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Room Temperature Synthesis and Crystal Structure of *mer*-[$MoBr_3Py_3$], the Vibrational Spectra of *mer*-[$MoBr_3Py_3$], *mer*-[MoI_3Py_3] and *trans*,*trans*-[$MoBr_2Py_4$][$MoBr_4Py_2$]

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Abstract. The reaction of $MoBr_3$ and pyridine at room temperature provided single crystals of *mer*-[MoX_3Py_3]. *mer*-[$MoBr_3Py_3$] crystallizes in $P2_1/n$ monoclinic space group with cell dimensions a = 9.2297(5) Å, b = 12.911(8) Å, c = 15.7022(9) Å and β = 90.479(3)°. There are four formula units in a unit cell. Mo–N distances are in the range 2.196(8)–2.214(8) Å and Mo–Br distances are 2.573(1) Å and 2.574(1) Å. Fundamental vibrational frequencies of pyridine molecules are strongly affected upon coordination in all three coordination compounds: *mer*-[$MoBr_3Py_3$], *mer*-[MoI_3Py_3] and *trans*,*trans*-[$MoBr_2Py_4$]-[$MoBr_4Py_2$].

Introduction

The first literature on neutral monomeric trihalo-tripyridine molybdenum(III) coordination compounds dates back to the year 1931, when *Rosenheim* described synthesis of *mer*-[$MoCl_3Py_3$] and *mer*-[$MoBr_3Py_3$] (Py = pyridine)[1] by the reaction of the corresponding molybdenum trihalides in boiling pyridine. The use of $(NH_4)_2[MoX_5H_2O]$ (X = Cl, Br, I) have been demonstrated to lead to the same products, while the presence of methanol in the reaction mixture resulted in the precipitation of ionic *trans*,*trans*-[MoX_2Py_4][MoX_4Py_2].[2,3] The crystal structure of *mer*-[$MoCl_3Py_3$] was determined, while for *mer*-[$MoBr_3Py_3$] the cell parameters were derived from powder data and authors expressed believe that *mer*-[$MoCl_3Py_3$] and *mer*-[$MoBr_3Py_3$] are isostructural.[2] The d^3 transition metal coordination compounds were studied for the photo-initiated two-electron oxidation process which is expected to be a common feature in second and third row transition metal coordination compounds. *mer*-[MoX_3Py_3] (X = Br, I), and especially *mer*-[$MoCl_3Py_3$], which was found to phosphoresce in solid state were considered for such a study.[4] The precise crystal structure of *mer*-[$MoBr_3Py_3$] would possibly also contribute to the knowledge on photochemical processes associated to this compound. Precipitation of *mer*-[$MoBr_3Py_3$] as the last step in the synthesis[1] did not provide crystals suitable for X-ray measurements. To reduce the crystallization rate the reaction of molybdenum tribromide and pyridine was conducted at room temperature, which provided crystals of appropriate quality for X-ray crystal structure determination. In this paper the room temperature synthesis and the crystal structure of *mer*-[$MoBr_3Py_3$] is described and tentative assignment of vibrational data are provided.

Results and Discussion

Due to the slight solubility[5] of *mer*-[$MoBr_3Py_3$] in pyridine it was anticipated, the $MoBr_3$ reaction with pyridine might proceed at lower temperatures albeit at lower reaction rates. The reaction between finely divided $MoBr_3$ and pyridine took three weeks to complete at room temperature yielding almost pure *mer*-[$MoBr_3Py_3$]. The side product in traces were plate crystals, identified by single-crystal X-ray diffraction as *trans*,*trans*-[$MoBr_2Py_4$][$MoBr_4Py_2$], which was already reported to appear as the side product in the reaction between $(NH_4)_2[MoBr_5.H_2O]$ and pyridine diluted with methanol.[3]

Crystal Structure

The *mer*-[$MoBr_3Py_3$] crystallizes in the monoclinic space group $P2_1/n$ with four formula units in a unit cell, Table 1. Cell parameters obtained (a = 9.2297(5) Å, b = 12.911(8) Å, c = 15.7022(9) Å, β = 90.479(3) °) differ from previously reported parameters based on powder diffraction data.[2] Molybdenum in *mer*-[$MoBr_3Py_3$] has octahedral surroundings of three bromine atoms and three nitrogen atoms (Figure 1), angles formed by central molybdenum atom and atoms in *trans* and *cis* positions are close to 180° and 90° with the highest deviation in angle Br2–Mo1–Br3 at 176.92°, and angle Br2–Mo1–N1 at 87.33°. The Mo–Br bond lengths at 2.573(1) Å and 2.574(1) Å correspond well with the average value 2.565(1) Å for bond lengths found in ionic coordination compounds with pyridine ligands, *trans*,*trans*-[$MoBr_2Py_4$][$MoBr_4Py_2$][3] and *trans*-[$Mo^{III}Br_2Py_4$]Br_3.[6] The

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three Mo–N bond lengths in *mer*-[MoBr$_3$Py$_3$] are slightly different but in a very narrow range from 2.196(8) Å to 2.214(8) Å, the corresponding Mo–N bond lengths in *trans*,*trans*-[MoBr$_2$Py$_4$][MoBr$_4$Py$_2$][3] and *trans*-[Mo^{III}Br$_2$Py$_4$]Br$_3$[6] are in the range from 2.207(4) Å–2.237(4) Å. The pyridine ring is almost planar; the greatest torsion angle found is N2–C6–C7–C8 at 2.22°. The average C–N distance 1.344 Ä, C–C distance 1.374 Ä and average angles C–N–C 116.78°, N–C–C 123.57°, C–C–C 118.68° in pyridine rings are comparable to corresponding distances and angles in ionic molybdenum coordination compounds, *trans*,*trans*-[MoBr$_2$Py$_4$][MoBr$_4$Py$_2$] and *trans*-[Mo^{III}Br$_2$Py$_4$]Br$_3$.[3,6] The pyridine molecules are arranged in a propeller like formation around a plane formed by three nitrogen atoms and one bromine atom.

Table 1. Summary on crystal structure of *mer*-[MoBr$_3$Py$_3$].

Empirical formula	MoBr$_3$C$_{15}$N$_3$H$_{15}$
Formula weight	572.96
Temperature /K	200
Radiation	MoK$_\alpha$ (0.71069 Å)
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions /Å	
a /Å	9.2297(5)
b /Å	12.9112(8)
c /Å	15.7022(9)
β /°	90.48(0)
V /Å^3	1871.1(2)
Z	4
Calculated density /g·cm^{-3}	2.034
Absorption coeff. /mm^{-1}	7.106
F(000)	1192
Color	Orange-yellow
Theta range for data collection	6.09–73.96
Limiting indices	–12–8, –16–16, –9–20
Refinement method	Full-matrix on *F*^{2}
Measured reflections	8352
Independent used in refinement	4242
Free parameters	199
*R*1	0.0692
*wR*2	0.1615
Goodness-of-fit on *F*^{2}	1.056
Largest diff. peak and hole /e·Å^{-3}	1.399, –1.339,

Vibrational Spectroscopy

The study of resonance Raman effect was reported on *mer*-[MoBr$_3$Py$_3$] and *mer*-[MoCl$_3$Py$_3$][7] with laser excitation lines in the range from 647.1 to 476.5 nm and the highest sevenfold enhancement was observed in the 1606 cm^{-1} band associated with the carbon–carbon stretching vibration of the pyridine ring. The utilization of He-Ne excitation line at 632.8 nm to obtain Raman spectra of *mer*-[MoBr$_3$Py$_3$], *mer*-[MoI$_3$Py$_3$] and *trans*,*trans*-[MoBr$_2$Py$_4$][MoBr$_4$Py$_2$] in this work is not expected to provide strong pre-resonance enhancement according to electronic spectrum of *mer*-[MoBr$_3$Py$_3$] where principal bands appear at 385 and 310 nm.[5,8] Raman spectra of *mer*-[MoBr$_3$Py$_3$], *mer*-[MoI$_3$Py$_3$] and *trans*,*trans*-[MoBr$_2$Py$_4$][MoBr$_4$Py$_2$] are shown on Figure 2 and Figure 3. The band at 258 cm^{-1} in the low-frequency part of the Raman spectrum of *mer*-[MoBr$_3$Py$_3$] is assigned to the Mo–Br stretching vibration according to the assignment provided for the infrared bands at 260 cm^{-1} and 269 cm^{-1} for the same type of vibration.[7,9]

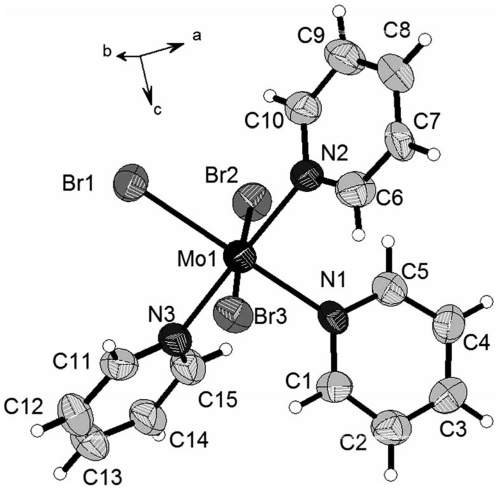

Figure 1. *mer*-[MoBr$_3$Py$_3$] molecular unit; thermal ellipsoids are given at 30 % probability level.

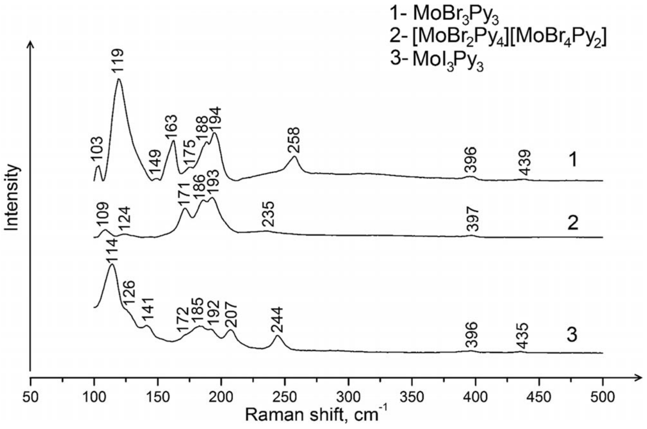

Figure 2. Raman spectra of *mer*-[MoBr$_3$Py$_3$], *trans*,*trans*-[MoBr$_2$Py$_4$]-[MoBr$_4$Py$_2$] and *mer*-[MoI$_3$Py$_3$] in the range 100–500 cm^{-1}.

Accordingly the band at 207 cm^{-1} in the Raman spectrum of the *mer*-[MoI$_3$Py$_3$] originates from the Mo–I stretching vibration. The frequency ratio between the two is 0.80 which corresponds well to Mo–I/Mo–Br stretching vibration frequency ratio (0.80) in octahedral [Rh(en)$_2$X$_2$]$^+$ (en = ethylendiamine) cations.[10] The band at 244 cm^{-1} in the Raman spectrum of *mer*-[MoI$_3$Py$_3$] is assigned to Mo–N stretching vibration, which is expected to occur in the range from 200 cm^{-1} to 287 cm^{-1}. The Mo–N stretching vibrations in general appear weaker than Mo–X vibrations and are not sensitive to the type of halogen.[11] Therefore, in *trans*,*trans*-[MoBr$_2$Py$_4$][MoBr$_4$Py$_2$] the weak Raman band at 235 cm^{-1} is assigned to the Mo–N vibration, the corresponding infrared band was found at 242 cm^{-1}.[3] In the Raman spectrum of *mer*-[MoBr$_3$Py$_3$] there is no discernible band around 240 cm^{-1}, but it is possible it is obscured by an uneven background. Other bands in the low-frequency region of

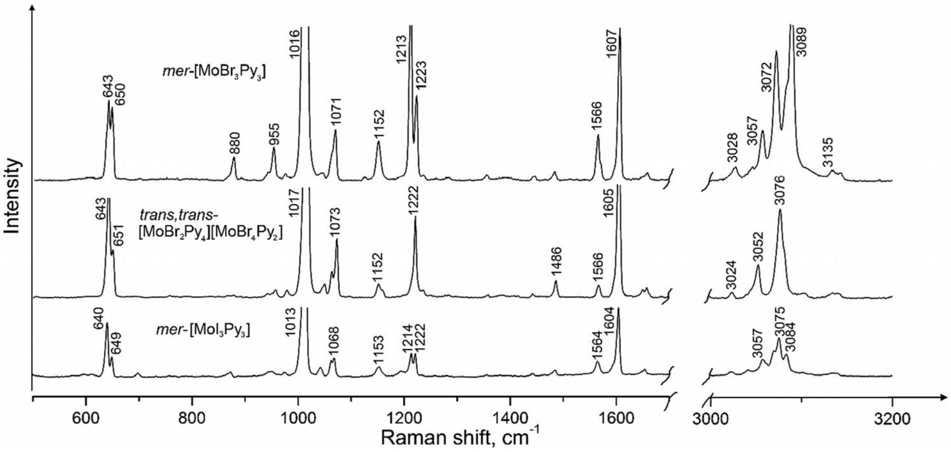

Figure 3. Raman spectra of *mer*-[$MoBr_3Py_3$], *trans*,*trans*-[$MoBr_2Py_4$][$MoBr_4Py_2$] and *mer*-[MoI_3Py_3] in the range 500–3300 cm^{-1}.

mer-[$MoBr_3Py_3$] and *trans*,*trans*-[$MoBr_2Py_4$][$MoBr_4Py_2$] Raman spectra we found uncertain to assign due to the appearance of Mo–X and Mo–N bands in the same region and the lack of isotopic substitution data, which was already pointed out by *Filippo* et al.[7]

The coordination of the pyridine molecule to the metal atom affects pyridine internal vibrations, which results in split and/or shifted bands in the vibrational spectra of pyridine coordination compounds.[5,12]

Conclusions

The *mer*-[$MoBr_3Py_3$] was synthesized at room temperature from finely divided $MoBr_3$ and anhydrous pyridine in three weeks. Molybdenum in *mer*-[$MoBr_3Py_3$] has octahedral surroundings of three bromine atoms and three nitrogen atoms and the pyridine molecules are arranged in a propeller like formation around a plane formed by three nitrogen atoms and one bromine atom. Vibrational spectra reveal the fundamental frequencies of pyridine molecules are strongly affected upon coordination in all three coordination compounds: *mer*-[$MoBr_3Py_3$], *mer*-[MoI_3Py_3] and *trans*,*trans*-[$MoBr_2Py_4$]-[$MoBr_4Py_2$].

Experimental Section

Materials and Syntheses: All material transfer and handling was performed on a vacuum line or in a glow box to avoid moisture. Molybdenum foil (Sigma–Aldrich, St. Louis, Missouri, USA, ≥ 99.9 %), bromine (Sigma–Aldrich, St. Louis, Missouri, USA, ≥ 99.5 %), iodine (Merck KGaA, Darmstadt, Germany, sublimed) and $Mo(CO)_6$ (Sigma–Aldrich, St. Louis, Missouri, USA, ≥ 99.9 %) were used as received. Anhydrous pyridine (Sigma–Aldrich, St. Louis, Missouri, USA, 99.8 %) was dried under CaH_2 and distilled prior to use. $MoBr_3$ was prepared by a modified procedure[13] from bromine vapor and molybdenum foil at 600 K in a quartz ampoule with the attached reservoir holding liquid bromine at room temperature. The synthesis of *mer*-[$MoBr_3Py_3$][1] was carried out at room temperature by the reaction of pyridine and $MoBr_3$. $MoBr_3$ (28 mg) was placed into a glass flask containing pyridine (5 mL) and was kept at room temperature. After disappearance of traces of $MoBr_3$ (three weeks) the pyridine was pumped out on a vacuum line and the product *mer*-[$MoBr_3Py_3$] was collected as orange-yellow needle crystals. Yield: 96 %. $MoI_3C_{15}H_{15}N_3$: C 31.44; H 2.64; N 7.33 ; found C 31.00; H 2.65; N 7.20 %. MoI_3 was prepared from $Mo(CO)_6$ and iodine and *mer*-[MoI_3Py_3] was prepared from MoI_3 and pyridine according to published procedures.[14]

Raman Spectroscopy: Raman spectra of crystalline samples were measured with a Horiba Jobin Yvon LabRAM HR spectrometer using the 632.81 nm excitation line of a He-Ne laser at 1.7 mW power. Scattered light was collected by an Olympus x50 long distance objective in backscattering configuration and spectra recorded were an average of 100 scans with an integration time of 5 seconds. The spectrometer zero-order grating position and the position of the polycrystalline silicon 520.6 cm^{-1} band were checked prior to and after each measurement to maintain the wavenumber accuracy of 0.5 cm^{-1}. Raman spectra were also measured on the same single crystals on which X-ray diffraction data were obtained.

Infrared Spectroscopy: IR spectra were measured with a Perkin–Elmer GX FTIR spectrometer in the range from 600–4000 cm^{-1} as Nujol mulls between NaCl windows and as KBr pellets with 1 cm^{-1} resolution. Continuous flow of nitrogen was kept through the sample chamber for 20 minutes prior to measurement in order to remove airborne carbon dioxide and water vapor.

Chemical Analyses: Analyses for C, H and N were performed with an Elementar Vario EL cube elemental analyzer.

Crystal Structure Analysis: Crystal data on orange-yellow needles, *mer*-$MoBr_3Py_3$ were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromatized Mo-K_α radiation. Data were treated using the Rigaku CrystalClear software suite package.[15] The structure was solved by direct methods using the SIR-92[16] program (teXan crystallographic software package of Molecular Structure Corporation[17]) and refined on F^2 with SHELXL-97[18] software implemented in the program package WinGX.[19] Hydrogen atoms were included on idealized positions and refined with geometrical restrictions. The figures were prepared using DIAMOND 3.1 software.[20] Details of the data collection and structure elucidation are listed in Table 1 and Table 2. Crystallographic data for the structure of *mer*-$MoBr_3Py_3$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data may be obtained on quoting

Table 2. Atomic coordinates and isotropic displacement parameters /$\times 10^{-2}$ for *mer*-[$MoBr_3Py_3$].

Atom	*x*	*y*	*Z*	*U*
Mo1	0.0074(1)	0.08748(7)	0.25774(6)	
Br1	–0.1302(1)	–0.01560(9)	0.14245(7)	
Br2	–0.0568(1)	0.25817(9)	0.18170(7)	
Br3	0.0785(1)	–0.07753(9)	0.34007(7)	
N1	0.1230(8)	0.1820(6)	0.3543(5)	
N2	0.2097(9)	0.0789(7)	0.1855(5)	
N3	–0.1923(9)	0.1003(7)	0.3339(5)	
C1	0.104(1)	0.1639(9)	0.4383(6)	
H1	0.04320	0.10990	0.45450	0.0580
C2	0.170(1)	0.223(1)	0.5009(7)	
H2	0.15370	0.21020	0.55830	0.0670
C3	0.262(1)	0.3003(9)	0.4748(7)	
H3	0.30830	0.34110	0.51550	0.0630
C4	0.286(1)	0.3190(9)	0.3892(7)	
H4	0.34930	0.37070	0.37140	0.0640
C5	0.213(1)	0.2578(9)	0.3324(7)	
H5	0.22730	0.26980	0.27470	0.0620
C6	0.334(1)	0.049(1)	0.2214(7)	
H6	0.33350	0.02880	0.27820	0.0710
C7	0.462(1)	0.047(1)	0.1797(7)	
H7	0.54550	0.02760	0.20870	0.0690
C8	0.469(1)	0.072(1)	0.0952(8)	
H8	0.55570	0.07000	0.06580	0.0770
C9	0.342(1)	0.102(1)	0.0561(8)	
H9	0.34070	0.11890	–0.00140	0.0760
C10	0.217(1)	0.105(1)	0.1022(7)	
H10	0.13250	0.12620	0.07480	0.0680
C11	–0.273(1)	0.0161(9)	0.3517(6)	
H11	–0.24040	–0.04810	0.33280	0.0590
C12	–0.401(1)	0.0196(9)	0.3963(8)	
H12	–0.45320	–0.04040	0.40780	0.0660
C13	–0.450(1)	0.1153(9)	0.4234(8)	
H13	–0.53670	0.12080	0.45230	0.0690
C14	–0.367(1)	0.204(1)	0.4070(7)	
H14	–0.39620	0.26850	0.42630	0.0740
C15	–0.242(1)	0.1920(9)	0.3618(7)	
H15	–0.18740	0.25090	0.34970	0.0610

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Supporting Information (see footnote on the first page of this article)**:** Tables containing band frequencies and tentative assignments.

Acknowledgments

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References

[1] A. Rosenheim, G. Abel, R. Lewy, *Z. Anorg. Allg. Chem.* **1931**, *197*, 189–211.
[2] J. V. Brenčič, *Z. Anorg. Allg. Chem.* **1974**, *403*, 218–224.
[3] J. V. Brenčič, L. Golič, I. Leban, R. Rotar, *Z. Anorg. Allg. Chem.* **1996**, *622*, 2124–2128.
[4] A. K. Mohammed, R. A. Isovitsch, A. W. Maverick, *Inorg. Chem.* **1998**, *37*, 2779–2785.
[5] E. König, H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)* **1960**, *26*, 371–404.
[6] J. V. Brenčič, A. N. Chernega, R. Rotar, *Acta Chim. Slov.* **1999**, *46*, 155–160.
[7] J. San Filippo Jr., M. A. S. King, *Inorg. Chem.* **1976**, *15*, 1228–1232.
[8] P. Ovesana, G. Furlani, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mater. Nat. Rend.* **1966**, *41*, 324–331.
[9] A. D. Westland, N. Muriithi, *Inorg. Chem.* **1972**, *11*, 2971–2975.
[10] D. M. Adams, *Metal-Ligand and Related Vibrations*, St. Martin's Press, New York, N. Y. **1967**, pp 71.
[11] R. J. H. Clark, C. S. Williams, *Inorg. Chem.* **1965**, *4*, 350–357.
[12] N. S. Gill, R. H. Nuttall, D. E. Scaife, D. W. A. Sharp, *J. Inorg. Nucl. Chem.* **1961**, *18*, 79–87.
[13] A. Rosenheim, G. Abel, R. Lewy, *Z. Anorg. Allg. Chem.* **1931**, *197*, 189–211.
[14] C. Djordjević, R. S. Nyholm, C. S. Pande, M. H. B. Stiddart, *J. Chem. Soc. A* **1966**, *26*, 16–17.
[15] *CrystalClear*, An integrated program for the Collection and Processing of Area Detector Data, Rigaku Corporation, **1997–2002**.
[16] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
[17] *TeXan for Windows*, version 1.06: Crystal Structure Analysis, Package, Molecular Structure Corporation, (**1997–9**).
[18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[19] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[20] *DIAMOND v3.1*, **2004–2005** Crystal Impact GbR, Bonn, Germany.

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