

Two new scorpionate oxomolybdenum(VI)-poly(pyrazolyl)borate complexes: synthesis, structure, and catalytic performance in the oxidation of cyclohexane

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Reagents and instruments. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C automatic analyzer. The infrared (IR) spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrophotometer with pressed KBr pellets from 200 to 4000 cm⁻¹. UV-Vis spectra were determined by JASCO V-570 UV-Vis spectrometer (200–1100 nm, in form of solid sample). TGA were performed under N₂ atmosphere at 1 atm with a heating rate of 10 °C/min on a Perkin Elmer Diamond TG/DTA. X-ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu K α radiation, in the range 5° < 2 θ < 50°, with a step size of 0.02° (2 θ) and an acquisition time of 2 s per step. The products of oxidation reaction were determined and analyzed by Shimadzu GC-16A series gas chromatograph equipped with a FID detector and a capillary column (PG2000, column length: 30 m; internal diameter: 0.25 mm). All the chemicals used were of analytical grade and without further purification. KTp and KTp⁴⁺ were synthesized according to the literature method¹.

X-ray data collection and refinement of crystal structure. The complexes of 1–2 were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD

diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a ω scan mode. All the measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS program².

5 All hydrogen atoms were positioned geometrically and refined using a riding model. The non-hydrogen atoms were refined with anisotropic thermal parameters. The crystallographic data, the experimental details of the data collection and the structure refinement are given. The drawings were made with Diamond program, and all calculations were performed using SHELX-97 program³.

10 Tables of atomic coordinates, an isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of these information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC 891375 for complex **1** and 891376 for **2**, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK
15 (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

References

- 1 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 6288–6294.
- 2 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction for Area Detector Data*, University of Göttingen, Göttingen, Germany, 1996.
- 3 G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

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Table S1 Selected bond lengths (Å) angles (°) for complexes **1** and **2**.

Complex 1					
Mo–O1	1.699(5)	Mo–O2	1.703(5)	Mo–O3	1.8753(7)
Mo–N6	2.206(6)	Mo–N2	2.278(6)	Mo–N4	2.301(6)
Mo#–O3	1.8753(7)	O1–Mo–O2	104.8(3)	O1–Mo–O3	102.8(2)
O2–Mo–O3	102.6(2)	O1–Mo–N6	90.3(2)	O2–Mo–N6	90.8(3)
O3–Mo–N6	157.99(17)	O1–Mo–N2	161.2(2)	O2–Mo–N2	89.2(3)
O3–Mo–N2	85.79(16)	N6–Mo–N2	76.9(2)	O1–Mo–N4	87.5(3)
O2–Mo–N4	163.4(3)	O3–Mo–N4	84.98(17)	N6–Mo–N4	77.9(2)
N2–Mo–N4	76.5(2)	C3–N2–Mo	128.8(6)	N1–N2–Mo	126.3(5)
C6–N4–Mo	128.8(6)	N3–N4–Mo	125.2(5)	C9–N6–Mo	127.6(6)
N5–N6–Mo	125.4(5)	Mo–O3–Mo1#	180.0		
Complex 2					
Mo–O1	1.695(3)	Mo–O2	1.701(3)	Mo#–O3	1.8830(4)
Mo–O3	1.8830(4)	Mo–N2	2.221(4)	Mo–N4	2.283(4)
Mo–N6	2.306(4)	O1–Mo–O2	104.39(18)	O1–Mo–O3	103.58(12)
O2–Mo–O3	103.46(18)	O1–Mo–N2	90.11(16)	O2–Mo–N2	90.09(16)
O3–Mo–N2	157.41(15)	O1–Mo–N4	161.04(16)	O2–Mo–N4	88.62(16)
O3–Mo–N4	86.29(11)	N2–Mo–N4	75.91(14)	O1–Mo–N6	86.51(16)
O2–Mo–N6	162.84(16)	O3–Mo–N6	86.39(16)	N2–Mo–N6	76.46(14)
N4–Mo–N6	77.89(14)	Mo–O3–Mo#	174.9(3)	C3–N2–Mo	126.3(3)
N1–N2–Mo	125.9(3)	C6–N4–Mo	126.1(3)	N3–N4–Mo	126.2(3)
C9–N6–Mo	126.9(3)	N5–N6–Mo	125.8(3)		

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Table S2 Hydrogen bonds (Å) of complexes **1** and **2**.

D–H···A	d(D–H)/ Å	d(H···A)/ Å	d(D···A)/ Å	∠D–H···A/ °
Complex 1				
C1–H1···O1#1	0.9300	2.4700	3.3200	153.00
C7–H7···O1#2	0.9300	2.5800	3.2934	134.00
Complex 2				
O3–H2···O1#3	0.9300	2.4000	3.1951	143.00

Symmetry transformation used to generate equivalent atoms: #1: 1-x, -0.5+y, 0.5-z; #2: x, 1.5-y, 0.5+z; #3: 1-x, 1-y, 2-z.

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10 **Table S3** A comparison of key bond lengths (Å) and angles (°) for complexes reported previously.

Entry	Complexes	Coordination modes	Mo=O	Mo-O	Mo-N	N-Mo-N	O-Mo-N	Mo-O-Mo
1	$\text{Tp}^*\text{Mo}^{\text{VI}}\text{OS}(\text{S}_2\text{PPh}_2)^3$	MoON3S2	1.662(3)		2.259(4)	79.97(1)	114.2(2)	
2	$\text{Tp}^*\text{Mo}^{\text{VI}}\text{OS}(\text{S}_2\text{PP}^{\text{ri}}_2)^3$	MoON3S2	1.702(4)		2.295(5)	80.1(2)	113.3(2)	
3	$\text{Tp}^*\text{Mo}^{\text{V}}\text{O}(\text{etp})_2^4$	MoO3N3	1.675(2)		2.215(2)	81.75(8)	115.49(9)	
4	$\text{Tp}^{\text{iPr}}\text{Mo}^{\text{VI}}\text{O}_2(2\text{-OC}_6\text{H}_4\text{CONHPh})^{16}$	MoO3N3	1.687(5)		2.264(5)	79.71(19)	116.0(2)	
5	$\text{Tp}^{\text{iPr}}\text{Mo}^{\text{VI}}\text{OS}(\text{OC}_6\text{H}_4^{\text{sBu-2}})^{17}$	MoO2N3S	1.692(5)		2.27(5)	79.18(19)	112.3(2)	
6	$(\text{Tp}^*)\text{Mo}^{\text{V}}\text{O}(\text{bdtCl}_2)^{18}$	MoON3S2	1.679(3)		2.245(3)	82.28(11)	116.75(12)	
7	$\text{Tp}^{\text{iPr}}\text{Mo}^{\text{V}}\text{O}_2(\text{SPh})^{19}$	MoO2N3S	1.698(3)		2.277(4)	79.3(14)	116.22(14)	
8	$[\text{Tp}^{\text{iPr}}\text{Mo}^{\text{V}}\text{O}]_2(\mu\text{-S})(\mu\text{-S}_2)^{20}$	MoON3S2	1.653(3)		2.32(6)	79.9(12)	111.98(13)	
9	$[\text{TpMo}^{\text{VI}}(\text{NAr})(\text{O})]_2\text{O}^5$	MoO2N4	1.706(8)	1.8789(12)	2.284(11)	77.5(4)	111.9(4)	180.0(0)
10	$[\text{Tp}^*\text{Mo}^{\text{V}}\text{OCl}]_2(\mu\text{-O})^6$	MoO2N3Cl	1.664(4)	1.887(5)	2.238(5)	81.6(2)	116.5(2)	177.4(4)
11	$[\text{Tp}^{\text{iPr}}\text{Mo}^{\text{V}}\text{O}]_2(\mu\text{-O})(\mu\text{-Mo}^{\text{VI}}\text{O}_4)^7$	MoO3N3	1.682(3)	1.875(3)	2.216(4)	83.54(15)	117.52(16)	159.28(19)
12	$(\text{TpMo}^{\text{IV}}\text{O}_2)_4^8$	MoO3N3	1.669(7)	1.886(3)	2.262(9)	79.56(3)	115.2(3)	152.7(5)

**etp=2-(ethylthio)phenolate, Tp*=hydrotris(3, 5-dimethylpyrazol-1-yl)borate, Ar = 2, 6-i-Pr₂-C₆H₃,
 Tp^{iPr}=hydrotris(3-isopropylpyrazol-1-yl)borate, bdtCl₂ = 3, 6-dichloro-1, 2-benzenedithiolate**

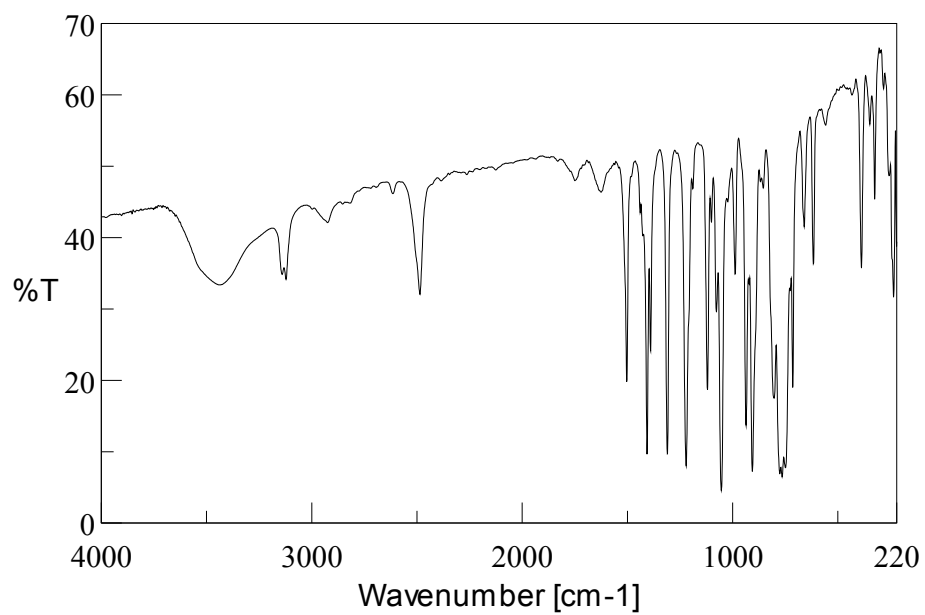


Fig. S1 The Solid-state IR spectra of complex **1** at room temperature

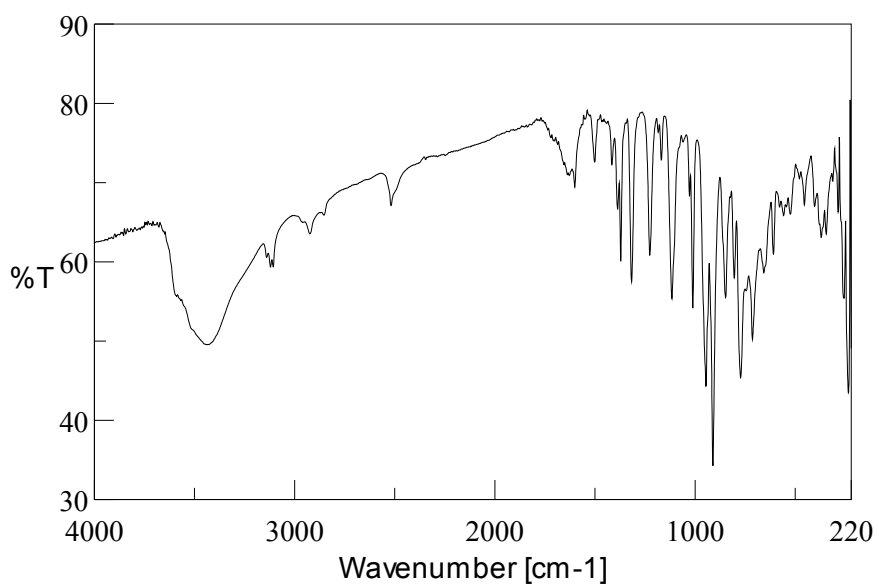


Fig. S2 The Solid-state IR spectra of complex **2** at room temperature

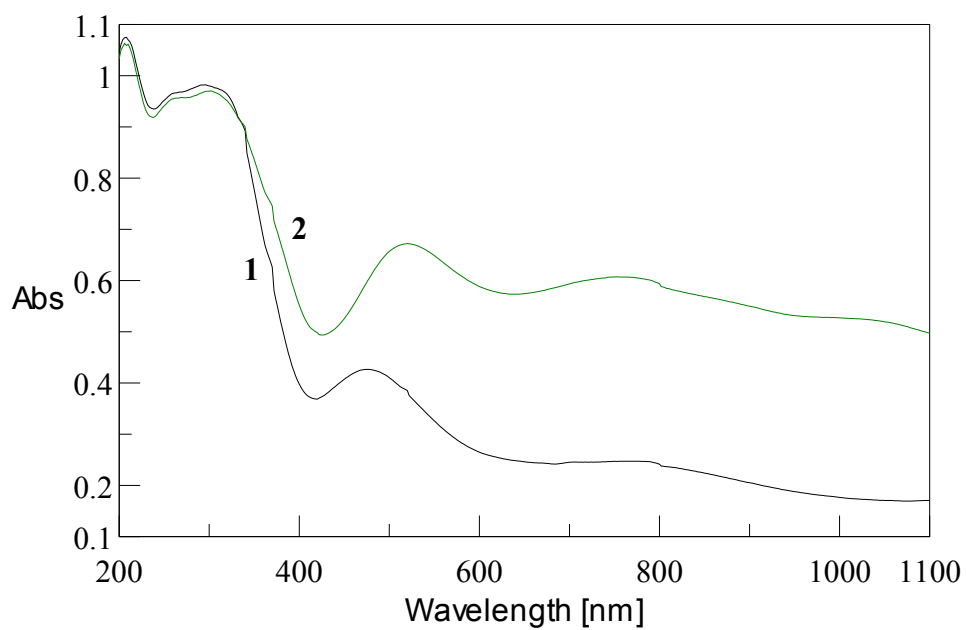


Fig. S3 The UV-Vis spectra for complexes 1 and 2

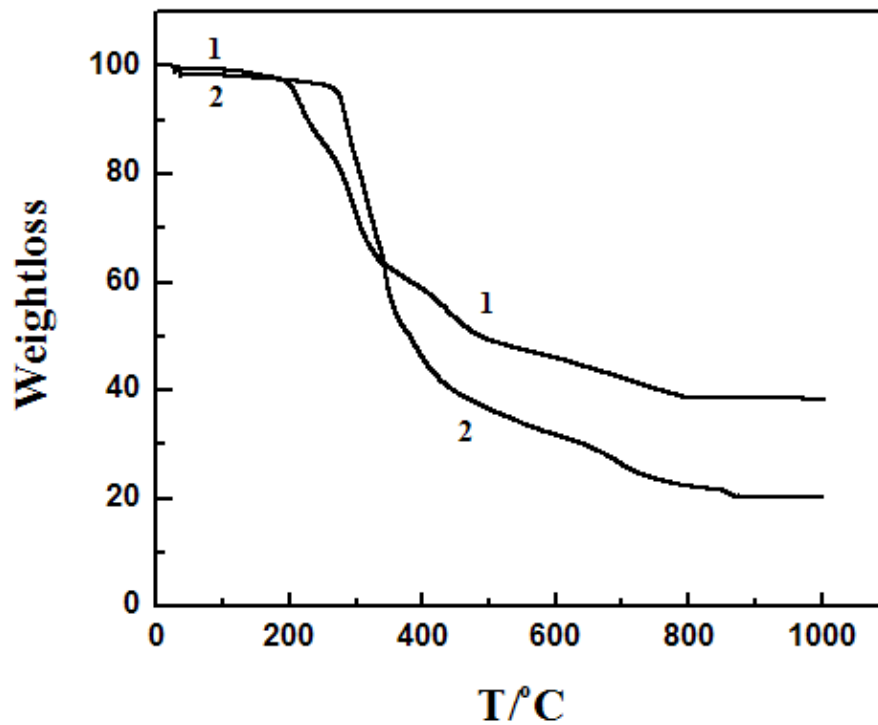


Fig. S4 The TG curves for complexes 1 and 2

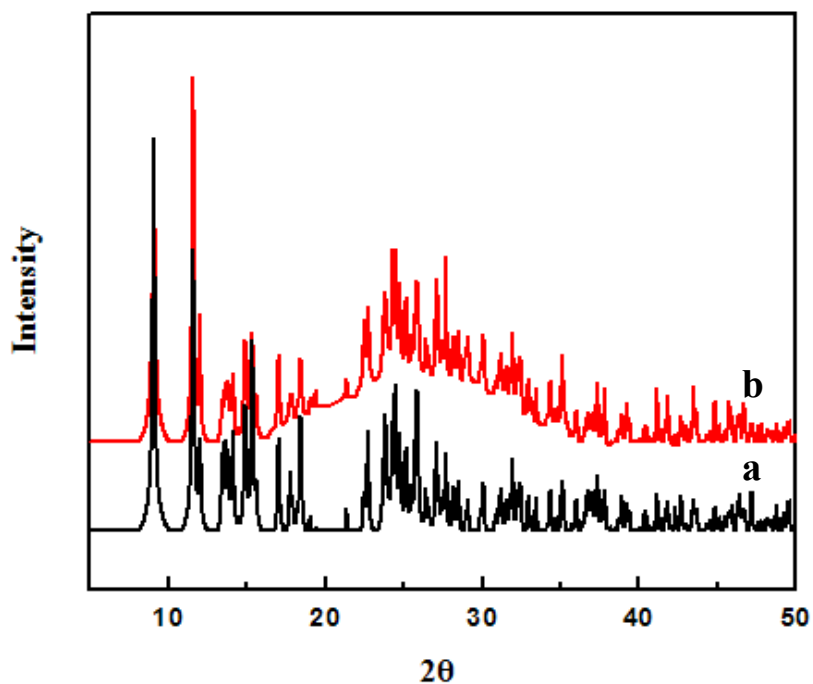


Fig. S5 XRD powder patterns: (a) the simulated XPRD pattern calculated from single-crystal structure of complex **1**; (b) experimental XPRD for complex **1**.

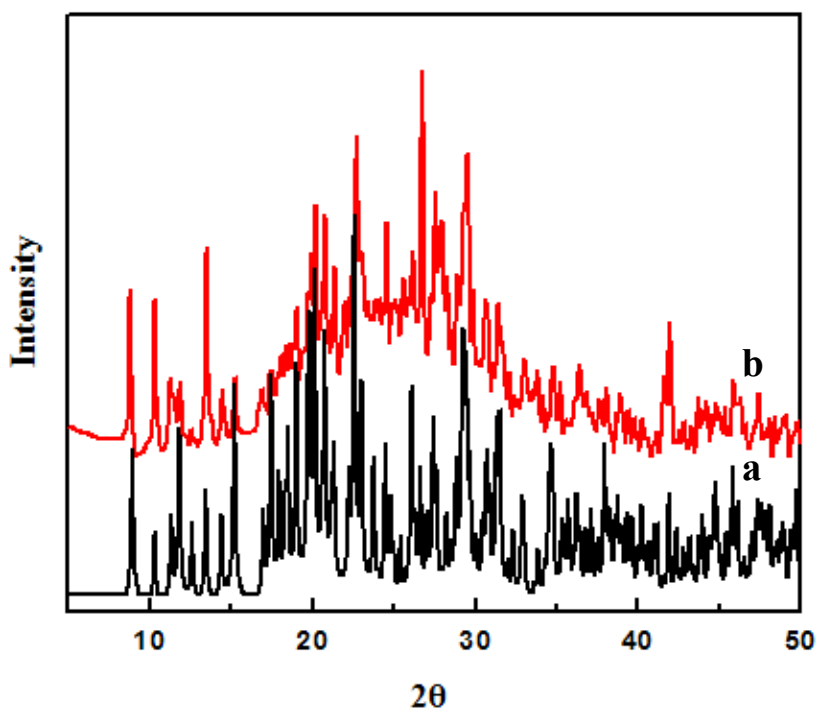


Fig. S6 XRD powder patterns: (a) the simulated XPRD pattern calculated from single-crystal structure of complex **2**; (b) experimental XPRD for complex **2**.