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ARTICLE

Synthesis and catalysis of Co13 disk surrounded by vanadium-oxygen crown

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By the reaction of binuclear cobalt-containing polyoxovanadate $[Co_2(H_2O)_2V_{10}O_{30}]^{6-}$ with methanol, tridecanuclear cobalt containing polyoxovanadate, $[Co_{13}(OH)_6(OCH_3)_6V_{24}O_{72}]^{10-}$ (**Co13**), was synthesized. Single crystals suitable for x-ray crystallographic analysis were obtained as trimethylphenylammonium salts. Tridecanuclear cobalt core exhibited the planar disk structure and the 24 vertex-sharing VO_4 units surrounded the edge of the disk. This is the largest VO_4-based polyoxovanadate as far as we know. Compound **Co13** was stable in the solution state. Electrochemical analysis showed the possibility of **Co13** to act as the oxydation catalyst for alcohol. Compound **Co13** acted as a catalyst for oxidation of several alcohols. After the reaction, **Co13** catalyst was retrieved by addition of excess amount of ethyl acetate and filtration. The structure of the catalyst was maintained and reused. The oxidation of not only aromatic but also aliphatic alcohols proceeded with **Co13**. Compound **Co13** showed catalytic performance for the oxidation of secondary alcohols even in the presence of alkenic and primary alcoholic functions.

Introduction

Vanadium-oxygen species exist as multinuclear species, called polyoxovanadates, in the aqueous solution except for under the strong acidic and strong basic conditions.[1] Octahedrally coordinated VO_6-based decavanadates and tetrahedrally coordinated VO_4-based oligomers are the dominant species in the acidic and basic solution, respectively. The VO_4-based structures are bridged by the vertex-sharing oxygen atoms to form circular structures. The circular polyoxovanadates act as inorganic ligands with nucleophilicity to stabilize cationic species at the centre of the circles.[2] Proton and various metal-cores stabilized by circular polyoxovanadates, such as $[HV_4O_{12}]^{3-}$, $[PdV_6O_{18}]^{4-}$, $[Cu_2V_8O_{24}]^{4-}$, $[Ni_4V_{10}O_{30}(OH)_2(H_2O)_6]^{4-}$ (**Ni4**), $[Mn_2(V_5O_{15})_2]^{6-}$, $[Co_2(H_2O)_2V_{10}O_{30}]^{6-}$ (**Co2**, Figure 1), $[(H_2O)M(V_4O_{12})_2]^{5-}$ (M = Y, Ho), $[LnV_9O_{27}]^{6-}$ (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy), and $[LnV_{10}O_{30}]^{7-}$ (Ln = La, Er, Tm, Yb, Lu) were reported.[2-8] Although the obtained structures showed the versatility, the synthetic procedures are almost same. Tetravanadate $[V_4O_{12}]^{4-}$ is dissolved in organic solvent and addition of metal cation gives the metal-containing polyoxovanadates. Tetravanadate easily changes the number of the VO_4 units and the conformations of the rings.[9] In comparison with the general organic ligands, circular polyoxovanadate ligands show high flexibility as if the ligands adjust their own structures to the central core structures. Lanthanide-surrounding polyoxovanadates vary the conformations depending on the ionic radii.[6,7] In the case of manganese and cobalt, the number of manganese and cobalt cations increased by the reaction of the additional metal cations to form $[M_3(H_2O)OAcV_{10}O_{30}]^{5-}$ (M = Co (**Co3**), Mn, OAc = acetate), and $[Mn_6O_6V_8O_{26}(OAc)_2]^{6-}$.[10,11]

The layered cobalt oxides and hydroxides are paid attention due to the application of the sustainable renewable energy generation and storage, superconductor, and catalysts.[12-15] The separation of the monolayers produced a hydroxide ion conductor and electrochemical catalysts especially for the water splitting.[16] To prepare the discrete monolayers, peeling reagents, and/or protecting ligands for the flat surface of monolayer are important.[17,18] In these cases, the monolayers show the size distribution. With the appropriate ligands

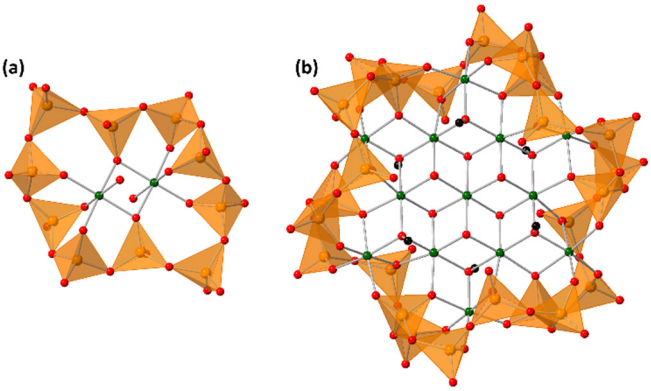

Figure 1. Anion structures of (a) **Co2** and (b) **Co13**. The green, orange, red, and black spheres represent cobalt, vanadium, oxygen, and carbon atoms, respectively. Orange tetrahedra represents VO_4 units.

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surrounding the edge of the monolayer, single species were obtained. Up to date, planar multinuclear cobalt-oxygen complexes were reported.[19-] Functionalized 6-methoxyphenoxides, planar heptanuclear cobalt hydroxide was stabilized with showing the unique electron transfer and oxidation catalyst.[19,20] With isobutyrate and N-butyldiethanolamine, decanuclear cobalt disk was synthesized. The disk contained both bridging hydroxide and alkoxide ligands.[21] By the reaction of cobalt sources with tris(hydroxymethyl)alkane, hepta- and tridecanuclear cobalt disks were prepared.[22,23] Triazacyclononane (tacn) was also act as terminal ligands. Terminal mononuclear cobalt-tacn complexes were prepared in the first step. Then, the coordination of 6 monomers to the heptanuclear cobalt core to afford the tridecanuclear cobalt disk under basic media. The terminal ligands prevented the further hydrolysis.[24] Not only organic ligand but also the rigid polyoxometalates can stabilize the planer cobalt cores, such as $[Co_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ (X = P, V) and $[Co_4(OH)_2(H_2O)_6(H_2SiW_{10}O_{36})_2]^{6-}$.[25-28] Compound $[Co_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ acted as the efficient homogeneous water oxidation catalysts. In this work, synthesis of multinuclear cobalt disk surrounded by VO_4-based polyoxovanadate and its catalytic properties for alcohol oxidation were investigated.

Results and discussion

Synthesis of tridecanuclear cobalt containing polyoxovanadate

The solid of the previously reported binuclear cobalt containing polyoxovandate **Co2** showed water-induced thermochromism.[5] The original colour of **Co2** was light green and by the exposure to the water vapor, the solid colour changed to brown and by heating to evaporate the adsorbed water, the light green colour was retrieved.[5] This result inspired us to investigate the colour change by addition of substrate to the **Co2** solution. Methanol or 2-propanol was added to the acetonitrile solution of **Co2**. In the case of methanol, the solution colour was changed from green to brown. Addition of 2-propanol caused no colour change. From the mixed solution of acetonitrile and methanol, tiny amounts of brown crystals were obtained. IR spectrum of the crystalline sample was different from that of **Co2**, showing the structure conversion (Figure S1). Although the quality of the crystals was too low to complete the x-ray crystallographic analysis, the anion structure was confirmed. It contained a tridecanuclear cobalt disk surrounded by 24 VO_4 units (**Co13**, Figure 1). To improve the yield, triethylamine was added to the synthetic solution to assist the proton removal of methanol. The product **Co13** was selectively precipitated from the synthetic solution. The low yield of **Co13** was due to the unidentified by-products in the solution. The yield clearly increased with increasing the amount of added triethylamine, while excess amount of triethylamine gave impurity. After dissolution of 200 mg of **Co2** in 0.8 mL of the mixed solvent of acetonitrile and methanol (3:1, v/v), addition 2, 3, 4, 5 equiv. of triethylamine with respect to **Co2** and standing for 3 days at room temperature yielded 5.5, 9.4, 13, 14 mg of the products, respectively. Under the optimized condition, the yield reached 24%. From the elemental analysis and thermogravimetric analysis, the formula of the product was $(Et_4N)_5(HEt_3N)_5[Co_{13}(OH)_6(OCH_3)_6V_{24}O_{72}]\cdot 10H_2O$. From the electrospray ionization mass (ESI-MS) spectrum, the corresponding ion pairs due to **Co13** was observed (Figure S2). The distribution of the ion pairs indicates that the bridging methoxide ligands and/or hydroxide ligands are exchangeable.

Single crystals suitable for x-ray crystallographic analysis were obtained by the cation exchange to trimethylphenylammonium. IR spectra in the fingerprint region of polyoxovanadates were same between ethylammonium salt and trimethylphenylammonium salts, showing that the anion structure was maintained during the cation exchange (Figure S1). The BVS values of cobalt and vanadium atoms were 2.00-2.10 and 4.96-5.17, showing cobalt and vanadium atoms were divalent and pentavalent, respectively.[29] Oxygen atoms surrounding the centred cobalt atom were hydroxide ligands. They bridged the centred cobalt atom and 6 cobalt atoms. The 6 cobalt atoms are bridged by methoxide ligands. The methyl groups located vertically to the tridecanuclear cobalt disk, and the directions were opposite to the next methoxide ligands. Methoxide ligands also bonded to the outer 6 cobalt atoms. The arrangement of the 13 cobalt atoms was similar to that of $[Co_{13}(OH)_{24}(tacn)_6]^{8+}$.[24] The tridecanuclear cobalt disk was surrounded by the $[V_{24}O_{72}]^{24-}$ crown. The crown was composed

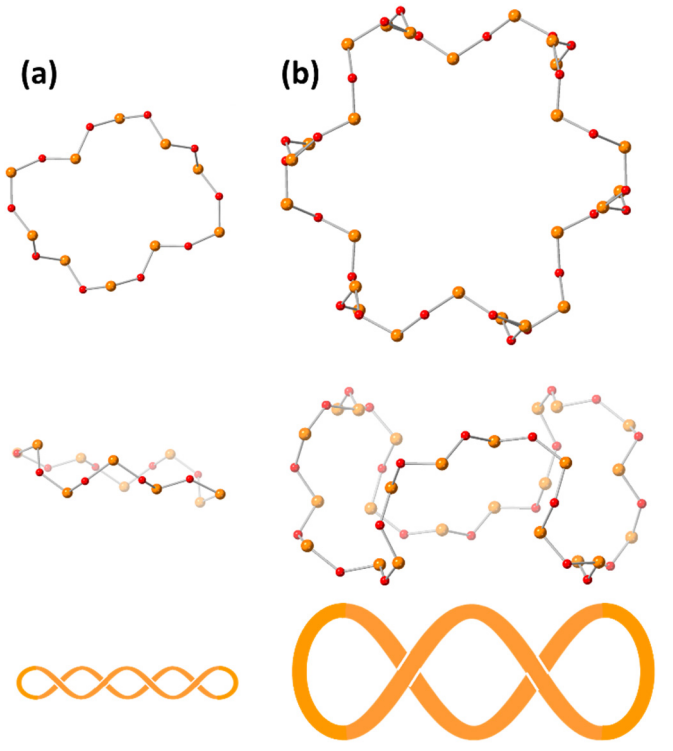


Figure 2. Top and side views and schematic representations of (a) $V_{10}O_{10}$ ring in **Co2** and (b) $V_{24}O_{24}$ ring in **Co13**. The orange and red spheres represent vanadium and oxygen atoms, respectively.

of 24 vertex-sharing VO_4 units. The 48 membered $V_{24}O_{24}$ ring could be drawn with a single stroke. Top view of the ring represented the gear shape (Figure 2). Side view of the ring contained three waves. The numbers of waves of the surrounding polyoxovanadate ligands in **Co2** and **Co3** were 5 and 4 respectively.[10] With increasing the number of the cobalt atoms in the crown, the number of waves of vanadium-oxygen ring decreased (Figure 2). The conformation relationship between the central disk and surrounding polyoxovanadate crowns in **Co13** was different from that in previously reported planer core-containing polyoxovanadate **Ni4**.[4] The polyoxovanadate crown of **Co13** sat in the same plane as tridecanuclear cobalt disk, while the crown of **Ni4** was perpendicular to the tetranuclear nickel plane.

The direct current magnetic measurement of trimethylphenylammonium salts of **Co13** was carried out using the crystalline sample. The $\chi_M T$ value of 48.3 $cm^3 K\ mol^{-1}$ was much larger than the value calculated from the spin-only equation for 13 high-spin Co^{II} ions (24.4 $cm^3\ K\ mol^{-1}$) due to the significant spin–orbit coupling of the octahedral Co^{II} ion (Figure S3). The $\chi_M T$ value gradually decreased to a minimum at 34 K and slightly increased to reach a value of 40.1 $cm^3\ K\ mol^{-1}$ at 19 K. Upon further cooling, the $\chi_M T$ abruptly decreased down to 24.6 $cm^3\ K\ mol^{-1}$. The slight increase at 34 K can be attributed to the ferromagnetic exchange coupling between Co^{II} centers. This feature was competed with the sharp decrease owing to the zero-field splitting. The alternating current susceptibility measurement was performed to observe slow magnetic relaxation behavior. However, no frequency dependence was observed for the out-of-phase signal (χ_M'') indicating that **Co13** is not a single-molecule magnet (Figure S4).

Oxidation property

Electrochemical property of **Co13** was investigated. In the range of 0 – 2.0 V vs ferrocene/ferrocenium (Fc/Fc^+), a weak and broad oxidation peak around 1.5 V was observed. By addition of methanol, increase of the catalytic current over 1.0 V was observed. In addition, an irreversible oxidation peak at 1.5 V was clearly appeared (Figure 3). IR spectra show that the **Co13** structure is maintained after the treatment with excess amount of methanol in the solution state (Figure S5). Without **Co13** or with typical metavanadate, $[V_4O_{12}]^{4-}$, the current increase was not observed. With $Co(NO_3)_2$, the catalytic current increase was observed over 1.4 V without a peak top (Figure S6). With **Co2**, addition of methanol caused the decomposition of the structure. The second cycle of **Co13** solution with methanol showed the weak current probably due to the adsorption of the inactive species on the surface of the electrode (Figure S7). In the case of water addition to the **Co13** solution, the peak current over 1.0 V increased (Figure S8). Addition of non-oxidative *tert*-butyl alcohol did not show the current increase (Figure S8). After the treatment of 5000 equiv. of water or 10000 equiv. of *tert*-butyl alcohol, the **Co13** structure was maintained (Figure S5).

By addition of 1-butanol to the **Co13** solution, the peak top potential was shifted to 1.4 V, indicating the ligand exchange (Figure 3). IR spectra also supported the ligand exchange (Figures S9). After the reaction with 1-butanol, 2-butanol, and benzyl alcohol, the peak at 860 cm^{-1} of the original **Co13** was sifted to 843, 847, and 853 cm^{-1} respectively. In the case of balky *tert*-butyl alcohol, no peak shift was observed (Figure S5). After the constant potential electrolysis at 1.5 V in the presence of 1-butanol with **Co13**, trace amount of butanal was detected by the GC-MS measurement.

Next, chemical oxidation of alcohol was investigated (Table 1). *Tert*-butyl hydroperoxide (TBHP) was used as an oxidant. IR spectrum of the solid collected by filtration after addition of ethyl acetate in to the **Co13** solution in the presence of 500 equiv. of TBHP, was identical to that of the authentic samples of **Co13**, showing the stability of **Co13** towards TBHP (Figure S10). The reaction was carried out in the mixed solvent of propylene carbonate and acetonitrile (1:1, v/v) to dissolve the catalysts. With **Co13** as a catalyst, oxidation of diphenyl methanol proceeded smoothly to afford the corresponding ketone in 95% yield in 24 h (entry 1).

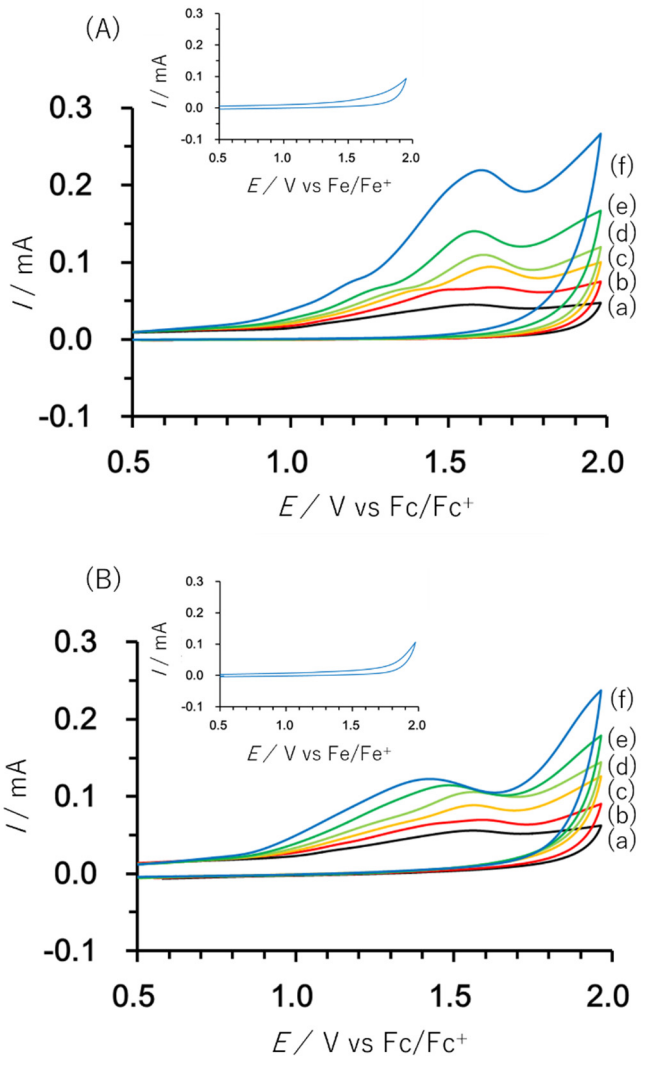
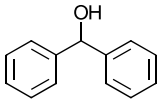
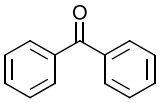
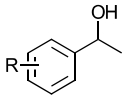
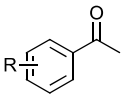
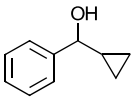
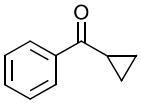
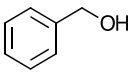
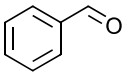
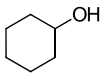
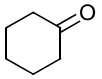
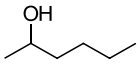
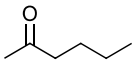
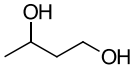
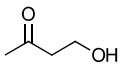
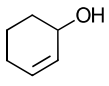


Figure 3. First cycle of cyclic voltammograms of **Co13** in the presence of (a) 0 equiv., (b) 100 equiv., (c) 300 equiv., (d) 500 equiv., (e) 1000 equiv., and (f) 3000 equiv. of (A) methanol and (B) 1-buthanol. The insertion represents voltammograms under the condition (f) without **Co13**.

After the reaction, the catalyst was collected by filtration after addition of excess amount of ethyl acetate. IR spectrum of the retrieved catalyst were same as those of the authentic samples (Figure S11). ESI-MS spectrum of the retrieved catalyst showed the related peak sets of **Co13** (Figure S12). The retrieved catalyst was reused for the alcohol oxidation. The oxidation of diphenyl methanol with the retrieved catalyst gave in 93% yield (Figure S13). The reactivity of $Co(NO_3)_2$ was lower than **Co13** (entry 2). Although the reactivities of **Co2** and $[V_4O_{12}]^{4-}$ were similar to that of **Co13**, their structures were decomposed during the reaction (entry 3,4, Figures S14, S15). The second run with retrieved catalysts of **Co2** and $[V_4O_{12}]^{4-}$ gave the lower yields (Figure S13). The simple mixture of $Co(NO_3)_2$ and $[V_4O_{12}]^{4-}$ gave the middle yield of the product (entry 5). Without catalysts, reaction hardly proceeded (entry 6). The oxidation of 1-phenyl ethanol and its derivatives smoothly proceeded to give the corresponding acetophenone derivatives (entry 7-10). The derivatives with both electron donative group and an electron attracting groups efficiently oxidized. The oxidation of the radical-clock substrate exclusively produced cyclopropyl phenyl ketone without the ring-opened products, indicating that free-radical intermediates are not involved in the present alcohol oxidation (entry 11).[30] The oxidation of benzyl alcohol with **Co13** gave higher yield of benzaldehyde than that with $[V_4O_{12}]^{4-}$ in 2 h, although the yield was low due to the substrate inhibition (entry 12,13, Figure S9). The oxidations of cyclic and linear

Table 1. Oxidation of various alcohol.[a]

entry	substrate	product	catalyst (μmol)	time / h	conversion / %	yield / %
1			**Co13** (2)	24	99	99
2			$Co(NO_3)_2$ (26)	24	45	45
3			**Co2** (13)	24	91	88
4			$\{Et_4N\}_4[V_4O_{12}]$ (12)	24	93	93
5			$Co(NO_3)_2$ (26) $\{Et_4N\}_4[V_4O_{12}]$ (12)	24	78	78
6			–	24	8	7
7	 R = H	 R = H	**Co13** (2)	36	96	95
8	R = *p*-Me	R = *p*-Me	**Co13** (2)	36	95	92
9	R = *p*-Cl	R = *p*-Cl	**Co13** (2)	36	99	99
10	R = *m*-NO_2	R = *m*-NO_2	**Co13** (2)	36	98	98
11			**Co13** (2)	35	94	94
12			**Co13** (2)	2	33	32
13			$\{Et_4N\}_4[V_4O_{12}]$ (12)	2	24	15
14			**Co13** (2)	24	54	54
15			**Co13** (2)	21	46	46
16[b]			**Co13** (2)	10	44	29
17[c]			**Co13** (2)	10	71	47

[a] Reaction conditions: Substrate (1 mmol), catalysts (2-26 μmol), 5.5 M decan solution of TBHP (1 mmol), acetonitrile (1 mL), propylene carbonate (1 mL), internal standard (0.2 mmol), 32°C, 800 rpm with a Teflon-coated magnetic stirrer bar. Conversion and yields were Determined by GC. [b] Primary alcohol oxidation product was not detected. [c] Alcohol was selectively oxidized without formation of epoxide.

aliphatic alcohols proceeded to afford the corresponding aliphatic ketones with middle yields with stopping the reactions probably due to the inhibition of substrates by the coordination to active centres (entry 14-17). The alcohol oxidation with **Co13** was secondary selective. The oxidation of 1,3-butanediol selectively took place at the secondary position (entry 16). 2-cyclohexene-1-ol possess the two oxidative functions. In the presence of **Co13**, alcohol oxidation selectively proceeded without formation of the epoxy products (entry 17). The oxidative products observed in GC chart was only 2-cyclohexene-1-one.

After the treatment of **Co13** with TBHP, IR peak at 860 cm^{-1} was slightly shifted, indicating that the coordination of TBHP (Figure S10). The isolated samples after the treatment with TBHP was utilized for the oxidation of diphenyl methanol. Without additional oxidant, ca. 6 equiv. of benzophenone was obtained, showing the coordination of TBHP to **Co13** is included in reaction paths. In the previous work, tetrahedrally coordinated vanadium centre has a potential to activate TBHP.[31] Based on the results herein and previous reports, we propose possible reaction paths. The oxidant TBHP was activated by the coordination to vanadium and/or cobalt centres. The approach of the substrates to the activated TBHP gives the products.

Experimental

Materials.

All reagents were obtained from commercial suppliers and were used without further purification unless otherwise noted. $\{Et_4N\}_4[V_4O_{12}]$ and $\{Et_4N\}_6[Co_2(H_2O)_2V_{10}O_{30}]$ (**Co2**) were synthesized following the literature method.[5,32] 7-Oxabicyclo[4.1.0]heptan-2-ol (2,3-Epoxycyclohexanol) was obtained with the previously reported system with $\{n\text{-}Bu_4N\}_5[V_{18}O_{46}(NO_3)]^{5-}$.[33]

Synthesis of tridecanuclear cobalt-containing polyoxovanadate, $[Co_{13}(OH)_6(OCH_3)_6V_{24}O_{72}]^{10-}$ (Co13).

$\{Et_4N\}_6[Co_2(H_2O)_2V_{10}O_{30}]$ 200 mg (0.10 mmol) was dissolved in 0.8 mL of the mixed solvent of acetonitrile and methanol (3:1, v/v). After the addition of triethylamine 58 μL (0.40 mmol), the solution was stirred for 1 h. Then the solution was filtrated to remove the insoluble materials. The solution kept standing 2 days at 35°C. The brown powder of **Co13** 21 mg was obtained (24% yield based on cobalt). Elemental analysis calcd. for $\{Et_4N\}_6\{Et_3HN\}_4[Co_{13}(OH)_6(OCH_3)_6V_{24}O_{72}]\cdot 12H_2O$: C 19.37%, H 4.84%, N 2.90%; found: C 19.44%, H 4.61%, N 2.82%. Ethylammonium salts of **Co13** were used for electrochemical analysis and catalytic reactions. The crystalline samples suitable for the single X-ray analysis were obtained by the cation exchange. **Co13** and 100 equiv. of trimethylphenylammonium bromide respective to **Co13** was dissolved in DMSO at 60°C. Vapor diffusion of ethyl acetate to the **Co13** solution at 35°C gave red crystals. Elemental analysis calcd. for $\{Me_3PhN\}_{10}[Co_{13}(OH)_6(OCH_3)_6V_{24}O_{72}]\cdot 4Me_2SO\cdot 10H_2O$: C 23.64%, H 3.97%, N 2.65%, S 2.43%; found: C 23.37%, H 3.99%, N 2.60%, S 2.45%. CCDC 2364056 contains the supplementary crystallographic data for **Co13** (Table S1). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Conclusions

Methanol-induced structure conversion from binuclear to tridecanuclear cobalt-containing polyoxovanadates under the basic condition was discovered by monitoring the colour change of the solution with additives. Among cobalt-containing VO_4-based polyoxovanadate crowns, the numbers of the wave in the V-O rings decrease with increasing the number of the central cobalt atoms. Compound **Co13** acted as oxidation catalyst for the alcohol. The ligand exchanges might assist the oxidation reactions. The size and conformation of polyoxovanadate crowns were controllable to adjust the central metal cores. Conversion of the central metal core structures induces the structure dependent properties. Polyoxovanadate crown is one of the candidates to support such phenomena.

Author contributions

Conceptualization, funding acquisition, Y.K.; characterization, R.M; spectroscopic analysis and catalytic reactions, I.Y.; synthesis and electrochemistry, M.Y.; supervision, Y.K and Y.H. All authors have contributed to write the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 C. F. Baes and R. E. Mesmer, The hydrolysis of cations, John Wiley, New York, 1976.
2 Y. Hayashi, *Coord. Chem. Rev*. 2011, **255**, 2270.
3 J. Fuchs, S. Mahjour and J. Pickardt, *Angew. Chem. Int. Ed. Engl*. 1976, **15**, 374.
4 T. Kurata, A. Uehara, Y. Hayashi and K. Isobe, *Inorg. Chem.* 2005, **44**, 2524.
5 S. Inami, M. Nishio, Y. Hayashi, K. Isobe, H. Kameda and T. Shimoda, *Eur. J. Inorg. Chem.* 2009, 5253.
6 M. Nishio, S. Inami, M. Katayama, K. Ozutsumi and Y. Hayashi, *Inorg. Chem*. 2012, **51**, 784.
7 M. Nishio, S. Inami and Y. Hayashi, *Eur. J. Inorg. Chem*. 2013, 1876.
8 T. Maruyama, H. Kawabata, Y. Kikukawa and Y. Hayashi, *Eur. J. Inorg. Chem*. 2019, 529.
9 Y. Kikukawa, H. Kawabata and Y. Hayashi, *RSC Adv*. 2021, **11**, 31688.
10 T. Maruyama, Y. Kikukawa, H. Sakiyama, M. Katayama, Y. Inada and Y. Hayashi, *RSC. Adv*. 2017, **7**, 37666.

11 T. Maruyama, A. Namekata, H. Sakiyama, Y. Kikukawa and Y. Hayashi, *New J. Chem*. 2019. **43**. 17703.
12 Y. Zhang and H. Ohta, *NPG Asia Mater*. 2023, **15**, 67.
13 Y. Lyu, X. Wu, K. Wang, Z. Feng, T. Cheng, Y. Liu, M. Wang, R. Chen, L. Xu, J. Zhou, Y. Lu and B. Guo, *Adv. Energy Mater*. 2021, **11**, 2000982.
14 J. V. Badding, *Nat. Mater*. 2003, **2**, 208.
15 G. Chen, H. Wan, W. Ma, N. Zhang, Y. Cao, X. Liu, J. Wang and R. Ma, *Adv. Energy Mater*. 2020, **10**, 1902535.
16 G. Song and X. Hu, *Nat. Commun.* 2014, **5**, 4477.
17 R. Ma, Z. Liu, L. Li, N. Iyi and T. Sasaki, *J. Mater. Chem.* 2006, **16**, 3809.
18 N. Tarutani, S. Kimura, T. Sakata, K. Suzuki, K. Katagiri and K. Inumaru, *ACS Materials Lett*. 2022, **4**, 1430.
19 A. M. Ulman and D. F. Nocera, *J. Am. Chem. Soc*. 2013, **135**, 15053.
20 T. S. Mahapatra, D. Basak, S. Chand, J. Lengyel, M. Shatruk, V. Bertolasi and D. Ray, *Dalton Trans*. 2016, **45**, 13576.
21 S. Schmitz, T. Secker, M. Batool, J. van Leusen, M. A. Nadee and. P. Kögerler, *Inorg. Chim. Acta*, 2018, **482**, 522.
22 K.-D. Leng, S.-K. Xing, R. Herchel, J.-L. Liu and M.-L. Tong, *Inorg. Chem.* 2014, **53**, 5458.
23 Y. Peng, C.-B. Tian, Y.-H. Lan, N. Magnani, Q.-P. Li, H.-B. Zhang, A. K. Powell and S.-W. Du, *Eur. J. Inorg. Chem*. 2013, 5534.
24 Sugiarto, Y. Imai and Y. Hayashi, *Inorg. Chem.* 2023, **62**, 1845.
25 Q. Yin, J. M. Tan, C. Besson, Y. V Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C. L. Hill, *Science*, 2010, **328**, 342–345.
26 H. Lv, J. Song, Y. V. Geletii, J. W. Vickes, J. M. Sumliner, D. G. Musaev, P. Kögerler, P. F. Zhuk, J. Bacsa, G. Zhu and C. L. Hill, *J. Am. Chem. Soc.* 2014, **136**, 9268.
27 Y. Kikukawa, K. Suzuki, K. Yamaguchi and N. Mizuno, *Inorg. Chem*. 2013, **52**, 8644.
28 Y. Kuriyama, Y. Kikukawa, K. Suzuki, K. Yamaguchi and N. Mizuno, *Chem. Eur. J*. 2016, **22**, 3962.
29 D. Altermatt and I. D. Brown, *Acta Crystallogr*. 1985, **B41**, 244.
30 D. Griller and K. U. Ingold, *Acc. Chem. Res.* 1980, **13**, 317.
31 Y. Kikukawa, Y. Sakamoto, H. Hirasawa, Y. Kurimoto, H. Iwai and Y. Hayashi, *Catal. Sci. Technol.* 2022, **12**, 2438.
32 H. Nakano, T. Ozeki and A. Yagasaki, *Acta Crystallogr*. 2002, **C58**, m464.
33 I. Yoshida, Y. Kikukawa, R. Mitsuhashi, Y. Hayashi, *Nanoscale*, 2024, **16**, 10584.

Data availability statements

Crystallographic data for **Co13** has been deposited at CCDC under 2364056 and can be obtained from https://www.ccdc.cam.ac.uk/.