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

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Dedicated to the memory of Professor Ljubo Golič

Abstract

(P(C6H5)4)2[MoO(NCS)5] (1) crystallized after addition of (P(C6H5)4)Br to the mixture obtained by refluxing (pyH)5[MoOCl4(H2O)]3Cl2 (py = pyridine) and KSCN in acetonitrile, and also by oxidation of ((γ-pic)2H)[Mo(NCS)4] (γ-pic) with Br2 in air. The oxidation of ((γ-pic)2H)[Mo(NCS)4] with a considerably lower concentration of Br2 in air gave ((γ-picH)[Mo2O3(SO4)(NCS)6](SO4)2)2 (pyH)8[Mo2O3(NCS)8]X4 (X = Br, 3; X = Cl, 4) were isolated after addition of pyHX to the hydrolysis product of [MoO(NCS)5]2−. 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)5]2−, [Mo2O3(SO4)(NCS)6]4− and [Mo2O3(NCS)8]4− ions, namely (P(C6H5)4)2[MoO(NCS)5]1, (γ-picH)6[Mo2O3(SO4)(NCS)6](SO4)2 (pic = picoline) and (pyH)8[Mo2O3(NCS)8]X4 (X = Br, 3; X = Cl, 4). Coordination anions of these types are already known, R2[MoO(NCS)5] (R = pyH+, α-picH+, C6H9N+, NH(CH3)3+, N(CH3)4+, bzpyH+ (bzpy = benzoylpyridine), lutH+ (lut = lutidine)),1,2 (pyH)3[Mo2O3(SO4)3(NCS)6]3,4 K4[Mo2O3(NCS)8]5 ⋅ 4(CH3)2CO6 and were obtained by different synthetic pathways than ours. The crystal structures of related complexes with [MOX]2− species (M(IV) = Mo,7,8 V,9 W,10 M(V) = Mo,11 Nb,12–17 Re,18 V,19 W,18,20,21 M(VI) = Re,22 Ta,23 W,24–27 X = F,14,15,19,23,24 Cl,11,16–18,20–22,25–27 Br,21 CN,7,8,10 NCS4,13) and [Re2O5(NC)8]4−4,28 were also reported in the literature.4

2. Experimental

All reagents and organic solvents, which were obtained from commercial sources, were of analytical grade quality and used without further purification. (pyH)5[MoOCl4(H2O)]3Cl2 was prepared as described previously,29 and ((γ-pic)2H)[Mo(NCS)4] by refluxing a mixture of (NH4)2MoCl5(H2O)Cl with Br2 in air. The identity was checked by elemental (CHN) analysis, the powder diffraction technique4,30 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−1 region and on a Perkin-Elmer 2000-FT-IR instrument in the 700–30 cm−1 region. X-ray powder diffraction data of the prepared starting materials, (pyH)5[MoOCl4(H2O)]3Cl2 and ((γ-pic)2H)[Mo(NCS)4((γ-pic)2)2], were obtained using
an Enraf Nonius FR 552 Guinier camera with CuKα 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 MoKα radiation. The data were processed using the DENZO program. Structures were solved by direct methods using the SIR97 program. Structures were refined by full matrix least squares on 

$F^2$ using Xtal3.6. The positions of hydrogen atoms for compounds 1, 2, and 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

(P(C6H5)4)2MoO(NCS)5 1. Synthesis 1: A mixture of KSCN (5.0 g, 0.052 mol) and (pyH)4MoOCl4(H2O)Cl2 (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 P(C6H5)4Br (8.4 g, 0.020 mol) to the red-brown filtrate (the filtrate was also used to obtain micro crystals of 1) were isolated (9.2 g, 8.5 mmol, 85%). Anal. Calcd. for C38H32N8MoO5S8 (M = 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 MoO(NCS)52– 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 Br2 (1.14 mol) in acetonitrile was slowly added to 40 mL of the acetonitrile suspension of ((py-pic)H)Mo(NCS)5(py-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 P(C6H5)4Br (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%).

(pyH)4Mo2O3(NCS)8(SO4)2– (X = Br 3. X = Cl 4). The red-brown filtrate, obtained in the synthesis of 1 was diluted with water (45 mL). 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 C48H48N12Mo2O11S8Br4 (M = 1665.05): C 34.63, H 2.91, N 12.55; Found: C 34.25, H 2.75, N 13.28. Anal. Calcd. for 4 C48H48N12Mo2O11S8BCl4 (M = 487.24): C 38.77, H 3.25, N 15.07; Found: C 388.25, H 3.16, N 14.42.

3. Results and Discussion

3.1. Crystal Structures

The asymmetric unit of compound 1 consists of two (P(C6H5)4)3+ cations and the molybdenum(V) complex anion [MoO(NCS)5]2– (Figure 1). The coordination polyhedron of the Mo1O6 moiety is a distorted octahedron. The NCS moieties are nearly linear (N–C–S = 177.6(11)–179.3(9)°), while the equatorial NCS moieties are bent away from the oxygen atom, the average O–Mo–N angle being 95.8°. The axial Mo–N3 bond (2.209(14) Å), trans to 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 (N(CH3)4)2[MoO(NCS)5]1.1

Figure 1. PLUTON–334 drawing of the [MoO(NCS)5]2– anion.

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The structure of compound 2 consists of picolinium cations, sulfate and $[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6]^{4–}$ 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 $[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6]^{4–}$ anion (which also has $mm$ symmetry). Mo, N2, C2, S2, S3, O2, and O3 lie on the first mirror plane, O1, O4 and S3 on the mirror plane perpendicular to the first one and S1 and O1 on the two fold axis on the intersection of the two mirror planes. Each of the two Mo atoms in binuclear $[\text{Mo}_2\text{O}_3(\text{SO}_4)(\text{NCS})_6]^{4–}$ 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.3 The Mo...Mo 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...
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 unit is linear, and the terminal oxygen atoms (O2, O2') are in a trans position (Figure 3). The Mo–Mo', 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 MoO₆ moiety.⁵,⁶ 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.⁵,⁶ The crystal structure is completed with almost planar \((\text{pyH})_4\text{X}_2^{2+}\) moieties (\(D_{2h}\) symmetry). Both halide anions from the asymmetric unit are connected by three hydrogen 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⁺, 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⁺, 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.

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

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<td>178.8(11)</td>
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Symmetry operation: \(-x, 1-y, 1-z\)
3.2. Spectroscopy

For all four compounds 1–4, the positions and the widths of the CN broad bands within the 2150–1850 cm⁻¹ region indicate N-bonding of the NCS ligands. The CN stretching band exhibits strong splitting for 1 (2096, 2034 cm⁻¹) and weak splitting for 3 (2067, 2036 cm⁻¹) and 4 (2067, 2032 cm⁻¹). No splitting could be observed in the spectrum of 2. The strong band at about 950 cm⁻¹ (956 cm⁻¹ 1, 952 cm⁻¹ 3, 950 cm⁻¹ 4), which can be assigned as ν(Mo=O), is split in the spectrum of 2 (947, 935 cm⁻¹). In the spectra of 3 and 4, a strong band at about 745 cm⁻¹ (744 cm⁻¹ 3, 747 cm⁻¹ 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 vibration of the Mo–O–Mo unit.
stretching vibration of Mo–O–Mo at about 400 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 cm\(^{-1}\).\(^{36}\) The N-bonding of NCS in compound 1 is also indicated by the \(\delta\)(NCS) vibration at 481 cm\(^{-1}\) (Figure 5).\(^{35}\) Due to possible overlap with the bending vibration of the Mo–O–Mo unit in 2–4,\(^{36}\) and one of the bending vibrations of the bidentately bonded sulfate (\(\delta_{d1}(SO_4)\)) in 2,\(^{37}\) the \(\delta\)(NCS) band cannot be unambiguously assigned for all three dinuclear compounds. Nevertheless, for (NR\(_4\))\(_4[Mo_2O_3(NCS)_8]2((CH_3)\_2CO)\) (R = CH\(_3\), C\(_2\)H\(_5\))\(^6\) the medium intensity band at about 480 cm\(^{-1}\) (480 cm\(^{-1}\) for R = CH\(_3\) and 482 cm\(^{-1}\) for R = C\(_2\)H\(_5\)) is assigned as a \(\delta\)(NCS) band. For 3 and 4 a vibration at 485 cm\(^{-1}\) was noticed. The widest and the most intensive band within the 350–250 cm\(^{-1}\) region for 1 and 320–240 for 2–4, which exhibits splitting for 2, can be assigned as the Mo–N(NCS) stretching vibration (Figure 5).\(^{35,38}\) The bands at 1587, 1188, 1162, 1108, 998, 752, 689, 616, 528 cm\(^{-1}\) probably belong to the vibrations of the tetraphenylephosphonium cation in 1. The typical absorption for pyridinium around 1525 cm\(^{-1}\) is observed in spectra of 3 and 4, at 1523 and 1525 cm\(^{-1}\), respectively.\(^{39}\)

4. Conclusions

In the prepared oxido compounds of Mo(V), the octahedrally coordinated species [MoO(NCS)\(_5\)]\(^{2-}\) (1), [Mo\(_2\)O\(_3\)(SO\(_4\))(NCS)\(_6\)]\(^{4-}\) (2), and [Mo\(_2\)O\(_5\)(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](image-url)
atom via nitrogen atoms in all four compounds. The results of vibrational spectroscopy in agreement with the Mo–N bonding, and spectra of 3 and 4 reveal identical bands, since their coordination spheres are similar.

[MoO(NCS)₅]²⁻ was prepared from [MoOCl₄(H₂O)]⁻ by the substitution of four chlorido ligands and water molecules with thiocyanato-N ligands, and also by the oxidation of [Mo(NCS)₄(γ-pic)]²⁻ with bromine. We did not succeed in obtaining higher yields of compound 2. We believe the formation of the species [Mo₂O₃(SO₄)(NCS)₆]⁴⁻ could be the result of combined oxidation of [Mo(NCS)₄(γ-pic)]²⁻ by bromine as well as oxygen (formation of SO₄²⁻ from NCS⁻).

Also, in the literature, the formation of this anion is in not clearly described.³ [Mo₂O₃(NCS)₆]⁴⁻ is photosensitive in CH₃CN, the purple solution becomes orange under ambient light, the photolysis product being [MoO(NCS)₅]²⁻.⁶

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

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Povzetek

Po dodatku (P(C6H5)4)Br v filtrat, ki nastane pri refluksu (pyH)8[MoOCl4(H2O)]Cl2 (py = piridin) in KSCN v acetonitrilu, izkristalizira (P(C6H5)4)[MoO(NCS)3] (1), ki nastane tudi pri oksidaciji (γ-pircH)2[Mo(NCS)5] (2). (pyH)8[MoOCl4(H2O)]Cl2 (py = piridin) z bromom na zrak. Oksidacija (((γ-pircH)2)[MoOCl4(H2O)]Cl2) γ-pircH2[MoOCl4(H2O)]Cl2 z nižjo koncentracijo broma, ki prav tako poteka v prisotnosti zraka, vodi tudi do nastanka γ-pircH2[MoOCl4(H2O)]Cl2 (pyH)8[MoOCl4(H2O)]Cl2 (X = Br, 3; X = Cl, 4) se izloči po dodatku pyHX vraztopino nastalo pri hidrolizi [MoO(NCS)5]2−. Spojine smo okarakterizirali z IR spektroskopijo ter rentgensko difraktijsko analizo monokristalov. Položaja ν(CN) in δ(NCS) trakov kažeta na N-vezavo NCS skupine, kar potrdijo tudi rezultati rentgenske difrakcije.