Yu Youzhu*, Shen Yanhong, Niu Yongsheng, Zheng Xiaoming, Han Xi and Chang Songyang
Crystal structure of diazido-bis(μ_2 -pyridin-2-ylmethanolato- $\kappa^2N:O$)-bis(pyridin-2-ylmethanolato- κ^2N,O)dicobalt(III) – methanol (1/3),
 $C_{27}H_{35}Co_2N_{10}O_7$

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Abstract

$C_{27}H_{35}Co_2N_{10}O_7$, orthorhombic, $Pna2_1$ (no. 33),
 $a = 29.6280(13)$ Å, $b = 7.5784(3)$ Å, $c = 14.3600(7)$ Å,
 $V = 3224.3(2)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0409$, $wR_{ref}(F^2) = 0.1133$,
 $T = 296(2)$ K.

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The crystal structure is shown in the figure. Solvent methanol molecules are omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Yu Youzhu, College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang, Henan 455000, P.R. China, e-mail: 119yyz@163.com

Shen Yanhong, Niu Yongsheng, Zheng Xiaoming, Han Xi and Chang Songyang: College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang, Henan 455000, P.R. China

Table 1: Data collection and handling.

Crystal:	Dark block
Size:	$0.19 \times 0.17 \times 0.16$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	41911, 7954, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7048
$N(\text{param})_{\text{refined}}$:	418
Programs:	Bruker programs [1], SHELX [2, 3]

Source of material

A mixture of 2-pyridinemethanol (2 mmol, 0.218 g), $CoCl_2 \cdot 6H_2O$ (1 mmol, 0.238 g), NaN_3 (1 mmol, 0.065 g) and methanol (12 mL) was sealed in a Teflon-lined stainless vessel (15 mL) and heated at 413 K for 24 h under autogenous pressure. The vessel was then cooled at 5 K h^{-1} to 373 K, followed by slow cooling to room temperature. The resulting solution was then filtrated and the dark filtrate was left slowly evaporating at room temperature. After about one week large black cuboid crystals suitable for X-ray diffraction had formed from the solution. One of them was picked up for the measurement and the remaining ones were collected by filtration, washed with methanol under vacuum. Yield: 0.124 g. (ca. 34%).

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. A Flack-Parsons parameter of 0.036(5) was obtained based on 3083 quotients [3].

Discussion

In recent years, coordination chemists have reported a considerable amount of work in the area of single-molecule magnets (SMMs) [4–6]. The potential applications of SMMs are vast. These include information processing, data storage, quantum computing, spintronics, biomedical applications, or magnetic refrigeration [7].

Some efforts have been mainly made on Mn^{3+} or Fe^{3+} based SMMs [8, 9]. As a large anisotropic ion, Co^{2+} might be another possible candidate ion for SMMs due to its strong Ising-type anisotropic contribution in single-chain magnets

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Co1	0.11229(2)	0.16234(7)	0.16336(4)	0.03097(14)
Co2	0.12304(2)	−0.00906(7)	0.34487(5)	0.03113(14)
N1	0.17202(12)	0.1010(5)	0.1221(3)	0.0352(8)
N2	0.04853(13)	0.2024(5)	0.1833(3)	0.0380(9)
N3	0.07055(13)	0.1135(5)	0.3917(3)	0.0338(8)
N4	0.17915(13)	−0.1194(5)	0.3112(3)	0.0361(8)
N5	0.10254(14)	−0.2296(5)	0.3962(3)	0.0404(9)
N6	0.12068(14)	−0.2838(5)	0.4644(3)	0.0399(9)
N7	0.1370(2)	−0.3456(7)	0.5296(5)	0.0719(16)
N8	0.12103(16)	0.4053(6)	0.1236(4)	0.0516(12)
N9	0.1451(2)	0.4496(6)	0.0659(4)	0.0584(13)
N10	0.1688(4)	0.5031(10)	0.0129(8)	0.153(6)
O1	0.09412(11)	0.0809(5)	0.0457(2)	0.0409(7)
O2	0.13555(10)	0.2135(4)	0.2863(2)	0.0317(6)
O3	0.09957(10)	−0.0618(4)	0.2218(2)	0.0300(6)
O4	0.15363(13)	0.0563(5)	0.4541(2)	0.0460(8)
O5	0.3276(3)	0.3676(11)	0.2671(6)	0.154(4)
H5	0.3415	0.4192	0.2260	0.184*
O6	0.1341(2)	0.0751(8)	0.6302(4)	0.0940(18)
H6	0.1404	0.0475	0.5766	0.113*
O7	0.04290(19)	0.2846(8)	0.9369(5)	0.0962(19)
H7	0.0571	0.2216	0.9729	0.115*
C1	0.21125(14)	0.1599(7)	0.1576(5)	0.0445(11)
C2	0.25190(18)	0.1161(9)	0.1149(5)	0.0564(14)
H2	0.2790	0.1563	0.1399	0.068*
C3	0.2521(2)	0.0158(9)	0.0378(5)	0.0645(17)
H3	0.2793	−0.0155	0.0099	0.077*
C4	0.2117(2)	−0.0404(9)	0.0001(5)	0.0588(16)
H4	0.2113	−0.1084	−0.0538	0.071*
C5	0.17197(17)	0.0055(7)	0.0433(4)	0.0423(11)
C6	0.12534(18)	−0.0415(9)	0.0109(4)	0.0518(14)
H6A	0.1244	−0.0415	−0.0566	0.062*
H6B	0.1176	−0.1589	0.0325	0.062*
C7	0.05419(15)	−0.1093(6)	0.2087(4)	0.0391(10)
H7A	0.0436	−0.1742	0.2627	0.047*
H7B	0.0516	−0.1856	0.1547	0.047*
C8	0.02547(16)	0.0519(7)	0.1949(4)	0.0428(11)
C9	−0.0209(2)	0.0474(10)	0.1890(5)	0.0679(18)
H9	−0.0364	−0.0580	0.1981	0.082*
C10	−0.0445(2)	0.2018(12)	0.1694(7)	0.079(2)
H10	−0.0758	0.2008	0.1628	0.095*
C11	−0.0208(2)	0.3534(11)	0.1600(6)	0.075(2)
H11	−0.0359	0.4587	0.1487	0.090*
C12	0.02570(18)	0.3533(7)	0.1671(5)	0.0537(13)
H12	0.0415	0.4587	0.1605	0.064*
C13	0.11597(16)	0.3522(6)	0.3400(4)	0.0417(11)
H13A	0.1095	0.4521	0.3000	0.050*
H13B	0.1371	0.3904	0.3874	0.050*
C14	0.07364(15)	0.2903(6)	0.3849(3)	0.0346(9)
C15	0.04009(19)	0.3999(7)	0.4175(4)	0.0470(12)
H15	0.0431	0.5219	0.4137	0.056*
C16	0.0016(2)	0.3241(8)	0.4561(4)	0.0512(13)
H16	−0.0218	0.3950	0.4775	0.061*
C17	−0.00142(18)	0.1444(7)	0.4622(4)	0.0480(12)
H17	−0.0270	0.0920	0.4875	0.058*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C18	0.03383(17)	0.0417(6)	0.4306(4)	0.0392(10)
H18	0.0320	−0.0803	0.4365	0.047*
C19	0.2003(2)	0.0633(10)	0.4375(5)	0.0636(17)
H19A	0.2165	0.0420	0.4951	0.076*
H19B	0.2085	0.1798	0.4151	0.076*
C20	0.21348(17)	−0.0719(8)	0.3670(4)	0.0492(13)
C21	0.2554(2)	−0.1518(10)	0.3573(6)	0.0703(19)
H21	0.2791	−0.1202	0.3964	0.084*
C22	0.2616(2)	−0.2778(10)	0.2900(6)	0.073(2)
H22	0.2896	−0.3315	0.2830	0.087*
C23	0.2266(2)	−0.3243(8)	0.2330(5)	0.0627(17)
H23	0.2306	−0.4078	0.1863	0.075*
C24	0.18538(17)	−0.2449(6)	0.2464(4)	0.0419(11)
H24	0.1611	−0.2791	0.2095	0.050*
C25	0.3485(5)	0.2159(14)	0.2875(8)	0.120(4)
H25A	0.3797	0.2391	0.3011	0.181*
H25B	0.3465	0.1373	0.2352	0.181*
H25C	0.3344	0.1626	0.3407	0.181*
C26	0.1297(3)	0.2573(12)	0.6363(8)	0.097(3)
H26A	0.1237	0.2899	0.6997	0.146*
H26B	0.1053	0.2955	0.5974	0.146*
H26C	0.1572	0.3123	0.6160	0.146*
C27	0.0690(5)	0.3270(18)	0.8651(7)	0.138(5)
H27A	0.0530	0.4064	0.8247	0.208*
H27B	0.0768	0.2222	0.8313	0.208*
H27C	0.0959	0.3832	0.8873	0.208*

(SCMs) [10]. However, among the abundant Co²⁺ clusters, only a few behave as SMMs [11]. It is still a big challenge in discovering the ingredients for Co²⁺-based SMMs at present. It is well known that azido-bridged clusters have been exploited as SMMs for end-on (EO) azido bridges, which is propitious to F coupling [12]. The versatility bridging modes of the azido ligand, along with its to couple paramagnetic metal centers ferromagnetically under suitable conditions, makes it a very popular choice [13–15]. The 2-(hydroxymethyl)pyridine (hmpH) group has been used previously in chemistry by Christou and Hendrickson [16] who reported the cubane cluster [Co^{II}₄Cl₄(hmp)₄(MeOH)₄]; this cluster proved to be the first cobalt SMM. By now, only few cobalt clusters containing hmp[−] and azido have been reported. It is meaningful to continue to syntheses and study structure of Co complex using hmpH and azido ligands.

The structure of title compound contains two Co³⁺ atoms, four hmp[−] ligands, two azido ligands and three methanol molecules. Each Co³⁺ ion displays a distorted octahedral coordination environment. Among the four deprotonated hmpH ligands, there are two hmp[−] ligands provided that coordinate to one Co(III), and there are two hmp[−] ligands which bridge the two Co³⁺ atoms (*cf.* the figure). Each azido

ligand only provides one coordination site with Co^{3+} . The distance between the two Co^{3+} atoms is 2.930 Å. The average bond length (1.934 Å) of $Co(1)-N(1)$, $Co(1)-N(2)$ and $Co(1)-N(8)$ is typical and comparable with those observed in the related complex (1.938 Å) [17].

In the crystal structure, the molecular conformation is stabilized by $O-H\cdots O$ hydrogen bonds of complexes and methanol.

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