Short Communication

# Preparation and Crystal Structure of Tetrakis-(μ-1,8-naphthyridine)dimolybdenum(II) Tetrafluoroborate

Anders Døssing,[a],* Sine Larsen,[b] Alexander van Lelieveld[a] and Rikke Mattsson Bruun[b]

[a]Department of Inorganic Chemistry and [b]Centre for Crystallographic Studies, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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Numerous molybdenum(II) complexes containing a $[Mo_2]^{4+}$ core have been prepared over recent decades.[1] The vast majority of these complexes contain negatively charged ligands giving uncharged or negatively charged complexes. Homoleptic complexes containing uncharged ligands are scarce and so far complexes of *N,N*-dimethylformamide,[2] ammonia,[2] 1,2-diaminoethane,[3] 1,2-diaminopropane[4] and acetonitrile[5] have been isolated in the solid state. Only the acetonitrile complex has been structurally characterized.[5] This prompted us to a search for suitable uncharged ligands with the aim of preparing cationic dimolybdenum(II) complexes. The bidentate nitrogen donor 1,8-naphthyridine (abbreviated hereafter as napy), with a distance between the two nitrogen atoms[6] of 2.307 Å, proved useful in this regard. With this background we report here the synthesis, crystal structure and spectral properties of the dimolybdenum(II) complex $[Mo_2(napy)_4(NCCH_3)_2](BF_4)_4 \cdot CH_3CN$.
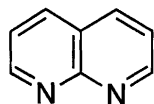
1,8-naphthyridine,
napy

Experimental

Materials. All manipulations were carried out under nitrogen by the use of standard Schlenk techniques. All

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* To whom correspondence should be addressed.

solvents used were HPLC grade, and the acetonitrile (MeCN) was distilled under nitrogen from CaH_2 prior to use. The compounds $[Mo_2(NCCH_3)_8](BF_4)_4$[7] and napy[8] were prepared according to previously described methods.

$[Mo_2(napy)_4(NCCH_3)_2](BF_4)_4 \cdot CH_3CN$ (1). $[Mo_2(NCCH_3)_8](BF_4)_4$ (0.370 g, 0.427 mmol) was dissolved in MeCN (10 ml). Then a solution of napy (0.250 g, 1.92 mmol) in MeCN (4 ml) was added to the blue $[Mo_2(NCCH_3)_8](BF_4)_4$ solution. The mixture turned brown–yellow and was stirred for 30 min. Diethyl ether (16 ml) was then added dropwise in order to precipitate 1. The resulting green precipitate was filtered off, washed twice with diethyl ether and dried under a current of nitrogen, yielding 0.40 g (79%) of crude 1. For recrystallization 0.40 g of the crude product was dissolved in MeCN (10 ml). The solution was filtered and 1 was reprecipitated by addition of diethyl ether (6 ml). Yield: 0.30 g of pure 1. Calc. for $C_{38}H_{33}B_4F_{16}Mo_2N_{11}$: C, 38.59; H, 2.81; N, 13.03. Found: C, 38.52; H, 2.86; N, 13.03. UV–Vis (in CH_3CN): λ_{max}/nm ($\varepsilon/M^{-1} cm^{-1}$): 699(717), 454(406), 286(48.4 × 10³). IR (KBr, v/cm^{-1}) 2253 (C≡N). ¹H NMR (CD_3CN) δ 8.15, 9.00, 9.35.

X-Ray crystallography. Crystals of 1 suitable for the single-crystal X-ray diffraction study were grown in a test tube (70 × 8 mm). The tube was sealed with a rubber septum and all manipulations were carried out with syringes under nitrogen. About 20 mg of the crude crystalline product of 1 obtained as described above were dissolved in 0.5 ml of MeCN, allowing 0.5 ml of diethyl ether to diffuse into the MeCN solution through a 0.25 ml hexane layer. Crystals of 1 appeared as green

plates after 1–2 days. They were very air-sensitive and had to be coated with mineral oil in the short period they were exposed to air. Several crystals were examined before one was found that could be used for the data collection performed with a CAD-4 diffractometer. The crystal was relatively small (0.25 × 0.13 × 0.08 mm) and showed very weak diffraction. It was therefore decided to use Cu Kα radiation for the data collection to obtain measurable intensities of the reflections despite the high linear absorption coefficient. The crystal was cooled to 122.4(5) K by an Oxford Cryostream low-temperature device. The ω–2θ scan mode was employed, and reflections were measured to $\theta_{max} = 75°$. The intensities of four standard reflections were recorded every 10^4 s, and the orientation of the crystal checked after every 600 reflections. The data set comprised 12 221 reflections. Data reduction was performed with the DREADD[9] program system and included corrections for background, Lorentz, polarization and absorption effects. The Gaussian integration procedure was used for the latter correction, with transmission factors in the range 0.422–0.707. Analysis of the intensities of the standard reflections revealed an overall decrease of up to 5% with exposure time; the data were also corrected for this variation. Analysis of the diffraction data showed that it possesses the Laue symmetry $2/m$ and that the systematically absent reflections are consistent with the space group $P2_1/n$, a non-standard setting of $P2_1/c$. Symmetry related reflections were averaged ($R_{int} = 0.052$) to give 5952 reflections used in the structure determination and refinement. SHELXL-97[10] program package was used for the structure determination and refinement, minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The weights were chosen to give an even and smooth distribution of $\langle w(\Delta F^2)^2 \rangle$ with $|F^2|$ and $\sin \theta/\lambda$. The atomic scattering[11] factors were used as contained in the program. During the refinement it became apparent that the structure is slightly disordered, indicated by the large displacement parameters for one of the tetrafluoroborate groups and by residual electron density close to one of the crystallographic inversion centers. These peaks were subsequently interpreted as being due to a partly populated MeCN molecule in addition to the ordered one also present in the crystal. Refinements were also attempted in the space group Pn to examine if this would eliminate the disorder, but this did not lead to an improvement of the model. The hydrogen atoms in the structure were introduced in idealized positions and given isotropic displacement parameters that are 1.2 times the equivalent isotropic parameter for the parent atom except for the methyl groups, where the displacement parameter is multiplied by 1.5. The final model included anisotropic displacement parameters for all fully populated non-hydrogen atoms. As the disordered MeCN (non-coordinated) in the structure is found at an inversion center, it must correspond to two different centrosymmetrically related orientations of the molecule, with the positions of the nitrogen atom and the methyl carbon atom superimposed and the

central carbon atom almost at the inversion centre. Carbon atoms were used for both atoms; the site occupancy factor of the terminal atom was scaled relative to the central atom to account for the superposition of the carbon and the nitrogen atoms. The numerically high peaks and holes in the final difference electron density were found close to Mo; they reflect the low accuracy of the diffraction data. A summary of the crystallographic data is given in Table 1 and the final positional and equivalent isotropic thermal parameters are listed in Table 2.

Other physical measurements. Elemental analyses of C, H and N were made at the H. C. Ørsted Institute, University of Copenhagen. Infrared spectra were measured on a Perkin–Elmer 1600 FTIR instrument and ^{1}H NMR spectra on a Varian 400 MHz instrument. Optical absorption spectra were recorded on a Cary 5E UV–Vis–NIR spectrophotometer.

Results and discussion

Acetonitrile complexes of the transition metals are widely used as synthetic precursors, and the title compound 1 was conveniently prepared by the following reaction:

$[Mo_2(NCCH_3)_8](BF_4)_4 + 4napy$

$\rightarrow [Mo_2(napy)_4(NCCH_3)_2](BF_4)_4 \cdot CH_3CN + 5CH_3CN$
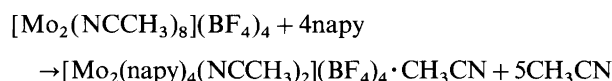
An ORTEP plot of the cation in 1 is shown in Fig. 1, and selected bond lengths and angles are compiled in Table 3.

The dimolybdenum cation is found at a crystallographic inversion center as illustrated in the ORTEP drawing in Fig. 1. The $[Mo_2]^{4+}$ unit is bridged by four centrosymmetrically related napy molecules and with the two MeCN molecules in axial positions. Each molybdenum atom is surrounded by six ligands in a distorted octahedral geometry with the other molybdenum atom *trans* to the MeCN molecule. The Mo–Mo bond length

Table 1. Summary of crystallographic data for 1.

Chemical formula	$C_{42}H_{39}B_4F_{16}Mo_2N_{13}$
FW/g mol^{-1}	1264.98
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.6494(16)
b/Å	11.852(2)
c/Å	18.574(2)
b/°	102.551(11)
V/Å^3	2503.2(6)
Z	2
T/K	122.4(5)
Density (calc)/Mg m^{-3}	1.678
Wavelength/Å	1.541 84
Abs. coeff./mm^{-1}	5.064
R-indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0774$, $wR_2 = 0.1927$
R-indices (all data)^a	$R_1 = 0.0882$, $wR_2 = 0.1996$

$^a R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 2. Fractional atomic coordinates and equivalent iso-
tropic thermal parameters (in $Å^2$) in **1**.

Atom	x	y	z	U_{eq}[a]
Mo	0.50665(3)	0.02055(4)	0.94597(2)	0.02040(18)
N1	0.5656(4)	−0.1522(4)	0.9269(2)	0.0231(9)
N2	0.3178(4)	−0.0116(4)	0.9029(3)	0.0232(9)
N3	0.5393(4)	−0.1970(4)	1.0434(3)	0.0241(9)
N4	0.3079(4)	−0.0665(4)	1.0205(3)	0.0265(10)
C11	0.6018(5)	−0.1815(5)	0.8659(3)	0.0291(12)
C12	0.5711(4)	−0.2329(5)	0.9807(3)	0.0229(10)
C13	0.6430(5)	−0.2899(5)	0.8545(3)	0.0320(13)
C14	0.6105(5)	−0.3430(5)	0.9725(3)	0.0280(12)
C15	0.6460(5)	−0.3708(5)	0.9063(3)	0.0312(12)
C21	0.2631(5)	0.0090(5)	0.8333(3)	0.0269(11)
C22	0.2500(4)	−0.0517(5)	0.9497(3)	0.0214(10)
C23	0.1408(5)	−0.0047(5)	0.8065(3)	0.0297(12)
C24	0.1284(5)	−0.0719(5)	0.9257(3)	0.0277(12)
C25	0.0739(5)	−0.0467(5)	0.8523(4)	0.0327(13)
C31	0.5436(5)	−0.2719(5)	1.0979(3)	0.0290(12)
C33	0.5799(6)	−0.3838(5)	1.0930(4)	0.0384(14)
C35	0.6136(6)	−0.4193(5)	1.0309(4)	0.0362(14)
C41	0.2482(5)	−0.1103(6)	1.0682(4)	0.0348(14)
C43	0.1277(5)	−0.1358(6)	1.0475(4)	0.0415(16)
C45	0.0686(5)	−0.1160(6)	0.9781(4)	0.0374(14)
N5	0.4792(4)	0.9370(5)	0.1954(3)	0.0336(11)
C51	0.4710(5)	0.8995(5)	0.2517(4)	0.0316(12)
C52	0.4610(6)	0.8536(6)	0.3223(4)	0.0425(15)
B1	0.2747(6)	0.6281(7)	0.2120(5)	0.0395(17)
F11	0.1975(5)	0.5601(6)	0.1656(5)	0.106(3)
F12	0.2314(5)	0.7379(4)	0.2039(3)	0.0634(13)
F13	0.2885(5)	0.5970(5)	0.2850(3)	0.0743(17)
F14	0.3832(4)	0.6258(5)	0.1932(3)	0.0670(14)
B2	0.7257(7)	0.3295(7)	0.1560(6)	0.050(2)
F21	0.7741(4)	0.4361(4)	0.1648(2)	0.0485(10)
F22	0.7187(6)	0.2902(5)	0.0852(4)	0.089(2)
F23	0.7914(5)	0.2596(4)	0.2067(4)	0.0827(19)
F24	0.6123(4)	0.3383(6)	0.1671(4)	0.090(2)
N6	0.8412(5)	0.7947(5)	0.0496(4)	0.0439(14)
C61	0.8695(5)	0.7453(6)	0.1029(4)	0.0391(15)
C62	0.9071(7)	0.6801(8)	0.1699(5)	0.062(2)
C300	0.0000(8)	0.4999(15)	0.0000(7)	0.048(6)
C400	−0.1021(8)	0.4955(15)	0.0070(8)	0.026(4)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i \cdot a_j$.

Fig. 1. ORTEP II drawing of the cation in **1**. The thermal
ellipsoids are scaled to include 50% probability. The hydro-
gen atoms are omitted for clarity.

Table 3. Selected interatomic distances (in Å) and angles
(in °) for complex **1**.[a]

Mo–N1	2.212(5)	Mo–N5	2.714(5)
Mo–N2	2.204(5)	N5–C51	1.159(8)
Mo–N3'	2.178(5)	C51–C52	1.447(9)
Mo–N4'	2.183(4)	Mo–Mo'	2.1037(8)
Mo'–Mo–N1	91.60(12)	N1–Mo–N4'	87.38(18)
Mo'–Mo–N2	91.79(13)	N2–Mo–N3'	87.30(17)
Mo'–Mo–N3'	93.74(13)	N2–Mo–N4'	173.84(17)
Mo'–Mo–N4'	93.36(12)	N3'–Mo–N4'	88.99(18)
Mo'–Mo–N5	177.19(12)	Mo–N5–C51	168.1(5)
N1–Mo–N2	95.86(17)	N5–C51–C52	179.5(8)
N1–Mo–N3'	173.72(16)		

[a] Primed atoms are generated by the symmetry operation
$(1-x, -y, 2-z)$.

is 2.1037(8) Å and the average Mo–N(napy) distance is
2.193(2) Å, which is significantly longer than in related
molybdenum complexes with anionic nitrogen atoms.
The two napy ligands display the same geometrical
features, which compare well to the results from six
structure determinations[12-16] extracted from the
Cambridge Structural Database (version 5.15)[17] where
napy serves as the bridging ligand between two identical
metal ions. The distance between the two ligating nitro-
gen atoms in these structures is in the range
2.308–2.366 Å, with a mean value of 2.339 Å. The
N1–N3 and N2–N4 distances are in the lower end of
this range [2.311(6) and 2.304(6) Å, respectively], but
are significantly longer than the Mo–Mo distance.
Comparing napy in these structures to the free molecule[6]
reveals some changes to the bond lengths with coordina-
tion. Most significant is the elongation of the bonds from
the nitrogen atoms to the external carbon atoms; in the
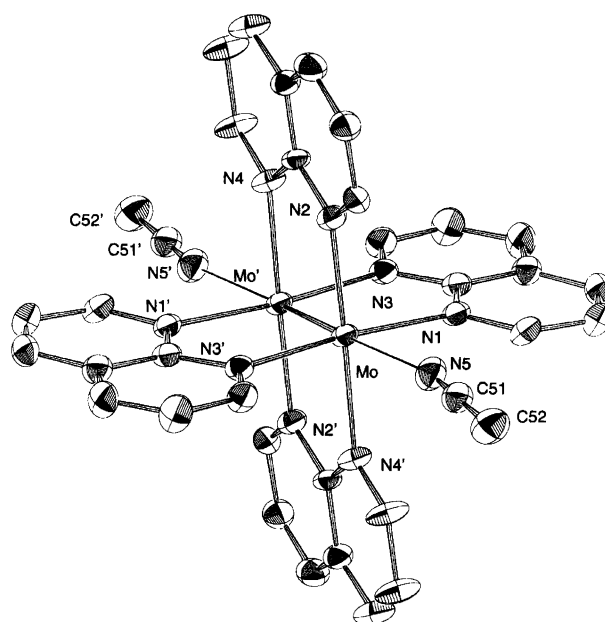present structure the average value is 1.3395 Å, compared

to 1.315 Å found in free napy. Both napy ligands display
a very small twist of the ring system around the bond
common for the two six-membered rings. The interplanar
angle between the two pyridine moieties is 2.4(3) and
2.0(3)° in the two napy ligands in the present structure.
The N1–Mo–Mo'–N3 and N2–Mo–Mo'–N4 dihedral
angles are −3.3(2)° and 3.4(2)°, respectively which
illustrates that the molybdenum atoms are displaced
slightly from the mean planes defined by the napy ligands.

From the overall symmetry of the dinuclear cation one
would have expected the two napy planes to be ortho-
gonal; however, the interplanar angle between the two
mean planes for the napy ligands is 82.0(1)°, showing
that the conformation of the cation in the crystal deviates
markedly from the idealized geometry. A similar discrep-
ancy is found for the MeCN molecule that acts as the
sixth ligand to Mo. The Mo–N(acetonitrile) distance is

so long, 2.714(5) Å, that it must correspond to a very weak Mo–ligand interaction. The Mo–N5–C51 angle is 168.1(5)°, which shows that the MeCN molecule is interacting differently with the two napy ligands. Looking for explanations for these gross deviations from the expected D_{4h} symmetry, the structure was examined for interactions to N5. The distances between N5 and the four ortho-hydrogen atoms from the surrounding napy molecules are in the range 2.43–2.50 Å. The shortest and longest distances are to the hydrogen atoms attached to C11 and C31', which are in the same equatorial plane, whereas the corresponding distances in the other independent plane are almost identical, 2.48 Å. The crystal packing is dominated by C–H–F hydrogen bond interactions, with corresponding C–F distances between 3.2 and 3.35 Å. From the napy ligands only the protons attached to C33, C35, C43 and C45 do not take part in these hydrogen bonds. The origin of this may lie in the irregular geometry of the dinuclear cation in these intermolecular interactions.

The ^{1}H NMR spectrum of **1** in acetonitrile-d_3 displays only three resonances of equal area in the aromatic region. The four napy ligands in **1** in solution are (on the NMR timescale) thus equivalent, in contrast to the four napy ligands in **1** in the solid state. Resonances originating from uncoordinated napy were absent. The optical absorption spectrum of **1** in MeCN solution is shown in Fig. 2. When napy was added to a blue MeCN solution of $[Mo_2(NCCH_3)_8](BF_4)_4$ the spectrum changed until four equivalents of napy were added, and addition of further equivalents of napy did not lead to spectral changes. The resulting spectrum was identical to that of a solution of **1** (Fig. 2). This shows that the $[Mo_2(napy)_4]^{4+}$ cation remains intact in MeCN solution, and that no substitution of coordinated napy molecules

with solvent molecules occurs. The lowest-energy transition in dimolybdenum(II) complexes ($\lambda = 699$ nm in the present case) has conclusively been assigned as a $\delta \rightarrow \delta^*$ transition.[1] The factors that govern the transition energy are the Mo–Mo bond length,[18,19] the internal twist angle around the Mo–Mo axis[20,21] and the π donor/acceptor properties of the ligand.[22] The transition energy $(14.3 \times 10^3\ cm^{-1})$ is remarkably lower than in the recently[23] synthesized and structurally characterized complex $[Mo_2(hpp)_4]$, where hpp$^-$ represents the deprotonated form of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine. The amidinato ligand, hpp$^-$, structurally

hpp⁻
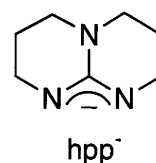
resembles the napy ligand, and the Mo–Mo bond length in $[Mo_2(hpp)_4]$ was found to be 2.067(1) Å. The energy of the $\delta \rightarrow \delta^*$ transition in the $[Mo_2(hpp)_4]$ complex was found to be $21.7 \times 10^3\ cm^{-1}$. This significantly higher transition energy can hardly be explained by the small difference in the Mo–Mo bond length alone, and a more likely explanation may have its background in a difference in the π donor/acceptor properties of the napy and hpp$^-$ ligands. The nature of the transitions with energies higher than the $\delta \rightarrow \delta^*$ transition is not yet fully understood, and the assignment of the second transition in **1** at 454 nm therefore requires further study.
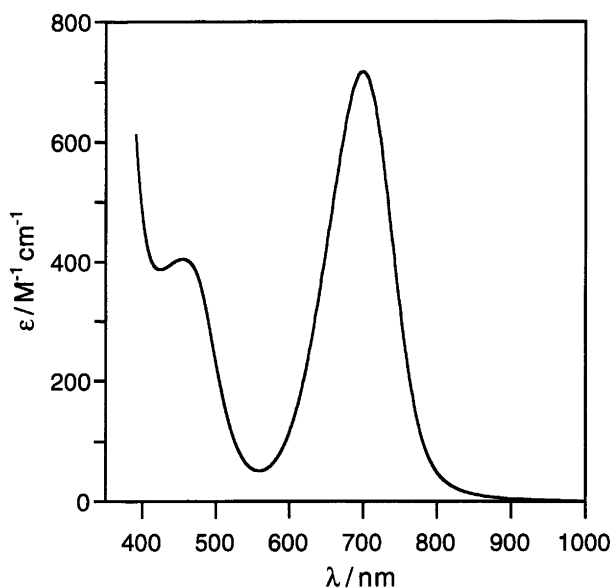
Fig. 2. Optical absorption spectrum of **1** in acetonitrile at room temperature.

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