

Hexaaquacobalt(II) tetrapotassium diethylene-diaminetetraacetato(4−)cobaltate(III) β -octamolybdate hexahydrate

Uk Lee,^{a*} Hea-Chung Joo^a and Mi-Ae Cho^b

^aDepartment of Chemistry, Pukyong National University, 599-1 Daeyeon-dong Nam-ku, Pusan 608-737, South Korea, and ^bDepartment of Chemistry, Pusan National University, 24, Chang jeon-dong, Kumjeong-ku, Pusan 660-701, South Korea

Correspondence e-mail: uklee@mail.pknu.ac.kr

Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

H-atom completeness 51%

R factor = 0.036

wR factor = 0.085

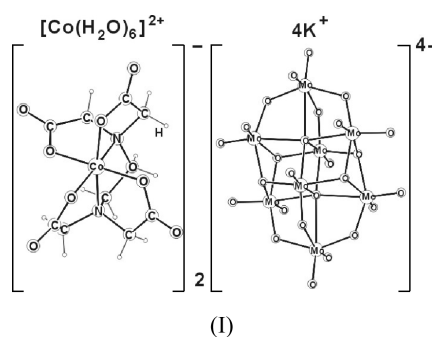
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of the title double salt, $\text{K}_4[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6][\text{Co}^{\text{III}}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)_2][\beta\text{-Mo}_8\text{O}_{26}]\cdot 6\text{H}_2\text{O}$, were prepared by the hydrothermal reaction of $\text{K}_3[\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{18}(\text{OH})_6]\cdot n\text{H}_2\text{O}$ with $\text{Na}_2\text{H}_2\text{edta}$ and CoCl_2 (edta is ethylenediamine tetraacetic acid). The compounds contain β -octamolybdate, $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$, and ethylenediaminetetraacetato(4−)cobaltate(III), $[\text{Co}^{\text{III}}(\text{edta})]^-$, complex anions. The counter-cations are $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ and K^+ . The $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion and $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ cations have inversion centers. The bond-length ranges are as follows: $\text{Co}^{\text{III}}-\text{O}$ in $[\text{Co}(\text{edta})]^-$ 1.882 (4)–1.917 (4) \AA , $\text{Co}^{\text{III}}-\text{N}$ in $[\text{Co}(\text{edta})]^-$ 1.922 (4)–1.931 (4) \AA , $\text{Co}^{\text{II}}-\text{O}$ in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 2.062 (4)–2.141 (4) \AA , and $\text{Mo}-\text{O}$ in $[\text{Mo}_8\text{O}_{26}]^{4-}$ 1.690 (4)–1.716 (4) \AA (*Ot*), 1.742 (3)–2.265 (3) \AA (*Ob*), 1.939 (3)–2.348 (3) \AA (*Oc*), 2.187 (3)–2.472 (3) \AA (*Of*), where *Ot* are terminal O atoms, *Ob* bridging O atoms bound to two Mo atoms, *Oc* central O atoms bound to three Mo atoms and *Of* central O atoms bound to five Mo atoms.

Comment

Almost all the polyoxometalate species are synthesized as self-assembled by pH control. The attempt to separate new polyoxometalate species by the degradation of complicated heteropolyoxometalate species is meaningful. The title double salt compound, (I), was obtained by the reaction of $\text{K}_2[\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{18}(\text{OH})_6]\cdot n\text{H}_2\text{O}$ with Na_2edta and CoCl_2 solutions.



The octamolybdate anion, $[\text{Mo}_8\text{O}_{26}]^{4-}$, shows the most structural variety among isopolymolybdates; the α (Fuchs & Hartl, 1976; Hsieh *et al.*, 1987; Day *et al.*, 1977), β (Lindqvist, 1952; William *et al.*, 1983; Xu *et al.*, 1994; Fun *et al.*, 1996; Zheng *et al.*, 2001; Wu *et al.*, 2001), and γ isomers (Niven *et al.*, 1991; Xi *et al.*, 1994; Inoue & Yamase, 1995; Hagrman & Zubieta, 1999) have been reported.

Fig. 1 shows a view of the $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ anion. Its structural characteristics are normal. The $\text{Mo}-\text{O}$ bonds can be classified into four types, *Ot*, *Ob*, *Oc* and *Of*, according to their coordinating modes; *Ot* is a terminal O atom, *Ob* represents a

Received 13 September 2002

Accepted 23 September 2002

Online 30 September 2002

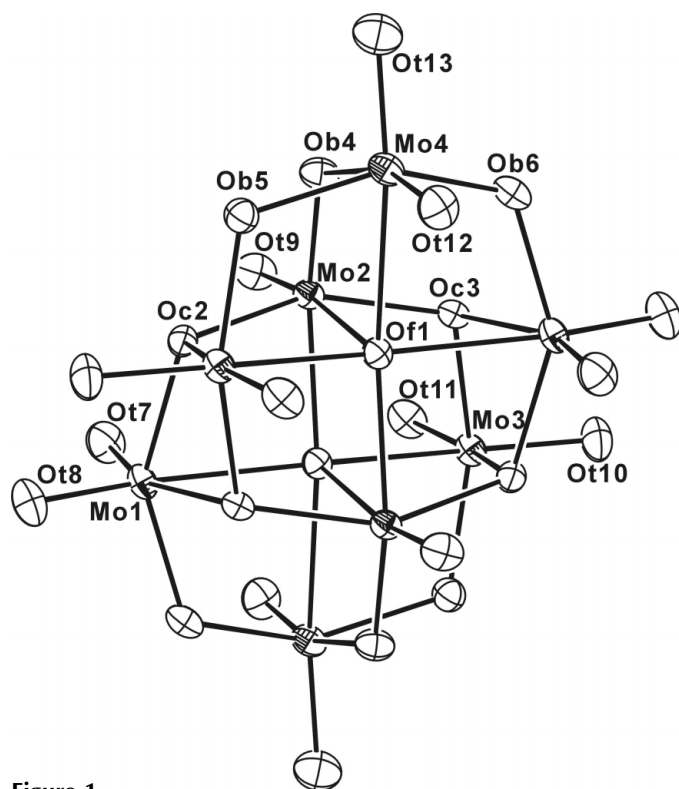


Figure 1
Perspective view of $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$. Displacement ellipsoids are drawn at the 50% probability level.

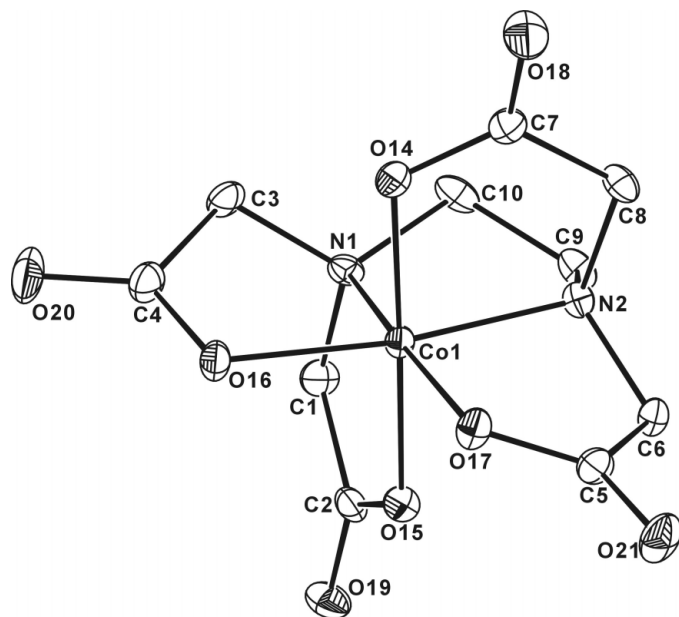


Figure 2
Perspective view of $[\text{Co}^{\text{III}}\text{-edta}]^-$. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

bridging O atom bound to two Mo atoms, Oc represents a central O atom coordinated to three Mo atoms and Of represents a central O atom coordinated to five Mo atoms. The ranges of the Mo–O distances are 1.690 (4)–1.716 (4), 1.742 (3)–2.265 (3), 1.939 (3)–2.348 (3), and 2.187 (3)–2.473 (4) Å for Ot, Ob, Oc and Of, respectively.

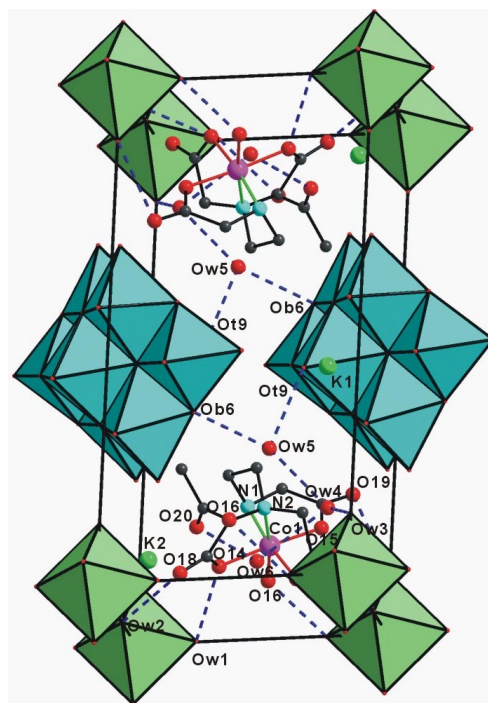
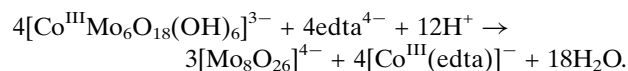


Figure 3
Packing diagram of one unit cell, showing the hydrogen bonds.

Ethylenediaminetetraacetic acid (H_4edta) is a well-known chelating agent (Ogino & Shimura, 1986), with six potential sites of four carboxyl and two amino groups available for binding with metal cations. The anion edta^{4-} forms chelate complexes with many metal cations, and most of these complexes are stable. Therefore, edta^{4-} can extract Co^{3+} from $[\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ and form $[\text{Mo}_8\text{O}_{26}]^{4-}$ and $[\text{Co}^{\text{III}}(\text{edta})]^-$ complexes. The following chemical reaction is expected:



The crystal structures of $\text{Co}^{\text{III}}\text{-edta}$ (Weakliem & Hoard, 1959; Okazaki *et al.*, 1983; Zubkowski *et al.*, 1995) and $\text{Co}^{\text{II}}\text{-edta}$ (McCandlish *et al.*, 1978; Gomez-Romero *et al.*, 1986; Solans & Font-Bardia, 1987) complexes have been reported. Fig. 2 shows the $[\text{Co}^{\text{III}}(\text{edta})]^-$ structure as found in the present study. As is expected, the Co–O and Co–N bond distances are shorter than those in $[\text{Co}^{\text{II}}(\text{edta})]^{2-}$. The apical bond lengths, Co1–O15 [1.882 (4) Å] and Co1–O14 [1.894 (4) Å], are shorter than the equatorial bond lengths Co1–O16 [1.917 (4) Å], Co1–O17 [1.915 (4) Å], Co1–N1 [1.922 (4) Å], and Co1–N2 [1.931 (4) Å]. On the other hand, the apical bond lengths, Co2–OW2 [2.141 (4) Å], are longer than the equatorial bond lengths, such as Co2–OW1 [2.062 (4) Å] and Co2–OW3 [2.082 (4) Å], in the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion, which has crystallographic inversion symmetry.

All water molecules are involved in strong hydrogen bonds with carbonyl O atoms of edta and β -[Mo₈O₂₆]⁴⁻ (Table 2 and Fig. 3).

Experimental

The title compound was synthesized by mixing stoichiometric quantities of K₃[CoMo₆O₁₈(OH)₆] \cdot nH₂O (Lee *et al.*, 2001), Na₂H₂edta and CoCl₂ in aqueous solution. The resulting solution was concentrated in a water bath. After one day, stable violet-coloured crystals were obtained at room temperature.

Crystal data

K ₄ [Co(H ₂ O) ₆][Co(C ₁₀ H ₁₂ N ₂ O ₈) ₂ · [Mo ₈ O ₂₆] \cdot 6H ₂ O	Z = 1
M _r = 2309.34	D _x = 2.597 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
a = 8.3607 (8) Å	Cell parameters from 30 reflections
b = 10.685 (2) Å	θ = 9.6–10.5°
c = 16.922 (1) Å	μ = 2.87 mm ⁻¹
α = 90.32 (1)°	T = 298 (2) K
β = 95.86 (2)°	Tetragonal prism, violet
γ = 100.79 (1)°	0.60 \times 0.40 \times 0.30 mm
V = 1476.8 (3) Å ³	

Data collection

Stoe Stadi-4 diffractometer	θ_{\max} = 27.5°
$\omega/2\theta$ scans	h = -10 \rightarrow 10
Absorption correction: ψ scan	k = -13 \rightarrow 13
(X-SHAPE; Stoe & Cie, 1996)	l = 0 \rightarrow 21
T _{min} = 0.273, T _{max} = 0.425	3 standard reflections
6733 measured reflections	frequency: 60 min
6733 independent reflections	intensity decay: 3.2%
5391 reflections with $>2\sigma(I)$	

Refinement

Refinement on F ²	w = 1/[$\sigma^2(F_o^2) + (0.0288P)^2$
R[F ² > 2 $\sigma(F^2)$] = 0.036	+ 3.9688P]
wR(F ²) = 0.085	where P = (F _o ² + 2F _c ²)/3
S = 1.15	(Δ/σ) _{max} = 0.001
6733 reflections	$\Delta\rho_{\max}$ = 0.72 e Å ⁻³
421 parameters	$\Delta\rho_{\min}$ = -0.91 e Å ⁻³
H-atom parameters constrained	

Table 1

Selected interatomic distances (Å).

Mo1—Mo2	3.2217 (9)	Mo3—Or11	1.711 (4)
Mo1—Mo4 ⁱ	3.2846 (8)	Mo3—Ob5 ⁱ	1.904 (4)
Mo1—Mo3 ⁱ	3.4126 (9)	Mo3—Oc3	2.004 (3)
Mo1—Mo2 ⁱ	3.4972 (7)	Mo3—Oc2 ⁱ	2.296 (3)
Mo2—Mo3	3.2207 (8)	Mo3—Of1 ⁱ	2.309 (3)
Mo2—Mo4	3.4307 (9)	Mo4—Or13	1.698 (4)
Mo3—Mo4 ⁱ	3.2522 (9)	Mo4—Or12	1.716 (4)
Mo1—Or8	1.692 (4)	Mo4—Ob6	1.926 (4)
Mo1—Or7	1.708 (4)	Mo4—Ob5	1.929 (3)
Mo1—Ob6 ⁱ	1.911 (4)	Mo4—Ob4	2.265 (3)
Mo1—Oc2	1.999 (3)	Mo4—Of1	2.472 (3)
Mo1—Of1 ⁱ	2.307 (3)	Co1—O15	1.882 (4)
Mo1—Oc3 ⁱ	2.348 (3)	Co1—O14	1.894 (4)
Mo2—Or9	1.693 (3)	Co1—O17	1.915 (4)
Mo2—Ob4	1.742 (3)	Co1—O16	1.917 (4)
Mo2—Oc3	1.939 (3)	Co1—N1	1.922 (4)
Mo2—Oc2	1.962 (3)	Co1—N2	1.931 (4)
Mo2—Of1 ⁱ	2.187 (3)	Co2—OW1	2.062 (4)
Mo2—Of1	2.323 (3)	Co2—OW3	2.082 (4)
Mo3—Or10	1.690 (4)	Co2—OW2	2.141 (4)

Symmetry code: (i) -x, 1 - y, 1 - z.

Table 2

Hydrogen-bonding D...A distances (Å).

OW1...O16 ⁱ	2.726 (5)	OW4...OW5	2.935 (8)
OW1...O14 ⁱⁱ	2.745 (5)	OW4...OW6	2.970 (11)
OW2...O18 ⁱⁱⁱ	2.805 (6)	OW5...OB6 ^{iv}	2.832 (6)
OW2...O17 ⁱ	2.899 (5)	OW6...O20 ⁱ	2.862 (8)
OW3...OW4	2.677 (7)	OW6...O18 ⁱⁱ	3.188 (8)
OW3...O19 ⁱ	2.918 (6)		

Symmetry codes: (i) 1 - x, -y, 1 - z; (ii) x, y, z - 1; (iii) -x, -y, 1 - z; (iv) 1 - x, 1 - y, 1 - z.

H atoms were located in difference Fourier maps, then positioned geometrically and allowed to ride on their respective parent atoms.

Data collection: *STADIA* (Stoe, 1996); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Pukyong National University Research Fund in 2000.

References

- Brandenburg, K. (1998). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.
- Day, V. W., Friedrich, M. F., Klemperer, W. G. & Shum, W. (1977). *J. Am. Chem. Soc.* **99**, 952–953.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fuchs, J. & Hartl, H. (1976). *Angew. Chem. Int. Ed. Engl.* p. 15. 375–376.
- Fun, H.-K., Yip, B. C., Niu, J. Y. & You, X. Z. (1996). *Acta Cryst.* **C52**, 506–509.
- Gomez-Romero, P., Jameson, G. B., Casan-Pastor, N., Coronado, E. & Beltran, D. (1986). *Inorg. Chem.* **17**, 1383–1394.
- Hagrman, P. J. & Zubieta, J. (1999). *Inorg. Chem.* **38**, 4480–4485.
- Hsieh, T. C., Shaikh, S. N. & Zubieta, J. (1987). *Inorg. Chem.* **26**, 4079–4089.
- Inoue, M. & Yamase, T. (1995). *Bull. Chem. Soc. Jpn.* **68**, 3055–3063.
- Lee, U., Joo, H. C., Kwon, J. S. & Cho, M. A. (2001). *Acta Cryst.* **E57**, i112–i114.
- Lindqvist, I. (1952). *Acta Cryst.* **5**, 667–670.
- McCandlish, E. F. K., Michail, T. K., Neal, J. A., Lingafelter, E. C. & Rose, N. J. (1978). *Inorg. Chem.* **17**, 1383–1394.
- Niven, M. L., Cruywagen, J. J. & Heyns, J. B. B. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2007–2011.
- Ogino, H. & Shimura, M. (1986). *Advances in Inorganic and Bioinorganic Mechanism*, Vol. 4. p. 329. London: Academic Press.
- Okazaki, H., Tomioka, K. & Yoneda, H. (1983). *Inorg. Chim. Acta*, **74**, 169–178.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Solans, X., Font-Bardia, M., Aguiló, M., Arostegui, M. & Oliva, J. (1987). *Acta Cryst.* **C43**, 648–651.
- Stoe & Cie (1996). *STADIA*, *X-RED* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
- Weakliem, H. A. & Hoard, J. L. (1959). *J. Am. Chem. Soc.* **81**, 549–555.
- William, J. K., John, P. F. Jr & Anthony, M. M. (1983). *Inorg. Chem.* **22**, 2412–2416.
- Wu, C. D., Lu, C. Z., Zhuang, H. H. & Huang, J. S. (2001). *Acta Cryst.* **E57**, m349–m351.
- Xi, R., Wang, B., Isobe, K., Nishioka, T., Toriumi, K. & Ozawa, Y. (1994). *Inorg. Chem.* **33**, 833–836.
- Xu, X.-X., You, X.-Z. & Wang, X. (1994). *Polyhedron*, **13**, 1011–1014.
- Zheng, L. M., Wang, Y., Wang, X., Korp, J. D. & Jacobson, A. J. (2001). *Inorg. Chem.* **40**, 1380–1385.
- Zubkowski, J. D., Perry D. L., Valente, E. J. & Lott, S. (1995). *Inorg. Chem.* **34**, 6409–6411.