

Metavanadates and Dihydrogendecavanadates with Cations of Macrocyclic Tetraamines

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Summary. From the reaction systems *Cyclam/Mecyclam*- KVO_3 - H_2O - HCl - EtOH (*Cyclam* = 1,4,8,11-tetraazacyclotetradecane; *Mecyclam* = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), the first polyvanadates with cations of macrocyclic amines were isolated: $(\text{CyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28}\cdot 2\text{H}_2\text{O}$, $(\text{MecyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$, $(\text{CyclamH}_2)(\text{VO}_3)_2\cdot 3\text{H}_2\text{O}$, $(\text{CyclamH}_2)(\text{VO}_3)_2\cdot 2\text{H}_2\text{O}$, and $(\text{MecyclamH}_2)(\text{VO}_3)_2\cdot \text{H}_2\text{O}$. The metavanadates with the CyclamH_2^{2+} cation differ markedly in their IR spectra, obviously due to the different structure of the polyanion. The interruption of dynamic heating at the thermal analysis of the crystallohydrates of dihydrogendecavanadates resulted in the formation of corresponding anhydrous dihydrogendecavanadates.

Keywords. Metavanadates; Dihydrogendecavanadates; Macrocyclic tetraamines; *Cyclam*; Hexamethyl-*cyclam*.

Metavanadate und Dihydrogendecavanadate mit Kationen aus makrocyclischen Tetraaminen

Zusammenfassung. Aus dem *Cyclam/Mecyclam*- KVO_3 - H_2O - HCl - EtOH Reaktionssystem (*Cyclam* = 1,4,8,11-tetraazacyclotetradecane; *Mecyclam* = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) wurden die ersten Polyvanadate mit cyclischen Aminen als Kationen isoliert: $(\text{CyclamH}_2)_2\text{V}_{10}\text{O}_{28}\cdot \text{H}_2\text{O}$, $(\text{MecyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$, $(\text{CyclamH}_2)(\text{VO}_3)_2\cdot 3\text{H}_2\text{O}$, $(\text{CyclamH}_2)(\text{VO}_3)_2\cdot 2\text{H}_2\text{O}$ und $(\text{MecyclamH}_2)(\text{VO}_3)_2\cdot \text{H}_2\text{O}$. Die zwei Metavanadate mit dem Kation CyclamH_2^{2+} unterscheiden sich wesentlich in ihren Infrarotspektren, was auf unterschiedliche Polyanionstruktur der Metavanadate hinweist. Durch Unterbrechen der dynamischen Erhitzung bei der thermischen Analyse von Kristallhydraten der Dihydrogendekavanadate wurden entsprechende Verbindungen ohne Kristallwasser gewonnen.

Introduction

After decades of extensive studies of different types of polyvanadates with inorganic cations, the attention is now focussed on vanadates formed in reaction systems containing different organic compounds. In such systems, similarly as in the presence of inorganic cations, decavanadates with isolated $\text{V}_{10}\text{O}_{28}^{6-}$ ions or metavanadates with linear chain structures of the polyanion are usually formed [1–3]. However, in some cases decavanadates with higher protonation degree [4, 5] or metavanadates containing an isolated cyclic $\text{V}_4\text{O}_{12}^{4-}$ ion have been also prepared

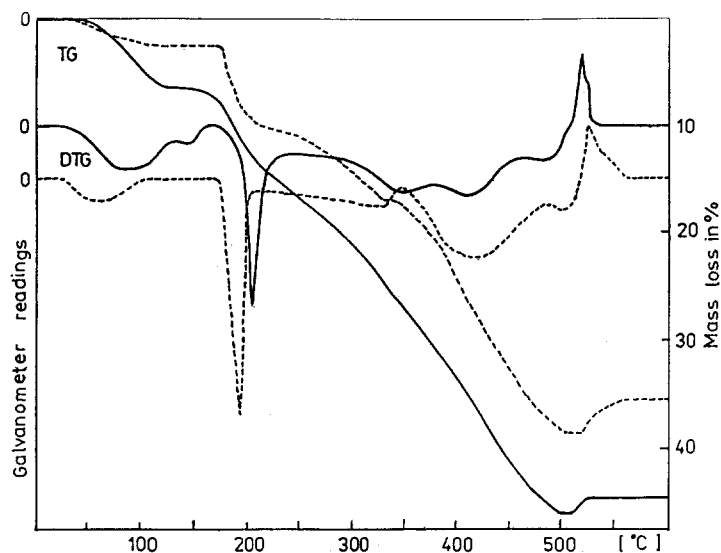


Fig. 1. TG and DTG curves of $(\text{CyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28}\cdot 2\text{H}_2\text{O}$ (dashed line) and $(\text{MecyclamH}_2)_2\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$ (full line); conditions: sample weight, 100 mg; heating rate, $5^\circ\text{C}/\text{min}$; air atmosphere

[6, 7]. The interaction of polyvanadates with dipeptides has been studied as a model for polyoxometallate-protein interactions in connection with the observed anti-AIDS activity of the polyoxometallates [8].

Recently, we have prepared and characterized the benzylammonium, imidazolium, and pyridinium deca-, meta-, and first hexavanadates with organic cations [9]. Herein, we report the synthesis and properties of new meta- and dihydrogendecavanadates with divalent cations of macrocyclic tetraamines, CyclamH_2^{2+} and MecyclamH_2^{2+} .

Results and Discussion

Dihydrogendecavanadates

At the thermal decomposition of the crystallohydrates of dihydrogendecavanadates **1** and **2** (Fig. 1), the process of crystal water release is markedly separated from the decomposition of the organic cations and the polyvanadate ion.

The mass losses on the TG curves corresponding to the first decomposition processes in the temperature interval $35\text{--}150^\circ\text{C}$, 2.40% for **1** and 6.50% for **2**, are in very good agreement with calculated values for loss of crystal water (2.57 and 6.59%, respectively). The products obtained by interruption of dynamic heating at temperatures corresponding to the first plateau on the TG curves (120°C for **1** and 135°C for **2**) were identified by chemical analysis [11] and IR spectra (Table 1) as the anhydrous dihydrogendecavanadates $(\text{CyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28}$ (**8**), and $(\text{MecyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28}$ (**9**). After water release, the thermal decomposition of **1** and **2** is accompanied by a continuous mass loss up to 500°C for **1** and 510°C for **2**. The products obtained by interruption of heating at those temperatures were found by X-ray phase analysis to be mixtures of V_2O_5 and VO_2 . The final product of thermal

Table 1. IR bands of the $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ anion in the 400–1000 cm^{-1} region in the crystallohydrates and in the corresponding anhydrous dihydrogendecavanadates

$(\text{CyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28} \cdot x\text{H}_2\text{O}$		$(\text{MecyclamH}_2)_2\text{H}_2\text{V}_{10}\text{O}_{28} \cdot x\text{H}_2\text{O}$		assignment
x = 2 (1)	x = 0 (8)	x = 6 (2)	x = 0 (9)	
975sh ^a	972sh ^a	985s ^a	982s ^a	ν(V–O _t)
983vs	960vs	970vs ^a	965vs ^a	
945s ^a	945sh ^a	945s ^a	945 ^a	
920m	920m	920m	920m	
		850s ^a	845s ^a	ν(V–O _b)
832s	830s	835s	825s	
745s	740s	738s	735sh	
608s	608m	595s	600s	
558m	560m	535m	520w	
480w	480w			
455m ^a	455m ^a	442m ^a	442w ^a	
435w	435vw			

^a V–O stretchings combined with bands of the cation

decomposition, after oxidation of VO_2 to V_2O_5 connected with mass increase in the temperature intervals 520–570 °C for **1** and 510–535 °C for **2**, is pure V_2O_5 . At the thermal decomposition of the metavanadates prepared, the decomposition processes proceed simultaneously, *i.e.* the corresponding anhydrous metavanadates cannot be prepared by this method.

Based on comparison of the IR spectra of polyvanadates prepared with spectra of the chlorides **6** and **7** [12], we have identified the bands of CyclamH_2^{2+} and MecyclamH_2^{2+} cations and assigned the characteristic bands corresponding to ν(V–O_t) and ν(V–O_b) (O_b: bridging oxygen; O_t: terminal oxygen) vibrations. The band positions in the dihydrogendecavanadates (Table 1) are in agreement with those found in decavanadates with organic [9, 13] and inorganic [14] cations, thus indicating the same polyanion structure as found so far in structures of all decavanadates. The IR spectra of **8** and **9** confirm that the crystal water release, unlike the water release from crystallohydrates of decavanadates with inorganic cation leading to formation of meta- [15], hexa- [16], ortho- [17], or pentavanadates [18], is not connected with structure decomposition of the isolated $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ ion.

Metavanadates

The metavanadates with a polymeric chain structure consisting of the $\text{V}_n\text{O}_{3n}^{n-}$ anion made up by VO_4 tetrahedra, *i.e.* anhydrous metavanadates with inorganic cations [19] and crystallohydrates or anhydrous metavanadates with organic cations [20, 21], all have a characteristic IR spectrum in the region of the V–O vibrations (400–1000 cm^{-1}) due to the same structure of the polyanion. Among the metavanadates prepared, **3** and **5** exhibit such a characteristic spectrum (Fig. 2, a and b): ν_s(V–O_t): 930 and 900 cm^{-1} ; ν_{as}(V–O_t): 870 and 810 cm^{-1} ; ν_{as} + ν_s(V–O_b): 640 and

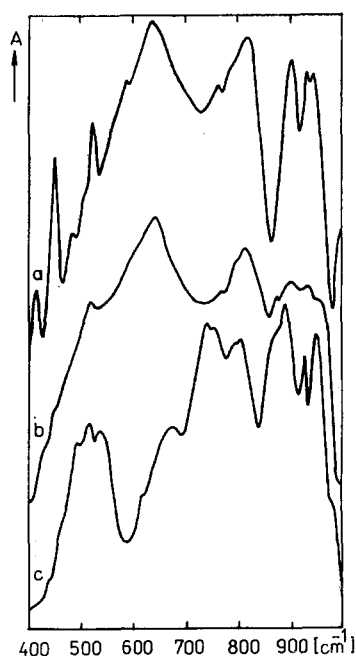


Fig. 2. IR spectra of metavanadates in the region of 400–1000 cm^{-1} : (*CyclamH*₂)(VO₃)₂·3H₂O (a), (*MecyclamH*₂)(VO₃)₂·H₂O (b), and (*CyclamH*₂)(VO₃)₂·2H₂O (c)

525 cm^{-1} for **3**; the same stretching vibrations can be found at 930 and 900 cm^{-1} ; 870 and 815 cm^{-1} ; and at 635 and 520 cm^{-1} for **5**. In both metavanadates, a pyroxene like chain structure of the polyanion can thus be proposed.

The spectra of metavanadates **3** and **4**, both containing the same *CyclamH*₂²⁺ cation (Fig. 2, b and c), markedly differ in the region of asymmetric and symmetric V–O_b–V vibrations, 400–800 cm^{-1} , obviously due to a different structure of the metavanadate anions. The spectrum of **4** exhibits strong bands at 740 and 675 cm^{-1} , and the most intensive band at about 640 cm^{-1} , characteristic for all metavanadates with polymeric chain structure, is missing. Up to date, only two metavanadates with a crystal structure built up of isolated cyclic V₄O₁₂⁴⁻ resp. HV₄O₁₂³⁻ ions formed by four VO₄ tetrahedra were prepared and structurally characterized: (*i*-Bu₄N)₄(V₄O₁₂) [6, 7] and (*n*-Bu₄N)₃(HV₄O₁₂) [22]. The IR spectrum is available only for the isobutylammonium salt. It not only exhibits the bands at 735 and 660 cm^{-1} as the spectrum of **4**, but also the same bands in the region of V–O_t stretching vibrations: 935, 890, and 810 cm^{-1} , compared with 930, 890, and 805 cm^{-1} for **4**. The difference in the spectra of **3** and **4**, and the similarities in the spectra of **4** and (*i*-Bu₄N)₄(V₄O₁₂) indicate that **4** will also probably have a structure containing the cyclic V₄O₁₂⁴⁻ ions. The isolation of monocrystals of **4** suitable for X-ray structure analysis which would unambiguously support this proposal is in progress in our laboratory.

The results obtained showed that not only the nature of the organic cation, but also the different reaction conditions, in presence of the same cation, seem to be responsible for the different structures of the polyanion in the metavanadates formed.

Experimental

V₂O₅ was prepared by thermal decomposition of NH₄VO₃. *Mecyclam*·2H₂O was prepared according to Ref. [10]; the other chemicals were of analytical grade (supplied from Aldrich or Lachema).

*Cyclam*H₂Cl₂·2H₂O (**6**) and *Mecyclam*H₂Cl₂·2H₂O (**7**) were prepared by crystallization from a 5:2 ethanol-water solution of the cyclic amine with a *pH* adjusted to 7.2 for **6** and 3.5 for **7** with HCl (1:3) and their composition was verified by chemical analysis. V(V) was determined by titration with FeSO₄ (diphenylamine as indicator). C, H, N and Cl were determined with a Carlo Erba 1106 analyzer. The IR spectra in Nujol mull were registered on a Specord M 80 spectrophotometer (Zeiss, Jena). The X-ray diffraction patterns were registered on a Philips diffractograph with a PW 1050 goniometer using CuK_α radiation. The thermal analysis was performed on a OD-102 Derivatograph (MOM, Budapest).

(*Cyclam* H₂)₂V₁₀O₂₈·2H₂O (**1**)

Cyclam (0.2 g, 1 mmol) was dissolved in 100 ml EtOH and KVO₃ (0.28 g, 2 mmol) in 100 ml H₂O. The *pH* of both solutions was adjusted to 3.0–3.5 before mixing with HCl (1:3). In this region **1** can be isolated as a pure substance. Calcd.: V, 36.38; C, 17.16; H, 4.17; N, 8.00%; found: V, 36.40; C, 17.25; H, 4.03; N, 8.03%.

(*Mecyclam*H₂)₂H₂V₁₀O₂₈·6H₂O (**2**)

Mecyclam·2H₂O (0.24 g, 0.75 mmol) was dissolved in 200 ml EtOH and KVO₃ (0.34 g, 2.5 mmol) in 100 ml H₂O. The *pH* of both solutions was adjusted as for **1** but within the range of 2.5–6.5 in which pure **2** crystallizes. Calcd.: V, 31.05; C, 23.43; H, 5.53; N, 6.83%; found: V, 31.00; C, 23.53; H, 5.30; N, 6.81%.

(*Cyclam*H₂)(VO₃)₂·3H₂O (**3**)

Cyclam (0.2 g, 1 mmol) was dissolved in 100 ml EtOH. The solution was filtered, and 1:3 HCl was added until a *pH* of 7.5. KVO₃ (0.28 g, 2 mmol) was dissolved in 100 ml H₂O. The solutions were mixed (*pH* 8.0), and acetone was added until a weak turbidity was formed. Pure **3** can be prepared in the *pH* range of 8.0–10.5 of the water-ethanol solution (the higher *pH* values adjusted with cyclam addition). Calcd.: V, 22.43; C, 26.20; H, 7.10; N, 12.33%; found: V, 22.50; C, 26.20; H, 7.15; N, 12.24%.

(*Cyclam*H₂)(VO₃)₂·2H₂O (**4**)

Cyclam (0.2 g, 1 mmol) was dissolved in 300 ml EtOH. The solution was filtered and the *pH* adjusted with HCl (1:3) to 8.5. KVO₃ (0.28 g, 2 mmol) was dissolved in 100 ml H₂O. The solutions were mixed (*pH* 9.0), acidified with HCl (1:3) to *pH* 8.5 and left to crystallize in the dark at room temperature. **4** was formed in 2–3 days. Calcd.: V, 23.44; C, 27.53; H, 6.93; N, 12.84%; found: V, 23.44; C, 27.36; H, 6.93; N, 12.84%.

(*Mecyclam*H₂)(VO₃)₂·H₂O (**5**)

Mecyclam·2H₂O (0.32 g, 1 mmol) was dissolved in 60 ml EtOH and the *pH* adjusted as for **3**. KVO₃ (0.28 g, 2 mmol) was dissolved in 40 ml H₂O. The solutions were mixed and left to crystallize. **5** can be prepared from solutions with a *pH* in the range of 7.6–10.5. Calcd.: V, 20.28; C, 38.25; H, 8.00; N, 11.15%; found: V, 20.10; C, 38.31; H, 7.83; N, 11.14%.

1 and **2** are orange, **3–5** pale yellow microcrystalline substances, all almost insoluble in water, ethanol, and common organic solvents. The given *pH* values are meter readings for aqueous, water-ethanol, or ethanol solutions.

As identification data, the interplanar distances and relative intensities (nm (*I*_{rel})) for the ten most intensive diffractions in **1–5** are given: **1**: 1.026(100), 0.859(65), 0.816(85), 0.4026(67), 0.3705(64), 0.3604(67), 0.3386(64), 0.3309(56), 0.3149(66), 0.2714(66); **2**: 1.016(90), 0.884(100), 0.734(50), 0.6159(11), 0.5197(22), 0.4366(20), 0.3666(30), 0.3490(11), 0.3341(60), 0.3075(14); **3**: 1.081(61), 0.849(43), 0.3990(69),

0.3934(72), 0.3853(63), 0.3738(43), 0.3633(100), 0.3528(53), 0.3326(32), 0.3068(35); 4: 0.815(28), 0.6211(28), 0.4439(30), 0.4125(100), 0.3962(60), 0.3763(70), 0.3363(80), 0.3250(25), 0.2942(20), 0.2344(30); 5: 0.6193(38), 0.5179(65), 0.4561(85), 0.3962(100), 0.3847(65), 0.3805(50), 0.3584(40), 0.3537(73), 0.3317(78), 0.3140(30).

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- [11] Calcd. for **8**: C, 17.61; H, 3.99; N, 8.21; V, 37.34%; found: C, 17.80; H, 4.06; N, 8.10; V, 36.95%.
Calcd. for **9**: C, 25.08; H, 5.13; N, 7.31; V, 33.24%; found: C, 24.78; H, 5.16; N, 7.20; V, 32.85%
- [12] IR spectra of **6**: 520m; 563vw; 608m; 625m; 640m; 682w; 762s; 790m; 808m, 852vs; 870m; 890m; 913m; 945s; 975w, and **7**: 415vw; 440m; 475sh; 504m; 520m; 555m; 595sh; 640m; 685s; 755m; 792s; 855m; 880w; 945s; 975vs; 992s
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