

Nonstoichiometric Bromo-chloro-pyridine-Mo^{III} Complexes

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By a selective exchange of ligand Br by Cl, a series of nonstoichiometric bromo-chloro-pyridine-molybdenum(III) octahedral compounds of the type (cat)[MoBr_aCl_(4-a)py₂] (cat = pyH, $a = 3-1$ (**1**, **4**, **7**)); cat = [(C₂H₅)₃NH], $a = 2.744$ (**2**); cat = Rb, $a = 2.278$ (**5**); cat = [(C₆H₅)₄As], $a = 1.258$ (**8**) and [MoBr_aCl_(3-a)py₃] ($a = 2-1$ (**3**, **6**)) have been prepared and characterized. Owing to great similarity of the powder diffraction patterns and IR spectra of compounds *mer*-[MoBr_aCl_(3-a)py₃] ($a = 3-0$) with the known monoclinic modification in the space group $P2_1/c$ and compounds [MoBr_aCl_(3-a)py₃] ($a = 2-1$ (**3**, **6**)), the same type of crystal lattice was confirmed. Isostructurality was observed also for the orthorhombic *trans*-(pyH)[MoBr₄py₂] ($Pnma$) and compounds **1** and **4**, while compound **7** is isostructural to *trans*-(pyH)[MoCl₄py₂]. X-ray crystallographic analyses of **2**, **5** and **8**, obtained by recrystallization of (pyH)[MoBr_aCl_(4-a)py₂] ($a = 3-1$) with different cations, were performed. In these compounds, Mo^{III} is octahedrally coordinated with four halogenido ions at distances 2.4953(6)–2.5920(10) Å and two pyridine molecules at distances 2.195(4)–2.220(4) Å. *Trans* oriented pyridine rings in compounds **5** and **8** are co-planar, while deviation from co-planarity was noticed for compound **2** (8.9(3)°). The stoichiometry of four coordinated Br and Cl atoms in these compounds is not ideal, since the structure analysis results for **2**, **5** and **8** show a mixed occupancy of crystallographic sites; thus, refined population parameters for both atoms (Br and Cl) were calculated.

Keywords

molybdenum(III) complexes
bromo, chloro, pyridine ligands
X-ray analysis

INTRODUCTION

Numerous trivalent d-transition elements, such as Ti, V, Ta, Cr, Mo, W, Tc, Re, Fe, Ru, Os, Rh, and Ir were found to be present in the *trans*-[MX₄py₂][−] and *mer*-[MX₃py₃] (X = Br, Cl; py = pyridine) coordination species. There are also several *cis*-[MX₄py₂][−] (M = Mo, Re, Os) complexes whose structures have been described.¹ Mo^{III} species can be obtained by the reaction of MoX₃, (NH₄)₂[MoX₅(H₂O)] or (pyH)₃[MoX₆] (X = Br, Cl) in pyridine. Bromide compounds are more reactive towards substitution with pyridine than chlorides, and are substituted at lower temperatures.² (pyH)₂[MoX₅py] (X = Br, Cl)

is the first product of the stepwise substitution of halides in [MoX₆]^{3−} with pyridine. Depending on the reaction conditions (mainly temperature and time), the [MoX₅py]^{2−} reacts further, and the products are *cis* and *trans* isomers of (cat)[MoX₄py₂] (cat = pyH, py₂H) or *mer*-[MoX₃py₃]. *Cis* compounds, obtained at lower temperature, convert into *trans* compounds when the temperature increases.^{2,3} (NH₄)₂[MoX₅(H₂O)] reacts with boiling pyridine yielding *trans*-(pyH)[MoX₄py₂] and then *mer*-[MoX₃py₃]. *Trans*-(pyH)[MoX₄py₂] can be also obtained by melt reaction between *mer*-[MoX₃py₃] and pyHX (X = Br, Cl). *Trans*-[MoX₄py₂][−] can have two extreme positions of pyridine rings: eclipsed and staggered. Thus far, only the

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staggered isomer of *trans*-(pyH)[MoBr₄py₂]^{1,4,5} is known, while both isomers have been isolated in the case of *trans*-(pyH)[MoCl₄py₂].⁴ *mer*-[MoCl₃py₃] crystallizes in the monoclinic space group *P*2₁/*c*, while *mer*-[MoBr₃py₃] (X = Br, Cl) can have two polymorphic forms.^{1,4,6,7} *Fac*-[MoX₃py₃] compounds are not known.^{1,4}

To our knowledge, no such types of compounds, containing bromide and chloride ligands together, have been described in the literature. This paper reports the synthesis and characterization of bromo-chloro-pyridine species of molybdenum(III) of the types [MoBr_{*a*}Cl_{*b*}(3-*a*)py₃] (*a* = 2-1) and [MoBr_{*a*}Cl_{*b*}(4-*a*)py₂]⁻ (*a* = 3-1).

EXPERIMENTAL

Synthesis

All starting compounds and solvents were of analytical grade quality. [MoX₃py₃] (X = Cl, Br) were prepared as reported elsewhere; we used (NH₄)₂[MoX₅(H₂O)] instead of MoX₃.^{8,9} The purity was checked by elemental C,H,N-analysis, powder diffraction technique and vibrational spectroscopy. PyHCl and pyHBr, obtained by the reaction between pyridine and conc. hydrochloric or hydrobromic acid, were dried in vacuum at a temperature between 140 and 160 °C.

(pyH)[MoBr₃Clpy₂]^{*} (**1**) (*, proposed formula; see Results). Due to the hygroscopic nature of pyHCl, solid reactants [MoBr₃py₃] and pyHCl (mole ratio 1:1) were weighed in a glove-box, where the mixture was thoroughly ground and placed into a glass ampoule. The reaction was performed in a closed system in vacuum at about 150–160 °C. The solid mixture of 5.334 g of the reactants in the ampoule changed its colour and lumped when the reaction temperature was reached. The extent of the particular reaction was followed by pumping out the released pyridine (0.613 g; 7.75 mmol), and weighing the remaining reaction mixture. The reaction was carried out until a constant mass (4.721 g) of the solid in the ampoule was reached. To remove possible traces of the remaining reactants, the product was washed with methanol and dried in vacuum. UV-Vis(CH₃CN) λ_{max}/nm: 252 (sh), 255, 281, 310 (sh), 380; IR(nujol) ν_{max}/cm⁻¹: 1630, 1603, 1596, 1534 (pyH⁺), 1481, 1445, 1221, 1215, 1194, 1156, 1073, 1062, 1045, 1010, 1005, 979, 775, 765, 749, 737, 695 (C–H), 676, 639, 439, 389, 302 (ν(Mo–Cl)), 270 (sh), 257, 245 (sh), 209, 180; A(CH₃CN) / S cm² mol⁻¹: 129. *Anal.* Calcd. for C₁₅H₁₆N₃Br₃ClMo (*M*_r = 609.42): C 29.56, H 2.65, N 6.90; found: C 30.07, H 2.66, N 7.10.

[(C₂H₅)₃NH][MoBr_{2.7}Cl_{1.3}py₂] (**2**). 0.12 g of compound **1** was dissolved in 4 mL of a mixture of acetonitrile, water, and triethylamine (volume ratio 9:6:5). The solution was filtered, and after cooling the filtrate to 4 °C, orange crystals suitable for X-ray analysis were obtained after 5 hours (0.027 g; 22 %).

[MoBr₂Clpy₃]^{*} (**3**) (*, proposed formula; see Results). 3.0 g of compound **1** was refluxed in pyridine (40 ml) under an argon atmosphere for half-an-hour. The transparent solution was gradually cooled down close to 3 °C and the

resulting yellow precipitate was filtered off after two days. The precipitate was washed with diethylether and dried in vacuum (0.94 g; 36 %). Better yield (2.1 g; 81 %) was obtained when cold water (100 mL) was added into the filtrate and the solution was allowed to stand on ice for several hours. UV-Vis(CH₃CN) λ_{max}/nm: 252 (sh), 255, 281, 375; IR(nujol) ν_{max}/cm⁻¹: 1605, 1482, 1445, 1233, 1216, 1154, 1065, 1045, 1010, 777 (C–H), 760 (C–H), 754 (C–H), 704 (C–H), 697 (C–H), 691 (C–H), 640, 442, 321 (ν(Mo–Cl)), 308 (ν(Mo–Cl)), 269 (sh), 263, 251, 208, 177; A(CH₃CN) / S cm² mol⁻¹: 4. *Anal.* Calcd. for C₁₅H₁₅N₃Br₂ClMo (*M*_r = 528.51): C 34.09, H 2.86, N 7.95; found: C 34.53, H 2.93, N 7.87.

(pyH)[MoBr₂Cl₂py₂]^{*} (**4**) (*, proposed formula; see Results). The synthesis procedure was similar to that of compound **1**. 4.881 g of a thoroughly ground solid equimolar mixture of compound **3** and pyHCl was used. During the reaction, 0.600 g (7.58 mmol) of pyridine was pumped off and the mass of the solid product was 4.281 g. UV-Vis(CH₃CN) λ_{max}/nm: 233 (sh), 252 (sh), 255, 280 (sh), 305 (sh), 385; IR(nujol) ν_{max}/cm⁻¹: 1631, 1604, 1596, 1533 (pyH⁺), 1481, 1447, 1222, 1212, 1194, 1157, 1073, 1062, 1045, 1015, 1006, 980, 764, 749, 737, 696, 675, 639, 439, 388, 303 (ν(Mo–Cl)), 256, 244, 209, 178; A(CH₃CN)/S cm² mol⁻¹: 121. *Anal.* Calcd. for C₁₅H₁₆N₃Br₂Cl₂Mo (*M*_r = 564.97): C 31.89, H 2.85, N 7.44; found: C 32.02, H 2.78, N 7.45.

Rb[MoBr_{2.3}Cl_{1.7}py₂] · H₂O (**5**). 0.048 g of compound **4** was added to 4 mL of 25 % ammonia solution. After stirring and filtration of the obtained solution, 0.13 g of RbI was dissolved in the resulting filtrate. The solution was subsequently kept at 0 °C for 15 hours. Orange crystals suitable for X-ray analysis were obtained (0.018 g; 35 %).

[MoBrCl₂py₃]^{*} (**6**) (*, proposed formula; see Results). The synthesis was similar to that of compound **3**. The starting compound was compound **4** (3.0 g). The yield was 74 % (1.9 g). UV-Vis(CH₃CN) λ_{max}/nm: 251, 290 (sh), 365; IR(nujol) ν_{max}/cm⁻¹: 1605, 1482, 1446, 1233, 1215, 1154, 1065, 1045, 1011, 778 (C–H), 761 (C–H), 755 (C–H), 704 (C–H), 697 (C–H), 691 (C–H), 641, 442, 322 (ν(Mo–Cl)), 308 (ν(Mo–Cl)), 274(sh), 261, 251, 208, 177; A(CH₃CN) / S cm² mol⁻¹: 1. *Anal.* Calcd. for C₁₅H₁₅N₃Br₂Cl₂Mo (*M*_r = 484.05): C 37.22, H 3.12, N 8.68; Found: C 36.80, H 3.17, N 8.52.

(pyH)[MoBrCl₃py₂]^{*} (**7**) (*, proposed formula; see Results). Following the procedure described for **1**, an equimolar solid mixture of [MoCl₃py₃] and pyHBr was used. The mass of the solid mixture in the ampoule was 4.684 g. After removing pyridine (0.618 g; 7.81 mmol), 4.066 g of the solid residue remained in the ampoule. UV-Vis(CH₃CN) λ_{max}/nm: 233, 251, 307, 380; IR(nujol) ν_{max}/cm⁻¹: 1633, 1604, 1529 (pyH⁺), 1482, 1447, 1320, 1235, 1212, 1193, 1158, 1062, 1045, 1011, 978, 780, 762, 753, 737, 696, 671, 340, 443, 390, 307 (ν(Mo–Cl)), 249, 222, 209, 175; A(CH₃CN)/S cm² mol⁻¹: 124. *Anal.* Calcd. for C₁₅H₁₆N₃BrCl₃Mo (*M*_r = 520.52): C 34.61, H 3.10, N 8.07; found: C 34.92, H 3.05, N 8.03.

$[(C_6H_5)_4As][MoBr_{1.3}Cl_{2.7}py_2]$ (**8**). $[(C_6H_5)_4As]Cl$ (0.23 g) was added to 0.094 g of compound **7**, previously dissolved in 7 mL acetonitrile. After cooling the solution on ice, prismatic orange crystals suitable for X-ray analysis were isolated (0.039 g; 26 %).

Comments on IR bands. Bands above 400 cm⁻¹ belong to pyridine vibrations. Due to the overlapping of the Mo–N(py) and Mo–Br stretching frequencies, the bands below 275 cm⁻¹ cannot be unambiguously assigned.

Physical Measurements

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

Conductivity measurements were performed with 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 a nujol suspension using a Perkin-Elmer 1720 X FT-IR instrument in the region of 4000–400 cm⁻¹ (with KBr plates) and a Perkin-Elmer 2000 FT-IR instrument within the range 700–150 cm⁻¹.

Electronic spectra were measured with a Perkin-Elmer UV/Vis/NIR spectrophotometer Lambda 19. Samples were prepared as 8.0×10^{-5} M solutions in acetonitrile.

X-ray powder diffraction data were obtained using a Guinier-de Wolf camera with Cu-K α radiation ($\lambda = 1.54178$ Å).

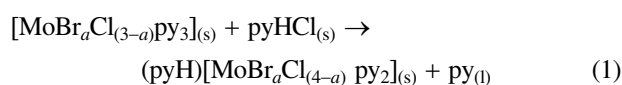
X-ray diffraction data of compounds **2**, **5** and **8** were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 20 °C. In all the three cases, the unit cell parameters and the orientation matrix for data collection were determined from 25 standard reflections ($10^\circ < \theta < 18^\circ$). Refinement of the unit cell parameters was performed on 75 reflections ($10^\circ < \theta < 18^\circ$) for compounds **2** and **8**, and on 100 reflections for compound **5**. Intensity control reflections were measured every 20000 seconds and the intensity decay was insignificant. Analytical absorption corrections based on the real shape of the crystals were made for all data sets. The positions of Mo atoms were determined from the Patterson map and the other non-hydrogen atoms were revealed by iterative Fourier synthesis. Anisotropic refinement was applied to all non-hydrogen atoms. In the case of compound **2**, all C–C and C–N bonds in the cation (triethylammonium) were restrained to keep the distances reasonable, while no restraints on the geometry of non-hydrogen atoms were applied for compounds **5** and **8**. Hydrogen atoms were found in the difference Fourier maps for all three compounds, and their isotropic atomic displacement parameters were fixed to the values of 1.5 and 1.25 times those of the corresponding values of methyl C atoms and other atoms to which H atoms were bound, respectively. Further treatment was as follows: for **2** and **5**, the positional parameters of H atoms were refined using restraints, while for compound **8**, only two H atoms (H15 and H16) were restrained and positional parameters of the rest of H atoms were refined independently. The so-called soft restraints were used where the expected distances (*e.g.* 1.05 for C–H bond) were added as

additional observations into the LS matrix, while their weights were calculated from the given expected *e.s.d.*'s (*e.g.*, reciprocal 0.01 for C–H bond). Scattering factors for neutral atoms from Tables II.2B and II.3.1 (Int. Tables Vol. IV)¹⁰ were used throughout. All calculations were performed using the XTAL program package,¹¹ while the illustrations were drawn with ORTEP¹¹ and PLATON.¹²

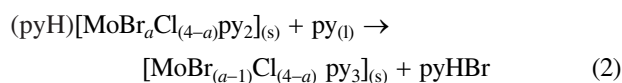
Crystal data and further experimental details of the data collection and handling are given in Table I.

RESULTS AND DISCUSSION

The synthesis, performed in a melt, and described by the reaction:



serves as the basis for replacement of the pyridine molecule in the Mo^{III} coordination sphere with the Cl ion, resulting in an increase of the number of Cl ligands from 3–*a* to 4–*a* (*a* = 3–0). On the other hand, by reflux of compounds $(pyH)[MoBr_aCl_{(4-a)}py_2]$ in boiling pyridine, a selective exchange of Br ligand through the pyridine molecule takes place:



Therefore, by an alternate mode of performing these two reactions (Eqs. 1, 2) subsequently (Figure 1: steps I, III (Eq. 1), steps II, IV (Eq. 2)), one-way selective replacements of Cl ligand with Br can be achieved.

Compounds **1** and **7**, can be prepared directly by melting $[MoX_3py_3]$ (*X* = Br, Cl) with either *pyHCl* or *pyHBr*. However, after reflux of compound **7** in pyridine, the reversible reaction resulting in the starting material (*X*-ray powder diffraction pattern) occurs.

IR absorption spectra of **1**, **4**, **7** and *trans*-(*pyH*)- $[MoX_4py_2]$ (*X* = Br, Cl) in the 4000–400 cm⁻¹ region, where absorption bands attributed to pyridine ligand are found, show almost identical features, indicating the same *trans* arrangement of the ligands around Mo^{III}. Bands around 1530 cm⁻¹ confirm the presence of the pyridine cation.¹³ Analogy is also observed at *mer*- $[MoX_3py_3]$ (*X* = Br, Cl) and compounds **3** and **6**. In the case of *mer*- $[MoX_3py_3]$ (*X* = Br, Cl), the triple splitting of the pyridine out-of-plane C–H absorption bands at 748 (into 783, 768, 760 and 780, 762, 755 cm⁻¹ for *X* = Br and Cl, respectively) and 703 cm⁻¹ (into 712, 702, 698 and 704, 695, 690 cm⁻¹ for *X* = Br and Cl, respectively) indicates a monoclinic modification. According to the literature,⁶ a smaller splitting is characteristic for orthorhombic modification. Mo–N(*py*), Mo–Br and Mo–Cl stretching bands may be found in the far-IR region below 400 cm⁻¹, where

TABLE I. Crystallographic data for compounds **2**, **5** and **8**

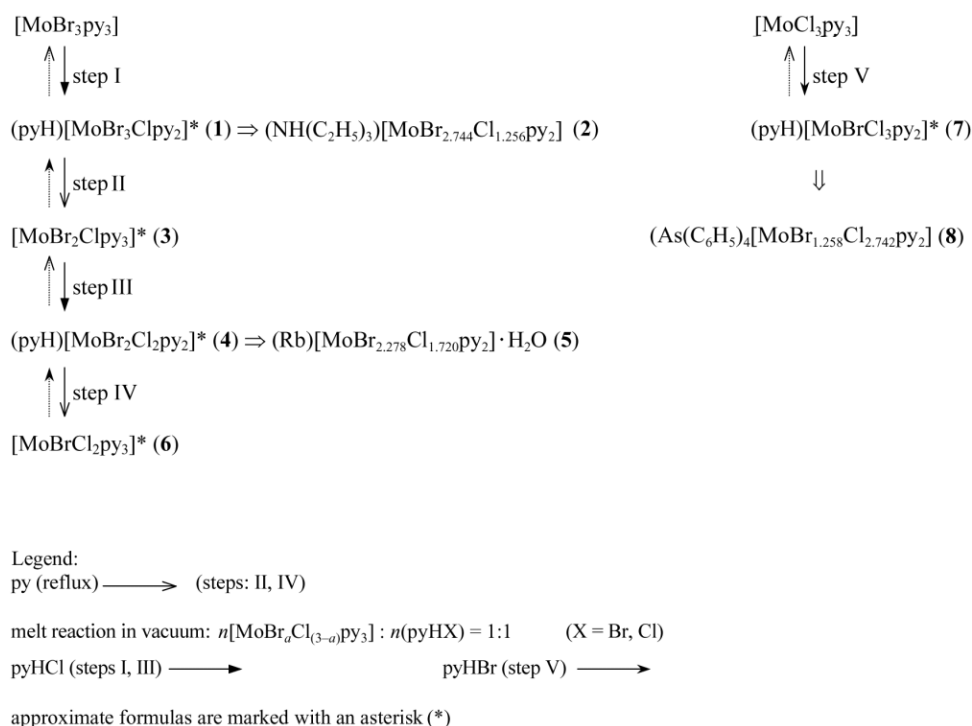
	2	5	8
Formula	C ₁₆ H ₂₆ Br _{2.744} Cl _{1.256} MoN ₃	C ₁₀ H ₁₂ Br _{2.278} Cl _{1.720} MoN ₂ ORb	C ₃₄ H ₃₀ AsBr _{1.258} Cl _{2.742} MoN ₂
Formula weight	622.53	600.63	835.22
Crystal shape	prism	prism	prism
Dimensions /mm	0.23 × 0.18 × 0.10	0.32 × 0.25 × 0.10	0.31 × 0.20 × 0.15
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	14.893(1)	8.431(1)	23.395(2)
<i>b</i> /Å	10.553(1)	8.947(1)	7.936(1)
<i>c</i> /Å	15.345(2)	12.013(1)	17.987(2)
α /°	90	101.31(1)	90
β /°	113.333(7)	98.51(1)	91.50(1)
γ /°	90	91.68(1)	90
<i>V</i> /Å ³	2214.5(4)	877.2(2)	3338.4(6)
<i>Z</i>	4	2	4
<i>D</i> _{calc} / (g cm ⁻³)	1.860	2.275	1.663
μ (Mo-K α) /cm ⁻¹	56.43	89.51	31.28
max. / min. absorption	3.157 / 1.525	7.143 / 2.778	1.848 / 1.370
Scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Range of $\sin \theta/\lambda$	0.0396–0.6605	0.0430–0.7016	0.0428–0.7019
Range of <i>h, k, l</i>	–20 –14 –21 / 20 14 21	–11 –12 –16 / 11 12 16	–32 –11 –13 / 32 11 13
No. of refl. measured	13395	10409	14124
No. of independent refl.	5336	5061	3513
No. of observed refl.	2904	2603	2275
Condition for obs. refl.	<i>I</i> > 2.5 σ (<i>I</i>)	<i>I</i> > 2.5 σ (<i>I</i>)	<i>I</i> > 2.5 σ (<i>I</i>)
<i>R</i>	0.037	0.035	0.033
<i>R</i> _w	0.036	0.030	0.013
<i>S</i> (goodness of fit)	1.033	1.099	1.093
No. of refined parameters	281	215	239

absorptions of pyridine molecule are not present.¹³ Due to the possible overlapping of the Mo–N(py) and Mo–Br stretching frequencies within the regions 265–240 cm⁻¹ and 280–230 cm⁻¹, respectively, the corresponding bands cannot always be unambiguously assigned when both ligands (Br, py) are present. Nevertheless, in some cases, the position of ν (Mo–Br) can be evaluated by ν (Mo–Cl) (330–280 cm⁻¹),^{3,5,14,15} from the frequency ratio ν (Mo–Br)/ ν (Mo–Cl) = 0.77.^{16,17,18} For *trans*-(pyH)[MoCl₄py₂], the corresponding strong ν (Mo–Cl) at 307 cm⁻¹ with the shoulder at 320 cm⁻¹ and medium ν (Mo–N(py)) at 249 cm⁻¹ are noticed,^{14,15} while in the spectrum of *trans*-(pyH)[MoBr₄py₂], a strong band at 256 cm⁻¹ (ν (Mo–Br)) and the shoulder at 250 cm⁻¹ (ν (Mo–N(py))) are observed.^{5,15} In the spectra of the prepared bromo-chloro-pyridine-molybdenum(III) compounds (**1**, **3**, **4**, **6**, **7**), a band around 210 cm⁻¹ and a band at 175–180 cm⁻¹ are also noticed. With a decrease of the Br/Cl ratio, the intensity of the band at *ca.* 210 cm⁻¹ rises whereas the intensity of the band at *ca.* 180 cm⁻¹ decreases. This is in agreement with the fact that the former band is observed in the spectra of

chloro compounds *mer*-[MoCl₃py₃] (209 cm⁻¹), *trans*-(pyH)[MoCl₄py₂] (210 cm⁻¹), while the one at *ca.* 180 cm⁻¹ is present only in the spectra of *mer*-[MoBr₃py₃] (at 178 cm⁻¹) and *trans*-(pyH)[MoBr₄py₂] (183 cm⁻¹).

For comparison, stoichiometric mixtures of pure bromo and chloro complexes at mole ratios 1:0, 3:1, 1:1, 1:3, 0:1 for (pyH)[MoBr₄py₂]/(pyH)[MoCl₄py₂] and 1:0, 2:1, 1:2, 0:1 for [MoBr₃py₃]/[MoCl₃py₃] were prepared. The UV-Vis spectra of these mixtures and stoichiometrically related compounds **1**, **4**, **7** and **3**, **6**, measured at the same concentrations (8.0 × 10⁻⁵ mol dm⁻³), differ significantly; therefore, a potentially possible existence of pure bromo and chloro compounds, which could arise or remain during the synthesis, was excluded.

Comparison of powder diffraction patterns of *mer*-[MoCl₃py₃]^{1,6,19} (monoclinic *P*2₁/*c*) and compounds **3** and **6** undoubtedly confirms their isostructurality (Table II). Analogy is observed also for *trans*-(pyH)[MoBr₄py₂] (orthorhombic, *Pnma*, staggered)^{1,19,20} and compounds **1** and **4** (Table III), while compound **7** is isostructural to *trans*-(pyH)[MoCl₄py₂]²⁰ (Table IV). A slight increase at inter-

Figure 1. Scheme of the synthesis of mixed bromo-chloro-pyridine-Mo^{III} complexes.

planar spacings, accompanied by a higher content of Br in both types of complexes, ($[\text{MoBr}_a\text{Cl}_{(3-a)}\text{py}_3]$ and $(\text{pyH})[\text{MoBr}_a\text{Cl}_{(4-a)}\text{py}_2]$), and monoclinic modification of compounds **3**, **6** are in agreement with some conclusions derived from vibrational spectroscopy.

By exchange of the pyH^+ ion in compounds **1**, **4** and **7** with appropriate cations, the crystals suitable for X-ray analysis of three complexes, $[(\text{C}_2\text{H}_5)_3\text{NH}][\text{MoBr}_{2.7}\text{Cl}_{1.3}\text{py}_2]$ (**2**), $\text{Rb}[\text{MoBr}_{2.3}\text{Cl}_{1.7}\text{py}_2] \cdot \text{H}_2\text{O}$ (**5**) and $[(\text{C}_6\text{H}_5)_4\text{As}][\text{MoBr}_{1.3}\text{Cl}_{2.7}\text{py}_2]$ (**8**), were obtained. Similarly to related $[\text{MoX}_4\text{py}_2]^-$ complexes, four halogenido ligands form the square-plane around the central molybdenum ion at the distances 2.4953(6)–2.5920(10) Å in all three com-

pounds (**2**, **5**, **8**), while the other two positions, below and above the halogenido plane, in octahedral anions are occupied by two pyridine molecules *via* nitrogen atoms at 2.195(4)–2.220(4) Å (Figures 2–4, Tables V–VII). In the related $[\text{MoX}_4\text{py}_2]^-$ complexes, Mo–N(py) distances range between 2.18–2.23 Å.^{3,5,14,15,21–24} *Trans* oriented pyridine rings are co-planar in **5** and **8**, while a slight deviation from co-planarity was noticed in **2** (8.9 (3)°).

Major differences between crystal structures thus arise from the different cations, which constitute the driving force for different crystal packing. The results of structure analysis show occupancy of crystallographic sites by Br and Cl ions. The population parameters of Br

TABLE II. Comparison of interplanar spacings (*d*) in compounds **3** and **6**^(a) with those in *mer*- $[\text{MoX}_3\text{py}_3]$ ^(b)

<i>h, k, l</i> (c)	$[\text{MoCl}_3\text{py}_3]$				$[\text{MoBr}_3\text{py}_3]$		3		6	
	<i>d</i> /Å (c)	<i>I</i> (c)	<i>d</i> /Å (d)	<i>I</i> (d)	<i>d</i> /Å (d)	<i>I</i> (d)	<i>d</i> /Å	<i>I</i>	<i>d</i> /Å	<i>I</i>
0,0,-2	7.81	10	7.8	8	7.9	7	7.82	9	7.77	8
1,1,-1	7.43	10	7.4	10	7.5	10	7.46	10	7.44	10
1,1,-2	6.65	2	6.6	4			6.71	1	6.64	1
0,2,0	6.28	1	6.3	3	6.5	3	6.40	2	6.26	1
0,2,-1	5.83	9	5.8	10	6.0	5	5.91	6	5.85	6
1,1,1	5.45	2	5.45	3			5.44	4	5.43	3
1,1,-3	5.32	8	5.30	10	5.45	10	5.36	7	5.34	7
0,2,-2	4.89	2	4.85	4	5.00	1	4.98	2	4.91	1
2,0,0	4.02	6			4.00	10	4.00	10	4.00	9

^(a) $[\text{MoBr}_a\text{Cl}_{(3-a)}\text{py}_3]$ *a* = 2–1; ^(b) X = Br, Cl. Monoclinic modification *P2₁/c*.^(c) CLPYMO10^{1,19}; ^(d) Ref. 6.

TABLE III. Interplanar spacings (d) in compounds **1** and **4**; a comparison with the orthorhombic *trans*-(pyH)[MoBr₄py₂] (*Pnma*)

(pyH)[MoBr ₄ py ₂]				1		4		
h,k,l ^(a)	$d/\text{Å}$ ^(a)	I ^(a)	$d/\text{Å}$ ^(b)	I ^(b)	$d/\text{Å}$	I	$d/\text{Å}$	I
2,0,0	8.10	1	8.0	1	8.02	1	7.94	1
1,0,1	7.61	5	7.5	5	7.45	5	7.45	4
0,1,1	7.34	4	7.3	6	7.21	6	7.16	6
2,1,0	7.01	7	6.9	10	6.90	10	6.88	10
1,1,1	6.68	8	6.6	8	6.57	8	6.51	9
2,0,1	5.91	1	5.8	3	5.84	2	5.81	3
2,1,1	5.43	3	5.38	4	5.37	3	5.34	3
2,2,0	5.29	2	5.26	3	5.22	3	5.21	3
1,2,1	5.15	1	5.1	2	5.10	2	5.06	2
2,2,1	4.51	1	4.6	4	4.54	3	4.52	2

(a)JUYROK^{1,19}; (b)Ref. 20.

and Cl at the same site were refined (the sum was constrained to 1.00). In compound **2** Cl prefers site X4, in compound **5** Br prefers site X21, and in compound **8** there is more Br at site X1 (Figures 2–4, Tables V–VII). These preferences for Br and Cl are in a good agreement with the observed Mo–X bond lengths, where longer bonds correspond to a higher Br occupancy (Mo–Br and Mo–Cl distances in compounds with [MoX₄py₂][−] (X = Br, Cl) are between 2.55–2.61 Å^{3,5,15,21} and 2.42–2.45

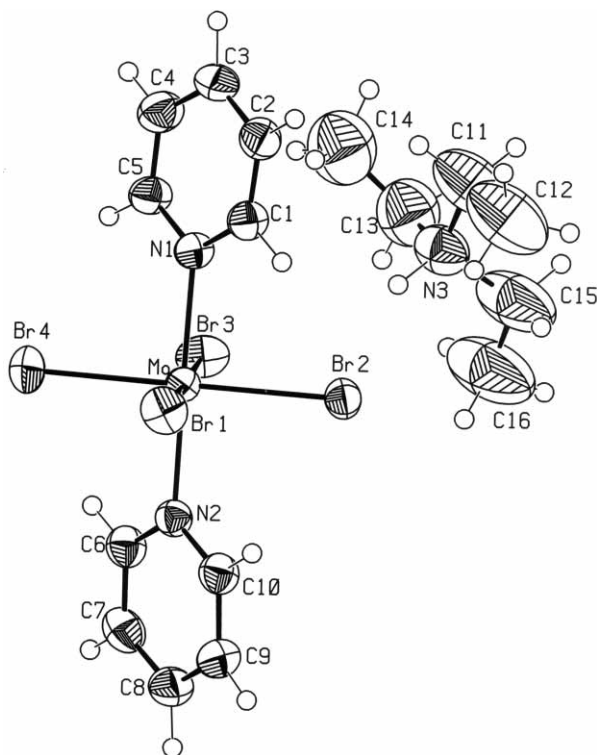


Figure 2. ORTEP drawing of the asymmetric unit of compound **2** showing the atomic labels (note that Br is used to denote Br and Cl sites with mixed occupancy). The ellipsoids are plotted at 50% probability.

TABLE IV. Comparison of interplanar spacings (d) in compound **7** with those in *trans*-(pyH)[MoCl₄py₂]

(pyH)[MoCl ₄ py ₂] ^(a)		7	
$d/\text{Å}$	I	$d/\text{Å}$	I
11.2	6	11.5	5
7.6	10	7.68	10
6.5	8	6.68	8
6.2	9	6.27	9
5.9	2	(b)	
5.6	3	5.73	2
5.05	3	5.20	1
4.96	1	5.04	1
4.6	2	4.70	1
4.25	6	4.32	7

(a)Ref. 20. (b)The line for the value was not observed, possibly due to its low intensity.

Å^{14,15,22–24}). The only noticeable exception from this pattern is the Mo–X2 distance (2.5920(10) Å) in **2**, which is ≈ 0.05 Å longer than expected (Table V). The reason for this exception may be a hydrogen bond N3–H3B...X2 (N3–H3B...X2 = 156.7(15)°, N3...X2 = 3.396(7) Å, X2...H3B = 2.456(14) Å, N3–H3B = 0.998(13) Å) to the nitrogen atom of the triethylammonium cation (Figure 5). It can be seen that the thermal ellipsoids of C atoms in the cation ($[(C_2H_5)_3NH]^+$) are large, showing that a disorder is present in this case (Figure 2). An attempt to model a disorder with more than one position of each C atom failed. For this reason, the bond lengths and angles were restrained and large atomic displacement parameters accounted for the disorder. In the structure of **5**, rubidium cations connect two neighboring coordination anions through two halogenido ions (3.3303(11)–3.4045(11) Å; Table VI) on each Mo–octahedron, thus forming halogenido zigzag ribbons with Rb⁺ at corner positions (Figure 6). Next to this four halogenido ions, additional two water molecules (at 2.947(7) and 2.968(7) Å; Table VII) and a nitrogen atom are coordinated to the Rb⁺ cation, forming an RbX₄O₂N chromophore, with four halogenido atoms and two water molecules at the corners of the capped trigonal prism, and the nitrogen atom (of pyridine molecule) perpendicular to one prism side. Simultaneously, these two water molecules are coordinated also to another Rb⁺ ion from the adjacent ribbon, enabling two mono-atomic bridges between the ribbons. Each water molecule is also involved in two hydrogen bonds to two X ions from one Mo^{III} anion (O–H1A...X12 = 159(7)°, O...X12 = 3.302(6) Å, X12...H1A = 2.34(7) Å, O–H1A = 1.01(7) Å; O–H1B...X11 = 139(6)°, O...X11 = 3.275(6) Å, X11...H1B = 2.45(9) Å, O–H1B = 1.00(7) Å). Alternate layers of Mo^{III} coordination anions and $[(C_6H_5)_4As]^+$ cations were found in **8**; Mo atoms occupy the inversion centers while As atoms are positioned on the twofold axis.

TABLE V. Selected bond distances / Å, angles / ° and the atom site occupancy of Br and Cl for compound **2**^(a)

Mo–X1	2.5564(11)	Mo–X2	2.5920(10)	Mo–X3	2.5661(11)
Mo–X4	2.5146(12)	Mo–N1	2.195(4)	Mo–N2	2.220(4)
X1–Mo–X2	90.51(4)	X1–Mo–X3	179.35(4)	X1–Mo–X4	88.91(4)
X1–Mo–N1	90.28(15)	X1–Mo–N2	91.37(15)	X2–Mo–X3	89.28(3)
X2–Mo–X4	179.29(5)	X2–Mo–N1	89.49(14)	X2–Mo–N2	89.84(14)
X3–Mo–X4	91.30(4)	X3–Mo–N1	89.11(15)	X3–Mo–N2	89.24(15)
X4–Mo–N1	90.12(14)	X4–Mo–N2	90.57(14)	N1–Mo–N2	178.2(2)
Br1	0.785(9)	Cl1	0.215(9)		
Br2	0.650(8)	Cl2	0.350(8)		
Br3	0.739(9)	Cl3	0.261(9)		
Br4	0.570(9)	Cl4	0.430(9)		
Br	2.744(9)	Cl	1.256(9)		

^(a)X is used for Br and Cl occupying the same site.

From the refined population parameters, the overall number of Br atoms in the anions can be calculated. These are 2.744, 2.278 and 1.258 for compounds **2**, **5** and **8**, respectively (Tables V–VII). Deviations from the expected formulas (3, 2 and 1) are not large, but due to the considerable difference between the scattering powers of Br and Cl, they can be regarded as significant.

Different local concentrations of pyHX (X = Br, Cl) in the melt, where the reaction takes place, probably allow a redistribution of the halogenido ions in the reaction equilibrium and filling of X positions in octahedra with both anions (Br, Cl). Therefore, the suggested formulas marked with an asterisk probably show only average stoi-

chiometric values for Br and Cl in the pyH⁺ complexes, since one pyridine molecule was released in the reaction (Eq. 1). As a consequence, addition of a certain cation results in structures with a nonstoichiometric distribution of Br and Cl atoms. To confirm this assumption, several crystals from the same sample should be crystallographically analyzed.

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Supplementary Materials. – Crystallographic data for the structures reported in this paper have been deposited

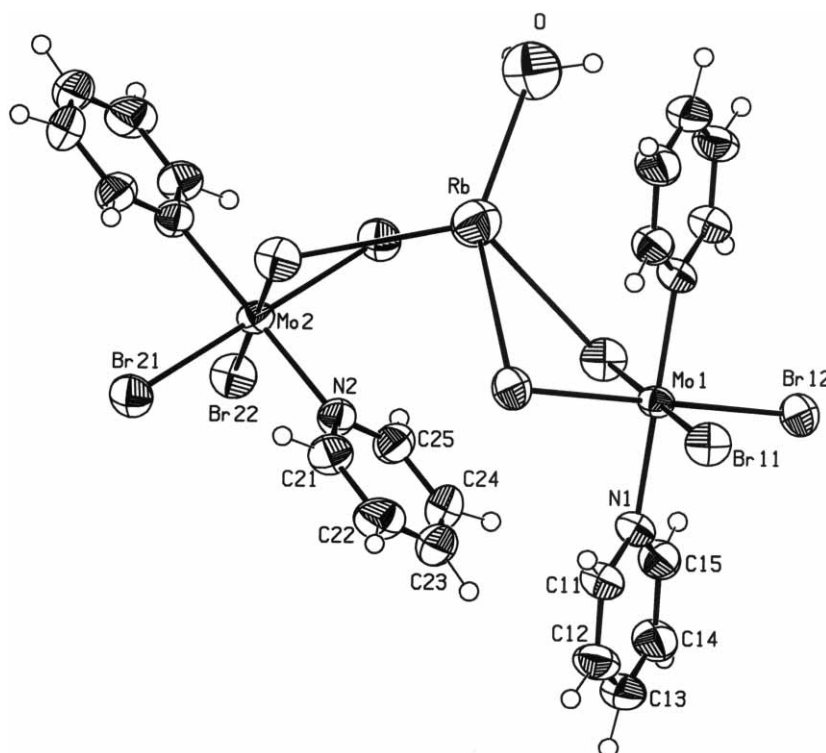


Figure 3. Extended asymmetric unit of compound **5**; Br is used to denote Br and Cl sites with mixed occupancy, ORTEP plot. Thermal displacement ellipsoids are drawn at 50 % probability level.

TABLE VI. Some bond distances / Å, angles / ° and the atom site occupancy of halogen sites for compound **5**^{(a),(b)}

Mo1–X11	2.5371(7)	Mo1–X12	2.5386(8)	Mo2–X21	2.5626(7)
Mo2–X22	2.5509(8)	Mo1–N1	2.206(5)	Mo2–N2	2.191(4)
Rb–X11	3.3613(12)	Rb–X12	3.4045(11)	Rb–X21	3.3521(10)
Rb–X22	3.3303(11)	Rb–O	2.947(7)	Rb–O'	2.968(7)
X11–Mo1–X12	88.91(3)	X11–Mo1–N1	90.64(10)	X12–Mo1–N1	91.32(10)
X21–Mo2–N22	89.84(3)	X21–Mo2–N2	89.02(11)	X22–Mo2–N2	89.58(11)
X11–Rb–X12	63.39(2)	X11–Rb–X21	84.55(3)	X11–Rb–X22	121.19(3)
X11–Rb–O	103.92(12)	X11–Rb–O'	150.37(11)	X12–Rb–X21	120.14(3)
X12–Rb–X22	88.91(3)	X12–Rb–O	150.06(11)	X12–Rb–O'	105.21(11)
X21–Rb–X22	65.41(2)	X21–Rb–O	82.92(12)	X21–Rb–O'	122.81(10)
X22–Rb–O	119.62(11)	X22–Rb–O'	83.84(12)	O–Rb–O'	71.84(17)
Br11	0.502(7)			Cl1	0.498(7)
Br12	0.541(7)			Cl2	0.459(7)
Br21	0.653(7)			C21	0.347(7)
Br22	0.582(7)			C22	0.416(7)
Br	2.278(7)			Cl	1.720(7)

^(a)X is used to denote Br and Cl. ^(b)The oxygen atom from another asymmetric unit for a symmetry equivalent position (1–x, 1–y, –z) is marked with an apostrophe (').

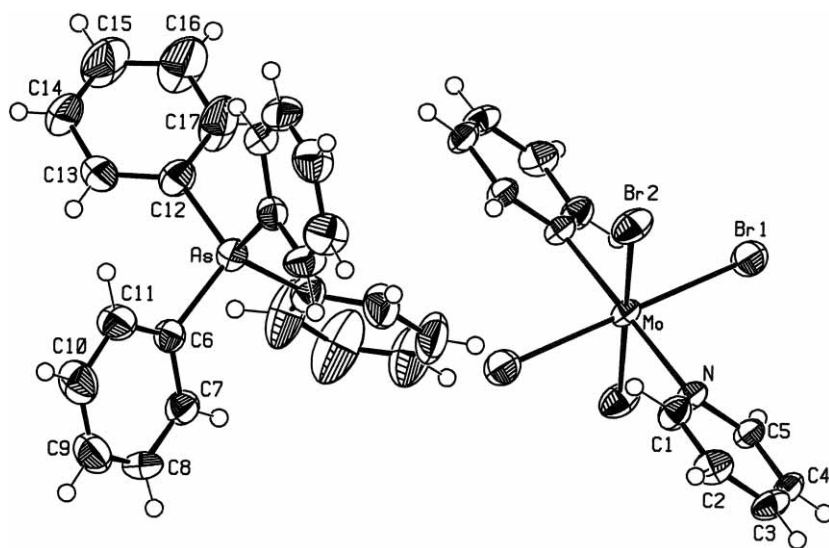


Figure 4. ORTEP plot of the extended asymmetric unit of compound **8** (Br denotes Br and Cl sites with mixed occupancy). The ellipsoids are plotted at 50 % probability.

TABLE VII. Selected bond distances / Å, angles / ° and the atom site occupancy of X sites for compound **8**^{(a),(b)}

Mo–X1	2.5242(5)	Mo–X2	2.4953(6)	Mo–N	2.193(2)
As–C6	1.914(3)	As–C12	1.907(3)		
X1–Mo–X2	91.51(3)	X1–Mo–N	88.52(7)	X2–Mo–N	90.47(6)
C6–As–C6'	104.18(12)	C6–As–C12	108.16(14)	C6–As–C12'	113.80(13)
C12–As–C12'	108.82(14)				
Br1	0.365(4)			Cl1	0.635(4)
Br2	0.264(4)			Cl2	0.736(4)
Br	1.258(4)			Cl	2.742(4)

^(a)X denotes Br and Cl sites with mixed occupancy. ^(b)Carbon atoms from another asymmetric unit for a symmetry equivalent position (1–x, +y, 1/2–z) are marked with an apostrophe (').

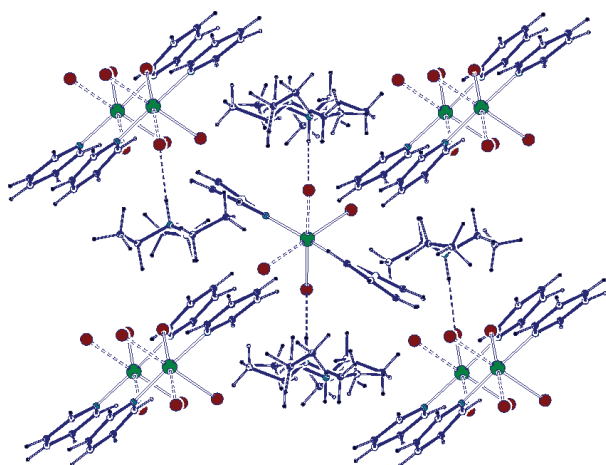


Figure 5. The crystal packing of compound **2**, PLATON drawing.

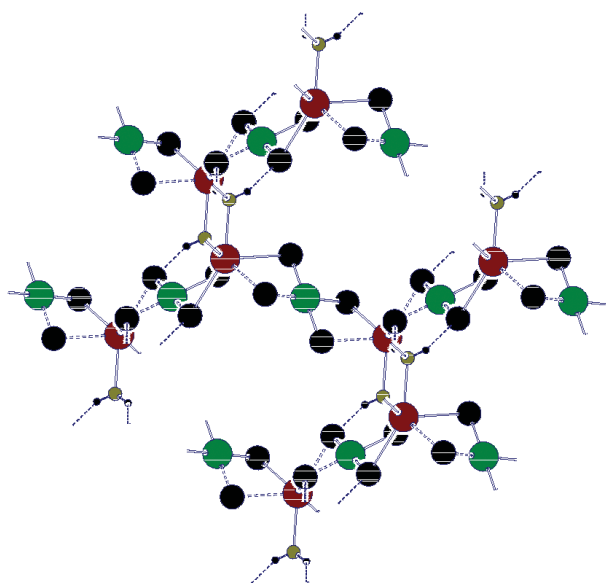


Figure 6. PLATON plot of the crystal packing of compound **5**.

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REFERENCES

1. F. H. Allen and O. Kennard, *Chem. Des. Autom. News* **8** (1993) 31–37.
2. J. V. Brenčič, I. Leban, B. Modec, and O. Carugo, *Inorg. Chim. Acta* **229** (1995) 421–424.
3. V. Brenčič, I. Leban, and B. Modec, *Z. Anorg. Allg. Chem.* **620** (1994) 950–954.
4. J. V. Brenčič, *Acta Chim. Slov.* **44** (1997) 131–141.
5. J. V. Brenčič, B. Čeh, I. Leban, B. Modec, and R. Rotar, *Z. Anorg. Allg. Chem.* **619** (1993) 796–800.
6. J. V. Brenčič, B. Čeh, and C. Kríželj, *Vestn. Slov. Kem. Druš.* **24** (1977) 41–46.
7. J. V. Brenčič, *Z. Anorg. Allg. Chem.* **403** (1974) 218–224.
8. A. Rosenheim, G. Abel, and R. Lewy, *Z. Anorg. Allg. Chem.* **197** (1931) 189–221.
9. J. H. Balthis, *J. Inorg. Nucl. Chem.* **24** (1962) 1017.
10. *International tables for X-ray Crystallography*, Vol. IV. Birmingham, Kynoch Press. Present distributor D. Reidel, Dordrecht, Holland, 1974.
11. S. R. Hall, D. J. du Boulay, and R. Olthof-Hazekamp (Eds.), *Xtal3.6 System*, University of Western Australia, Lamb, Perth, 1999.
12. A. L. Spek, *Platon, Acta. Crystallogr., Sect. A* **46** (1990) C34.
13. N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. Sharp, *J. Inorg. Nucl. Chem.* **18** (1961) 79–87.
14. J. V. Brenčič, I. Leban, and B. Modec, *Polyhedron* **13** (1994) 3171–3176.
15. J. V. Brenčič, L. Golič, I. Leban, and R. Rotar, *Z. Anorg. Allg. Chem.* **622** (1996) 2124–2128.
16. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., J. Wiley and Sons, New York, 1973.
17. G. Socrates, *Infrared Characteristic Group Frequencies, Tables and Charts*, 2nd ed., J. Wiley & Sons, Chichester, 1998.
18. R. J. H. Clark and C. S. Williams, *Inorg. Chem.* **4** (1965), 350–357.
19. E. Dowty, *Cryscon Shape Software*, Hidden Valley Road, Kingsport, USA, 1965.
20. J. V. Brenčič, B. Čeh, and I. Leban, *Z. Anorg. Allg. Chem.* **538** (1986) 212–220.
21. J. V. Brenčič and B. Modec, *Acta Crystallogr., Sect. C* **51** (1995) 197–198.
22. J. V. Brenčič and B. Čeh, *Inorg. Chim. Acta* **160** (1989) 143–145.
23. J. V. Brenčič, B. Čeh, and I. Leban, *Acta Crystallogr., Sect. C* **45** (1989) 1144–1146.
24. I. Leban, B. Modec, and J. V. Brenčič, *Acta Crystallogr., Sect. C* **50** (1994) 1546–1548.

SAŽETAK

Nestehimetrijski bromo-kloro-piridin-Mo^{III} kompleksi

Nives Kitanovski, Ljubo Golič, Anton Meden i Boris Čeh

Selektivnom zamjenom bromovoga liganda klorovim dobijena je i karakterizirana serija nestehimetrijskih bromo-kloro-piridin-Mo^{III} kompleksa tipa (cat)[MoBr_aCl_(4-a)py₂] (cat = pyH, $a = 3-1$ (**1**, **4**, **7**); cat = [(C₂H₅)₃NH], $a = 2.744$ (**2**); cat = Rb, $a = 2.278$ (**5**); cat = [(C₆H₅)₄As], $a = 1.258$ (**8**)) i [MoBr_aCl_(3-a)py₃] ($a = 2-1$ (**3**, **6**)). Usljed velike sličnosti difraktograma praha i IR spektara spojeva *mer*-[MoBr_aCl_(3-a)py₃] ($a = 3-0$) poznate monoklinske modifikacije u prostornoj grupi $P2_1/c$ i spojeva [MoBr_aCl_(3-a)py₃] ($a = 2-1$ (**3**, **6**)), potvrđen je isti tip kristalne rešetke. Opažena je izostruktornost rompskoga *trans*-(pyH)[MoBr₄py₂] ($Pnma$) i spojeva **1** i **4**, dok je spoj **7** izostrukturiran s *trans*-(pyH)[MoCl₄py₂]. Načinjena je rentgenska strukturalna analiza spojeva **2**, **5** i **8** dobijenih prekrizacijom (pyH)[MoBr_aCl_(4-a)py₂] ($a = 3-1$) s različitim kationima. U tim je spojevima Mo^{III} oktaedarski koordiniran s četiri halogenidna iona na udaljenostima 2.4953(6)–2.5920(10) Å i dvije molekule piridina na udaljenostima 2.195(4)–2.220(4) Å. *Trans* orijentirani piridinski prstenovi u spojevima **5** i **8** su koplanarni dok je kod spoja **2** ustanovljena devijacija od koplanarnosti (8.9(3)°). Strukturnom analizom utočnjeni su faktori zauzetosti četiri koordinirana atoma (Br, Cl) u spojevima **2**, **5** i **8**. Nađeno je da su navedeni kristalografski položaji zauzeti atomima Cl i Br u nestehimetrijskome omjeru.