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Synthesis and Characterization of *trans*-(pyH)[Mo(NCS)$_4$py$_2$] and *trans*-(py$_2$H)[Mo(NCS)$_4$py$_2$]. Crystal Structure of *trans*-(py$_2$H)[Mo(NCS)$_4$py$_2$]

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(pyH)[Mo(NCS)$_4$py$_2$] (**1**) (py = pyridine) was prepared by refluxing of the mixture of KSCN and [MoCl$_3$py$_3$] in pyridine. After the recrystallization of **1** in pyridine, single crystals of *trans*-(py$_2$H)[Mo(NCS)$_4$py$_2$] (**2**) were obtained. X-ray structure determination of **2** reveals *trans* slightly elongated (4 + 2) octahedral arrangement of two staggered conformated (85.9(4)°) N-bond pyridine molecules (Mo–N(py) = 2.191(6), 2.176(5) Å) and four isothiocyanato groups in square-planar orientation, bonded within the range 2.083(7)–2.106(7) Å to molybdenum atom in the anion. In the (py$_2$H)$^+$ cation, pyridine molecules are held together by a strong hydrogen bond with contact distance N7···N8 = 2.708(12) Å (N8–H8'···N7 geometry: N8–H8'···N7 = 175(7)°, N7···H8' = 1.65(7) Å, N8–H8' = 1.06(7) Å). The angle between the best planes through the pyridine–cation rings is 70.7(6)°. The results of IR and UV/Vis spectroscopy indicate the same arrangement of the ligands in the compounds **1** and **2**.

INTRODUCTION

The NCS group is interesting because of its versatile coordination nature to the central metal atom. The bonding mode depends on the metal (size, charge), on the additional ligands in the coordination sphere (charge, size, shape) and also on the conditions of the synthesis (temperature, solvent). In some cases both linkage isomers were isolated.[1–4] Solvents with high dielectric constants promote M–SCN bonding, whereas those with the low dielectricity promote M–NCS bonding.[3] Nitrogen atom is better electron donor than sulphur, so according to the concept developed by Pearson, the NCS group coordinated through nitrogen represents a »hard base«, whereas a sulphur-coordinated NCS group is considered as a »soft base«.[1,2] Because Mo^{III} belongs to »hard acids«, it should be coordinated preferably *via* nitrogen.[5] The steric requirements for the angular M–S–CN linkage are greater than for the linear M–NCS bonding. Thus the presence of the large ligands in the coordination sphere, tend to generate strains in M–SCN and promote M–NCS bonding.[2,4] Though the sulphur atom is a weaker σ-donor of electrons than the nitrogen atom, M–S bonding is stabilized by π back-bonding from metal to sulphur. However, when the additional ligand in the coordination sphere is a strong π-electron acceptor, the M–S π back-bond is reduced in strength, so N-bonded isomer is more stable.[2,4,6,7]

The aim of our work was the synthesis and characterization of pseudohalogenido complexes with chromium and molybdenum as a central atom and pyridine (py) or γ-picoline (pic) molecule as an additional ligand,

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of the types $[MX_3L_3]$ and $[MX_4L_2]^-$ (M = Cr, Mo; L = py, pic, X = NCS, NCO). We have found only the structures of four compounds of related types (*mer*-$[Os(NCS)_3py_3]$,[8] *trans*-$Hg[Co(NCS)_4py_2]$,[9] *trans*-$(picH)_2[Mn(NCS)_4pic_2] \cdot$ 2pic[10] and *trans*-$(picH)_2[Fe(NCS)_4pic_2]\cdot$2pic[10] in the literature. Although the synthesis of $(py_2H)[Mo(NCS)_4py_2]$ and several other compounds with $[Mo(NCS)_4py_2]^-$ have already been reported,[11] the X-ray structure analysis of the single crystals have not been presented. In this paper, we present the synthesis and characterization of *trans*-(cat)$[Mo(NCS)_4py_2]$ (cat = $(pyH)^+$, $(py_2H)^+$) and the crystal structure of *trans*-$(py_2H)[Mo(NCS)_4py_2]$.

EXPERIMENTAL

All starting compounds and solvents were of analytical grade quality. *mer*-$[MoCl_3py_3]$ was prepared as described previously.[11,12] The purity was checked by elemental (C, H, N) analysis, powder diffraction technique and vibrational spectroscopy.

Synthesis

trans-*(pyH)[Mo(NCS)$_4$py$_2$] (**1**)*

The mixture of KSCN (5.8 g, 0.060 mol) and *mer*-$[MoCl_3py_3]$ (8.8 g, 0.020 mol) in pyridine (45 mL) was refluxed in argon atmosphere for 5 hours. The solution was left at room temperature during the night (in argon atmosphere) and resulting yellow precipitate was filtered (the filtrate was used to obtain compound **2**). To remove the by-products and the remains of the reactants, the precipitate was washed with water and subsequently with methanol, and than dried at 135 °C, to remove all molecules of solvated pyridine. Yield: 4.2 g (49 %); UV/Vis(nujol) λ_{max}/nm: 259, 362; UV/Vis(CH_3CN) λ_{max}/nm: 252, 330, 346, 767; IR(nujol) ν_{max}/cm^{-1}: 2047, 1524, 487, 441, 307, 278, 210; Λ(CH_3CN)/S cm^2 mol^{-1}: 121.

Anal. Calcd. for $C_{19}H_{16}MoN_7S_4$ (M_r = 566.56): C 40.28, H 2.85, N 17.31 %; found: C 39.99, H 2.72, N 16.97 %.

trans-*(py$_2$H)[Mo(NCS)$_4$py$_2$]* (**2**)

The filtrate was cooled down to 4 °C and yellow crystals of the compound **2** precipitated and were filtered after 18 hours (1.5 g, 15 %). The single crystals of compound **2** suitable for X-ray diffraction were isolated as follows: *trans*-(pyH)$[Mo(NCS)_4py_2]$ (**1**) (0.77 g) was dissolved in pyridine (10 mL) at room temperature and the solution was filtered. After tree days of the slow diffusion of ether (into the solution) single crystals were obtained (0.28 g, 32 %). UV/Vis(nujol) λ_{max}/nm: 259, 361; UV/Vis(CH_3CN) λ_{max}/nm: 252, 330, 347, 768; IR(nujol) ν_{max}/cm^{-1}: 2052, 481, 434, 311, 280, 197; Λ(CH_3CN)/S cm^2 mol^{-1}: 127.

Anal. Calcd. for $C_{24}H_{21}MoN_8S_4$ (M_r = 645.66): C 44.65, H 3.28, N 17.35 %; found: C 44.19, H 3.05, N 17.54 %.

Measurements

Elemental (C, H, N) analyses were obtained using a Perkin-Elmer Elemental Analyzer 2400 CHN.

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

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

Electronic spectra were measured with a Perkin-Elmer UV/VIS/NIR spectrophotometer Lambda 19. Samples were prepared as nujol suspensions and as solutions in acetonitrile.

Thermogravimetric curve was recorded in the air by a Perkin-Elmer Thermogravimetric Analyzer TGA 7; the temperature range was 25–600 °C and the heating rate 5 K min^{-1} was applied.

X-ray powder diffraction data were obtained using Guinier camera Enraf Nonius FR 552 with Cu-Kα radiation.

The X-ray single crystal data were collected using Enraf Nonius CAD-4 with Mo-Kα radiation (λ = 0.71069 Å) at 20 °C. Crystal was mounted in thin-walled glass capillary together with some mother liquor to prevent the release of pyridine molecules. Cell parameters were determined from setting angles of 75 reflections ($8.00° < \theta < 13.66°$). Crystal stability was monitored by periodic measurements of the standard reflections every 333 minutes. A change of –2.81 % intensity was observed and correction applied. The reflection data were also corrected for Lorentz and polarization effects. The absorption correction was done using numerical analytical method. Since the space group $P2_12_12_1$ is non-centrosymmetric the Friedel pairs were not merged and Flack parameter was refined. Structure was solved by direct methods using SIR92.[13] The positions of H-atoms were calculated regarding the geometry with the exception of a proton from the cation. Difference Fourier map indicated that this proton is disordered over at least two positions, located in the area between the two nitrogen atoms of the non-coordinated pyridines (N7 and N8). We tried to resolve this disorder by the refinement of the positions of two maxima (one in the closeness to N7 and the other to N8 atom) with 50 % occupancy, but we were not successful. Finally, the strongest peak in the difference Fourier map in the region in between atoms N7 and N8 was assigned as H atom (H8') and its position was refined resulting in a reasonable N8–H8'···N7 geometry (N8–H8'···N7 angle 175(7)°, N7···N8, N7···H8' and N8–H8' distances of 2.708(12), 1.65(7) and 1.06(7) Å, respectively). Nevertheless, small peaks in the final difference Fourier map that remained in the vicinity of N7 are a sign of a hydrogen atom disorder. For a better description of this situation we would need not only better X-ray diffraction data, but also neutron diffraction data due to the fact that H atoms have small scattering power for X-rays and significantly larger for neutrons. Full-matrix least-squares refinement of F^2 magnitudes with anisotropic temperature factors for all non-hydrogen atoms was employed. The parameters of H-atoms (with the exception of that from $(py_2H)^+$ cation) were not refined. For the correlation and reduction of the structure data and for the refinement and interpretation, the XTAL3.6 system of crystallographic programs was used.[14] The crystal data and details of the data collection and refinement are collected in

TABLE I. Crystal data, data collection and refinement

formula	$C_{24}H_{21}MoN_8S_4$
*M*r	645.66
crystal system, space group	orthorhombic, $P2_12_12_1$
a, *b*, *c* /Å	8.430(1), 10.699(1), 33.761(3)
volume /Å^3	3045.0(5)
Z	4
D_x /Mg m^{-3}]	1.408
μ /mm^{-1}	0.73
crystal shape, color	plate, yellow
crystal size / mm	0.10 × 0.36 × 0.56
T_{min} / T_{max}	0.7737 / 0.9195
θ_{max} /°	27.96
h / *k* / *l* (min., max.)	–11, 11 / 0, 14 / –44, 0
No. of measured reflections	7873
No. of independent reflections	7291
R_{int}	0.0245
No. of observed reflections ($I > 2.5\sigma(I)$)	3320
No. of contributing reflections$^{(a)}$	5776
No. of parameters	338
No. of Friedel pairs	3158
Flack parameter	–0.08(6)
R	0.037
R_w	0.022
$\Delta\rho_{max}$ / eÅ^{-3}	0.672
$\Delta\rho_{min}$ / eÅ^{-3}	–0.645

(a) Reflections contributed to the Least-Square matrix; all observed reflections and those less-than ($I < 2.5\sigma(I)$) reflections, whose calculated magnitude of structure factor was larger than the observed one.

Table I. Selected bond lengths and the angles are given in Table II. The asymmetric unit with atom-numbering scheme is shown in Figure 1 (ORTEP–3).[15]

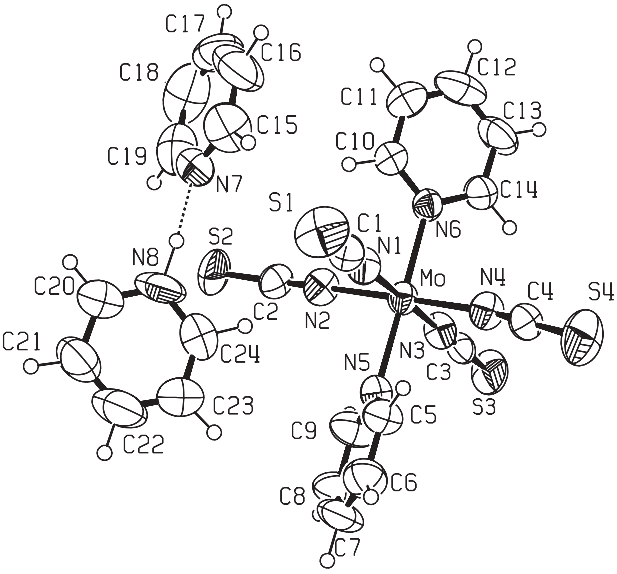

Figure 1. ORTEP–3 (Ref. 15) drawing of the asymmetric unit of the compound **2**. Thermal displacement ellipsoids are drawn at 50 % probability level.

RESULTS AND DISCUSSION

Crystal Structure of trans-*(py_2H)[Mo(NCS)$_4$ py$_2$] (2)*

The asymmetric unit of compound **2** (Figure 1) consists of (py_2H)$^+$ cation and molybdenum(III) complex anion. In the coordination anion, molybdenum is coordinated *via* nitrogen atoms by four isothiocyanato and two pyridine ligands in *trans* position. The coordination polyhedron of the MoN_6 moiety is slightly elongated octahedron. Four isothiocyanato nitrogen atoms are bonded to Mo^{III} ion at the distances ranging between 2.083(7) and 2.106(7) Å. Similar Mo–N bond lengths (from 2.034(18) to 2.119(14) Å) were found in $K_3[Mo(NCS)_6]\cdot H_2O\cdot CH_3COOH$ complex.[16] The two pyridine ligands are bonded to molybdenum at distances 2.191(6) and 2.176(5) Å which is close to 2.196 Å, the Mo–N bond distance found in the [MoCl$_4$py$_2$] complex anione.[17] Similar to *mer*-[Os(NCS)$_3$py$_3$],[8] *trans*-Hg[Co(NCS)$_4$py$_2$][9] and *trans*-(picH)$_2$[M(NCS)$_4$pic$_2$] · 2pic (M = Mn, Fe)[10] the NCS moieties are nearly linear (N–C–S = 177.4(9)–179.8(8)°). The best planes through pyridine–ligand rings are almost perpendicular to each other (85.9(4)°). Such orientation of pyridine ligands was also found in *trans*-(pyH)[MoBr$_4$py$_2$].[18] In the (py_2H)$^+$ cation, pyridine molecules are held together by a strong hydro-

TABLE II. Selected contact bond distances / Å and angles / °

Mo–N1	2.092(7)	Mo–N2	2.087(7)	Mo–N3	2.083(7)
Mo–N4	2.106(7)	Mo–N5	2.191(6)	Mo–N6	2.176(5)
N7···N8	2.708(12)	N7···H8'	1.65(7)	N8–H8'	1.06(7)
N1–Mo–N2	90.1(3)	N1–Mo–N3	178.5(3)	N1–Mo–N4	87.8(3)
N1–Mo–N5	88.4(3)	N1–Mo–N6	89.8(2)	N2–Mo–N3	90.8(3)
N2–Mo–N4	177.5(3)	N2–Mo–N5	89.9(3)	N2–Mo–N6	90.3(3)
N3–Mo–N4	91.3(3)	N3–Mo–N5	90.4(3)	N3–Mo–N6	91.4(3)
N4–Mo–N5	88.8(3)	N4–Mo–N6	90.9(2)	N5–Mo–N6	178.2(2)
Mo–N1–C1	171.0(7)	Mo–N2–C2	176.4(7)	Mo–N3–C3	177.5(7)
Mo–N4–C4	165.4(6)	N1–C1–S1	179.3(8)	N2–C2–S2	177.4(9)
N3–C3–S3	179.8(8)	N4–C4–S4	179.6(8)	N7···H8'–N8	175(7)

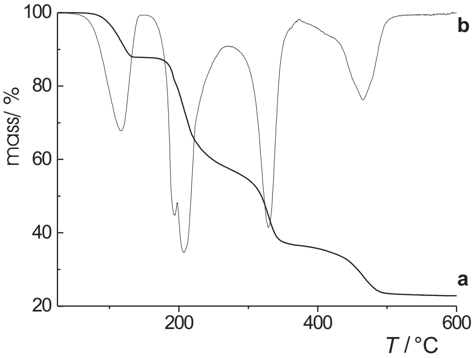

Figure 2. Thermogravimetric curve of the compound 2 (a) and its derivative (b), within the range 25–600 °C.

gen bond with the N7···N8 contact distance of 2.708(12) Å. The N···N contact distances in other structures containing $(py_2H)^+$ cation range in between 2.634 and 2.757 Å.[19–33] The angle between the best planes through the pyridine–cation rings is 70.7(6)°.

Thermal Analysis of trans-*$(py_2H)[Mo(NCS)_4py_2]$ (**2**)*

In the thermogravimetric curve, four well-defined mass-loss steps in the temperature range 50–500 °C were noticed. The first step, completed at 130 °C, is attributed to the removal of one pyridine molecule (calculated: 12.3 %; found: 11.8 %). The second step (180–225 °C) can be ascribed to the loss of two pyridine molecules (calculated: 24.5 %; found: 25.3 %). The end of the combustion at about 500 °C results in an appearance of MoO_3 (calculated: 22.3 %; found: 23.2 %). The identity of the oxidation product was confirmed by vibrational spectra and powder X-ray diffraction measurements.

Spectroscopy

The bonding mode of the NCS group can be predicted from IR spectra. 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 (for the free ion, as in KSCN, these frequencies are: ν (CN) = 2066 cm^{-1}, ν (CS) = 743 cm^{-1}, δ (NCS) = 470 cm^{-1}).[4,34] In general, the ν (CN) absorption is strong and exhibits a broad band below or close to 2100 cm^{-1} for isothiocyanato and a sharp band above 2100 cm^{-1} for thiocyanato compounds.[2,4,7,34,35] The ν (CS) absorption, ranging between 690–730 cm^{-1} for thiocyanato and between 780–860 cm^{-1} for isothiocyanato compounds, is weak.[6,7,34,36] The δ (NCS) frequency in isothiocyanato complexes is very similar to that in KSCN; one band of medium intensity within the range 450–490 cm^{-1} is observed. In S-bonded complexes, several bands ranging between 400–480 cm^{-1} appear (the strongest one close to 400 cm^{-1} and weaker satellites at higher energies).[6,7,34]

All Mo–N stretching bands (Mo–N(NCS) and Mo–N(py)) occur only in the far-infrared region.[34] The ν (Mo–N(py)) vibrations are expected to lie within 200–270 cm^{-1}.[37] The energy of the ν (M–N(NCS)) is higher than that of ν (M–S(SCN).[38] Assuming the same symmetry, the isothiocyanato compounds give rise to strong bands at the values slightly above the M–Cl stretches of the corresponding chloro complexes, whereas S--bonded complexes give bands of medium intensity, which fall approximately midway between the M–X (X = Cl, Br) stretches of the corresponding chloro and bromo complexes.[39] For the corresponding *trans*-$(pyH)[MoCl_4py_2]$, the strong Mo–Cl stretch at 307 cm^{-1} with the shoulder at 320 cm^{-1} and medium Mo–N(py) stretch at 249 cm^{-1} is noticed.[40] In the spectrum of *trans*-$(pyH)[MoBr_4py_2]$, a very strong band at 256 cm^{-1} and the shoulder at 250 cm^{-1} are observed.[18]

Significant distinctions between IR spectra of the non-dried and dried (135 °C) compound **2** (Figure 3) were observed. The most interesting change after the drying is an appearance of the characteristic band for the pyridinium cation at 1524 cm^{-1},[41] that is not observed in the vibration spectrum of the non-dried compound. It is worth

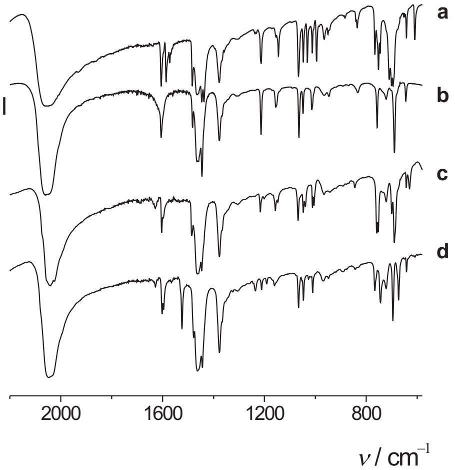

Figure 3. Vibrational spectra of the compound **2**, within the range 2200–580 cm^{-1}; immediately after filtration (a), after two hours at room temperature (b), after 24 hours at room temperature (c), after drying at 135 °C (d).

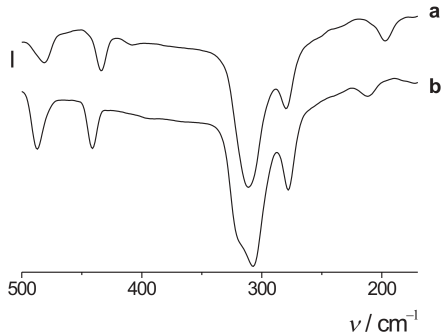

Figure 4. Vibrational spectra of the compound **2**, within the range 500–170 cm^{-1}; immediately after filtration (a), after drying at 135 °C (b).

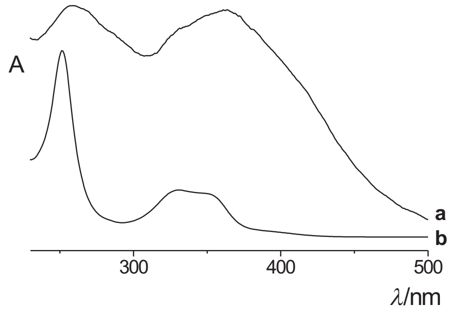

Figure 5. Electronic spectra of the compound **2**, within the range 230–500 nm; nujol suspension (a), 1.0 × 10^{-6} M solution in CH$_3$CN (b).

to note that after the drying the vibrational spectrum of **2** remains almost the same within the 500–170 cm^{-1} region (Figure 4), where only a small shift of the individual bands is noticed. The IR spectrum of the compound **1** is identical to the IR spectrum of compound **2**, dried at 135 °C. The position and the width of ν (CN) (*ca.* 2050 cm^{-1}, Figure 3) and the position of δ (NCS) band (*ca.* 485 cm^{-1}, Figure 4) confirm that thiocyanato ligands are bonded through nitrogen.[2,4,6,7,34] In the 690–860 cm^{-1} region, the δ(CH) absorption bands of pyridine mask the weak ν (CS) band,[17] so its position can not be determined.[6,7,34,36] The band at *ca.* 440 cm^{-1} (Figure 4) can be assigned as a shift of 403 cm^{-1} band of free pyridine.[37,41] Bands with the frequency below 400 cm^{-1} are assigned to the Mo–N stretching vibrations (Mo–N(NCS) at *ca.* 310 cm^{-1} (Figure 4)).[18,34]

In the electronic spectra of the compound **2**, solvated in acetonitrile and suspended in nujol, several bands within the region 230–850 nm are observed. The intensity of the band close to 770 nm is much weaker than the others and it is noticed in the spectra of the solutions with concentration 1.0 × 10^{-3} mol dm^{-3} or higher. In the spectra of the suspensions this band is not observed. Therefore, the yellow colour of both compounds **1** and **2** is a consequence of the broad band at *ca.* 350 nm, with partially absorption of violet light also from visible part of the spectrum (Figure 5). The electronic spectra of compound **1** and compound **2** non-dried and dried at 135 °C are identical.

CONCLUSIONS

The comparison of the electronic (Figure 5) and IR spectra below 350 cm^{-1} (Mo–N bonds) (Figure 4) of the compound **2** before and after the drying at 135 °C reveals almost identical feature, so the affect of the drying to the coordination sphere is negligible. Therefore, the pyridine molecule that leaves the compound **2** during first mass-loss step (Figure 2), as indicated by the thermogravimetric analysis, derives from the cation and not from the coordination anion. The spectroscopy and powder diffraction analysis provide clear evidence for the identity of compound **1** and compound **2**, dried at 135 °C. Due to this identity of compound **1** and compound **2** dried at 135 °C and to the fact that coordination sphere of compound **2** before and after the drying at 135 °C remains the same, very similar arrangement of the ligands around molybdenum may be proposed for both compounds **1** and **2**.

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Supplementary Materials.– CCDC–207518 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ /retrieving.html for from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk.

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SAŽETAK

Sinteza i karakterizacija *trans*-(pyH)[Mo(NCS)$_4$py$_2$] i *trans*-(py$_2$H)[Mo(NCS)$_4$py$_2$]. Kristalna struktura *trans*-(py$_2$H)[Mo(NCS)$_4$py$_2$]

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Spoj (pyH)[Mo(NCS)$_4$py$_2$] (**1**) (py = piridin) priređen je refluksiranjem smjese KSCN i [MoCl$_3$py$_3$] u piridinu. Rekristalizacijom **1** iz piridina dobiveni su jedinični kristali *trans*-(py$_2$H)[Mo(NCS)$_4$py$_2$] (**2**). Određivanjem strukture **2** difrakcijom rentgenskih zraka ustanovljeno je da u anionu atom molibdena ima oktaedarsku koordinaciju s tetragonskom distorzijom (4+2). Dvije piridinske molekule u zasjenjenoj konformaciji [85,9(4)°] koordinirane su na atom Mo u *trans* položaju [*d*(Mo-N(py)) = 2,176(5) i 2,191(6) Å], dok su četiri izotiocijanatne skupine koordinirane na molibden u ekvatorijalnoj ravnini s veznim udaljenostima molibden-dušik u rasponu 2,083(7) – 2,106(7) Å. Piridinske molekule u kationu (py$_2$H)$^+$ drže se zajedno jakom vodikovom vezom N-H···N na dodirnoj udaljenosti N···N koja iznosi 2,708(12) Å [geometrija vodikove veze: *d*(N8-H8') = 1,06(7) Å, *d*(N7···H8') = 1,65(7) Å, ∠ N8-H8'···N7 = 175(7)°]. Ravnine piridinskih prstenova u kationu zakrenute su jedna u odnosu na drugu pod kutom od 70,7(6)°. Rezultati IR i UV/Vis spektroskopske analize ukazuju na isti razmještaj liganada u spojevima **1** i **2**.