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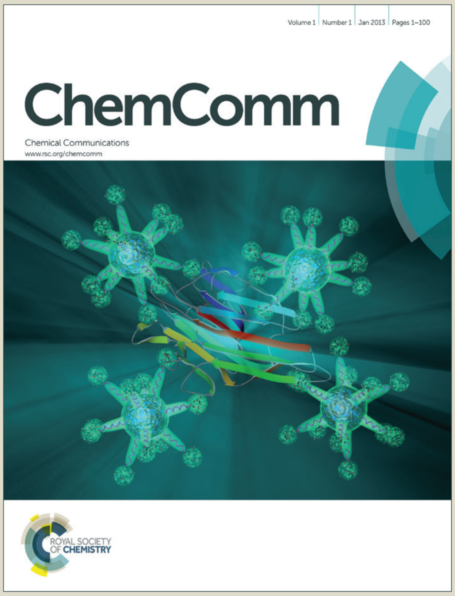

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The anion-binding polyanion: a molecular cobalt vanadium oxide with anion-sensitive visual response

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An anionic molecular cobalt vanadium oxide cluster, (n-$Bu_4N)_3[Co(AcO)V_4O_{12}]$ and its use as anion binding site is reported. Cluster formation is controlled by an anion-dependent dynamic solution equilibrium. Reversible anion binding in solution leads to significant spectral changes, allowing the ratiometric optical detection of the anion concentration *in situ*, even under harsh thermal conditions (T = 90 °C). Comparative studies showed that the spectral response is dependent on the type of anion so that carboxylates, weakly coordinating anions and halides can be distinguished.

Anion sensing by molecular compounds holds great promise for applications in medicine, biology and chemistry.[1] However, the development of anion sensors is still challenging, as anions are pH-sensitive, often feature low charge-to-size ratios and are affected by competing solvent binding.[2] Anion binding by molecular units is typically achieved using electrostatic, coordinative, hydrogen-bonding and other intermolecular interactions.[1] Further, a reporter subunit is necessary which signals the successful anion binding through a colorimetric, luminescent, electrochemical or other response.[2, 3] Considering the requirements outlined above, coordination compounds are ideally suited as sensors, as anion binding and sensing can be achieved by a multitude of structural motifs.[4] However, for anion sensing in harsh environments, classical coordination compounds might not always be suitable. Promising alternatives are molecular metal oxide anions, so-called polyoxometalates (POMs) as they combine high chemical and thermal resistance with remarkable structural and functional tunability.[5] The versatile supramolecular chemistry of POMs[6] and their ability to bind substrates by a variety of intermolecular interactions[7] makes them interesting candidates as molecular ion binding sites.[8]

Most POM-based sensor research is currently focused on electrode modification where the high redox-activity of POM is used as principal means of detection.[8] In contrast, supramolecular POM-systems for ion binding and sensing are rare: research has been focused on cation binding as this is favoured by electrostatic interactions with anionic POMs. A series of ring-shaped "inorganic crown ether" analogues capable of binding inorganic[9] and organic[10] cations have recently been reported. Further, uptake of anionic carboxylates in giant Keplerate capsules was observed.[11]

However bringing together the binding and sensing of anions within one POM species is still challenging. In the present study, we set out to develop a cluster capable of reversibly binding anionic ligands (acetate was used as a model). As binding site and reporter unit, Co^{II} was chosen as its spectral changes upon coordination and anion binding are well-established.[12] As the maximum exposure of the cobalt centre to the environment was desired, we opted to use a small, flexible vanadate ring $[V_4O_{12}]^{4-}$ (= **{V_4}**) for cobalt coordination.[13] Here, we report how a molecular polyanion can be employed for the colorimetric detection of anions in solution, providing initial proof of concept and opening new avenues for the development of inorganic POM-based anion sensors.

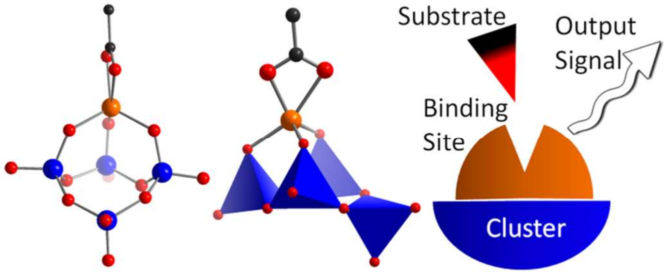

Figure 1. Top: The cluster anion $[Co(AcO)V_4O_{12}]^{3-}$ (= **{CoV_4}**). Ball-and-stick (left) and polyhedral (centre) illustration of **{CoV_4}** highlighting the distorted trigonal-bipyramidal cobalt coordination mode and the cluster-bound acetate ligand. Right: General detection principle used in this study. Colour scheme: V: blue; O: red; Co: orange; C: black. H-atoms are omitted for clarity.

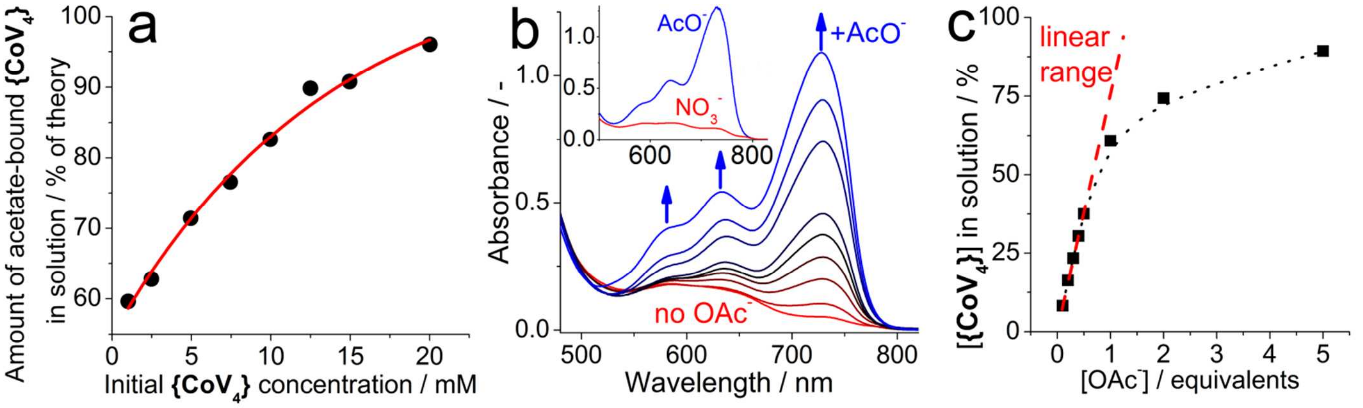

Figure 2. (**a**) Equilibrium concentration of acetate-bound **{CoV$_4$}** (in percent of theory) obtained by dissolving crystalline **{CoV$_4$}** ([**{CoV$_4$}**] = 1-20 mM) in DMF.[14] (**b**) Main: UV-Vis spectrometric detection of acetate by formation of **{CoV$_4$}:** addition of acetate to a 1:1 mixture of **{V$_4$}** and $Co(NO_3)_2 \times 6H_2O$ results in the instantaneous formation of **{CoV$_4$}** as indicated by the characteristic absorption features between λ = 550 – 800 nm. Inset: Absorption features for 1:1 mixtures of **{V$_4$}** and CoX_2 (X = NO_3^- (red), AcO^- (blue). (**c**) Linear ratiometric range for acetate binding, showing the amount of acetate-bound **{CoV$_4$}** in solution (in percent of theory). Conditions: $[Co(X)_2]$ = [**{V$_4$}**] = 5 mM; $[AcO^-]$ = 0.5 mM (gray line) – 25 mM (black line).

Co^{II} coordination to **{V$_4$}** was achieved by reaction of $Co(AcO)_2 \times 4\ H_2O$ with $(n\text{-}Bu_4N)_4$**{V$_4$}** in N,N-dimethyl formamide (DMF). Single crystals of compound **1**, $(n\text{-}Bu_4N)_3[Co(AcO)V_4O_{12}]$ (= $(n\text{-}Bu_4N)_3$**{CoV$_4$}**) suitable for crystallographic analysis[†] were obtained in yields of *ca.* 71 %. Structural analysis gave a pentanuclear cluster where a $[Co^{II}(AcO)]^+$ moiety is coordinated to **{V$_4$}** *via* three terminal V=O oxo ligands, see Fig. 1. The Co^{II} coordination environment is completed by a κ^2-coordinated acetate ligand with unsymmetrical Co-O bond lengths of 2.02 Å and 2.31 Å, resulting in a distorted trigonal bipyramidal coordination. Bond valence sum (BVS) calculations support the assigned metal oxidation states (Co^{II}; V^V) and no protonation of the oxo-ligands is observed.

While studying the stability of **{CoV$_4$}** in DMF solution, a dynamic equilibrium was observed and partial dissociation of the AcO^- ligand from the **{CoV$_4$}** cluster is found, see Fig. 2. Dissociation of AcO^- was also observed under high-resolution ESI-mass spectrometric conditions, where the non-acetate-bound cluster $(n\text{-}Bu_4N)[CoV_4O_{12}]^-$ was observed at m/z = 696.93 (calcd: 696.93). The equilibrium was investigated by concentration-dependent UV-Vis spectroscopy: crystalline **{CoV$_4$}** was dissolved in DMF and the solution concentration of intact, AcO^--bound **{CoV$_4$}** was determined photometrically, see Fig. 2a.[14] At low dissolved concentrations ([**{CoV$_4$}**] = 1 mM), solution concentrations of intact **{CoV$_4$}** (with bound AcO^-) were *ca.* 60 % of the theory. The corresponding dissociation constant K_d was 2.78×10^{-1} mM.[15] At [**{CoV$_4$}**] = 20 mM, *ca.* 96 % of the theory of intact, AcO^--bound **{CoV$_4$}** were observed[14] with a dissociation constant of 3.23×10^{-2} mM.[15] This suggests that solution stability of **{CoV$_4$}** increases with concentration and is in line with Ostwald's law of dilution which states that for weak electrolytes, dissociation increases with increasing dilution.[16] As the equilibrium is acetate-dependent, we were able to show that acetate addition to a **{CoV$_4$}** solution results in an increase of the characteristic **{CoV$_4$}** absorption features, see Fig. S13, ESI.

Based on these initial results, we hypothesized that the presence of acetate in the reaction mixture is a vital prerequisite for **{CoV$_4$}** formation. When $Co(NO_3)_2 \times 6H_2O$ was used as cobalt source, no cluster formation was observed UV-Vis spectroscopically. In contrast, when $Co(AcO)_2 \times 4H_2O$ was employed, instantaneous formation of **{CoV$_4$}** was observed, see Fig. 2b, inset. The observations suggest that successful **{CoV$_4$}** formation depends on the presence of the three components Co^{II}, **{V$_4$}** and AcO^-.

Based on the significant changes in UV-Vis response when comparing the nitrate and acetate based reactions, a homogeneous acetate detecting system was devised: in its resting state, the system features a 1:1 mixture of $Co(NO_3)_2$ and **{V$_4$}** in DMF. Ratiometric detection of acetate is possible by addition of the test solution (here: acetate solutions containing 0.1 – 5 equivalents $n\text{-}Bu_4NAcO$), see Fig. 2b,c. UV-Vis spectroscopy shows that upon acetate addition, the characteristic **{CoV$_4$}** absorption features are obtained, and instantaneous formation of **{CoV$_4$}** is observed. When five equivalents of acetate were added to a 1:1 mixture of $Co(NO_3)_2 \times 6H_2O$ and **{V$_4$}**, a **{CoV$_4$}** yield of *ca.* 89 % was observed spectroscopically, showing the efficient, acetate-triggered cluster assembly. Under the given conditions, the response time for acetate detection was < 1 s;[16] the detailed ligand exchange kinetics will be investigated using stopped-flow methods;[17] maximum signal/noise ratios of *ca.* 23 were observed[18] and the acetate detection limit of the current (non-optimized) system was *ca.* 0.5 mM. Linear, ratiometric behavior was observed for $[AcO^-]$ *ca.* 0.5 - 4 mM (= 0.1 - 0.9 eq.), see Fig. 2b,c.

The thermal stability of **{CoV$_4$}** was investigated and a sample of the acetate-coordinated cluster was dissolved in DMF and heated to T = 90 °C for 24 h. UV-Vis spectroscopic analysis before and after the heat-treatment showed virtually no spectral changes, demonstrating that the **{CoV$_4$}** carboxylate binding capability and stability is not affected by harsh thermal conditions (see Fig. S18, SI).

The broad applicability of **{CoV$_4$}** as anion binding site was investigated by studying the spectral response of the system when exposed to a range of anions. To this end, DMF solutions containing **{V$_4$}** (5 mM), $Co(NO_3)_2 \times 6H_2O$ (5 mM) and n-Bu_4NX (X = PF_6^-, $PhCOO^-$, Cl^-, [X] = 0.5 - 25 mM) were prepared and the resulting UV-Vis spectra were measured. As illustrated in Fig. 3, addition of weakly coordinating anions (here: PF_6^-, red line) resulted in no distinct spectral change and only gave a reduction of the reference signal intensity at λ_{max} = 578 nm. In contrast, addition of a carboxylate (here: $PhCOO^-$, blue line) gave the distinct absorption bands between λ = 550 - 800 nm reported for the acetate-coordinating species above (see Fig. 2). This suggests that **{CoV$_4$}** can be used to detect aliphatic and aromatic carboxylates. The $PhCOO^-$-based cluster $(n\text{-}Bu_4N)_3[Co(PhCOO)V_4O_{12}]$ (**2**) has been isolated and characterized by single-cystal XRD,† see ESI. When a halide (here: Cl^-, green line) was used, a different spectral response was detected and a new signals at $\lambda_{max,1}$ = 690 nm and $\lambda_{max,2}$ = 737 nm were observed. In addition, two shoulders were observed between λ ca. 600 - 650 nm, see Fig. 3. The chloride-based cluster $(n\text{-}Bu_4N)_3[Co(Cl)V_4O_{12}]$ has already been reported in the literature.[13, 14]

The comparative study shows that the cluster can be used to distinguish and detect various types of anions.

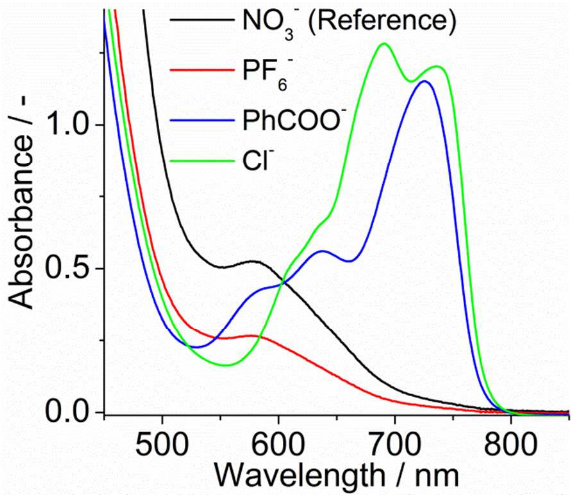

Figure 3. Anion-dependent UV-Vis spectroscopic response of **{CoV$_4$}**: a 1:1 mixture of **{V$_4$}** and $Co(NO_3)_2 \times 6H_2O$ (black reference line) shows distinct spectral responses to the presence of $(n\text{-}Bu_4N)PF_6$ (25 mM), $(n\text{-}Bu_4N)PhCOO$ (25 mM), and $(n\text{-}Bu_4N)Cl$ (25 mM). Conditions: $[\{V_4\}]$ = 5 mM, solvent: DMF, T = 25 °C.

Conclusions

In summary, we present a polyoxometalate-based molecular colorimetric anion sensor based on the acetate-dependent *in situ* formation of a cobalt vanadium oxide cluster, $[Co(AcO)V_4O_{12}]^{3-}$. Spectroscopic studies show that the cluster forms an acetate-dependent equilibrium in solution and cluster formation is dependent of the presence of three components (Co^{II}, $[V_4O_{12}]^{4-}$, AcO^-). Acetate detection is achieved by addition of acetate into a Co^{II} and $[V_4O_{12}]^{4-}$ containing solution. Short anion response times < 1 s are found and ratiometric behaviour at relevant anion concentrations is reported. The system can easily be assembled based on commercial precursors. High thermal stability up to *ca.* 90 °C was observed. It was shown that distinct spectral responses are found depending on the type of anion present, so that multiple anion detection becomes possible.

Future work will target the development of a multi-anion binding system for quantitative anion analysis as well as competitive anion binding. Further, detection of more complex carboxylates will be evaluated to determine whether sensor applications in biological systems would be possible. Cluster immobilization in supramolecular gels for the assembly of colorimetric solid-state anion sensors will be targeted.

Acknowledgements

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Notes and references

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† **Synthesis of 1, $(n\text{-}Bu_4N)_3[Co(AcO)V_4O_{12}]$:** $(n\text{-}Bu_4N)_4[V_4O_{12}]$ (200 mg, 146.5 mmol) was dissolved in DMF (2 mL) and added to a solution of $Co(AcO)_2 \times 4H_2O$ (18.2 mg, 73.1 mmol) in DMF (4 mL). The solution was stirred at room temperature for 2 h. Diffusion of diethyl ether or ethyl acetate into the mother liquor gave compound **1**. Yield: 65 mg (52.4 mmol, 71.4 % based on Co). Elemental analysis in wt.-% for $C_{50}H_{111}N_3O_{14}V_4Co$ (calculated values in brackets): C 48.63 (48.39), H 9.25 (9.01), N 3.47 (3.39), V 16.58 (16.41), Co 4.48 (4.75)

Crystallographic details: Crystallographic data and structure refinements for **1**: $C_{50}H_{111}Co_1N_3O_{14}V_4$, M_r = 1241.11 g mol^{-1}; block crystal: 0.18 × 0.15 × 0.13 mm^3; T = 150(2) K. Monoclinic, space group $P2_1$, a = 11.8530(7), b = 21.6446(12), c = 12.5652(11) Å, β = 93.647(6), V = 3217.1(4) Å^3, Z = 2, D_{calc} = 1.281 g cm^{-3}, μ(Mo*K*α) = 0.868 mm^{-1}, F(000) = 1326, 89091 reflections measured, 14733 unique (R_{int} = 0.039), 659 refined parameters, R_1 = 0.0455 (I > 2σ(I)), wR_2 = 0.1140 (all data).

Crystallographic data and structure refinements for **2**: $C_{55}H_{113}CoN_3O_{14}V_4$ (M =1303.17): monoclinic, space group Cc, a = 24.1500(4) Å, b = 23.6855(4) Å, c = 23.9678(4) Å, β = 93.9267(14)°, V = 13677.5(4) Å^3, Z = 8, T = 180.00(14) K, μ(Mo*K*α) = 0.820 mm^{-1}, D_{calc} = 1.266 g/mm^3, 54985 reflections measured, 31955 unique (R_{int} = 0.0279, R_{sigma} = 0.0466) R_1 = 0.0436 ($I > 2\sigma(I)$), wR_2 = 0.1036 (all data).

The supplementary crystallographic data for **1 (**CSD 834843) and **2 (**CSD 1001987) is available from the Cambridge Crystallographic Data Centre CCDC. Electronic

Supplementary Information (ESI) available: Synthetic, analytical, crystallographic and spectroscopic details are provided. See DOI: 10.1039/c000000x/

[‡]These authors contributed equally to this work.

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14. The equilibrium concentration of acetate-bound **{CoV$_4$}** in solution was calculated as: **[{CoV$_4$}$_{solution}$]** / [**{CoV$_4$}$_{weighed-in}$**] x 100; [**{CoV$_4$}$_{solution}$**] = [$Co(AcO)V_4O_{12}^{3-}$] in solution, determined photometrically; [**{CoV$_4$}$_{weighed-in}$**] = crystalline [$Co(AcO)V_4O_{12}^{3-}$] initially weighed in.
15. The dissociation constant K_d was calculated as K_d = [$CoV_4O_{12}^{2-}$] x [AcO^-] / [$Co(AcO)V_4O_{12}^{3-}$], based on a simplified equilibrium involving only the three components [$Co(AcO)V_4O_{12}^{3-}$], [AcO^-] and [$CoV_4O_{12}^{2-}$].
16. The exhange of AcO- for an equimolar amount of Cl^- was also too fast for detection by standard UV-Vis spectroscopic methods and will be investigated using stopped-flow methods.
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18. Signal/noise (S/N) ratios are calculated as follows:
S/N = Abs_{724nm}(after acetate addition) / Abs_{724nm}(before acetate addition).