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PREPARATION, CRYSTAL STRUCTURE AND THERMAL BEHAVIOUR OF COBALT-ETHYLENEDIAMINE-VANADATE

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ABSTRACT A new cobalt-ethylenediamine-vanadate $[Co(en)_3]^{3+}_2V_2O_7^{4-}HVO_4^{2-.}6H_2O$ has been synthesized and structurally characterized. The unit cell is triclinic, space group P1, a = 8.782(3)Å, b = 8.967(3)Å, c = 12.562(2)Å, α = 89.89(2)°, β = 105.30(2)°, γ = 116.01(3)°, V = 850.1(3)Å³, Z = 1. The thermal decomposition has been studied by thermogravimetry and simultaneous mass spectrometry (TG/MS) in different atmospheres, i.e. H₂, N₂ and O₂. As solid products elemental cobalt on V₂O₃, Co₂V₂O₇, Co₃V₂O₈ and VO_x have been obtained, and depending on the actual atmosphere different volatile products such as NH₃, H₂O, NO and CO₂. Independent of the pretreatment, reoxidation of the product phases leads to the ternary oxides Co₂V₂O₇ and Co₃V₂O₈. The microstructures have been studied by scanning electron microscopy (SEM). The product formed in hydrogen has been tested with respect to its catalytic activity for the reduction of NO with CO. MATERIALS INDEX : cobalt, oxides, vanadates, ethylenediamine

Introduction

In the ternary system Co-V-O only few phases with defined structures, i.e. $Co_3V_2O_8$, $Co_2V_2O_7$ and CoV_2O_6 , are known. In the compound $Co_3V_2O_8$ (orthorhombic, Cmca, (1)) cobalt (II+) occupies edge sharing oxygen octahedra and vanadium (V+) adopts a distorted tetrahedral coordination. Also in $Co_2V_2O_7$ (monoclinic, $P2_1/c$, (2)) cobalt occupies an octahedral coordination. The edge sharing CoO_6 -units form zig-zag-chains which are connected to neighboured chains by common edges. Vanadium (V+) shows tetrahedral coordination in form of $V_2O_7^{4-}$ -units.

In CoV_2O_6 (monoclinic, P2/m, (3)) the CoO_6 -octahedra are also edge sharing but they form isolated straight chains. The coordination of vanadium is changing as well. The oxygen polyhedra can be described as distorted trigonal bipyramids which are nearly identical to the ones observed in $V_2\text{O}_5$.

Of main interest was the question about the influence of the introduction of ethylenediamine (en) as a sterically demanding ligand on the coordination-polyhedra of the metals. The assumed answer was confirmed by this work : there is a transition from connected chain-elements to isolated building-units.

For the first time it was possible to obtain a vanadate with two different building-species. Those units are well known in the phase diagram of the polyvanadates (4). $V_2O_7^{4-}$ and HVO_4^{2-} exist in the same pH-range but at different vanadium concentrations.

A ternary vanadate containing cobalt in the oxidation state of +III was not known until now (5). This contribution focusses on the synthesis, structure determination and the characterization of the thermochemical reactivity of the new cobalt-en-vanadate, $[Co(en)_3]^{3+}_2V_2O_7^{4-}HVO_4^{2-}.6H_2O$, tris(ethylenediamine)cobalt(3+)divanadate(4-)hydrogenvanadate(2-)hexahydrate.

The role of the atmosphere is studied in order to determine its possible influences on the course of the decomposition. The properties of catalytically relevant degradation products depend strongly on their pretreatment, i.e. the thermochemical behaviour of the title compound. Thus the fundamental problem of a direct control of the product properties, e. g. catalytically active dispersed metal particles generated on defined supports at relatively low temperatures, can be tackled (6).

Experimental

<u>Preparation</u>: 1 - 10 g grained cobalt metal (purum, Fluka AG, Buchs/CH) is given to a 20% aqueous ethylenediamine solution (purum, 97%, Fluka AG, Buchs/CH). The solution was covered with parafilm (American Can Company/USA) and kept for three months at room temperature. Addition of 0.5g NH₄VO₃ or V₂O₅ to this solution ([Co] > 0.3 g/100ml, pH > 12 and -log [V] \approx 1) leads to the formation of orange crystals of tris(ethylenediamine)cobalt(3+)divanadate(4-)-hydrogenvanadate(2-)hexahydrate, [Co(en)₃]³⁺₂V₂O7⁴⁻HVO4^{2-.}6H₂O, up to 1 mm³ in size after two months. The crystals were isolated by filtration and washed with methanol.

<u>Characterization</u>: The thermal decomposition of the title compound was registered in different atmospheres on a modified Perkin-Elmer thermogravimetric system TGS-2. Evolved gas analysis was performed simultaneously with a Balzers QMG-511 quadrupole mass spectrometer coupled to the thermobalance. X-ray investigations of the solid products were performed using a Guinier-IV and a Guinier-Lenné camera with $CuK_{\alpha 1}$ radiation.

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Crystal Structure Determination: A single crystal with dimensions 0.53 x 0.23 x 0.09 mm³ was mounted on an Enraf-Nonius CAD4 single crystal diffractometer. Lattice parameters as well as the orientation matrix were determined with a standard least-squares routine using 25 automatically centered reflections (12.5°< θ <19.5°). Out to $\theta \le 30^\circ$ a total of 5272 (incl. standard reflections) data were collected using the ω -2 θ -scan technique with Miller indices -12 \leq h \leq 12, -12 \leq k \leq 12 and $0 \le 1 \le 17$. Four intensity control reflections remeasured every three hours gave no evidence for serious decay ($\leq 2\%$). The orientation was checked by five reflections which were remeasured every 300 data. Lorentz, polarization and numerical absorption corrections (min. and max. transmission factors are 0.5183 and 0.8779) were applied with six crystal faces. The structure was solved using the automatic Patterson interpretation routine in SHELXS-86 (7) with 5160 unique reflections. The mean | E²-1 | values for all groups (0kl, h0l, hk0 and hkl) compared with the theoretical values unambigously showed that the structure most probably was acentric. Therefore the first trial to solve the structure in the space group P $\overline{1}$ failed. Switching to the acentric space group P 1 revealed the solution of the structure. Some spurious peaks had to be omitted. The water molecules were found in a later stage in the difference maps. The R-values of the isotropic refinement were 6.97% and 7.43%. Two relatively high temperature parameters were observed for O(9) and O(10) : 0.114(6)Å² and 0.103(5)Å², these for the six water oxygen were between 0.042(2)Å² and 0.064(3)Å². In the stage of the refinement using anisotropic temperature parameters, the 46 non-hydrogen atoms were refined in two groups, with 217 and 196 parameters respectively. All H-atoms (except HW62 which was postulated) could be located in several difference Fourier syntheses. The positional parameters of the hydrogen atoms were not refined, their isotropic temperature parameters were set to fixed values $u_{iso} = 0.04 \text{Å}^2$. The final R- and R_w -values are 0.034 and 0.041, respectively using 4781 reflections with $F_0 > 6\sigma(F_0)$, at convergence $(\Delta/\sigma) \le 0.04$. The weighting scheme w = k/($\sigma^2(F)$ + 0.000075 F²) (k refined to 1.0403) based on intensity statistics and showed no significant dependence on the function minimized upon the magnitude of F_0 or $(\sin\theta/\lambda)$. The final difference Fourier map was nearly featureless with the highest residue of 0.82 e⁻/Å³ and -0.75 e⁻/Å³ (0.35Å from O(9)) as hole. The absorption correction and the refinement of the structure were carried out with SHELX-76 (8). The final structure was drawn with SCHAKAL 86 (9) und ORTEP (10). The scattering

(8). The final structure was drawn with SCHAKAL 86 (9) und ORTEP (10). The scattering factors as well as the corrections for anomalous dispersion for the neutral atoms were taken from (11).

Results and Discussion

Structural part: The crystallographic investigation led to the parameters given in Table 1. The positional and thermal parameters are summarized in Table 2. The bond distances are listed in Table 3.

TABLE 1 Crystallographic Data for [Co(en)3]2V2O7HVO4 • 6H2O.

Crystal system	triclinic
Space group	P 1
Cell dimensions	a = 8.782(3) Å
	b = 8.967(3) Å
	c = 12.562(2) A
	$\alpha = 89.89(2)^{\circ}$
	$\beta = 105.30(2)^{\circ}$
	$\gamma = 116.01(3)$
Z	1
Molecular weight	916.382 g/mol
Volume	850.1(3) Å ³
Density _{calc.}	1.790 g/cm ³
Density _{meas.}	1.77(3) g/cm ³
Final R-Value	0.0344
Final R _w -Value	0.0408

The observed Co-N distances are in accordance with reported values (12).

With a variation of only 0.017Å the two CoN₆-octahedra are nearly undistorted. As well the C-N-, C-C-, N-H- as the C-H-bond lengths correspond to observed values.

As expected the terminal V-O bonds are shorter (from 1.594Å to 1.695Å) than the distances between vanadium and the bridging oxygen atoms (O(11) : 1.780Å / 1.809Å, resp. O(4) : 1.817Å).

A selection of angles of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$ is listed in Table 4.

The standard deviations of the angles including H-atoms are about a factor ten too small because the H-positions are not refined. The difference of the angles in CoN_6 compared with ideal octahedra is max. 5° and is also observed in $[Co(NO_2)(en)_2]NO_3$ (12).

The N-C-C angles are fixed by the geometry of the ligand and show only slight variation $(107^{\circ} \pm 2^{\circ})$.

Comparing the angles around vanadium leads to an analogous result as observed for the bond lengths : the VO₄-tetrahedra of the $V_2O_7^{4-}$ -unit are more distorted than the one in the HVO₄²⁻-unit. The V-O-V angle is not far from the ones found in metavanadates (145° ± 2°), but much different from the V-O-V angle of 117° in Co₂V₂O₇.

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TABLE 2

Atomic Coordinates for $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$,

 $U_{eq} = 1/3 \Sigma_i \Sigma_j u_{ij} \cdot a^*_i \cdot a^*_j \cdot a_i \cdot a_j.$

Atom	x/a	y/b	z/c	Ueq [Å ²]
Co(1)	0.0000	0.0000	0.0000	0.0250(1)
N(11)	-0.0457(5)	0.1698(4)	0.0657(3)	0.0377(7)
C(11)	0.0921(6)	0.3388(5)	0.0596(4)	0.044(1)
C(21)	0.1277(6)	0.3313(5)	-0.0507(5)	0.051(1)
N(21)	0.1619(5)	0.1854(5)	-0.0613(3)	0.0507(9)
N(12)	-0.1815(5)	-0.1785(4)	0.0539(3)	0.0364(7)
C(12)	-0.3590(6)	-0.2192(5)	-0.0205(4)	0.045(1)
$\hat{C}(22)$	0.6542(6)	-0.2093(5)	-0.1383(4)	0.0389(9)
N(22)	-0.1948(5)	-0.0459(4)	-0.1358(3)	0.0379(7)
N(13)	0.1939(5)	0.0343(5)	0.1352(3)	0.0405(8)
C(13)	0.2928(8)	-0.0564(8)	0.1138(5)	0.074(1)
C(23)	0.1712(9)	-0.2068(7)	0.0371(5)	0.071(1)
N(23)	0.0618(5)	-0.1617(4)	-0.0595(3)	0.0404(8)
Co(2)	0.75696(8)	0.40303(7)	0.54321(5)	0.0221(1)
N(14)	0.5557(5)	0.2409(5)	0.4211(3)	0.0381(8)
C(14)	0.5251(7)	0.0696(6)	0.4440(4)	0.048(1)
C(24)	0.5441(6)	0.0668(5)	0.5657(4)	0.049(1)
N(24)	0.7155(5)	0.2099(5)	0.6274(3)	0.0425(8)
N(15)	0.9654(5)	0.5468(4)	0.6661(3)	0.0366(7)
C(15)	1.1137(6)	0.5093(5)	0.6654(3)	0.0385(9)
C(25)	1.1099(6)	0.4958(6)	0.5455(4)	0.044(1)
N(25)	0.9258(5)	0.3719(5)	0.4809(3)	0.0420(8)
N(16)	0.7790(5)	0.5936(4)	0.4591(2)	0.0374(8)
C(16)	0.6318(6)	0.6332(5)	0.4604(4)	0.0433(9)
C(26)	0.6162(6)	0.6245(5)	0.5762(4)	0.044(1)
N(26)	0.6060(5)	0.4626(4)	0.6071(3)	0.0365(7)
V(1)	0.0638(1)	0.04918(9)	0.59567(6)	0.0258(1)
O(1)	-0.0357(4)	0.0618(4)	0.4646(2)	0.0439(7)
O(2)	0.0860(5)	-0.1267(4)	0.6006(3)	0.059(1)
O(3)	-0.0462(5)	0.0606(4)	0.6832(3)	0.0547(8)
0(4)	0.2811(4)	0.2296(4)	0.6356(2)	0.0393(6)
V(2)	0.7008(1)	0.3989(1)	0.17101(6)	0.0364(1)
V(3)	0.6672(1)	0.36197(9)	-0.10144(6)	0.0282(1)
O(5)	0.8073(5)	0.5034(4)	-0.1639(2)	0.0510(8)
O(6)	0.4679(4)	0.3493(4)	-0.1522(3)	0.0526(8)
0(7)	0.6604(5)	0.1754(4)	-0.1252(4)	0.075(1)
O(8)	0.5015(7)	0.3780(6)	0.1624(5)	0.122(2)
O(9)	0.8605(11)	0.5590(8)	0.2660(5)	0.144(2)
O(10)	0.7132(9)	0.2388(9)	0.2192(7)	0.170(3)
0(11)	0.7556(5)	0.4468(5)	0.0444(2)	0.067(1)
O(W1)	0.2098(6)	0.2632(5)	0.3468(4)	0.081(1)
O(W2)	-0.2475(5)	-0.0319(5)	0.2444(3)	0.0557(9)
O(W3)	0.0800(7)	0.8721(6)	0.3225(4)	0.093(1)
O(W4)	0.3178(5)	0.9137(5)	0.8143(3)	0.062(1)
U(W5)	0.4476(4)	0.6610(4)	0.1887(3)	0.0555(9)
U(W0)	0.2203(7)	0.5/13(6)	0.3208(4)	0.109(1)

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TABLE 3

Bond Distances in Å of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$.

Co(1) Co(1)	- - -	N(11) N(12) N(13)	1.968(5) 1.972(4) 1.974(4)	Co(1) - Co(1) - Co(1) -	N(21) N(22) N(23)	1.969(4) 1.962(4) 1.966(5)
N(11) C(21) N(11) C(11) C(21) N(21)		C(11) N(21) H(112) H(114) H(214) H(212)	1.486(5) 1.478(9) 0.901(4) 0.834(7) 1.028(6) 1.121(5)	C(11) - N(11) - C(11) - C(21) - N(21) -	C(21) H(111) H(113) H(213) H(211)	1.507(9) 0.918(4) 0.920(5) 0.989(5) 0.956(4)
N(12) C(22) N(12) C(12) C(22) N(22)		C(12) N(22) H(122) H(124) H(224) H(222)	1.473(6) 1.477(5) 1.036(5) 0.917(7) 0.925(5) 0.971(4)	C(12) - N(12) - C(12) - C(22) - N(22) -	C(22) H(121) H(123) H(223) H(221)	1.513(8) 0.883(4) 0.940(5) 0.972(6) 1.050(5)
N(13) C(23) N(13) C(13) C(23) N(23)	-	C(13) N(23) H(132) H(134) H(234) H(232)	1.494(11) 1.511(8) 1.015(4) 0.989(7) 1.095(7) 0.918(5)	C(13) - N(13) - C(13) - C(23) - N(23) -	C(23) H(131) H(133) H(233) H(231)	1.445(8) 0.920(5) 1.085(7) 1.190(9) 0.805(3)
V(1) V(1) O(4)	- -	O(1) O(3) H(O4)	1.678(4) 1.673(5) 0.889(3)	V(1) - V(1) -	O(2) O(4)	1.671(5) 1.817(3)
V(2) V(2) V(3) V(3) Co(2) Co(2) Co(2)	-	O(8) O(10) O(11) O(6) N(14) N(15) N(16)	1.649(7) 1.594(9) 1.809(4) 1.649(4) 1.978(3) 1.961(3) 1.971(4)	V(2) - V(2) - V(3) - V(3) - Co(2) - Co(2) - Co(2) -	O(9) O(11) O(5) O(7) N(24) N(25) N(26)	1.676(6) 1.780(4) 1.695(4) 1.673(5) 1.973(4) 1.966(6) 1.968(5)
N(14) C(24) N(14) C(14) C(24) N(24)		C(14) N(24) H(142) H(144) H(244) H(242)	1.480(7) 1.486(5) 0.923(5) 0.965(4) 0.795(7) 1.017(5)	C(14) - N(14) - C(14) - C(24) - N(24) -	C(24) H(141) H(143) H(243) H(241)	1.495(9) 0.863(4) 0.832(7) 1.009(6) 1.052(6)
N(15) C(25)	-	C(15) N(25)	1.483(8) 1.497(5)	C(15) - N(15) -	C(25) H(151)	1.502(7) 0.902(4)
N(15) C(15) C(25) N(25)	- - -	H(152) H(154) H(254) H(252)	0.965(5) 0.982(5) 0.915(5) 0.989(4)	C(15) - C(25) - N(25) -	H(153) H(253) H(251)	0.878(4) 0.884(7) 0.951(5)

N(16)	-	C(16)	1.487(9)	C(16) -	C(26)	1.496(8)
C(26)	-	N(26)	1.472(7)	N(16) -	H(161)	1.181(4)
N(16)	-	H(162)	0.867(3)	C(16) -	H(163)	0.882(4)
C(16)	-	H(164)	0.743(5)	C(26) -	H(263)	0.916(4)
C(26)	-	H(264)	0.941(6)	N(26) -	H(261)	0.945(4)
N(26)	-	H(262)	0.928(4)			
O(W1)	-	H(W11)	0.971(5)	O(W1) -	H(W12)	0.994(5)
O(W2)	-	H(W21)	0.907(4)	O(W2) -	H(W22)	0.933(5)
O(W3)	-	H(W31)	0.894(5)	O(W3) -	H(W32)	0.998(7)
O(W4)	-	H(W41)	0.757(3)	O(W4) -	H(W42)	0.784(5)
O(W5)	-	H(W51)	0.864(3)	O(W5) -	H(W52)	0.844(5)
O(W6)	-	H(W61)	0.755(6)	O(W6) -	H(W62)	1.003(8)

TABLE 4

Angles [°] of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O_1$.

N(11)	-	Co(1)	-	N(21)	85.9(2)	N(11)	-	Co(1)	- N(12)	90.5(2)
N(12)	-	Co(1)	-	N(21)	174.0(2)	N(11)	-	Co(1)	- N(22)	91.4(2)
N(21)	-	Co(1)	-	N(22)	90.2(2)	N(12)	-	Co(1)	- N(22)	85.1(2)
N(11)	-	Co(1)	-	N(13)	91.2(2)	N(13)	-	Co(1)	- N(21)	91.4(2)
N(12)	-	Co(1)	-	N(13)	93.5(2)	N(13)	-	Co(1)	- N(22)	177.1(2)
N(11)	-	Co(1)	-	N(23)	176.2(1)	N(21)	-	Co(1)	- N(23)	92.4(2)
N(12)	-	Co(1)	-	N(23)	91.4(2)	N(22)	-	$C_0(1)$	- N(23)	92.0(2)
N(13)	-	Co(1)	-	N(23)	85.5(2)	. ,			xy	
N(11)	-	C(11)	-	C(21)	107.0(4)	N(21)	-	C(21)	- C(11)	107.7(5)
N(12)	-	C(12)	-	C(22)	107.5(5)	N(22)	-	C(22)	- $C(12)$	106.2(3)
N(13)	-	C(13)	-	C(23)	109.2(6)	N(23)	-	$\hat{C}(23)$	-C(13)	108.4(6)
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N(14)	-	Co(2)	-	N(24)	85.4(2)	N(14)	-	Co(2)	- N(15)	174.2(2)
N(15)	-	Co(2)	-	N(24)	90.5(2)	N(14)	-	Co(2)	- N(25)	90.7(2)
N(24)	-	Co(2)	-	N(25)	94.3(2)	N(15)	-	$C_0(2)$	- N(25)	85.5(2)
N(14)	-	Co(2)	-	N(16)	92.6(2)	N(16)	-	$C_0(2)$	- N(24)	1753(2)
N(15)	-	Co(2)	-	N(16)	91.8(2)	N(16)	-	$C_0(2)$	- N(25)	90.0(2)
N(14)	-	Co(2)	-	N(26)	93.9(2)	N(15)	-	$C_0(2)$	- N(26)	90.3(2)
N(16)	-	Co(2)	-	N(26)	84.9(2)	N(24)	-	$C_0(2)$	- N(26)	91.0(2)
N(25)	-	$C_0(2)$	-	N(26)	173.3(2)			00(2)	11(20)	1.0(2)
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N(14)	-	C(14)	-	C(24)	106.6(4)	N(24)	_	C(24)	-C(14)	108 1(4)
N(15)	-	C(15)	-	C(25)	105.5(4)	N(25)	-	C(25)	-C(15)	107 1(4)
N(16)	-	C(16)	-	C(26)	106.9(4)	N(26)	-	C(26)	- C(16)	107.0(5)
								-()	-()	
0(1)	-	V(1)	-	O(2)	110.0(2)	0(1)	-	V(1)	- O(3)	111.6(2)
O(2)	-	V(1)	-	0(3)	111.0(2)	$\dot{0}(1)$	-	V(1)	- 0(4)	106.1(2)
O(2)	-	VÌÌ	-	0(4)	109.7(2)	0(3)	-	$\mathbf{v}_{(1)}$	- 0(4)	108.2(2)
V(1)	-	O(4)	-	H(O4)	116.8(3)	0(5)		•(•)	0(1)	100.2(2)
. ,		- ()								
O(8)	-	V(2)	-	0(9)	112.2(4)	O(8)	-	V(2)	-0(10)	107.7(4)
0(9)	-	V(2)	-	0(10)	103.7(4)	O(8)	-	$v(\bar{2})$	- 0(11)	112.1(3)
0(9)	-	$\dot{V(2)}$	-	0(11)	104,4(3)	O(10)	-	V(2)	- 0(11)	116.6(4)
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O(5) O(6) O(6) V(2)		V(3) V(3) V(3) O(11)		O(6) O(7) O(11) V(3)	109.2(2) 110.1(2) 109.9(2) 138.9(2)	0(5) 0(5) 0(7)	-	V(3) V(3) V(3)	• • •	O(7) O(11) O(11)	109.: 104.9 113.:	3(3) 9(2) 2(3)
H(W11) H(W31) H(W51)	- - -	O(W1) O(W3) O(W5)	- - -	H(W12) H(W32) H(W52)	105.3(6) 134.9(8) 95.2(4)	H(W21) H(W41) H(W61)	- - -	O(W2) O(W4) O(W6)	•	H(W22) H(W42) H(W62)	88.3 118.2 104.3	3(3) 2(6) 8(7)

The hydrogen bonds found are listed in Table 5. 23 linear N-H-O and 13 O-H-O hydrogen bridges are observed with usual distances and angles.

TABLE 5

Hydrogen Bonds of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$.

i	-	j	k	ij	jk	ik	< ijk	sym.code
N(12)	-	H(122)	0(11)	1.036(5)	2.280(5)	3.155(7)	141.1(2)°	-1+x, -1+y, z
N(13)	-	H(131)	O(W3)	0.920(5)	2.051(6)	2.933(8)	160.1(4)°	x, -1+y, z
N(13)	-	H(132)	O(8)	1.015(4)	2.035(5)	3.022(6)	163.4(4)°	x, y, z
N(21)	-	H(211)	O(8)	0.956(4)	2.379(6)	3.294(7)	160.1(4)°	x, y, z
N(21)	-	H(212)	O(3)	1.121(5)	2.341(3)	3.166(6)	128.7(3)°	x, y, -1+z
N(21)	-	H(212)	O(6)	1.121(5)	2.371(4)	2.972(7)	111.6(2)°	x, y, z
N(22)	-	H(221)	O(7)	1.050(5)	1.762(6)	2.806(8)	172.3(3)°	x, y, z
N(22)	-	H(222)	O(3)	0.971(4)	1.930(4)	2.872(6)	162.8(3)°	x, y, -1+z
N(23)	-	H(231)	O(5)	0.805(4)	2.146(4)	2.884(4)	152.6(3)°	-1+x, $-1+y$, z
N(23)	-	H(232)	O(W4)	0.918(5)	2.040(6)	2.927(7)	162.2(4)°	x, -1+y, -1+z
N(14)	-	H(141)	O(10)	0.863(4)	2.38 (1)	3.20 (1)	158.9(4)°	x, y, z
N(14)	-	H(142)	O(W1)	0.923(5)	2.147(6)	3.029(8)	159.6(3)°	x, y, z
N(15)	-	H(151)	0(5)	0.902(4)	1.998(5)	2.779(6)	144.1(3)°	x, y, 1+z
N(15)	-	H(152)	O(2)	0.965(5)	2.013(4)	2.846(6)	143.5(3)°	1+x, 1+y, z
N(16)	-	H(161)	O(9)	1.181(4)	1.74 (1)	2.76 (1)	140.5(4)°	x, y, z
N(16)	-	H(162)	0(2)	0.867(3)	2.311(3)	2.877(5)	123.0(3)°	1+x, 1+y, z
N(24)	-	H(241)	O(3)	1.052(6)	1.873(5)	2.889(8)	161.4(3)°	1+x, y, z
N(24)	-	H(242)	O(7)	1.017(5)	2.312(6)	3.264(8)	155.4(3)°	x, y, 1+z
N(25)	-	H(251)	O(1)	0.951(5)	2.014(5)	2.959(7)	172.2(3)°	1+x, y, z
N(25)	-	H(252)	O(10)	0.989(4)	2.379(8)	3.246(9)	146.0(3)°	x, y, z
N(25)	-	H(252)	O(9)	0.989(4)	2.387(8)	3.231(9)	142.8(3)°	x, y, z
N(26)	-	H(261)	O(5)	0.945(4)	1.951(4)	2.879(5)	166.5(4)°	x, y, 1+z
N(26)	-	H(262)	O(4)	0.928(4)	1.946(4)	2.818(5)	155.6(3)°	x, y, z
O(4)	-	H (O4)	O(6)	0.889(3)	1.806(3)	2.666(5)	162.3(3)°	x, y, 1+z
O(W1)	-	H(W11)	O(W6)	0.971(6)	1.775(7)	2.745(9)	176.8(3)°	x, y, z
O(W1)	-	H(W12)	O(1)	0.994(6)	1.917(4)	2.891(7)	165.8(4)°	x, y, z
O(W2)	-	H(W21)	O(1)	0.907(4)	1.875(3)	2.781(5)	178.2(4)°	x, y z
O(W2)	-	H(W22)	O(10)	0.933(5)	1.72 (1)	2.61 (1)	156.1(3)°	-1+x, y, z
O(W3)	-	H(W31)	O(9)	0.894(5)	1.692(6)	2.577(8)	170.0(6)°	-1+x, y, z
O(W3)	-	H(W32)	O(1)	0.998(7)	2.209(5)	3.098(9)	147.6(4)°	x, 1+y, z
O(W4)	-	H(W41)	O(7)	0.757(4)	2.037(4)	2.783(5)	168.6(5)°	x, 1+y, 1+z
O(W4)	-	H(W42)	O(2)	0.784(5)	2.044(4)	2.820(6)	170.5(3)°	x, 1+y, z

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O(W5) -	H(W51) O(W2)	0.864(3)	1.930(4)	2.792(5)	175.0(4)°	1+x, 1+y, z
O(W5) -	H(W52) O(8)	0.844(5)	2.024(7)	2.813(9)	155.4(3)°	x, y, z
O(W6) -	H(W61) O(W5)	0.755(6)	2.076(5)	2.778(8)	154.8(6)°	x, y, z
O(W6) -	H(W62) O(9)	1.003(8)	2.318(9)	3.00 (1)	124.6(3)°	-1+x, y, z

The compound is built up of the quasi-isolated units $Co(en)_3^{3+}$, HVO_4^{2-} , $V_2O_7^{4-}$ and water, the hydrogen bridges being responsible for the stability of the structure.

The SCHAKAL-plot in FIG. 1 shows the building units of [Co(en)3]2V2O7HVO4 · 6H2O.



FIG. 1 Structural building units of [Co(en)₃]₂V₂O₇HVO₄ · 6H₂O.

The central $Co(2)(en)_3^{3+}$ -units are surrounded by vanadates and water-molecules. The $Co(1)(en)_3^{3+}$ -complexes in the corners of the cell (FIG. 2) are in direction **b** connected by Vander-Waals-contacts and in direction **a** surrounded by $V_2O_7^{4-}$ -units and water resp. in direction **c** by HVO_4^{2-} and H_2O .

Additional material to this structure can be ordered from (13).

<u>Thermal behaviour</u>: The decomposition of the starting material was studied by thermogravimetry and simultaneous mass spectrometry in different atmospheres, i.e. H₂, N₂ and O₂ at a temperature



FIG. 2 Stereo projection of the structure of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$.

range of 25 - 800°C. It was not possible to take REM-pictures of the initial crystals because of decomposition during evacuation. This instability of the compound was also observed by TG-measurements. The possibility of detecting the sixth water molecule was a function of the evacuation time.

In flowing hydrogen atmosphere the evaporation of the crystal water molecules is registered in three endothermic steps with the ratio 3:1:1 and is finished at 150°C. The sixth water molecule must be lost during evacuating. As it can be seen in FIG. 3 the actual decomposition takes place between 200°C - 500°C with a total weight loss of 62.4% (theoretical 62.6%, without crystal water 50.8%) and leads to the formation of Co° and V₂O₃. These products can be explained formally by the equation:

$$[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O + 6H_2 \rightarrow 2Co^* + 1\frac{1}{2}V_2O_3 + 6en + 12\frac{1}{2}H_2O_3$$

The weight loss of the first two endothermal steps and of the third exothermal step cannot be explained with specific stoichiometric changes, i.e. formation of defined intermediates. The mass spectrometric measurements show for the first two steps three different mass-signals with m/e = 17 (NH₃⁺, OH⁺), m/e = 18 (H₂O⁺) and m/e = 30 (NO⁺). The last step is accompanied by emission of only water and NH₃. During the whole experiment there was no CO₂ (m/e = 44) detected.

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Combined TG/MS curves of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$ in hydrogen. Sample weight, heating rate and gas flow are inserted.

The morphology of the crystals decomposed in hydrogen is shown in FIG. 4. The initial shape is more or less conserved, although without any strong indication for oriented decomposition. The reoxidation of the H₂-decomposed samples was examined by X-ray analysis using a Guinier-Lenné camera and summarized in the following scheme :

H₂-decomposed phases in O₂

Temperature [°C]



FIG. 4

Scanning electron micrographs of [Co(en)3]2V2O7HVO4 · 6H2O decomposed in H2 at 600°C.

The elemental cobalt in the starting material cannot be identified by X-ray analysis. At about 250°C the V_2O_3 is oxidized to V_2O_5 . During the course of the oxidation an amorphous and unknown phase precedes to the formation of ternary vanadates. At around 500°C the reflections of the stable products $Co_2V_2O_7$ und $Co_3V_2O_8$ are observed.

With respect to weight loss and gaseous reaction products, the decomposition of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$ in nitrogen is similar to the one in hydrogen, although its final point is shifted to a 200°C higher temperature. As solid products Co^o and V₂O₃ are formed as well.

In oxygen the loss of water takes place in two endothermic steps (FIG. 5) with the ratio 5:1 and is finished at 150°C. All six H₂O can be observed because in oxygen there was no need for previous evacuation of the thermobalance.

The actual decomposition takes place between 200°C - 500°C with a total weight loss of 51.7% (theoretical 52.1%, without crystal water 40.3%) and leads to the formation of the same products as after reoxidation, $Co_2V_2O_7$, $Co_3V_2O_8$ und V_2O_5 . The weight loss of the steps cannot be explained by the formation of well-defined intermediates.

The following formal equation explains the results :

 $4[\text{Co}(\text{en}_3)]_2\text{V}_2\text{O}_7\text{HVO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{Co}_2\text{V}_2\text{O}_7 + 2\text{Co}_3\text{V}_2\text{O}_8 + 3\text{V}_2\text{O}_5 + 24\text{en} + 26\text{H}_2\text{O} + 2\text{O}_2$

The MS-measurements show the distribution of the gaseous decomposition products. During the entire course of degradation there was no NH₃ found because the maxima at m/e = 17 originate from the OH-fragment peak of H₂O.

The first step of weight loss is accompanied by the evolution of H_2O (m/e = 18), NO (m/e = 30) and CO_2 (m/e = 44). During the second step mainly the formation of carbon dioxide is observed.

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The morphology of the oxidized crystals is fundamentally different from the ones in other atmospheres. The images are shown in FIG. 6. The shape of the initial crystals is not anymore recognizable because of sinter processes. The formation of the mixed phases $Co_2V_2O_7$, $Co_3V_2O_8$ (and V_2O_5) leads to a change of the morphology. Further magnifications of the surface show agglomerates of primary particles in the range of 1 µm up to 20 µm.

Catalytical activity: The catalytical behaviour was measured on the well known reaction :

 $2 \text{ NO} + 2 \text{ CO} \Rightarrow \text{N}_2 + 2 \text{ CO}_2$

The components of the reactor are described elsewhere (5). The NO was quantitatively analysed by the chemiluminescence-method using a CLD 502 (Tecan AG, Hombrechtikon/CH). Gas flow and concentrations were : 60ml/min 1250ppm NO and 2.25% CO in Ar.

1g of catalyst, i.e. Co^o on V₂O₃ obtained from the decomposition of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$ in H₂ was used. The results of the measurements of the catalytical activity are shown in FIG. 7. A 50% conversion is found at a temperature of 140°C. No NO was detected above 220°C, i.e. the catalyst reaches its full conversion rate. During a run of seven hours at 300°C the activity was

stable. Compared with other catalysts generated from different precursors (5) the activity of this compound is considered to be quite high.



FIG. 6 Scanning electron micrographs of [Co(en)3]2V2O7HVO4 • 6H2O decomposed in O2 at 550°C.



FIG. 7 Catalytical behaviour of Co^o on V₂O₃ obtained from the thermal decomposition of $[Co(en)_3]_2V_2O_7HVO_4 \cdot 6H_2O$ in hydrogen.

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Conclusions

This work demonstrates that by careful choice of nearby equilibrium conditions the generation of well defined complex precursor phases is possible, i.e. a cobalt(III) central ion surrounded by voluminous amine ligands, in combination with two different kinds of vanadate oxoanions. Their presence in one and the same structure is to our knowledge new. By varying the degradation conditions of such precursors a rich spectrum of solid products may be obtained and interesting, although complicated thermochemical behaviours are observed. In this context, the influence of the actual atmosphere on the mechanistic course of heterogeneous solid state reactions is decisive, and volatile decomposition products need to be carefully monitored e.g. by mass spectrometry.

To further elucidate the interrelation between preparation, studies of the reactivity and potential products of a given initial solid, it is necessary to test the decomposed materials obtained. Our results prove that catalytically relevant processes are most suitable respective means. In turn, these informations can be used for the appropriate preparation or treatment of the precursor respectively the pre-treatment of the catalyst. Further work and results of investigations on related heterogeneous catalysts are contained in (5).

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