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The crystal structure bis{hexakis(1-methyl-1*H*-imidazole- κ^1 N)cobalt(II)} tetrakis(μ_3 -oxido)-octakis(μ_2 -oxido)-tetradeca-oxido-octamolybdate(VI), $C_{24}H_{36}CoMo_4N_{12}O_{13}$

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Abstract

$C_{24}H_{36}CoMo_4N_{12}O_{13}$, triclinic, $P\bar{1}$ (no. 2), $a = 11.155(5)$ Å, $b = 13.889(6)$ Å, $c = 14.081(6)$ Å, $\alpha = 64.544(12)^\circ$, $\beta = 79.558(14)^\circ$, $\gamma = 87.084(14)^\circ$, $V = 1936.3(15)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0365$, $wR_{ref}(F^2) = 0.1171$, $T = 293(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

$(NH_4)_3[Co(Mo_6O_{24}H_6)] \cdot 7H_2O$ (0.3 g, 0.25 mmol) in 6 mL *N*-methylimidazole was sealed in a 25 mL Teflon-lined stainless steel autoclave and was heated under autogenous pressure at 120° for 72 h and then cooled to room temperature. Orange red block crystals were collected.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.25 × 0.20 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.75 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	34372, 6975, 0.047
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5844
$N(param)_{refined}$:	494
Programs:	Bruker [1], SHELX [2], Olex2 [3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Co1	0.13665(5)	0.17353(5)	0.14152(5)	0.02990(17)
N1	0.3255(4)	0.0157(4)	−0.0459(4)	0.0477(11)
N2	−0.0792(4)	−0.1214(3)	0.3041(3)	0.0416(10)
N3	−0.0526(4)	0.3045(3)	0.3503(3)	0.0383(9)
N4	−0.0557(4)	0.3341(3)	−0.1223(3)	0.0402(10)
N5	0.3235(4)	0.4797(3)	−0.0191(3)	0.0465(11)
N6	0.4343(4)	0.1212(3)	0.3109(4)	0.0441(11)
N7	0.0258(3)	0.2595(3)	0.2210(3)	0.0339(9)
N8	0.0251(4)	0.2258(3)	0.0171(3)	0.0356(9)
N9	0.2606(4)	0.1313(3)	0.2535(3)	0.0376(9)
N10	0.2421(4)	0.0778(3)	0.0697(3)	0.0400(10)
N11	0.0157(4)	0.0351(3)	0.2428(3)	0.0375(9)
N12	0.2500(3)	0.3163(3)	0.0412(3)	0.0349(9)
C1	0.3568(6)	0.0466(5)	0.3906(5)	0.0606(16)
H1	0.373232	−0.000422	0.457326	0.073*
C2	0.3638(7)	0.0092(6)	−0.1484(5)	0.078(2)
H2A	0.297172	0.027517	−0.187095	0.117*
H2B	0.387635	−0.062168	−0.135504	0.117*
H2C	0.431535	0.057921	−0.189671	0.117*
C3	0.2515(6)	0.0534(5)	0.3551(5)	0.0559(15)
H3	0.182052	0.010841	0.394251	0.067*
C4	0.3773(6)	0.4395(6)	−0.0882(5)	0.0682(19)
H4	0.433751	0.475160	−0.150251	0.082*
C5	0.3470(7)	0.5841(5)	−0.0236(6)	0.074(2)
H5A	0.276697	0.627060	−0.039346	0.111*
H5B	0.415980	0.618573	−0.078390	0.111*
H5C	0.363757	0.575422	0.044138	0.111*
C6	−0.0629(5)	0.3202(5)	0.4479(4)	0.0536(15)
H6A	−0.093007	0.255359	0.508746	0.080*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H6B	−0.118292	0.376311	0.444550	0.080*
H6C	0.015838	0.339221	0.454195	0.080*
C7	−0.0734(5)	0.4301(4)	−0.2181(5)	0.0536(14)
H7A	−0.011065	0.482837	−0.234393	0.080*
H7B	−0.152002	0.458156	−0.205207	0.080*
H7C	−0.068705	0.412118	−0.277276	0.080*
C8	0.3345(5)	0.3392(6)	−0.0509(5)	0.0605(17)
H8	0.357962	0.292550	−0.081960	0.073*
C9	0.2561(5)	0.0913(5)	−0.0299(4)	0.0483(13)
H9	0.222186	0.146292	−0.082809	0.058*
C10	0.0306(5)	0.3215(4)	−0.0632(4)	0.0424(12)
H10	0.087931	0.374354	−0.077252	0.051*
C11	−0.1378(5)	0.3265(5)	0.2857(5)	0.0543(15)
H11	−0.214446	0.354261	0.294881	0.065*
C12	−0.1076(6)	−0.2278(4)	0.3153(5)	0.0562(15)
H12A	−0.069079	−0.235289	0.252223	0.084*
H12B	−0.194286	−0.237259	0.324766	0.084*
H12C	−0.078030	−0.280620	0.376329	0.084*
C13	0.5600(5)	0.1418(5)	0.3119(5)	0.0554(15)
H13A	0.563075	0.163041	0.367911	0.083*
H13B	0.594965	0.197739	0.244366	0.083*
H13C	0.605321	0.078128	0.324081	0.083*
C14	−0.0769(5)	0.0228(4)	0.3267(4)	0.0511(14)
H14	−0.096478	0.073316	0.353448	0.061*
C15	−0.1187(5)	0.2395(5)	−0.0783(5)	0.0528(15)
H15	−0.182753	0.222083	−0.102722	0.063*
C16	0.3061(5)	−0.0119(4)	0.1205(4)	0.0444(12)
H16	0.313520	−0.040937	0.192165	0.053*
C17	−0.0879(5)	0.2997(5)	0.2058(5)	0.0503(14)
H17	−0.125003	0.307294	0.149028	0.060*
C18	0.3563(5)	−0.0512(5)	0.0502(5)	0.0514(14)
H18	0.402566	−0.111890	0.064397	0.062*
C19	0.0110(5)	−0.0556(4)	0.2335(4)	0.0441(12)
H19	0.064325	−0.071555	0.183632	0.053*
C20	0.2475(5)	0.4026(4)	0.0569(4)	0.0405(12)
H20	0.198455	0.409677	0.114379	0.049*
C21	0.3728(5)	0.1699(4)	0.2295(4)	0.0427(12)
H21	0.405908	0.224391	0.163992	0.051*
C22	−0.0701(5)	0.1758(4)	0.0078(5)	0.0471(13)
H22	−0.098201	0.106702	0.054539	0.057*
C23	−0.1351(5)	−0.0720(5)	0.3645(5)	0.0544(15)
H23	−0.200678	−0.098583	0.420730	0.065*
C24	0.0434(4)	0.2646(4)	0.3089(4)	0.0335(10)
H24	0.113791	0.243149	0.338320	0.040*
Mo1	0.36057(3)	0.46206(3)	0.60340(3)	0.02368(14)
Mo3	0.65764(3)	0.34676(3)	0.69012(3)	0.02933(14)
Mo4	0.36393(3)	0.38868(3)	0.36842(3)	0.02909(14)
Mo5	0.53790(3)	0.24414(3)	0.55060(3)	0.02940(14)
O1	0.2275(3)	0.4363(3)	0.6929(3)	0.0511(9)
O3	0.4859(3)	0.4573(3)	0.6674(2)	0.0359(7)
O4	0.7923(3)	0.2855(3)	0.6771(3)	0.0418(8)
O5	0.6749(3)	0.1932(3)	0.5238(3)	0.0450(9)
O6	0.4367(3)	0.1398(3)	0.5967(3)	0.0424(8)
O9	0.5450(3)	0.2526(2)	0.6818(2)	0.0339(7)
O10	0.6256(3)	0.3177(3)	0.8229(3)	0.0417(8)
O11	0.7216(3)	0.4918(2)	0.6272(3)	0.0337(7)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
O12	0.3855(3)	0.4178(3)	0.2355(3)	0.0465(9)
O16	0.2547(3)	0.2897(3)	0.4271(3)	0.0412(8)
O19	0.3786(3)	0.3650(2)	0.5501(2)	0.0302(7)
O20	0.5106(3)	0.3203(2)	0.4045(2)	0.0319(7)
O21	0.3567(3)	0.5930(2)	0.4967(2)	0.0316(7)

Experimental details

The structure was solved by direct methods. All H-atoms from C atoms were positioned with idealized geometry and $U_{iso}(H) = 1.2U_{eq}(C)$, C(imidazole)–H = 0.93 Å and C(methyl)–H = 0.96 Å.

Comment

Polyoxometalates (POMs) are metal-oxygen clusters composed of early transition metals in the highest valence state and oxygen atoms [4]. Recently, the organic-inorganic hybrid materials based on POMs have shown application prospects in many fields, such as catalysis [5–7], anti-cancer drugs [8], fluorescence [9], energy conversion [10, 11].

Based on this, a new organic-inorganic hybrid material based on one classical $[Mo_8O_{26}]^{4-}$ unit and two $[Co(N\text{-methylimidazole})_6]^{2+}$ units was prepared by a simple solvothermal method. In this structure, the cobalt atom is six-coordinated and the coordination atoms are N atoms from six N-methylimidazole ligands. The Mo atoms have different coordination geometries in the $[Mo_8O_{26}]^{4-}$ anion (see the Figure and the systematic name).

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References

1. Bruker. SAINTv8.37A. Bruker AXS Inc, Madison, WI, USA (2015).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
4. Long, D. L.; Tsunashima, R.; Cronin, L.: Polyoxometalates building blocks for functional nanoscale systems. *Angew. Chem. Int. Ed.* **49** (2010) 1736–1758.
5. Chen, B. K.; Huang, X. Q.; Wang, B.; Lin, Z. G.; Hu, J. F.; Chi, Y. N.; Hu, C. W.: Three new imidazole-functionalized hexanuclear oxidovanadium clusters with exceptional catalytic oxidation properties for alcohols. *Chem. Eur. J.* **19** (2013) 4408–4413.

6. Tucher, J.; Wu, Y. L.; Nye, L. C.; Ivanovic-Burmazovic, I.; Khusniyarov, M. M.; Streb, C.: Metal substitution in a Lindqvist polyoxometalate leads to improved photocatalytic performance. *Dalton Trans.* **41** (2012) 9938–9943.
7. Proust, A.; Thouvenot, R.; Gouzerh, P.: Functionalization of polyoxometalates: towards advanced applications in catalysis and materials science. *Chem. Commun.* **16** (2008) 1837–1852.
8. Bijelic, A.; Aureliano, M.; Rompel, A.: Polyoxometalates as potential next-generation metallodrugs in the combat against cancer. *Angew. Chem. Int. Ed.* **58** (2019) 2980–2999.
9. Zhang, B. F.; Song, J.; Li, D.; Hu, L.; Hill, C. L.; Liu, T. B.: Self-assembly of polyoxovanadate-containing fluorosurfactants. *Langmuir* **32** (2016) 12856–12861.
10. Dong, Y. Y.; Zhang, J.; Yang, Y. L.; Qiu, L. L.; Xia, D. B.; Lin, K. F.; Wang, J. Q.; Fan, X.; Fan, R. Q.: Self-assembly of hybrid oxidant POM@Cu-BTC for enhanced efficiency and long-term stability of perovskite solar cells. *Angew. Chem. Int. Ed.* **58** (2019) 17610–17615.
11. Chen, J. J.; Symes, M. D.; Fan, S. C.; Zheng, M. S.; Miras, H. N.; Dong, Q. F.; Cronin, L.: High-performance polyoxometalate-based cathode materials for rechargeable lithium-ion batteries. *Adv. Mater.* **27** (2015) 4649–4654.