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Crystal structure of poly[bis(μ_2 -1,4-di(1*H*-imidazol-1-yl)benzene- $\kappa^2N:N'$)-(μ_2 -tetraoxido-molybdate(VI)- $\kappa^2O:O'$)cobalt(II)], $C_{24}H_{20}N_8O_4MoCo$

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.15 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.26 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11555, 2979, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2759
$N(\text{param})_{\text{refined}}$:	174
Programs:	SHELX [1], Bruker [2, 3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.500000	0.500000	0.000000	0.01937(8)
Mo1	0.500000	0.29090(2)	0.250000	0.02043(6)
C1	0.35303(8)	0.39900(17)	0.03853(14)	0.0256(3)
H1	0.371855	0.331455	0.084137	0.031*
C2	0.34102(9)	0.5523(2)	−0.08210(15)	0.0339(4)
H2	0.350917	0.610938	−0.135839	0.041*
C3	0.27863(10)	0.5412(2)	−0.04470(16)	0.0364(4)
H3	0.238587	0.590083	−0.067022	0.044*
C4	0.23637(8)	0.40161(16)	0.10180(13)	0.0244(3)
C5	0.24514(9)	0.28318(17)	0.15896(15)	0.0289(3)
H5	0.282779	0.228364	0.150920	0.035*
C6	0.17989(9)	0.48283(18)	0.11331(16)	0.0321(4)
H6	0.174376	0.562566	0.075579	0.038*
C7	0.13181(9)	0.44530(17)	0.18081(16)	0.0314(4)
H7	0.093486	0.498901	0.187457	0.038*
C8	0.19744(9)	0.24705(18)	0.22815(15)	0.0280(3)
H8	0.203513	0.168598	0.267570	0.034*
C9	0.14082(8)	0.32779(16)	0.23849(13)	0.0240(3)
C10	0.07153(9)	0.17035(17)	0.33585(14)	0.0269(3)
H10	0.084476	0.093434	0.302311	0.032*
C11	0.02430(10)	0.30454(18)	0.43863(15)	0.0337(4)
H11	−0.001819	0.336771	0.490791	0.040*
C12	0.06195(10)	0.38047(18)	0.37785(16)	0.0342(4)
H12	0.066234	0.472302	0.379724	0.041*
N1	0.38765(7)	0.46393(15)	−0.02893(12)	0.0276(3)
N2	0.28634(7)	0.44266(15)	0.03346(12)	0.0267(3)
N3	0.09276(7)	0.29354(13)	0.31237(12)	0.0251(3)
N4	0.03010(7)	0.17309(15)	0.41243(12)	0.0268(3)
O1	0.50934(7)	0.39269(14)	0.13795(10)	0.0359(3)
O2	0.57374(9)	0.19295(15)	0.28367(15)	0.0548(4)

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Abstract

$C_{24}H_{20}N_8O_4MoCo$, monoclinic, $C2/c$ (no. 15), $a = 19.3535(7)$ Å, $b = 10.0870(4)$ Å, $c = 12.4174(5)$ Å, $\beta = 97.3700(10)^\circ$, $V = 2404.08(16)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0218$, $wR_{\text{ref}}(F^2) = 0.0577$, $T = 298(2)$ K.

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A part of the title coordination polymer is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents were purchased and used without further purification. A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.0484 g, 0.2 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.0582 g, 0.2 mmol), 1,4-di(1*H*-imidazol-1-yl)benzene (bib) (0.042 g, 0.2 mmol), 0.5 mL

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acetonitrile and 6 mL water was added to a 13 mL Teflon-lined stainless steel reactor and heated under autogenous pressure at 393 K for 72 h and then cooled to room temperature naturally. Purple block crystals of the title coordination polymer were obtained (yield 51%, based on Co).

Experimental details

H atoms were generated geometrically and refined as riding atoms with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$ for aromatic H atoms.

Comment

Polyoxometalates (POMs) possess a large number of terminal and bridging oxygen atoms as potential active coordination sites to be combined with transition metals, such as [MoO₄]^{2−} [5], [Mo₃O₁₀]^{2−} [6], [Mo₆O₁₉]^{6−} [7], [Mo₈O₂₆]^{4−} [8], and so on [9]. Currently, polyoxomolybdate-based metal–organic complexes (MOCs) have attracted attention, not only due to their diverse structures caused by different amounts of molybdenum centers [10], but also for their wide range of applications in the fields of fluorescent sensing [11], catalysis [12], magnetism [13], electrode materials [14] and nanotechnology [15]. Here, we report on an experiment to introduce the 1,4-di(1H-imidazol-1-yl)benzene (bib) ligand into the reaction system containing [MoO₄]^{2−} anions to synthesize a POM-based cobalt(II) complex.

The asymmetric unit of the title complex consists of a half crystallographically independent Co(II) ion, a half MoO₄^{2−} unit, and one bib ligand. The Co(II) center is six-coordinated with a slightly distorted octahedral (CoN₄O₂) geometry that is formed by two O atoms from two MoO₄^{2−} units and four N donors from four different μ_2 -bridging bib ligands [N1, N1ⁱ, N4ⁱⁱ, N4ⁱⁱⁱ, O1, and O1ⁱ, symmetry codes: (i) $-x + 1, -y + 1, -z$, (ii) $x + 1/2, -y + 1/2, z - 1/2$, (iii) $-x + 1/2, y + 1/2, -z + 1/2$]. The lengths of the Co–O (2.0147(12) Å) and Co–N (2.1755(14) and 2.1884(14) Å) bonds are comparable to those observed in the related literature [16–18]. The bib ligand acts as a bidentate ligand, each Co(II) ion is surrounded by four bib ligands, which extend into a 2D layer. The 2D sheets are pillared by the [MoO₄]^{2−} units to form a 3D pillar-layered framework. The important feature of the structure is that the [MoO₄]^{2−} units and Co(II) ions connect with each other forming 1D [–Co–MoO₄]_n chain-like assembly with Co···Co distances of 6.2087(3) Å.

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