

Scientific paper

# Synthesis And Characterization of Mo(V)-oxido Complexes Containing the Thiocyanato-N Ligand

Nives Kitanovski,\* Amalija Golobič and Boris Čeh

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, 1001 Ljubljana, Slovenia.

\* Corresponding author: E-mail: nives.kitanovski@fkt.uni-lj.si

Received: 17-09-2007

Dedicated to the memory of Professor Ljubo Golič

## Abstract

(P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)<sub>2</sub>[MoO(NCS)<sub>5</sub>] (**1**) crystallized after addition of (P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)Br to the mixture obtained by refluxing (pyH)<sub>5</sub>[MoOCl<sub>4</sub>(H<sub>2</sub>O)]<sub>3</sub>Cl<sub>2</sub> (py = pyridine) and KSCN in acetonitrile, and also by oxidation of ((γ-pic)<sub>2</sub>H)[Mo(NCS)<sub>4</sub>(γ-pic)<sub>2</sub>] (pic = picoline) with Br<sub>2</sub> in air. The oxidation of ((γ-pic)<sub>2</sub>H)[Mo(NCS)<sub>4</sub>(γ-pic)<sub>2</sub>] with a considerably lower concentration of Br<sub>2</sub> in air gave (γ-picH)<sub>6</sub>[Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>](SO<sub>4</sub>) (**2**). (pyH)<sub>8</sub>[Mo<sub>2</sub>O<sub>3</sub>(NCS)<sub>8</sub>]X<sub>4</sub> (X = Br, **3**; X = Cl, **4**) were isolated after addition of pyHX to the hydrolysis product of [MoO(NCS)<sub>5</sub>]<sup>2-</sup>. The compounds were characterized by IR spectroscopy and single crystal X-ray diffraction analysis. The positions of the ν(CN) and δ(NCS) bands indicate N-bonding of the NCS groups and are in agreement with the crystal-structure results.

**Keywords:** Molybdenum(V), thiocyanato-N, crystal structures.

## 1. Introduction

This paper presents the preparation and the characterization of four thiocyanato-N Mo(V) oxido coordination compounds with [MoO(NCS)<sub>5</sub>]<sup>2-</sup>, [Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>]<sup>4-</sup> and [Mo<sub>2</sub>O<sub>3</sub>(NCS)<sub>8</sub>]<sup>4-</sup> ions, namely (P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)<sub>2</sub>[MoO(NCS)<sub>5</sub>] **1**, (γ-picH)<sub>6</sub>[Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>](SO<sub>4</sub>) **2** (pic = picoline), and (pyH)<sub>8</sub>[Mo<sub>2</sub>O<sub>3</sub>(NCS)<sub>8</sub>]X<sub>4</sub> (py = pyridine) (X = Br **3**, X = Cl **4**). Coordination anions of these types are already known, R<sub>2</sub>[MoO(NCS)<sub>5</sub>] (R = pyH<sup>+</sup>, α-picH<sup>+</sup>, C<sub>6</sub>H<sub>9</sub>N<sup>+</sup>, NH(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>, bzpyH<sup>+</sup> (bzpy = benzoylpyridine), lutH<sup>+</sup> (lut = lutidine)),<sup>1,2</sup> (pyH)<sub>4</sub>[Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>],<sup>3,4</sup> K<sub>4</sub>[Mo<sub>2</sub>O<sub>3</sub>(NCS)<sub>8</sub>] · 4H<sub>2</sub>O,<sup>5</sup> (NR<sub>4</sub>)<sub>4</sub>[Mo<sub>2</sub>O<sub>3</sub>(NCS)<sub>8</sub>] · 2((CH<sub>3</sub>)<sub>2</sub>CO) (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>)<sup>6</sup> and were obtained by different synthetic pathways than ours. The crystal structures of related complexes with [MOX<sub>5</sub>]<sup>2-</sup> species (M(IV) = Mo,<sup>7,8</sup> V,<sup>9</sup> W,<sup>10</sup> M(V) = Mo,<sup>11</sup> Nb,<sup>12–17</sup> Re,<sup>4,18</sup> V,<sup>19</sup> W,<sup>18,20,21</sup> M(VI) = Re,<sup>22</sup> Ta,<sup>23</sup> W,<sup>24–27</sup> X = F,<sup>9,14,15,19,23,24</sup> Cl,<sup>11,16–18,20–22,25–27</sup> Br,<sup>21</sup> CN,<sup>7,8,10</sup> NCS<sup>4,13</sup>) and [Re<sub>2</sub>O<sub>3</sub>(NC)<sub>8</sub>]<sup>4–4,28</sup> were also reported in the literature.<sup>4</sup>

## 2. Experimental

All reagents and organic solvents, which were obtained from commercial sources, were of analytical grade quality and used without further purification. (pyH)<sub>5</sub>[MoOCl<sub>4</sub>(H<sub>2</sub>O)]<sub>3</sub>Cl<sub>2</sub> was prepared as described previously,<sup>29</sup> and ((γ-pic)<sub>2</sub>H)[Mo(NCS)<sub>4</sub>(γ-pic)<sub>2</sub>] by refluxing a mixture of (NH<sub>4</sub>)<sub>2</sub>[MoCl<sub>5</sub>(H<sub>2</sub>O)] and KSCN in γ-picoline. The identity was checked by elemental (CHN) analysis, the powder diffraction technique<sup>4,30</sup> and vibrational spectroscopy.

### 2.1. Measurements

Elemental (CHN) analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Infrared spectra were recorded as a nujol suspension on a Perkin-Elmer 1720-X FT-IR instrument in the 4000–400 cm<sup>-1</sup> region and on a Perkin-Elmer 2000-FT-IR instrument in the 700–30 cm<sup>-1</sup> region. X-ray powder diffraction data of the prepared starting materials, (pyH)<sub>5</sub>[MoOCl<sub>4</sub>(H<sub>2</sub>O)]<sub>3</sub>Cl<sub>2</sub> and ((γ-pic)<sub>2</sub>H)[Mo(NCS)<sub>4</sub>(γ-pic)<sub>2</sub>], were obtained using

an Enraf Nonius FR 552 Guinier camera with  $\text{CuK}_\alpha$  radiation.

## 2. 2. X-ray Structure Analysis

Diffraction data for all four compounds were collected on a Nonius Kappa CCD diffractometer at 293(2) K using graphite monochromated  $\text{MoK}_\alpha$  radiation. The data were processed using the DENZO program.<sup>31</sup> Structures were solved by direct methods using the SIR97 program.<sup>32</sup> Structures were refined by full matrix least squares on  $F$  using Xtal3.6.<sup>33</sup> The positions of hydrogen atoms for compound **3** were obtained from the difference Fourier map and were calculated regarding the expected geometry for compounds **1**, **2**, and **4**. The parameters of hydrogen atoms were not refined. The structure of compound **2** is partially disordered (a non-coordinated sulfate anion and a picolinium cation lying on the mirror plane). The resulting crystal data and details concerning data collection and refinement for all four compounds are quoted in Table 6. The crystallographic data for compounds **1–4** were also deposited with the Cambridge Crystallographic Data Centre as supplementary material with the deposition numbers: CCDC 657899–657902, respectively. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/const/retrieving.html>.

## 2. 3. Syntheses

$(\text{P}(\text{C}_6\text{H}_5)_4)_2[\text{MoO}(\text{NCS})_5]$  **1**. *Synthesis 1*: A mixture of KSCN (5.0 g, 0.052 mol) and  $(\text{pyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$  (4.5 g, 3.3 mmol) in acetonitrile (45 mL) was refluxed for 3 hours. The solution was cooled down to room temperature and the resulting precipitate was filtered off. After addition of  $\text{P}(\text{C}_6\text{H}_5)_4\text{Br}$  (8.4 g, 0.020 mol) to the red-brown filtrate (the filtrate was also used to obtain **3** and **4**) micro crystals of **1** were isolated (9.2 g, 8.5 mmol, 85%). *Anal. Calcd.* for  $\text{C}_{53}\text{H}_{40}\text{N}_5\text{MoOP}_2\text{S}_5$  ( $M_r = 1081.16$ ): C 58.88, H 3.73, N 6.48; *Found*: C 58.45, H 3.81, N 6.31. *Single crystals were isolated as follows*: 15 mL of filtrate containing  $[\text{MoO}(\text{NCS})_5]^{2-}$  was diluted with 4 mL of acetonitrile and gradually cooled down to 6 °C. Orange prismatic crystals were obtained after 8 days (432 mg, 0.400 mmol, 12.0%). *Synthesis 2*: 28.4 mL of 0.040 M solution of  $\text{Br}_2$  (1.14 mol) in acetonitrile was slowly added to 40 mL of the acetonitrile suspension of  $(\gamma\text{-pic})_2\text{H}[\text{Mo}(\text{NCS})_4(\gamma\text{-pic})_2]$  (800 mg, 1.14 mmol). During reaction the suspension was cooled to 10 °C. The red-brown solution was left at room temperature and the resulting precipitate was filtered. After addition of  $\text{P}(\text{C}_6\text{H}_5)_4\text{Br}$  (2.00 g, 4.77 mmol) to the filtrate, and cooling down to –20 °C, crystals suitable for X-ray analysis crystallized (988 mg, 0.914 mmol, 80%).

$(\gamma\text{-picH})_6[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6](\text{SO}_4)$  **2**.  $(\gamma\text{-pic})_2\text{H}[\text{Mo}(\text{NCS})_4(\gamma\text{-pic})_2]$  (1.12 g, 1.60 mmol) was suspended in 5 mL of acetonitrile and 62.2 mL of a 0.015 M solution of

$\text{Br}_2$  (0.933 mmol) in acetonitrile was gradually added at room temperature. The brown solution was left at room temperature for 5 days and the resulting precipitate was filtered. After 15 days single crystals appeared in the solution. *Anal. Calcd.* for  $\text{C}_{42}\text{H}_{42}\text{N}_{12}\text{Mo}_2\text{O}_{11}\text{S}_8$  ( $M_r = 1339.23$ ): C 37.67, H 3.16, N 12.55; *Found*: C 37.28, H 3.78, N 11.72.

$(\text{pyH})_8[\text{Mo}_2\text{O}_3(\text{NCS})_8]\text{X}_4$  (X = Br **3**, X = Cl **4**). The red-brown filtrate, obtained in the synthesis of **1** was diluted with water (45 mL).  $\text{pyHX}$  (0.060 mol) was dissolved in the purple solution. After slow evaporation violet crystals with a green lustre, suitable for X-ray analysis, were obtained (6.3 g, 3.8 mmol, 75% **3**; 6.1 g 4.1 mmol, 82% **4**). *Anal. Calcd.* for **3**  $\text{C}_{48}\text{H}_{48}\text{N}_{16}\text{Mo}_2\text{O}_3\text{S}_8\text{Br}_4$  ( $M_r = 1665.05$ ): C 34.63, H 2.91, N 13.46; *Found*: C 34.25, H 2.75, N 13.28. *Anal. Calcd.* for **4**  $\text{C}_{48}\text{H}_{48}\text{N}_{16}\text{Mo}_2\text{O}_3\text{S}_8\text{Cl}_4$  ( $M_r = 487.24$ ): C 38.77, H 3.25, N 15.07; *Found*: C 38.25, H 3.16, N 14.42.

## 3. Results and Discussion

### 3. 1. Crystal Structures

The asymmetric unit of compound **1** consists of two  $(\text{P}(\text{C}_6\text{H}_5)_4)^+$  cations and the molybdenum(V) complex anion  $[\text{MoO}(\text{NCS})_5]^{2-}$  (Figure 1). The coordination polyhedron of the  $\text{MoN}_5\text{O}$  moiety is a distorted octahedron. The NCS moieties are nearly linear ( $\text{N–C–S} = 177.6(11) - 179.3(9)^\circ$ ), while the equatorial NCS moieties are bent away from the oxygen atom, the average  $\text{O–Mo–N}$  angle being  $95.8^\circ$ . The axial  $\text{Mo–N3}$  bond (2.209(14) Å), *trans* to  $\text{Mo–O}$  (the distance is 1.647(14) Å), is 0.153 Å longer than the average bond length of the equatorial ones (2.056 Å), due to the *trans* effect of the terminal oxygen atom (Table 1). A similar distortion was observed in the compound  $(\text{N}(\text{CH}_3)_4)_2[\text{MoO}(\text{NCS})_5]$ .<sup>1</sup>

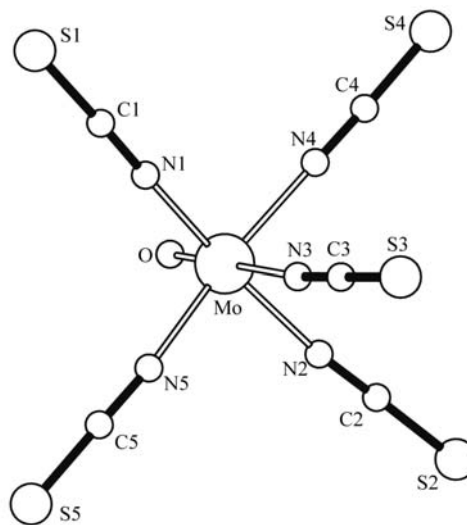


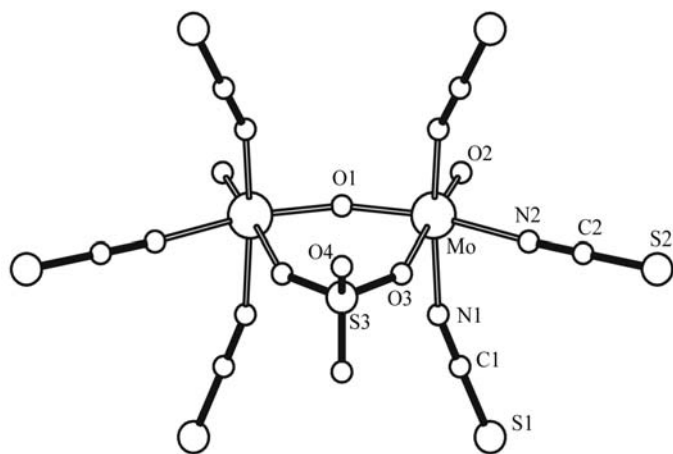
Figure 1. PLUTON-3<sup>34</sup> drawing of the  $[\text{MoO}(\text{NCS})_5]^{2-}$  anion.

**Table 1.** Bond distances [Å] and selected angles [°] for compound **1**.

Mo–O	1.647(14)	Mo–N1	2.053(14)	Mo–N2	2.066(15)
Mo–N3	2.209(14)	Mo–N4	2.058(8)	Mo–N5	2.048(7)
N1–C1	1.148(14)	N2–C2	1.144(15)	N3–C3	1.183(15)
N4–C4	1.142(9)	N5–C5	1.151(8)	C1–S1	1.614(14)
C2–S2	1.599(14)	C3–S3	1.591(14)	C4–S4	1.580(8)
C5–S5	1.591(8)				
O–Mo–N1	95.8(7)	O–Mo–N2	95.9(6)	O–Mo–N3	179.8(5)
O–Mo–N4	96.3(5)	O–Mo–N5	95.2(5)	N1–Mo–N2	168.3(7)
N1–Mo–N3	84.3(5)	N1–Mo–N4	89.7(4)	N1–Mo–N5	89.8(5)
N2–Mo–N3	84.0(5)	N2–Mo–N4	88.5(5)	N2–Mo–N5	89.7(4)
N3–Mo–N4	83.9(4)	N3–Mo–N5	84.6(4)	N4–Mo–N5	168.5(7)
Mo–N1–C1	176.3(9)	Mo–N2–C2	173.7(5)	Mo–N3–C3	174.2(5)
Mo–N4–C4	173.5(10)	Mo–N5–C5	170.1(10)	N1–C1–S1	177.6(11)
N2–C2–S2	179.1(7)	N3–C3–S3	179.0(9)	N4–C4–S4	178.3(11)
N5–C5–S5	179.3(9)				

**Table 2.** Selected distances [Å] and angles [°] for complex anion of **2**.

Mo <sup>i</sup> ...Mo <sup>i</sup>	3.6770(9)	Mo–O1	1.8709(19)	Mo–O2	1.649(10)
Mo–O3	2.195(9)	Mo–N1	2.101(6)	Mo–N2	2.125(9)
O3–S3	1.475(7)	O4–S3	1.436(9)	N1–C1	1.160(9)
N2–C2	1.142(12)	C1–S1	1.614(8)	C2–S2	1.620(9)
Mo–O1–Mo <sup>i</sup>	158.6(6)	O1–Mo–O2	100.7(4)	O1–Mo–O3	84.1(3)
O1–Mo–N1	93.26(17)	O1–Mo–N2	164.9(4)	O2–Mo–O3	175.2(3)
O2–Mo–N1	95.5(2)	O2–Mo–N2	94.4(3)	O3–Mo–N1	84.2(2)
O3–Mo–N2	80.8(3)	N1–Mo–N2	85.24(19)	N1–Mo–N1 <sup>ii</sup>	166.0(4)
O3–S3–O4	109.3(2)	O3–S3–O3 <sup>i</sup>	110.6(5)	O4–S3–O4 <sup>i</sup>	109.0(6)
Mo–O3–S3	142.5(7)	Mo–N1–C1	159.7(6)	Mo–N2–C2	175.4(9)
N1–C1–S1	179.6(7)	N2–C2–S2	179.6(10)		

Symmetry operations: <sup>i</sup> 1–x, 1–y, z; <sup>ii</sup> 1–x, y, z**Figure 2.** PLUTON-3<sup>34</sup> drawing of the [Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>]<sup>4-</sup> anion.

The structure of compound **2** consists of picolinium cations, sulfate and [Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>]<sup>4-</sup> anions (Figure 2). The asymmetric unit of compound **2** consists of one and a half picolinium cations (one lies on a mirror plane), a quarter of a sulfate anion (with *mm* symmetry) and a quarter of the [Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>]<sup>4-</sup> anion (which also has *mm* symmetry). Mo, N2, C2, S2, S3, O2,

**Table 3.** Hydrogen bonds parameters ([Å], [°]), and angles [°] between the best planes of picoline-cation rings, for compound **2**.

N3...O4	3.060(10)	N3–H1...O4	127.77
N3...O6	2.70(2)	N3–H1...O6	129.99
N3...O7	2.94(2)	N3–H1...O7	136.19
N4...O5	2.563(9)	N4–H2...O5	174.16
pic3...pic4	73.8(2)		

and O3 lie on the first mirror plane, O1, O4 and S3 on the mirror plane perpendicular to the first one and S3 and O1 on the two fold axis on the intersection of the two mirror planes. Each of the two Mo atoms in binuclear [Mo<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)(NCS)<sub>6</sub>]<sup>4-</sup> is coordinated by two oxido ligands (one terminal O2 and one bridging O1), three N atoms from three thiocyanato ligands, coordinated in *mer* mode, and one O atom (O3) of the bridging sulfato anion, attached by two symmetry related O atoms to both Mo atoms. The selected bond lengths and angles are shown in Table 2. The Mo–O3 bond length (2.195(9) Å) is lengthened as a result of *trans* influence of the terminal oxido ligand. A similar effect was also observed in the related compound with the pyridinium cation.<sup>3</sup> The Mo...Mo<sup>i</sup> contact distance is 3.6770(9) Å (Table 2). The structure is stabilized by the N–H...O hydrogen bonds, which connect both picolinium cations and O atoms of

coordinated and non-coordinated sulfate anions. N3...O4, N3...O6, N3...O7 and N4...O5 contact distances are 3.060(10), 2.79(2), 2.94(2) and 2.563(9) Å, respectively (Table 3).

The compounds **3** and **4** are isostuctural. They both consist of binuclear complex anions  $[\text{Mo}_2\text{O}_3(\text{NCS})_8]^{4-}$ , pyridinium cations and halides, bromides in **3** and chlorides in **4**. There is a distorted octahedral arrangement of two oxido ligands (one terminal O2 and one bridging O1) and four N-bonded thiocyanato ligands around the molybdenum atom. The bridging oxygen (O1) lies on a crystallographic inversion centre, so the Mo–O1–Mo<sup>i</sup> unit is linear, and the terminal oxygen atoms (O2, O2<sup>i</sup>) are in a *trans* position (Figure 3). The Mo–Mo<sup>i</sup>, Mo–O1 and Mo–O2 distances are 3.7153(5), 1.8577(4) and 1.664(4) Å in **3** and 3.725(1), 1.8623(7) and 1.683(7) Å in **4** (Table 4), and are similar to those found in other compounds containing the Mo<sub>2</sub>O<sub>3</sub> moiety.<sup>5,6</sup> The angle defined by Mo(V), bridging and terminal oxygens is 102.0(2)° and 102.3(2) for **3** and **4**, respectively. The NCS moieties are nearly linear, with the average N–C–S angles of 179.3° for **3** and 178.9° for **4**. As a result of the *trans* influence of the terminal oxido ligands, the Mo–N3 distance (2.254(4) Å for **3**, 2.276(8) Å for **4**) is significantly longer than the other Mo–N distances, ranging from 2.081(5) to 2.117(5) Å for **3** and 2.054(8) to 2.163(11) Å for **4**. Very similar distances and angles were also observed in both related compounds.<sup>5,6</sup> The crystal structure is completed with almost planar (pyH)<sub>4</sub>X<sub>2</sub><sup>2+</sup> moieties (*D*<sub>2h</sub> symmetry). Both halide anions from the asymmetric unit are connected by three hydro-

gen bonds to three neighbouring pyridinium cations. Two of the H-atoms are bridging and one is terminal (Figure 4). The shortest Br1...Br2 and Cl1...Cl2 contact distances are 4.2032(10) and 4.068(4), respectively. The N...X distances range from 3.439(4) to 3.651(5) Å for **3** (N11...Br2 and N11...Br1) and 3.254(10) to 3.628(10) Å for **4** (N11...Cl2 and N11...Cl1), for bridging pyH<sup>+</sup>, and from 3.187(6) to 3.234(6) Å for **3** (N21...Br1 and N41...Br2) and 3.033(10) to 3.099(14) Å for **4** (N21...Cl1 and N41...Cl2), for non-bridging pyH<sup>+</sup>, respectively (Table 5). The structure of both compounds consists of layers of complex anions separated by layers consisting of pyridinium-halide moieties. The layers are stacked along the *c* axis.

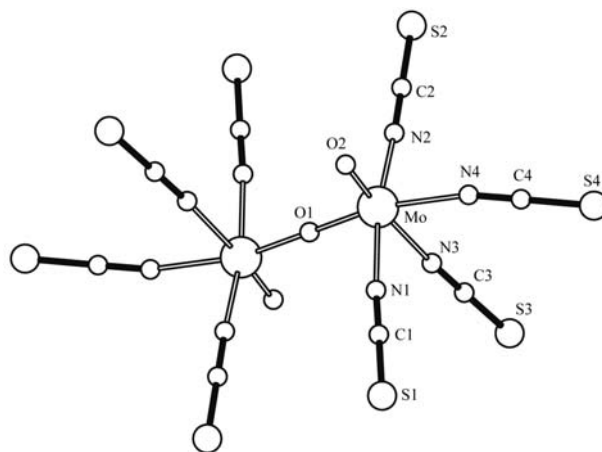


Figure 3. PLUTON-3<sup>34</sup> drawing of the  $[\text{Mo}_2\text{O}_3(\text{NCS})_8]^{4-}$  anion.

Table 4. Selected distances [Å] and angles [°] in  $[\text{Mo}_2\text{O}_3(\text{NCS})_8]^{4-}$  for **3** and **4**.

	<b>3</b>	<b>4</b>		<b>3</b>	<b>4</b>
Mo...Mo <sup>i</sup>	3.7153(5)	3.7245(10)	Mo–O1	1.8577(4)	1.8623(7)
Mo–O2	1.664(4)	1.683(7)	Mo–N1	2.094(5)	2.098(8)
Mo–N2	2.081(5)	2.054(8)	Mo–N3	2.254(4)	2.276(8)
Mo–N4	2.117(5)	2.163(11)	N1–C1	1.153(7)	1.139(13)
N2–C2	1.163(7)	1.144(13)	N3–C3	1.162(6)	1.157(12)
N4–C4	1.158(8)	1.116(15)	C1–S1	1.605(5)	1.613(10)
C2–S2	1.600(5)	1.636(11)	C3–S3	1.610(5)	1.588(9)
C4–S4	1.609(6)	1.608(11)			
O1–Mo–O2	101.97(16)	102.3(2)	O1–Mo–N1	90.27(13)	90.3(2)
O1–Mo–N2	91.91(13)	91.6(2)	O1–Mo–N3	84.37(12)	84.51(18)
O1–Mo–N4	164.45(15)	164.9(2)	O2–Mo–N1	95.32(19)	95.5(3)
O2–Mo–N2	95.3(2)	95.3(3)	O2–Mo–N3	173.6(2)	173.1(3)
O2–Mo–N4	93.5(2)	92.8(3)	N1–Mo–N2	168.44(18)	168.3(3)
N1–Mo–N3	83.77(16)	83.7(3)	N1–Mo–N4	86.6(2)	86.7(3)
N2–Mo–N3	85.15(17)	85.0(3)	N2–Mo–N4	88.3(2)	88.5(3)
N3–Mo–N4	80.15(19)	80.4(3)	Mo–N1–C1	175.1(4)	174.7(7)
Mo–N2–C2	172.9(4)	171.7(8)	Mo–N3–C3	173.1(4)	171.7(7)
Mo–N4–C4	164.7(5)	162.5(9)	N1–C1–S1	179.0(4)	178.7(8)
N2–C2–S2	179.7(4)	179.2(10)	N3–C3–S3	179.4(5)	179.0(8)
N4–C4–S4	179.0(4)	178.8(11)			

Symmetry operation: <sup>i</sup> –x, 1–y, 1–z

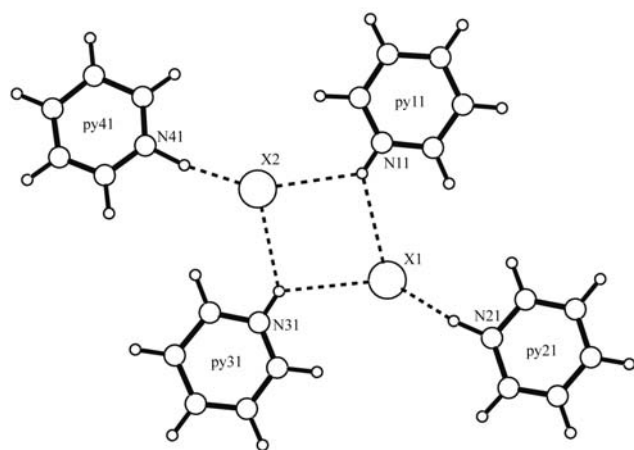


Figure 4. PLUTON-3<sup>34</sup> drawing of the ((pyH)<sub>4</sub>X<sub>2</sub>)<sup>2+</sup> moiety.

### 3. 2. Spectroscopy

For all four compounds **1–4**, the positions and the widths of the CN broad bands within the 2150–1850 cm<sup>-1</sup> region indicate N-bonding of the NCS ligands.<sup>35</sup> The CN stretching band exhibits strong splitting for **1** (2096, 2034 cm<sup>-1</sup>) and weak splitting for **3** (2067, 2036 cm<sup>-1</sup>) and **4** (2067, 2032 cm<sup>-1</sup>). No splitting could be observed in the spectrum of **2**. The strong band at about 950 cm<sup>-1</sup> (956 cm<sup>-1</sup> **1**, 952 cm<sup>-1</sup> **3**, 950 cm<sup>-1</sup> **4**), which can be assigned as  $\nu(\text{Mo}=\text{O})$ , is split in the spectrum of **2** (947, 935 cm<sup>-1</sup>). In the spectra of **3** and **4**, a strong band at about 745 cm<sup>-1</sup> (744 cm<sup>-1</sup> **3**, 747 cm<sup>-1</sup> **4**) is observed (Figure 5). Since that vibration is absent in the spectra of **2** it can be assigned as the asymmetrical stretching vibration of the linear Mo–O–Mo unit. The linearity of Mo–O–Mo causes the absence of the band characteristic of the symmetrical

Table 5. Hydrogen bonds parameters (Å, [°]), and angles [°] between the best planes of pyridine-cation rings, for compounds **3** and **4**.

	<b>3</b>	<b>4</b>		<b>3</b>	<b>4</b>
N11...X1	3.651(5)	3.628(10)	N11–H...X1	133.79	123.43
N11...X2	3.439(4)	3.254(10)	N11–H...X2	130.51	140.36
N21...X1	3.234(7)	3.099(14)	N21–H...X1	157.38	164.38
N31...X1	3.499(6)	3.283(13)	N31–H...X1	127.98	140.16
N31...X2	3.580(7)	3.507(13)	N31–H...X2	135.48	121.34
N41...X2	3.187(6)	3.033(10)	N41–H...X2	170.27	173.91
py11...py21	15.5(4)	19.2(8)	py11–py31	6.4(4)	8.2(7)
py11...py41	21.6(4)	20.9(7)	py21–py31	9.1(4)	11.1(8)
py21...py41	9.0(4)	9.4(8)	py31–py41	15.6(4)	13.6(8)

Table 6. Crystal data, data collection and structure refinement parameters for **1–4**.

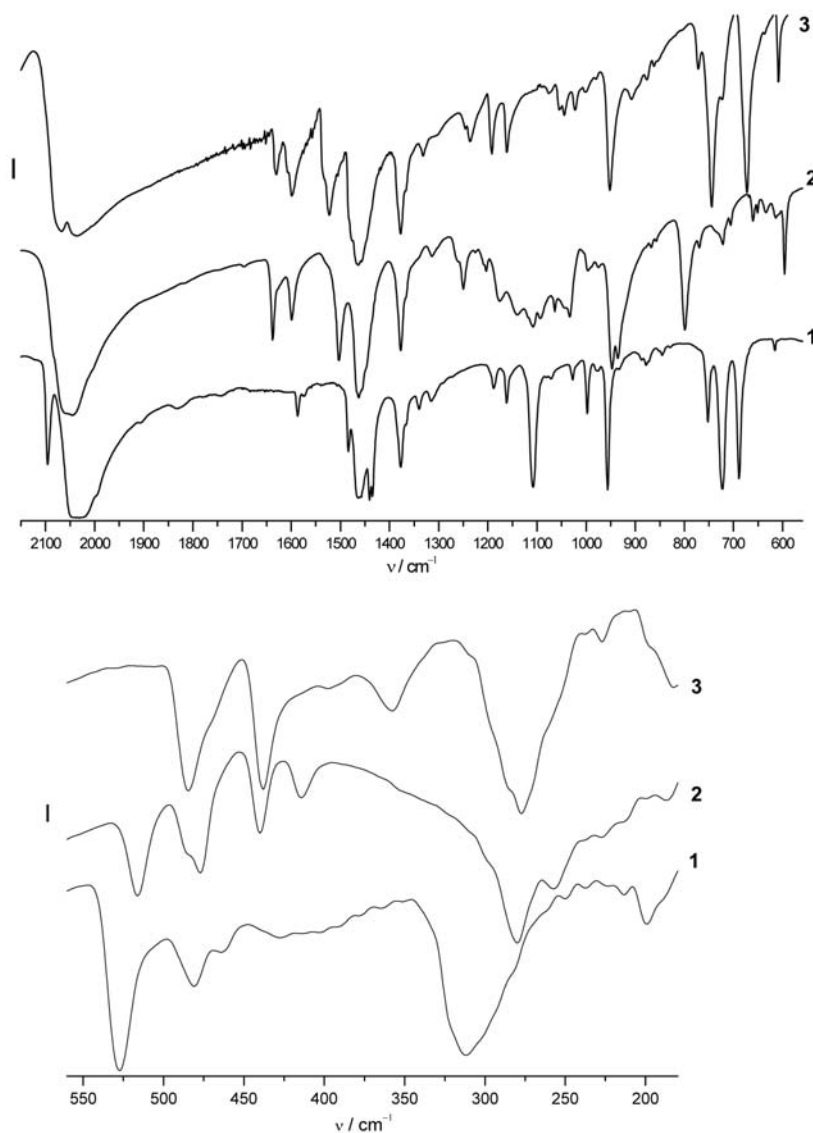
	Compound 1	Compound 2	Compound 3	Compound 4
Formula	C <sub>53</sub> H <sub>40</sub> MoN <sub>5</sub> OP <sub>2</sub> S <sub>5</sub>	C <sub>42</sub> H <sub>48</sub> Mo <sub>2</sub> N <sub>12</sub> O <sub>11</sub> S <sub>8</sub>	C <sub>48</sub> H <sub>48</sub> Br <sub>4</sub> Mo <sub>2</sub> N <sub>16</sub> O <sub>3</sub> S <sub>8</sub>	C <sub>48</sub> H <sub>48</sub> Cl <sub>4</sub> Mo <sub>2</sub> N <sub>16</sub> O <sub>3</sub> S <sub>8</sub>
<i>M<sub>r</sub></i>	1081.16	1345.32	1665.04	1487.24
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	<i>Pn</i> , No. 7	<i>Fmm</i> 2, No. 42	<i>P</i> -1, No. 2	<i>P</i> -1, No. 2
<i>a</i> (Å)	12.3714(1)	18.8567(3)	11.5832(1)	11.6406(4)
<i>b</i> (Å)	18.6921(2)	20.5554(4)	12.2379(2)	11.8869(5)
<i>c</i> (Å)	12.9422(1)	14.9393(2)	13.0981(2)	13.1693(6)
$\alpha$ (°)	90.00	90.00	90.9887(6)	91.5398(1)
$\beta$ (°)	116.5226(5)	90.00	109.9001(6)	110.1910(2)
$\gamma$ (°)	90.00	90.00	104.1873(6)	104.2451(2)
<i>V</i> (Å <sup>3</sup> )	2677.88(4)	5790.58(16)	1682.24(4)	1645.11(12)
<i>Z</i>	2	4	1	1
Color, shape	orange, prism	red, plate	violet, prism	violet, plate
$\rho$ (Mg m <sup>-3</sup> )	1.341	1.543	1.644	1.501
Total refl.	57282	26457	36626	23841
<i>R<sub>int</sub></i>	0.045	0.049	0.038	0.089
Independ. refl.	6036	1827	7652	7130
Observed refl.	5524	1623	5574	3007
Final <i>R</i> and <i>R<sub>w</sub></i>	0.042, 0.031	0.059, 0.041	0.042, 0.043	0.064, 0.042
Contribut. refl.	5885	1776	6878	5209
Parameters	604	154	367	367
$\Delta\rho_{\text{max}^{\text{min}}}$ (e Å <sup>-3</sup> )	0.411, -0.559	1.238, -1.823	0.976, -1.058	1.101, -1.354

stretching vibration of Mo–O–Mo at about  $400\text{ cm}^{-1}$ , which is IR active only in the case of a nonlinear Mo–O–Mo bridge, and is therefore observed only in the spectrum of **2** at  $414\text{ cm}^{-1}$ .<sup>36</sup> The N-bonding of NCS in compound **1** is also indicated by the  $\delta(\text{NCS})$  vibration at  $481\text{ cm}^{-1}$  (Figure 5).<sup>35</sup> Due to possible overlap with the bending vibration of the Mo–O–Mo unit in **2–4**,<sup>36</sup> and one of the bending vibrations of the bidentately bonded sulfate ( $\delta_{\text{d}(1)}(\text{SO}_4)$ ) in **2**,<sup>37</sup> the  $\delta(\text{NCS})$  band cannot be unambiguously assigned for all three dinuclear compounds. Nevertheless, for  $(\text{NR}_4)_4[\text{Mo}_2\text{O}_3(\text{NCS})_8] \cdot 2((\text{CH}_3)_2\text{CO})$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ )<sup>6</sup> the medium intensity band at about  $480\text{ cm}^{-1}$  ( $480\text{ cm}^{-1}$  for  $\text{R} = \text{CH}_3$  and  $482\text{ cm}^{-1}$  for  $\text{R} = \text{C}_2\text{H}_5$ ) is assigned as a  $\delta(\text{NCS})$  band. For **3** and **4** a vibration at  $485\text{ cm}^{-1}$  was noticed. The widest and the most intensive band within the  $350\text{--}250\text{ cm}^{-1}$  region for **1** and  $320\text{--}240$  for **2–4**, which exhibits splitting for **2**, can be as-

signed as the Mo–N(NCS) stretching vibration (Figure 5).<sup>35,38</sup> The bands at  $1587, 1188, 1162, 1108, 998, 752, 689, 616, 528\text{ cm}^{-1}$  probably belong to the vibrations of the tetraphenylephosphonium cation in **1**. The typical absorption for pyridinium around  $1525\text{ cm}^{-1}$  is observed in spectra of **3** and **4**, at  $1523$  and  $1525\text{ cm}^{-1}$ , respectively.<sup>39</sup>

## 4. Conclusions

In the prepared oxido compounds of Mo(V), the octahedrally coordinated species  $[\text{MoO}(\text{NCS})_5]^{2-}$  (**1**),  $[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6]^{4-}$  (**2**), and  $[\text{Mo}_2\text{O}_3(\text{NCS})_8]^{4-}$  (**3**, **4**), were identified. In the dinuclear units two molybdenum atoms are connected by the  $\mu$ -oxido bridge in **3** and **4**, and in the case of **2** also by the sulfato bridge. The X-ray diffraction analyses reveal that the NCS groups are bonded to the Mo

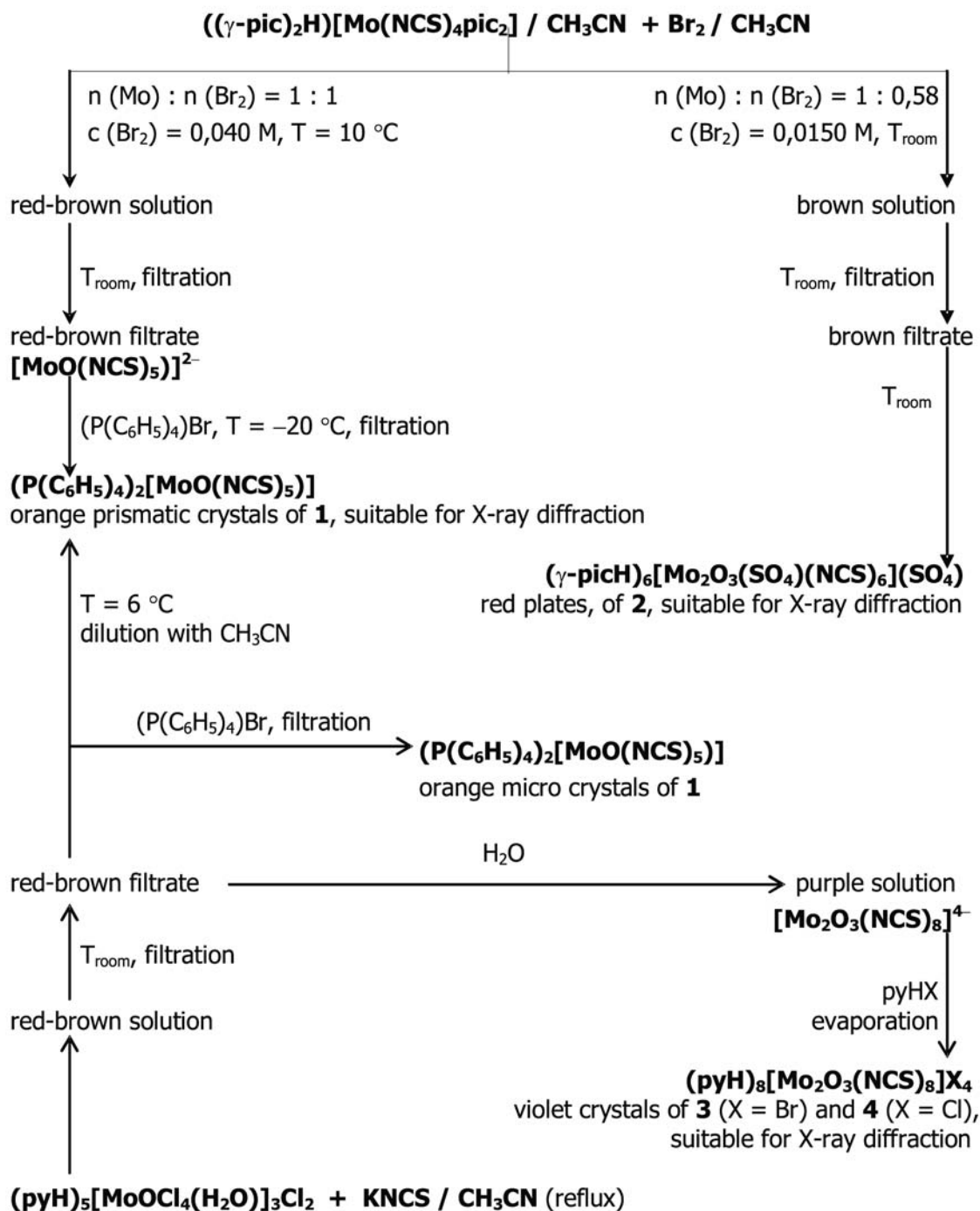


**Figure 5.** Vibration spectra of the compounds **1**, **2**, and **3**, within the range  $2150\text{--}560$  and  $560\text{--}180\text{ cm}^{-1}$ . The spectra of **4** reveals identical bands as **3**, since their coordination spheres are similar.

atom via nitrogen atoms in all four compounds. The results of vibrational spectroscopy are in agreement with the Mo–N bonding, and spectra of **3** and **4** reveal identical bands, since their coordination spheres are similar.

$[\text{MoO}(\text{NCS})_5]^{2-}$  was prepared from  $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$  by the substitution of four chlorido ligands and water molecules with thiocyanato-N ligands, and also by the oxidation of  $[\text{Mo}(\text{NCS})_4(\gamma\text{-pic})_2]^-$  with bromine. We did not succeed in

obtaining higher yields of compound **2**. We believe the formation of the species  $[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6]^{4-}$  could be the result of combined oxidation of  $[\text{Mo}(\text{NCS})_4(\gamma\text{-pic})_2]^-$  by bromine as well as oxygen (formation of  $\text{SO}_4^{2-}$  from  $\text{NCS}^-$ ). Also, in the literature, the formation of this anion is not clearly described.<sup>3</sup>  $[\text{Mo}_2\text{O}_3(\text{NCS})_8]^{4-}$  is photosensitive in  $\text{CH}_3\text{CN}$ , the purple solution becomes orange under ambient light, the photolysis product being  $[\text{MoO}(\text{NCS})_5]^{2-}$ .<sup>6</sup>



Scheme 1. Scheme of the syntheses.

## 5. Acknowledgements

The financial support of the Ministry of Higher Education, Science and Technology, Republic of Slovenia, through grants MVZT P1-0175, P1-0201 and X-2000, is gratefully acknowledged.

## 6. References

1. W. Clegg, *Acta Crystallogr., C*, **1987**, *43*, 791–792.
2. S.-O. Oh, C.-S. Kim, *J. Kor. Chem. Soc.*, **1981**, *25*, 263–269.
3. B. Kamenar, M. Cindrić, N. Strukan, *Acta Crystallogr., C*, **1994**, *50*, 1396–1399.
4. F. H. Allen, O. Kennard, *Chem. Des. Autom. News*, **1993**, *8*, 31–37.
5. A. Bino, S. Cohen, L. Tsimering, *Inorg. Chim. Acta*, **1983**, *77*, L79–L80.
6. P. C. Secrest, S. J. Geib, N. J. Cooper, *Inorg. Chem.*, **1997**, *36*, 4182–4186.
7. K. Wiegardt, G. Backes-Dahmann, W. Holzbach, W. J. Swiridoff, J. Weiss, *Z. Anorg. Allg. Chem.*, **1983**, *499*, 44–58.
8. H. Arzoumanian, M. Pierrot, F. Ridouane, J. Sanchez, *Transition Met. Chem.*, **1991**, *16*, 422–426.
9. A. Demšar, P. Bukovec, *Vestn. Slov. Kem. Drus.*, **1979**, *26*, 401–406C.
10. J. Szklarzewicz, D. Matoga, A. Samotus, J. Burgess, J. Fawcett, D. R. Russell, *Croat. Chem. Acta.*, **2001**, *74*, 529–544.
11. P. C. Junk, J. L. Atwood, *J. Coord. Chem.*, **1999**, *46*, 505–518.
12. J. Lipkovski, G. D. Andreetti, P. Sgarabotto, *Acta Crystallogr., A*, **1978**, *34*, 145.
13. B. Kamenar, C. K. Prout, *J. Chem. Soc. A*, **1970**, 2379–2384.
14. R. Stomberg, I. B. Svensson, L. Trysberg, *Acta Chem. Scand. A*, **1981**, *35*, 779–784.
15. U. Calov, M. Schneider, P. Leibnitz, *Z. Anorg. Allg. Chem.*, **1991**, *604*, 77–83.
16. J. Poitras, A. L. Beauchamp, *Can. J. Chem.*, **1996**, *72*, 1675–1683.
17. U. Muller, I. Lorenz, *Z. Anorg. Allg. Chem.*, **1980**, *463*, 110–116.
18. W. Massa, S. Hermann, K. Dehnicke, *Z. Naturforsch., B*, **1984**, *39*, 850–854.
19. H. Rieskamp, R. Mattes, K. Dehnicke, *Z. Naturforsch., B*, **1976**, *31*, 453–455.
20. P. Schreiber, K. Wiegardt, U. Florke, H. J. Haupt, *Z. Naturforsch., B*, **1984**, *42*, 1391–1397.
21. P. Hofacker, A. Werth, A. Neuhaus, B. Neumuller, F. Weller, K. Dehnicke, D. Fenske, *Chem. Zeit.*, **1991**, *115*, 321–325.
22. U. Lis, B. Jezowska-Trzebiatowska, *Acta Crystallogr., B*, **1995**, *33*, 1248–1250.
23. N. G. Furmanova, I. A. Verin, I. E. Zanin, A. N. Zozulin, E. G. Ilin, *Kristallografiya*, **1991**, *36*, 384–388.
24. W. Massa, S. Hermann, K. Dehnicke, *Z. Anorg. Allg. Chem.*, **1982**, *493*, 33–40.
25. L. Ying-Jie, R. H. Beer, *Polyhedron*, **1996**, *15*, 1667–1671.
26. P. C. Junk, J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, **1995**, 1551–1552.
27. P. C. Junk, J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, **1997**, 4393–4399.
28. P. Lumme, U. Turpeinen, Z. Stasička, *Acta Crystallogr., C*, **1991**, *47*, 501–503.
29. B. Modec, J. V. Brenčič, *Eur. J. Inorg. Chem.* **2005**, 1698–1709.
30. X'PERT HIGHSCORE PANalitical B. V. Almelo, (The Netherlands) **2005**.
31. Z. Otwinowski, W. Minor, *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A (Eds.: C. W. Carter Jr., R. M. Sweet), Academic Press, New York **1997**, pp. 307–326.
32. A. Altomare, M. C. Burla, M. Camalli, G. L. Casciarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR97, *J. Appl. Crystallogr.*, **1999**, *32*, 115–119.
33. S. R. Hall, D. J. du Boulay, and R. Olthof-Hazekamp (Eds.), *Tha XTAL3.6 System*, University of Western Australia, Lamb, Perth (Australia), **1999**.
34. A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2000**.  
A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
35. N. Kitanovski, A. Golobič, B. Čeh, *Croat. Chem. Acta*, **2004**, *77*, 593–598.
36. K. Nakamoto, *Infrared and Raman Rpectra of Rnorganic and Roordination Rompounds*, J. Wiley and Sons, New York, **1997**.
37. K. Nakamoto, J. Fujita, S. Tanaka, M. Kobayashi, *J. Am. Chem. Soc.*, **1957**, *79*, 4904–4908.
38. A. Sabatini, I. Bertini, *Inorg. Chem.*, **1965**, *4*, 959–961.
39. N. S. Gill, R. H. Nuttall, D. E. Scaife, D. W. Sharp, *J. Inorg. Nucl. Chem.*, **1961**, *18*, 79–87.

## Povzetek

Po dodatku  $(\text{P}(\text{C}_6\text{H}_5)_4)\text{Br}$  v filtrat, ki nastane pri refluxu  $(\text{pyH})_5[\text{MoOCl}_4(\text{H}_2\text{O})]_3\text{Cl}_2$  (py = piridin) in KSCN v acetoni-trilu, izkristalizira  $(\text{P}(\text{C}_6\text{H}_5)_4)_2[\text{MoO}(\text{NCS})_5]$  (**1**), ki nastane tudi pri oksidaciji  $(\gamma\text{-pic})_2\text{H}[\text{Mo}(\text{NCS})_4(\gamma\text{-pic})_2]$  (pic = pikolin) z bromom na zraku. Oksidacija  $(\gamma\text{-pic})_2\text{H}[\text{Mo}(\text{NCS})_4(\gamma\text{-pic})_2]$  z nižjo koncentracijo broma, ki prav tako poteka v prisotnosti zraka, vodi tudi do nastanka  $(\gamma\text{-picH})_6[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6](\text{SO}_4)$  (**2**).  $(\text{pyH})_8[\text{Mo}_2\text{O}_3(\text{NCS})_8]\text{X}_4$  (X = Br, **3**; X = Cl, **4**) se izloči po dodatku pyHX v raztopino nastalo pri hidrolizi  $[\text{MoO}(\text{NCS})_5]^{2-}$ . Spojine smo okarakterizirali z IR spektroskopijo ter rentgensko difracijsko analizo monokristalov. Položaja  $\nu(\text{CN})$  in  $\delta(\text{NCS})$  trakov kažeta na N-vezavo NCS skupine, kar potrjuje tudi rezultati rentgenske difrakcije.