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Electronic Supplementary Information (ESI):

New Mo(IV) complex with the pentadentate (N₃O₂) Schiff-base ligand: The first non-cyanide pentagonal-bipyramidal paramagnetic 4d complex

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Supporting Information

CONTENT:

1. Physical measurements	S2
2. Materials and methods	S2
3. Syntheses and characterization	S2
4. X-ray crystallography	S5
5. Theoretical calculations	S9
6. References	S14

1. PHYSICAL MEASUREMENTS

The infrared spectra were measured on solid samples using a Perkin Elmer Spectrum 100 Fourier Transform infrared spectrometer in the range of 4000–500 cm⁻¹. UV-Vis spectra were recorded using a HP 8451A DIODE ARRAY Spectrophotometer. Elemental analyses were carried out by the Analytical Department service at the Institute of Problems of Chemical Physics RAS using a Vario Micro cube (Elementar GmbH) equipment. Mass-spectra were recorded on a Shimadzu LCMS-2020 Single Quadrupole spectrometer with a scan range of m/z 10–2000 in the negative electrospray ionization mode (interface capillary voltage was of -3.0 kV and interface temperature of 350 °C). Simulations of the isotopic patterns were performed using *mMass 5.5* program. [1] The DC magnetic susceptibility of powder sample 1 was measured by a Quantum Design MPMS-5 SQUID magnetometer. The experimental data were corrected for the sample holder and for the diamagnetic contribution calculated from Pascal constants.

2. MATERIALS AND METHODS

All procedures described below were carried out under argon atmosphere using standard Schlenk-tube and vacuum line techniques. Unless otherwise stated, all reagents ((NH₄)₆Mo₇O₂₄·4H₂O, NH₄Cl, Sn (shots), 2,6-diacetylpyridine, benzoylhydrazide, Et₃N) were purchased from Aldrich and used without further purification. Methanol was dried upon refluxing with magnesium methoxide followed by distillation. Chloroform and dichloromethane were purified by distillation from CaH₂. All solvents were preliminary deoxygenated and stored under argon atmosphere over molecular sieves 3 Å.

3. SYNTHESES AND CHARACHTERIZATION

TheSchiff-baseligand(1,1'-(pyridine-2,6-diyl)bis(ethan-1-yl-1-ylidene))dibenzohydrazineylidene))dibenzohydrazine(H2DAPBH)wasobtainedfromthecondensationof2,6-diacetylpyridineand two equivalent of benzoylhydrazideaccording to literature procedure (Fig.S1). [2]



Fig. S1 Synthetic route to the H₂DAPBH ligand

 $(NH_4)_2[MoCl_5(H_2O)]$ was prepared as a stable brick-red crystalline solid according to published method. [3] Anal. Calc. for $Cl_5H_{10}MoN_2O$ (327.32): Cl, 54.16; H, 3.06; N, 8.56. Found: Cl: 52.6; H, 3.06; N, 8.43.

Preparation of [Mo^{IV}(DAPBH)Cl₂]

To a sample of $(NH_4)_2[MoCl_5(H_2O)]$ (0,2 g, 0,61 mmol) and H₂DAPBH (0,243 g, 0,61 mmol) placed in a round-bottomed Schlenk flask, equipped with stirring bar, methanol (23 mL) and Et₃N (0,17 mL, 1,22 mmol) were added. White-rose suspension obtained was stirred at room temperature for 1 h. The mixture gradually became deep green and complete dissolution of solids was observed. The reaction solution was stirred at r.t. for additional 1 hour to complete the reaction and then was filtered. The filtrate was left standing undisturbed at r. t. Large black crystals of 1 suitable for X-ray diffraction precipitated in a course of 3 days. Supernatant was then transferred to a Schlenk flask to collect the second crop of product 1 precipitated in 1 week. Two crops were combined, washed with cold methanol (3 ml) and dried *in vacuo* affording 0.12 g of product 1 of analytical purity. Yield 35%. Anal. Calculated for C₂₃H₂₁O₂N₅Cl₂ (%) C, 48.94; H, 3.72; N, 12.41; Cl, 12.59. Found (%) C, 48.52; H, 3.81; N, 12.21; Cl, 13.05. FT-IR (solid sample) v, cm⁻¹:693 s, 703vs, 710s, 713w, 799m, 1053 m, 1179 m, 1376vs, 1414 m, 1512m. ESI(-)-MS (CH₂Cl₂-CH₃OH, v/v= 1:1)): *m/z* 564.9 ([M]⁻), 100%; 595.9 ([M +CH₃O]⁻), 37%; 1126.0 ([2M+2H-Cl+CH₃O]⁻), 10%; 1157.0 ([2M+2H-Cl+2CH₃O]⁻), 7%.

The complex **1** is soluble in organic solvents such as chloroform and methylene chloride. When complex **1** was dissolved in chloroform, the red solution was formed and dark red crystals of **1A** suitable for X-ray diffraction precipitated from this solution in a course of a few days.



Fig. S2 A comparison of IR spectra of complex 1 and the free ligand DAPBH₂ in two ranges: <u>Left</u> - 1500–2000 cm⁻¹, <u>right</u> 2800–3800 cm⁻¹



Fig. S3 ESI(-)-MS spectrum of the complex 1 in CH_2Cl_2 - CH_3OH mixture. Inset: Experimental (top) and simulated (bottom; FWHM=0.6) isotopic patterns of the parent ion [M]⁻

Comments on the ESI-MS spectrum: the most intensive signal at m/z=564.9 corresponds to the molecular ion of the title compound. The simulated isotopic pattern of the parent ion excellently

matches the experimental one. The group of signals located at m/z=1120-1160 looks a bit puzzling at first sight. However, given that the dimerization of the DAPBH complexes in solution is not unprecedented (see for example [4]), we assigned these signals to the dimeric ions.

4. X-RAY CRYSTALLOGRAPHY

X-ray Structure Determination. X-ray diffraction data were collected on a APEX II DUO CCD diffractometer using molybdenum radiation [λ (MoK α) = 0.71072 Å, ω -scans] for 1 and 1A. The substantial redundancy in data allowed empirical absorption correction to be applied with SADABS by multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. C-H hydrogen atoms in all structures were placed in calculated positions and refined within the riding model. All calculations were performed with the SHELXTL software package [5]. Crystal data and structure refinement parameters are listed in Table S1. Crystallographic data for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary no.: CCDC-1558502 (for 1), CCDC-1558504 (for 1A). These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif.

Sample	<u>1</u>	<u>1A</u>
Brutto formula	$C_{23}H_{19}Cl_2MoN_5O_2$	$C_{23}H_{19}Cl_2MoN_5O_{2,}CHCl_3$
Formula weight	564.27	683.64
Т, К	120	120
Space group	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁
Z(Z')	4(1)	4(1)
a/Å	8.5326(8)	13.494(3)
b/Å	14.1129(14)	13.523(3)
c/Å	19.7994(19)	14.425(3)

Table S1. Crystal data and structure refinement parameters for 1 and 1A

β/	19.7994(19)	90
Volume/Å ³	2352.4(4)	2632.3(10)
$\rho_{calc}g/cm^3$	1.593	1.725
µ/cm ⁻¹	8.15	10.40
F(000)	1136	1368
2θ _{max} , °	58	58
Reflections collected (Rint)	28034 (0.0403)	31883 (0.0421)
Independent reflections	6260	6999
Reflections with I>2o(I)	4999	6271
R ₁ [I>2σ (I)]	0.0398	0.0386
wR ₂	0.0963	0.1068
GOF	1.063	1.044
Residual electron density, e·Å⁻³	-0.569/1.283	-0.735/1.461
(ρ _{min} /ρ _{max})		

 Table S2. Selected bond lengths (Å) and angles in 1 and 1A (°)

	1	1A
Mo1 01	2.0455(18)	2.048(3) .
Mo1 O2	2.042(2)	2.027(3) .
Mo1 N1	2.150(2)	2.125(4) .
Mo1 N2	2.142(2)	2.142(4) .
Mo1 N4	2.148(2)	2.135(4) .
Mo1 Cl1	2.3896(7)	2.3936(13)
Mo1 Cl2	2.3911(7)	2.3759(13)
O2 Mo1 O1	75.37(7)	74.61(13)
O2 Mo1 N2	71.68(9)	71.28(14)
O1 Mo1 N2	147.02(9)	145.87(15)
O2 Mo1 N1	142.56(9)	142.61(14)
O1 Mo1 N1	142.07(9)	142.73(13)
N2 Mo1 N1	70.88(10)	71.40(16)
O2 Mo1 N4	146.55(8)	146.10(14)

O1 Mo1 N4	71.19(8)	71.52(14)
N2 Mo1 N4	141.74(10)	142.51(15)
N1 Mo1 N4	70.88(9).	71.30(15)
O2 Mo1 Cl1	89.57(6)	91.40(11)
O1 Mo1 Cl1	90.99(6)	90.81(11)
N2 Mo1 Cl1	87.57(7)	88.03(11)
N1 Mo1 Cl1	88.96(6)	90.17(12)
N4 Mo1 Cl1	90.64(7)	88.48(11)
O2 Mo1 Cl2	90.96(6)	90.69(11)
O1 Mo1 Cl2	92.20(6)	93.54(11)
N2 Mo1 Cl2	89.59(6)	92.43(11)
N1 Mo1 Cl2	88.69(6)	85.79(12)
N4 Mo1 Cl2	90.67(7)	88.45(11)
Cl1 Mo1 Cl2	176.79(3)	175.55(4)



Fig S4. The general view of 1A in representation of atoms by thermal ellipsoids (p=50%).



Fig.S5 The scheme illustrating the difference of planarity of equatorial plane in 1 and 1A.



Fig. S6 Crystal packing diagram of 1 (view along *a* axis).

5. THEORETICAL CALCULATIONS



Fig. S7. Molecular structure of Mo^{IV}(DAPBH)Cl₂ complex obtained from DFT geometry optimization calculations. The deprotonated DAPBH ligand is perfectly planar and symmetric.



Fig. S8. Non-planar structure of (hypothetical) [Mo^{III}(HDAPBH)Cl₂] complex with monoprotonated (HDAPBH)⁻¹ ligand obtained from DFT geometry optimization calculations.

5.1. Ligand-field (LF) and angular-overlap model (AOM) calculations and simulation of magnetic susceptibility

Ligand-field (LF) calculations for the [Mo^{IV}(DAPBH)Cl₂] complex are performed in terms of a conventional model Hamiltonian

$$H = \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \zeta_{4d} \sum_i \mathbf{l}_i \mathbf{s}_i + V_{LF} + \mu_B (k\mathbf{L} + 2\mathbf{S})\mathbf{H}, \qquad (S1)$$

in which the first term represents Coulomb repulsion between 4d electron of Mo^{IV} (where i and j runs over 4d electrons), the second term is the spin-orbit coupling (SOC) of Mo^{IV} , V_{LF} is a ligand-field Hamiltonian, and the last term represents the Zeeman interaction with the external magnetic field **H**. In these calculations, the B = 475 and C = 2000 cm⁻¹ Racah parameters for the Coulomb term in (S1), the SOC constant $\zeta_{4d} = 700 \text{ cm}^{-1}$, and the k = 0.7 orbital reduction factor in the Zeeman term. [6] The one-electron operator $V_{\rm LF}$ is calculated in terms of the angular overlap model (AOM). [7] For N and O atoms in the N₃O₂ chelating ring we used the AOM parameters $e_{\sigma} = 13000 \text{ cm}^{-1}$ and $e_{\pi}/e_{\sigma} = 0.25$, which approximately correspond to a typical 10Dq $\approx 26000 \text{ cm}^{-1}$ crystal-field splitting energy of 4*d* metal ions with moderately strong ligands from the spectrochemical series, as can be estimated from the Jorgensen's equation [8]; AOM parameters for the apical Cl atoms are set to e_{σ} = 10000 cm⁻¹ and e_{π}/e_{σ} = 0.25. The radial dependence of the AOM parameters for N and O atoms in the N₃O₂ pentagon was approximated by $e_{\pi,\sigma}(R) = e_{\pi,\sigma}(R_0)(R_0/R)^n$ with n = 3 at the reference distance $R_0 = 2.15$ Å. Energy levels of the $4d^2$ LF states of Mo^{IV} are obtained by a numerical diagonalization of (S1) in the full set of $4d^2$ wave functions involving 45 $|LM_ISM_S\rangle$ microstates. The actual experimental geometry of [Mo^{IV}(DAPBH)Cl₂] complex was applied.

The components M_{α} ($\alpha = x, y, z$) of the magnetic moment M of [Mo^{IV}(DAPBH)Cl₂] in an external magnetic field H are obtained from the conventional equation

$$M_{\alpha} = Nk_{B}T \frac{\partial \ln Z(\boldsymbol{H})}{\partial H_{\alpha}}, \qquad (S2)$$

where Z(H) is the partition function

$$Z(\boldsymbol{H}) = \sum_{i} \exp(-E_{i} (\boldsymbol{H})/k_{B}T), \qquad (S3)$$

with $E_i(H)$ being the energy of the *i*-th electronic state of the Mo^{IV} ion in the magnetic field H obtained from diagonalization of the spin Hamiltonian (S1). Then the diagonal component $\chi_{\alpha\alpha}$ of the tensor of magnetic susceptibility is written as $\chi_{\alpha\alpha} = M_{\alpha}/H_{\alpha}$; magnetic susceptibility of

the powder sample is given by $\chi = (\chi_{xx} + \chi_{yy} + \chi_{zz})/3$. Calculations for 1 are performed at the experimental applied field of H = 1 kOe.

Calculated energies of 4*d* orbitals, $4d^2$ LF states, and spin-orbit $4d^2$ states of [Mo^{IV}(DAPBH)Cl₂] are presented, respectively, in Tables S3, S4, and S5.

Table S3. Calculated LF splitting energies (cm^{-1}) of 4*d* orbitals in complex 1.

4 <i>d</i> orbital	Ε
$4d_{zx}$	0
$4d_{zy}$	52
$4d_{xy}$	19501
4 <i>d</i> _{x2-y2}	22842
$4d_{z2}$	23157

Table S4. Calculated energies (cm^{-1}) of LF states $(4d^2)$ of complex 1.

Energy	^{2S+1} L atomic term composition, %			
0	³ F	84.61	³ Р	15.39
6957	¹ G	53.24	¹ D	46.76
6962	¹ G	53.56	¹ D	46.44
12599	¹ G	54.15	1S	25.04
18684	³ F	97.94	³ Р	2.06
18727	³ F	97.90	³ Р	2.10
21783	³ F	99.96	³ Р	0.04
21812	³ F	99.94	³ Р	0.06
25767	¹ D	81.06	¹ G	18.94
25805	¹ D	81.17	¹ G	18.83
28245	³ Р	97.82	³ F	2.18
28324	³ Р	97.89	³ F	2.11
30273	¹ G	81.25	¹ D	18.75
30314	¹ G	81.70	¹ D	18.30
31324	¹ G	99.65	¹ D	0.35
31391	¹ G	99.61	¹ D	0.39
41039	³ F	99.98	³ Р	0.02
44693	³ F	99.97	³ Р	0.03
47226	³ Р	84.58	³ F	15.42
47816	¹ G	52.10	¹ D	42.49
48903	¹ D	53.24	¹ G	46.76
51052	¹ G	99.95	¹ D	0.05
52554	¹ D	53.50	¹ G	46.50
52880	¹ G	64.66	¹ D	35.11
62762	¹ S	69.31	¹ G	29.10

Table S5. Calculated energies (cm⁻¹) of low-lying $4d^2$ states of complex 1 with spin-orbit coupling switched on. The three lowest energy levels (marked in bold) correspond to the zero-field splitting states of the ground triplet spin state with the ZFS anisotropy parameters $D \approx +50$ cm⁻¹ and $|E| \approx 0.025$ cm⁻¹.

Energy
0
49.84
49.89
6976
6977
12678
18192
18206
18730
18773
19136
19151
21777
21807
21823
21838



Fig. S9. (a) 4*d* orbital energies of $[Mo^{IV}(DAPBH)Cl_2]$ complex. Two electrons with parallel spins occupy the lowest nearly degenerate $4d_{zx}$ and $4d_{yz}$ orbitals to form a triplet (S = 1) ground spin state; (b) Energy spectrum of $4d^2$ LF states $[Mo^{IV}(DAPBH)Cl_2]$ complex. Triplet spin states are marked in bold blue lines. Energy positions of 4*d* orbitals and $4d^2$ states are obtained from LF calculations in terms of the LF Hamiltonian (S1) with parameters listed in the text. The energy positions are given in the actual energy scale.

5.2. Ligand-field and magnetic calculations for the $[W^{V}(CN)_{7}]^{3-}$ complex

LF and magnetic calculations for the PBP $[W^{IV}(CN)_7]^{3-}$ complex [9] are performed following the computational scheme described above in Section 5.1. For tungsten(IV) heptacyanometallate the B = 400 and C = 1800 cm⁻¹ Racah parameters, the SOC constant of $\zeta_{4d} = 1900$ cm⁻¹, and the k = 0.65 orbital reduction factor are employed. The AOM parameters $e_{\sigma} = 20000$ cm⁻¹ and $e_{\pi}/e_{\sigma} = 0.1$ are used for all W-CN metal-ligand pairs in $[W^{IV}(CN)_7]^{3-}$ complex with applying the radial dependence $e_{\pi,\sigma}(R) = e_{\pi,\sigma}(R_0)(R_0/R)^n$ with $R_0 = 2.15$ A and n = 3. The actual distorted PBP geometry of $[W^{IV}(CN)_7]^{3-}$ complex was used. These calculations result in a triplet spin ground state (S = 1), which undergoes a second-order spin-orbit splitting resulting in the ground singlet spin-orbit state and two excited closely spaced ZFS energy levels lying, respectively, at 278.88 and 279.15 cm⁻¹. This corresponds to a nearly uniaxial ZFS anisotropy with $D \approx +279$ cm⁻¹ and $|E| \approx 0.14$ cm⁻¹; the value of the axial D parameter is reasonably close to D = +330 cm⁻¹ reported in ref. [9], while a very small transverse magnetic anisotropy E is in sharp contrast to |E| = 110 cm⁻¹, which has been found for $[W^{IV}(CN)_7]^{3-}$ complex in ref. [9] from the fitting to the magnetic data. Importantly, the calculated $\chi_{mol}T$ versus T curve is nearly perfectly reproduced in terms of the LF Hamiltonian (S1) with the aforelisted set of parameters, Fig. S10.



Fig. S10. $\chi_{mol}T$ versus *T* for the $[W^{IV}(CN)_7]^{3-}$ complex (a moderately distorted pentagonal bipyramid), experimental (open circles) **[9]** and calculated with LF model (solid blue line) in terms of the Hamiltonian (S1) with the set of parameters B = 400, C = 1800 cm⁻¹, $\zeta_{4d} = 1900$ cm⁻¹, and k = 0.65; the $e_{\sigma} = 20000$ cm⁻¹ and $e_{\pi}/e_{\sigma} = 0.1$ AOM parameters are used. The calculated ZFS pattern of the ground S = 1 spin state (0, 278.88, 279.15 cm⁻¹) indicates the absence of the transverse magnetic anisotropy in the $[W^{IV}(CN)_7]^{3-}$ complex, $E \approx 0$.

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