403 cm^{-1} band of free pyridine.[32,33] In the spectrum of **2,** several bands originating from the γ-picoline vibrations are noticed. The Cr–N stretching bands occur only in the far-infrared region[30] while the *ν*(Cr–N(NCS)) bands are expected to lie slightly above the Cr–Cl ones of the corresponding chloro complexes.[2]

The IR-spectra and some relevant vibrations are given in Table VI. Since in **1** the Cr atom is positioned at an inversion centre, at least two IR-active frequencies (A$_u$) are expected for the Cr–N(NCS) stretching mode of the square-planar Cr–NCS skeleton, and one for the Cr–N(py) mode

TABLE VI. *ν*(CN), *δ*(NCS), *ν*(Cr–N(NCS)) and *ν*(Cr–N(L)) (L = py, γ-pic) infrared vibrations for **1**, **2** and their desolvated analogues

	ν(CN)	*δ*(NCS)	*ν*(Cr–N(NCS))	*δ*(Cr–N(L))[(a)]
K[Cr(NCS)$_4$py$_2$] · 4py	2076	484	383, 363, 340	212
K[Cr(NCS)$_4$py$_2$][(b)]	2071	484	383, 362, 340	213
K[Cr(NCS)$_4$py$_2$][(c)]	2074	484	382, 362, 335	213
[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic)	2085, 2043	498, 488[(d)]	396, 371, 349, 332	272, 261, 207
[Cr(NCS)$_3$(γ-pic)$_3$][(e)]	2085, 2055	498, 486[(d)]	394, 371, 349, 331	272, 260, 199

(a) These peaks are weak, all others are strong; (b) Compound K[Cr(NCS)$_4$py$_2$] obtained from **1** when dried at 110 °C; (c) Ref. 2; (d) Shoulder; (e) Compound [Cr(NCS)$_3$(γ-pic)$_3$] obtained from **2** when dried at 115 °C.

of the (py)N–Cr–N(py) group. There are no differences in the number of bands and values obtained from the spectrum of desolvated compound **1** and those observed elsewhere (Table VI).[2]

CONCLUSIONS

The N-bonding of the NCS groups in both compounds is confirmed by the results of X-ray diffraction analysis. The positions and the widths of the ν(CN) and δ(NCS) bands are in agreement with the crystal-structure results. Comparison of the electronic spectra and IR spectra below 400 cm^{-1} (Cr–N bonds) (Table VI), before and after drying at 110 °C (**1**) and 115 °C (**2**), respectively, reveals an almost identical feature. Therefore, in **1** and **2,** there is no change in coordination spheres via a loss of solvated py/γ-pic molecules.

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Supplementary Materials. – Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44–1223–336033; e.mail.: deposit@cc–dc.ca.ac.uk) and can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 284602 and 284603.

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SAŽETAK

Priprava i kristalne strukture *trans*-K[Cr(NCS)$_4$py$_2$] · 4py i *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic)

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trans-K[Cr(NCS)$_4$py$_2$] · 4py (**1**) (py-piridin) priređen je zagrijavanjem K$_3$[Cr(NCS)$_6$] u piridinu uz refluks, pri čemu je došlo do supstitucije dvaju tiocijanatnih liganada s dvije molekule piridina. Na sličan način ali uz dodatak γ-pikolina priređen je neutralni kompleks *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] · 4/3(γ-pic). Kristalna struktura spoja **1** sadrži polimerne lance *trans*-oktaedarski koordiniranih Cr^{III} u [Cr(NCS)$_4$py$_2$]$^-$ anionima i *trans*-oktaedarski koordiniranih K$^+$ povezanih nelinearnim K···SCN–Cr–NCS···K kontaktima. Struktura spoja **2** sadrži izolirane *mer*-[Cr(NCS)$_3$(γ-pic)$_3$] molekule i molekule kristalnog γ-pikolina. Podaci dobiveni IR spektroskopijom potvrđuju postojanje Cr–NCS veze u oba kompleksa.