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Syntheses and crystal structure of first octahedral d-metal complexes containing three and four isocyanato ligands, *mer*-[Mo(NCO)₃py₃] · 2py and *trans*-(py₂H)[Mo(NCO)₄py₂]

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Abstract

By refluxing of a mixture of $(NH_4)_2[MoCl_5(H_2O)]$ and KOCN in pyridine, the neutral *mer*- $[Mo(NCO)_3py_3]$ and anionic *trans*- $[Mo(NCO)_4py_2]^-$ species originated simultaneously at reflux temperature. After a separation of the water-unsoluble neutral and water-soluble ionic species, the single crystals of compounds $[Mo(NCO)_3py_3] \cdot 2py(1)$ and $(py_2H)[Mo(NCO)_4py_2](2)$ have been prepared and crystal structures of both were determined by X-ray crystallography. © 2005 Elsevier B.V. All rights reserved.

Keywords: Molybdenum(III); Isocyanate; Pyridine; Crystal structure

In the last 30 years, numerous transition metal complexes containing a mononuclear octahedral halogenopyridine/picoline species of type mer-[MX₃L₃] and *trans/cis*- $[MX_4L_2]^z$ (M = transition metal; X = Cl, Br, I; L = pyridine (py), 4-methylpyridine (pic); z =+1, 0, -1) were prepared and structurally characterized. Much more rare are corresponding compounds containing pseudo halogeno ligands like NCS and NCO, respectively. The crystal structure of only one mer-complex, [Os(NCS)₃py₃] [1], and a few *trans*-compounds, (picH)₂[Mn(NCS)₄pic₂] · 2pic [2] and (picH)₂ [Fe(NCS)₄ pic_2] · 2pic [2], Hg[Co(NCS)_4py_2] [3], and (py_2H) [Mo (NCS)₄py₂] [4] have been determined but none of the isocyanate complex of related stoichiometry has been noticed in the literature. We described here a synthesis [5], a separation of neutral $[Mo(NCO)_3py_3]$ and ionic $[Mo(NCO)_4 py_2]^-$ species [6], subsequently isolated in a

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crystalline form as *mer*-[Mo(NCO)₃py₃] \cdot 2py (1) and *trans*-(py₂H)[Mo(NCO)₄py₂] (2) [7], the structures of which were determined by a single crystal X-ray diffraction analysis [8].

The molecular structure of the compound 1 is shown in Fig. 1 with selected bond distances and angles in the caption of the figure. The central molybdenum atom is surrounded by six N-donor ligands, which constitute a typical distorted octahedral coordination sphere with a mer ligand arrangement of pyridine molecules and isocyanate groups. There is almost no difference between the Mo and N distances for NCO groups, which are in the range 2.080(4)-2.092(4) Å. Similar differences were found also for the Mo-N distances for the pyridine molecules, which are between 2.196(3) and 2.207(3) Å. The N-Mo-N angles range from 88.36(13)° to 91.98(14)° and deviate less than 2° from the ideal value of 90°. The N-C-O ligands are almost perfectly linear, the angles being in the range 178.6(6)-179.9(5)°. The angle between the axial pyridine rings is 87.5(3)°, which means nearly ideal staggered conformation. The dihedral

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Fig. 1. Molecular structure of **1** (labeled atoms from the asymmetric unit). Selected bond lenghts (Å) and angles (°): Mo(1)-N(1) 2.088(3), Mo(1)-N(2) 2.080(4), Mo(1)-N(3) 2.092(4), Mo(1)-N(4) 2.197(3), Mo(1)-N(5) 2.196(3), Mo(1)-N(6) 2.207(3), O(1)-C(1) 1.192(6), O(2)-C(2) 1.195(8), O(3)-C(3) 1.190(7), N(1)-C(1) 1.159(5), N(2)-C(2) 1.137(7), N(3)-C(3) 1.141(6) and N(1)-Mo(1)-N(2) 91.98(14), N(1)-Mo(1)-N(3) 177.02(14), N(1)-Mo(1)-N(4) 90.19(13), N(1)-Mo(1)-N(5) 90.93(12), N(1)-Mo(1)-N(6) 88.75(13), N(2)-Mo(1)-N(3) 90.90(14), N(2)-Mo(1)-N(4) 91.02(13), N(2)-Mo(1)-N(5) 89.51(13), N(2)-Mo(1)-N(6) 179.25(14), N(3)-Mo(1)-N(4) 89.02(13), N(3)-Mo(1)-N(5) 89.83(13), N(3)-Mo(1)-N(6) 88.36(13), N(4)-Mo(1)-N(5) 178.74(13), N(4)-Mo(1)-N(6) 89.10(12), N(5)-Mo(1)-N(6) 90.35(12), O(1)-C(1)-N(1) 179.9(5), O(2)-C(2)-N(2) 178.6(6), O(3)-C(3)-N(3) 179.3(6).

angles between the (least-square) plane Mo–N2–N4–N5–N6 and the pyridine rings containing N4, N5 and N6 atoms are $42.9(2)^{\circ}$, $49.7(2)^{\circ}$ and $53.8(2)^{\circ}$, respectively.

The molecular structure of the compound 2 is shown in Fig. 2 with selected bond distances and angles in the caption of the figure. Four $N_{\rm CO}$ and two $N_{\rm py}$ donor atoms depict an elongated octahedron around molybdenum atom. In both species, py_2H^+ and [Mo(N CO)₄py₂]⁻, only one of the pyridine rings lays in a mirror plane. This requires a perfect staggered conformation of the pyridine rings in both ions. The $Mo-N_{CO}$ distances 2.096(3) and 2.098(3) A are slightly longer and, oppositely, the mean $Mo-N_{py}$ length of 2.183(3) and 2.198(3) Å is slightly shorter than those in 1. The N-Mo-N angles deviate less than 0.7° from the ideal value of 90°. The pyridine molecule and pyridinium cation in py_2H^+ are held together by the strong hydrogen bond with the N···N distance of 2.706(6) Å and N–H···N angle of 169(9)°. Until now, the X-ray structures of less than a dozen species have been determinated in which the NCO group is bounded to the central molybdenum atom. In all compounds, the oxidation number of the molybdenum is +2, except in one with +4 where two



Fig. 2. Molecular structure of 2 (labeled atoms from the asymmetric unit). Selected bond lenghts (Å) and angles (°): Mo-N(1) 2.096(3), Mo-N(2) 2.098(3), Mo-N(3) 2.183(3), Mo-N(4) 2.198(3), O(1)-C(1) 1.198(5), O(2)-C(2) 1.197(5), N(1)-C(1) 1.155(4), N(2)-C(2) 1.152(4), N(3)-C(3) 1.336(5, N(3)-C(7) 1.349(5), N(4)-C(8) 1.340(4), C(3)-C(4) 1.379(7), C(4)-C(5) 1.362(8), C(5)-C(6) 1.369(8), C(6)-C(7) 1.372(7), C(8)-C(9) 1.376(5), C(9)-C(10) 1.361(5), N(5)···N(6) 2.706(6), N(5)-H(56) 1.04(9), N(6)···H(56) 1.68(9) and N(1)-Mo-N(2) 178.89(12), N(1)-Mo-N(3) 89.65(9), N(1)-Mo-N(4) 90.46(9), N(1)-Mo-N(1) 90.72(10), N(1)-Mo-N(2) 89.95(10), N(2)-Mo-N(3) 89.47(9), N(2)-Mo-N(4) 90.42(9), N(2)-Mo-N(2) 89.36(10), N(3)-Mo-N(4) 179.84(14), Mo-N(1)-C(1) 175.1(3), Mo-N(2)-C(2) 171.3(3), Mo-N(3)-C(3) 121.4(3), Mo-N(3)-C(7) 121.1(3), C(3)-N(3)-C(7) 117.4(4), Mo-N(4)-C(8) 120.9(2), C(8)-N(4)-C(8) 118.3(3), O(1)-C(1)-N(1) 179.3(4), O(2)-C(2)-N(2) 178.5(4), N(3)-C(3)-C(4) 122.9(4), C(3)-C(4)-C(5) 119.0(5), C(4)-C(5)-C(6) 118.9(5), C(5)-C(6)-C(7) 119.6(5), N(3)-C(7)-C(6) 122.1(4), N(4)-C(8)-C(9) 121.8(3), C(8)-C(9)-C(10) 119.5(4), C(9)–C(10)–C(9) 119.0(5), N(5)–H(56)···N(6) 169(9).

cis bounded NCO groups are part of the octahedral coordination sphere, and the Mo–N_{CO} distances are a bit longer [9].

The results of thermal gravimetric analyses (TGA) of compounds 1 and 2 are shown in Fig. 3 [10]. The initial sharp mass-loss step of 23.7% within the range 25–80 °C in 1 corresponds to the complete removal of two weakly



Fig. 3. Thermogravimetric analysis of 1 and 2.

bound solvated pyridine molecules (calc. 25.6%). The temperature range of the loss of one pyridine molecule from the py_2H^+ cation in **2** cannot be precisely determined, it starts at approximately 100 °C and is completed at about 150 °C. The removal of the corresponding molecule in an analog isothiocyanate complex (*trans*-(py_2H)[Mo(NCS)₄ py_2]) occurs at somewhat lower temperature range [4]. The course of both curves between 250 and 450 °C is very similar finishing by a complete oxidation of both substances into MoO₃ at about 450 °C (calc. 23.3%, found 22.8% for **1**, and calc. 24.8%, found 25.3% for **2**).

Because of an insignificant coupling of $v(Mo-N_{CO})$ and $v(Mo-N_{py})$ vibrations, and due to the close-to-90° geometry of all six N-Mo-N bond angles in both compounds, one obtains an ideal C_{2v} local point group symmetry for both $Mo(NCO)_3$ and $Mo(N_{py})_3$ frameworks in 1 (three IR active stretching vibrations, $2A_1 + B_1$), and D_{4h} and $D_{\infty h}$ symmetry for Mo(NCO)₄ and Mo $(N_{py})_2$ frameworks in 2 (in both cases, one IR active stretching vibration, E_u and Σ_u^+), respectively [11,12]. Because of the real symmetry (C_1 in 1 and C_s in 2), more than one band could usually be expected from the particular stretching. For v(NC): 2237(s), 2206(s), 2155(s) in 1, and 2224(sh), 2205(s), 2154(m) in 2. For v(CO): 1367(s), 1342(s), 1305(m) in 1, and 1355(w), 1338(m), 1331(s) in **2**. For δ (NCO): 607(s), 601(s) in **1**, and 605(s), 599(s) in **2.** For v(Mo-N_{CO}): 341(sh), 349(s) in 1, and 349(s), 344(sh) in 2. For $v(Mo-N_{py})$: 273(s) in **1**, and 277(s), in **2** [13].

Supplementary materials

All atoms parameters and other crystallographic data for both compounds have also been deposited with the Cambridge Crystallographic Data Centre as supplementary material with the deposition numbers: CCCD 244698 and 244699, for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc. cam.ac.uk/const/retrieving.html.

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- [5] *Synthesis*: All reagents and organic solvents were obtained from commercial sources and were used without further purification. All reactions were carried out under an atmosphere of argon or dinitrogen. Mixture of 2.00 g (6.1 mmol) of $(NH_{4})_2$ [MoCl₅(H₂O)], 5.00 g (62 mmol) of KCN and 20 ml of pyridine was refluxed for 10 h and cooled to room temperature. The dark black coloured mixture was filtrated and the crude product washed with several portions of cooled degassed water to remove by-products and remains of the reactants. The yellow solid product was subsequently washed with little portion of ethanol, diethyl ether and dried in vacuo. It was found that by reflux of (py_2H) [Mo(N-CO)₄py₂] in pyridine the final product is always [Mo(NCO)₃py₃]. Therefore, the mass ratio of both substances strongly depends on the reflux-time. With regard to the composition of the mixture, the total yield is between 50% and 60%.
- [6] Separation: To the purified mixture an appropriate portion of degassed water, warmed up to 60 °C, was added and the suspension thoroughly stirred. The pale yellow insoluble molecular product was removed by filtration and the soluble ionic one was precipitated by an excess of pyridinium chloride (pyHCl). The procedure was repeated several times until both substances were separated. It was found that approximately 0.6 g of ionic component of the purified mixture is dissolved in 100 ml of warmed water (60 °C).
- [7] *Crystallisation of* **1**: 0.10 g of $[Mo(NCO)_3py_3]$ was dissolved in 7 ml of degassed pyridine, the suspension warmed up to 35 °C, stirred for 15 min, filtrated and slowly cooled down to 10 °C. Yellowish crystals suitable for X-ray structure determination were isolated. *Anal.* Calc. for C₂₈H₂₅MoN₈O₃: C 54.46, H 4.08, N 18.15. Found: C 54.18, H 3.96, N 17.93. *Crystallisation of* **2**: 0.10 g of pyH[Mo(NCO)₄py₂] was dissolved in a warmed (40 °C) mixture of 3 ml of acetone and 4 ml of pyridine, the suspension was filtrated and slowly cooled down to room temperature. Yellow crystals were collected after filtration. *Anal.* Calc. for C₂₄H₂₁MoN₈O₄: C 49.58, H 3.64, N 19.27. Found: C 49.13, H 3.58, N 19.34.
- [8] Crystallographic data: For $C_{28}H_{25}MoN_8O_3$ (1), $M_r = 617.50$, monoclinic, $P2_1/n$, a = 8.305(1), b = 16.763(2), c = 20.884(6) Å, $\beta = 90.10(2)^\circ$, V = 2907(1) Å³, Z = 4, $D_c = 1.411$ Mg m⁻³, $\mu = 0.49 \text{ mm}^{-1}$, $F(0\ 0\ 0) = 1260$, yellow prism, $0.84 \times 0.48 \times$ 0.18 mm, T = 293(2) K. Of 15546 collected reflections 6971 were unique ($R_{int} = 0.0145$), 4868 observed [$I > 2.5\sigma(I)$], which refined to R = 0.041, wR = 0.044; for C₂₄H₂₁MoN₈O₄ (2):, $M_r = 581.42$, orthorhombic, *Pnma*, *a* = 8.188(1), *b* = 9.889(1), *c* = 32.034(4) Å, $V = 2593.8(5) \text{ Å}^3$, Z = 4, $D_c = 1.489 \text{ Mg m}^{-3}$, $\mu = 0.55 \text{ mm}^{-1}$ $F(0\ 0\ 0) = 1180$, yellow prism, $0.74 \times 0.36 \times 0.28$ mm, T =293(2) K. Of 6751 reflections 3286 were unique ($R_{int} = 0.0143$), 2477 observed $[I > 2.5\sigma(I)]$, which refined to R = 0.025, wR = 0.029. It was found that the freshly prepared crystals of 1 and 2 slowly lost the crystallinity on exposure to the atmosphere due to the escape of solvated pyridine molecules. Therefore, prismatic single crystals of 1 and 2 were sealed under argon into thin-walled glass capillaries together with a drop of mother liquor. X-ray diffraction studies on 1 and 2 were performed using data collected on Enraf Nonius CAD-4 diffractometer with graphitemonochromated MoK α radiation ($\lambda = 0.71069$ Å). The data were corrected for Lorentz polarisation and absorption. Structures were solved by direct methods using SIR97 [14]. We employed full-matirx least-squares refinements on F magnitudes with anisotropic displacement factors for all non-hydrogen atoms using Xtal 3.4 [15]. The exceptions were C and N atoms (labelled as C(24)-C(29) and N(81)-N(86)) from one of the solvate pyridine molecules in 1 which is disordered. These atoms were refined

isotropically. Since it could not be resolved which of the six atoms from the pyridine ring are N and which are C, each of the six maxima from the ring was treated as to be occupied partially (1/6) with N and partially(5/6) with C atom. The positions of H atoms in both structures were obtained from the difference Fourier maps, only those from a disordered solvate pyridine molecule of compound 1 were not located. For 1 only positional parameters of H atoms (the exception was H21) and for 2 the positional parameters of H atoms together with their anisotropic displacement factors were refined. In the final cycle of the refinement, we used 6121 and 3002 reflections (included were those "less than" reflections for which $F_c > F_o$) and 388 and 248 parameters for 1 and 2, respectively.

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