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Crystal structure of bis(μ_3 -2,2'-azanediy)bis(ethan-1-olato)- $\kappa^5 O:O, N, O':O'$ -tetrachlorido-bis(μ_2 -2-((2-hydroxyethyl)amino)ethan-1-olato- $\kappa^3 N, O:O$)dicobalt(II)dicobalt(III), $C_{16}H_{38}Cl_4Co_4N_4O_8$

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.20 × 0.18 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	28.9 cm $^{-1}$
Diffractometer, scan mode:	Bruker APEXII, φ and ω
$2\theta_{\max}$, completeness:	50.2°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	31371, 4718, 0.065
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3958
$N(\text{param})_{\text{refined}}$:	321
Programs:	Bruker [1], SHELX [2]

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $CoCl_2 \cdot 6H_2O$ (0.1 mmol), diethanolamine (0.1 mmol), triethylamine (0.1 mL) and water (15 mL) was stirred for ten minutes at room temperature. The mixture was then transferred in a 20 mL Teflon-lined stainless-steel reactor, heated to 433 K for 72 h, and then slowly cooled to room temperature at a rate of 5 K/h. Dark green block crystals were collected by filtration.

Experimental details

All H atoms were placed in idealized positions, refined with distance restraints of C–H = 0.97 Å and N–H = 0.91 Å and refined as riding atoms with $U_{\text{iso}}(H) = 1.2 U_{\text{eq}}(C, N)$, respectively.

Discussion

The construction of polynuclear metal complexes is one of the most active research areas in coordination chemistry, not only because of their intriguing variety of structures but also due to their potential applications as functional materials used in the area of molecular magnetism, quantum computing and biology [3–10]. It is well known that the structures of the

DOI 10.1515/ncrs-2017-0005

Received January 6, 2017; accepted June 16, 2017; available online July 6, 2017

Abstract

$C_{16}H_{38}Cl_4Co_4N_4O_8$, monoclinic, $P2_1/c$ (no. 14), $a = 9.070(3)$ Å, $b = 15.201(5)$ Å, $c = 20.786(6)$ Å, $\beta = 111.385(11)^\circ$, $V = 2668.5(15)$ Å 3 , $Z = 4$, $R_{\text{gt}}(F) = 0.0646$, $wR_{\text{ref}}(F^2) = 0.1743$, $T = 293$ K.

CCDC no.: 1556624

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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}
C1	0.2209(9)	0.0686(5)	0.3228(4)	0.0269(16)
H1A	0.1265	0.0392	0.2921	0.032*
H1B	0.2935	0.0243	0.3505	0.032*
C2	0.1794(8)	0.1307(5)	0.3678(4)	0.0226(15)
H2A	0.0880	0.1652	0.3406	0.027*
H2B	0.1525	0.0984	0.4023	0.027*
C3	0.3751(9)	0.0587(6)	0.2474(4)	0.0325(18)
H3A	0.4804	0.0454	0.2800	0.039*
H3B	0.3160	0.0040	0.2372	0.039*
C4	0.3896(10)	0.0911(6)	0.1829(4)	0.039(2)
H4A	0.4495	0.1456	0.1917	0.047*
H4B	0.4452	0.0482	0.1656	0.047*
C5	0.9019(9)	0.3882(5)	0.4864(4)	0.0275(16)
H5A	0.8233	0.4307	0.4601	0.033*
H5B	0.9936	0.4199	0.5169	0.033*
C6	0.9479(8)	0.3307(5)	0.4391(4)	0.0239(15)
H6A	0.9640	0.3658	0.4032	0.029*
H6B	1.0461	0.3004	0.4645	0.029*
C7	0.7657(9)	0.3812(5)	0.5713(4)	0.0317(18)
H7A	0.6893	0.3444	0.5813	0.038*
H7B	0.7104	0.4324	0.5461	0.038*
C8	0.8945(11)	0.4107(6)	0.6394(4)	0.039(2)
H8A	0.9696	0.4488	0.6297	0.047*
H8B	0.8467	0.4435	0.6668	0.047*
C9	0.8486(8)	0.1319(5)	0.5822(4)	0.0219(15)
H9A	0.9085	0.1773	0.6137	0.026*
H9B	0.8914	0.0751	0.6013	0.026*
C10	0.6743(7)	0.1376(5)	0.5731(3)	0.0193(14)
H10A	0.6216	0.0823	0.5558	0.023*
H10B	0.6640	0.1502	0.6170	0.023*
C11	0.8162(8)	0.0642(4)	0.4685(4)	0.0227(15)
H11A	0.8396	0.0119	0.4972	0.027*
H11B	0.8785	0.0619	0.4392	0.027*
C12	0.6396(8)	0.0658(4)	0.4234(4)	0.0215(14)
H12A	0.6155	0.0218	0.3872	0.026*
H12B	0.5756	0.0545	0.4510	0.026*
C13	0.2816(8)	0.3188(5)	0.2248(4)	0.0256(16)
H13A	0.2366	0.3749	0.2049	0.031*
H13B	0.2229	0.2723	0.1942	0.031*
C14	0.4536(8)	0.3147(5)	0.2333(4)	0.0233(15)
H14A	0.4637	0.3001	0.1897	0.028*
H14B	0.5042	0.3711	0.2488	0.028*
C15	0.3174(8)	0.3891(5)	0.3385(4)	0.0245(15)
H15A	0.2546	0.3929	0.3675	0.029*
H15B	0.2962	0.4410	0.3094	0.029*
C16	0.4943(8)	0.3861(5)	0.3842(4)	0.0221(15)
H16A	0.5591	0.3960	0.3567	0.026*
H16B	0.5192	0.4306	0.4200	0.026*
Cl1	0.3447(2)	0.38910(11)	0.51187(10)	0.0271(4)
Cl2	0.25233(19)	0.16641(11)	0.54815(8)	0.0212(4)
Cl3	0.7952(2)	0.07337(12)	0.29209(10)	0.0280(4)
Cl4	0.8692(2)	0.30582(13)	0.26128(9)	0.0265(4)
Co1	0.41717(10)	0.21633(6)	0.34264(4)	0.0144(2)
Co2	0.71356(9)	0.23657(6)	0.46548(4)	0.0130(2)
Co3	0.38507(10)	0.24570(6)	0.48920(5)	0.0157(2)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Co4	0.74714(10)	0.21329(6)	0.31869(5)	0.0188(3)
N1	0.2966(6)	0.1196(4)	0.2818(3)	0.0201(12)
H1	0.2160	0.1459	0.2472	0.024*
N2	0.8355(6)	0.3309(4)	0.5274(3)	0.0187(12)
H2C	0.9211	0.3032	0.5581	0.022*
N3	0.8600(7)	0.1439(4)	0.5130(3)	0.020
H3	0.9603	0.1604	0.5185	0.024*
N4	0.2712(6)	0.3082(4)	0.2941(3)	0.0188(12)
H4C	0.1709	0.2922	0.2891	0.023*
O1	0.3081(5)	0.1866(3)	0.4005(2)	0.0184(10)
O2	0.2366(8)	0.1053(7)	0.1337(4)	0.073(3)
H2	0.2283	0.0808	0.0974	0.109*
O3	0.8241(5)	0.2680(3)	0.4087(2)	0.0183(10)
O4	0.9745(7)	0.3354(4)	0.6770(3)	0.0391(14)
H4	0.9165	0.3097	0.6932	0.059*
O5	0.6056(5)	0.2062(3)	0.5252(2)	0.0171(10)
O6	0.6103(5)	0.1521(3)	0.3945(2)	0.0155(9)
O7	0.5259(5)	0.2478(3)	0.2838(2)	0.0173(10)
O8	0.5214(5)	0.3005(3)	0.4138(2)	0.0153(9)

coordination polymers are mainly dependent on the organic ligands and the metal ions [11–15]. So, through deliberate design and judicious choice of organic ligands and metal ions, such polynuclear metal complexes can be synthesized. Amino alcohols and their derivatives have been proved as powerful ligands in preparation of polynuclear metal complexes because their flexible coordination fashion and various coordination modes. The three heteroatoms can adjust their coordination number and orientation through rotation of C–N, C–O and C–C single bonds [16–19]. Herein, we reported a tetranuclear mixed valent cobalt complex.

The asymmetric unit of the title compound consists of two Co(II) ions (Co1, Co2), two Co(III) ions (Co3, Co4), four organic ligands, and four chlorido ligands. Both Co1 and Co2 exhibit a distorted octahedral coordination geometry, which is defined by two N atoms and four O atoms from three organic ligands, respectively. Co3 and Co4 are coordinated by two oxygen atoms from two organic ligands and two chlorido ligands, respectively, displaying the same distorted tetrahedral coordination geometries. In the crystal structure, there exist abundant hydrogen bonds, involving N–H···Cl, O–H···Cl and O–H···O hydrogen bonds forming a two-dimensional network.

Acknowledgements: This work was financial supported by Changsha Enviromental Protection College.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2009.

2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Makhankova, V. G.; Vassilyeva, O. Y.; Kokozay, V. N.; Skelton, B. W.; Reedijk, J.; Albada, G. A. V.; Soraced, L.; Gatteschi, D.: A unique heteropentanuclear $Cu^{II}_2Co^{II}Co^{III}_2$ complex, synthesised from metallic Cu and Co acetate in the presence of triethanolamine. Magnetic properties and a strong H-bond stabilised lattice. *New J. Chem.* **25** (2001) 685–689.
4. Bertaina, S.; Gambarelli, S.; Mitra, T.; Tsukerblat, B.; Müller, A.; Barbara, B.: Quantum oscillations in a molecular magnet. *Nature* **453** (2008) 203–206.
5. Stamp, P. C. E.; Gaita-Ariño, A.: Spin-based quantum computers made by chemistry: hows and whys. *J. Mater. Chem.* **19** (2009) 1718–1730.
6. Sanvito, S.: Molecular spintronics. *Chem. Soc. Rev.* **40** (2011) 3336–3355.
7. Goswami, S.; Mondal, A. K.; Konar, S.: Nanoscopic molecular magnets. *Inorg. Chem. Front.* **2** (2015) 687–712.
8. Bürgler, D. E.; Heß, V.; Esat, T.; Fahrendorf, S.; Matthes, F.; Schneider, C. M.; Besson, C.; Monakhov, K. Y.; Kögerler, P.; Ghisolfi, A.; Braunstein, P.; Atodiresi, N.; Caciuc, V.; Blügel, S.: Spin-Hybrids: a single-molecule approach to spintronics. *e-J. Surf. Sci. Nanotechnol.* **14** (2016) 17–22.
9. Schmitz, S.; Monakhov, Y. K.; Leusen, J.; Izarova, N. V.; Heß, V.; Kögerler, P.: $Co^{II/III}_5$ horseshoe and Ni^{II}_4 lacunary cubane coordination clusters: the isobutyrate/*N*-butyldiethanolamine reaction system. *RSC Adv.* **6** (2016) 100664–100669.
10. Sakiyama, H.; Chiba, H.; Tone, K.; Yamasaki, M.; Mikuriya, M.; Krzystek, J.; Ozarowski, A.: Magnetic Properties of a dinuclear nickel(II) complex with 2,6-bis[(2-hydroxyethyl)methylaminomethyl]-4-methylphenolate. *Inorg. Chem.* **56** (2017) 138–146.
11. Yang, J.; Ma, J. F.; Liu, Y. Y.; Ma, J. C.; Batten, S. R.: A series of Cu(II) complexes based on different bis(imidazole) ligands and organic acids: formation of water clusters and fixation of atmospheric carbon dioxide. *Cryst. Growth. Des.* **8** (2008) 4383–4393.
12. Bu, X. H.; Tong, M. L.; Chang, H. C.; Kitagawa, S.; Batten, S. R.: A neutral 3D copper coordination polymer showing 1D open channels and the first interpenetrating NbO-type network. *Angew. Chem. Int. Ed.* **43** (2004) 192–195.
13. Han, M. L.; Chang, X. H.; Feng, X.; Ma, L. F.; Wang, L. Y.: Temperature and pH driven self-assembly of Zn(II) coordination polymers: crystal structures, supramolecular isomerism, and photoluminescence. *CrystEngComm* **16** (2014) 1687–1695.
14. Meng, X.; Song, S. Y.; Song, X. Z.; Zhu, M.; Zhao, S. N.; Wu, L. L.; Zhang, H. J.: A Eu/Tb-codoped coordination polymer luminescent thermometer. *Inorg. Chem. Front.* **1** (2014) 757–760.
15. Liu, H. Y.; Wu, H.; Ma, J. F.; Liu, Y. Y.; Yang, J.; Ma, J. C.: Inorganic-organic hybrid compounds based on octamolybdates and metal-organic fragments with flexible multidentate ligand: syntheses, structures and characterization. *Dalton. Trans.* **40** (2011) 602–613.
16. Chen, Y.; Liu, Q.; Deng, Y.; Zhu, H.; Chen, C.; Fan, H.; Liao, D.; Gao, E.: Vanadium, molybdenum, and sodium triethanolamine complexes derived from an assembly system containing tetrathiometalate and triethanolamine. *Inorg. Chem.* **40** (2001) 3725–3733.
17. Nesterov, D. S.; Makhankova, V. G.; Vassilyeva, O. Y.; Kokozay, V. N.; Kovbasyuk, L. A.; Skelton, B. W.; Jezierska, J.: Assembling novel heterotrimetallic Cu/Co/Ni and Cu/Co/Cd cores supported by diethanolamine ligand in one-pot reactions of zerovalent copper with metal salts. *Inorg. Chem.* **43** (2004) 7868–7876.
18. Nesterov, D. S.; Makhankova, V. G.; Kokozay, V. N.; Skelton, B. W.: Direct synthesis and crystal structures of new heteropolynuclear complexes containing aminoalcohol ligands: From heterobi-(Co/Zn) to heterotrimetallic (Cu/Co/Zn) compounds. *Inorg. Chim. Acta* **358** (2005) 4519–4526.
19. Semenaka, V. V.; Nesterova, O. V.; Kokozay, V. N.; Zibatyuk, R. I.; Shishkin, O. V.; Boca, R.; Gómez-García, C. J.; Clemente-Juan, J. M.; Jezierska, J.: Structural and magnetic studies of tetranuclear heterometallic M/Cr ($M = Co, Mn$) complexes self-assembled from zerovalent cobalt or manganese, Reineckes salt and diethanolamine. *Polyhedron* **29** (2010) 1326–1336.