Electronic Supplementary Information

Catalysis of “Outer-Phase” Oxygen Atom Exchange Reactions by Encapsulated “Inner-Phase” Water in \( \{V_{15}Sb_6\}\)-type Polyoxovanadates

Michael Wendt\textsuperscript{a,*}, Ulrike Warzok\textsuperscript{b,*}, Christian Näther\textsuperscript{a}, Jan van Leusen\textsuperscript{c}, Paul Kögerler\textsuperscript{c}, Christoph A. Schalley\textsuperscript{c,#}, Wolfgang Bensch\textsuperscript{a,#}

\textsuperscript{a} Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany
\textsuperscript{b} Institut für Chemie und Biochemie der Freien Universität, Takustr. 3, 14195 Berlin, Germany
\textsuperscript{c} Institut für Anorganische Chemie, RWTH Aachen, Landoltweg 1, 52074 Aachen, Germany

Contents

Spectroscopic Characterization

Crystallographic Data

Magnetic Properties

Electrospray Mass Spectrometry

Figure S1 IR spectra of compounds I – III

Table S1 Assignment of the IR peaks of compounds I – III

Figure S2 TG curve of I

Figures S3 + S4 Powder Diffraction Patterns of I – III and IV

Figure S5 SEM pictures of all new compounds I – IV

Figure S6 UV/Vis Absorption spectra for Solubility Studies

Table S2 – S6 Crystallographic Data

Figure S7 Arrangement of the cluster anions and transition metal complex cations of IV

Table S7 – S10 Bond length and angles of the transition metal amine complexes in I – IV

Table S11 – S14 Hydrogen interactions in I – IV

Figure S8 Molar magnetization \( M_m \) as a function of the applied field \( B \)

Table S15 Parameters of the “full model” simulations

Electrospray Mass Spectrometry

References
1. IR Spectra

In Figure S1, the IR spectra of compounds I – III are displayed. As compound IV is a (pseudo)polymorph of I, both have equal IR spectra. All bands were assigned to the organic molecules or to the cluster vibrations. The values and assignments are listed in Table S1.

![IR Spectra of compounds I – III](image)

**Figure S1.** IR spectra of compounds I – III.

| wavenumber [cm⁻¹] | assignment                      |
|-------------------|---------------------------------|
|                  | **Compound I** | **Compound II** | **Compound III** |
| 3256             | crystal water, NH₂-stretch      |
| 2927             | CH₂ stretch                   |
| 2877             |                                |
| 1582             | NH₂ deformation               |
| 1458             | CH₃ deformation               |
| 1331             | OH deformation                |
| 954              | V⁴=O stretch                  |
| 700              | M-O-M stretch                 |
| 615              | M-O-M stretch                 |
2. Thermogravimetric Analysis

Figure S2 shows a DTA-TG curve of compound I as a representative example. For all compounds, first a weight loss due to water emission is observed being in accordance with the presence of ca. 15 water molecules in compounds I – III. The different not well resolved mass steps cannot be assigned to individual decomposition reactions. For compound IV, the first mass loss was ≈ 13 % and corresponds to the emission of ca. 28 water molecules.

Previous DTA-TG experiments on Sb-POVs\textsuperscript{1} displayed analogous behavior resulting in no distinct steps for the decomposition and the weight loss above 700 °C is assigned to the sublimation of antimony, which is in agreement with our measurements.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figureS2.png}
\caption{TG-curve (black) and DTG-curve (dotted) of compound I ([Ni(en)]\textsubscript{3} [V\textsubscript{15}Sb\textsubscript{6}O\textsubscript{42}(H\textsubscript{2}O)]xH\textsubscript{2}O (heating rate: 1 K min\textsuperscript{-1}).}
\end{figure}
3. Powder Diffraction Patterns

Figures S3 and S4 indicate phase purity of all four compounds I – IV as evidenced by a comparison of experimental powder patterns with calculated patterns using single crystal data. Both reflection intensities and 2θ angles are in excellent agreement with the calculated diffractions.

a)

b)
Figure S3. Measured (red) and calculated (black) powder diffraction patterns of compound I.

Figure S4. Measured (black) and calculated (red) powder diffraction patterns of compound IV.
4. Crystal Morphology

Figure S5 shows the morphology of the crystals of compounds I - IV. The crystal sizes could be determined to be around 1200 x 200 μm for I-III and 1000 x 125 μm for IV.

Figure S5. SEM pictures of compound I (top left), pseudopolymorphic compound IV (top right), bottom left: II and d) bottom right: III.
5. Calibration of the UV/Vis Absorption at 320 nm for Solubility Studies

The absorption vs. concentration calibration curve was obtained by dissolving I in different, defined concentrations in water (1.31·10⁻⁵ M, 2.30·10⁻⁵ M, 3.28·10⁻⁵ M, 4.27·10⁻⁵ M, 5.58·10⁻⁵ M) and measuring the UV/Vis spectra of these solutions. The peak maximum at 320 nm was evaluated and its absorption plotted against the sample concentration. A saturated solution of I in water was diluted by a factor of 1:25 to be in the concentration range of the calibration curve. The concentration was determined from its absorption at 320 nm and calculated back to that of the to determine the maximal solubility of I in water (1.19 g L⁻¹).

![Figure S6. UV/Vis spectrum of I dissolved in water (top) and the calibration curve obtained from the peak maxima at 320 nm used to determine the maximal solubility (bottom).](image-url)
6. Crystallographic Data

Table S2 summarizes information on single crystal structure refinement and shows clearly the similarity of the isostructural compounds I – III and the differences to the (pseudo)polymorphic compound IV.

Table S2 Selected crystal data and details of the structure refinement.

|                      | III C_{18}H_{92}N_{18}Fe_{3}V_{15}Sb_{6}O_{52} | II C_{18}H_{92}N_{18}Co_{3}V_{15}Sb_{6}O_{52} | I C_{18}H_{92}N_{18}Ni_{3}V_{15}Sb_{6}O_{52} | IV C_{18}H_{92}N_{18}Ni_{3}V_{15}Sb_{6}O_{43} |
|----------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Formula              | C_{18}H_{92}N_{18}Fe_{3} V_{15}Sb_{6}O_{52}   | C_{18}H_{92}N_{18}Co_{3} V_{15}Sb_{6}O_{52}   | C_{18}H_{92}N_{18}Ni_{3} V_{15}Sb_{6}O_{52}   | C_{18}H_{92}N_{18}Ni_{3} V_{15}Sb_{6}O_{43}   |
| MW / g·mol⁻¹         | 3055.24                                       | 3064.48                                       | 3063.82                                       | 2901.67                                       |
| crystal system       | monoclinic                                    | monoclinic                                    | monoclinic                                    | trigonal                                       |
| space group          | C2                                            | C2                                            | C2                                            | P321                                          |
| a /Å                 | 18.1991(4)                                    | 18.2302(14)                                   | 18.2404(7)                                    | 23.7437(5)                                    |
| b /Å                 | 22.6260(6)                                    | 22.6142(16)                                   | 22.7636(7)                                    | 23.7437(5)                                    |
| c /Å                 | 14.3614(3)                                    | 14.4067(11)                                   | 14.3542(5)                                    | 14.9586(3)                                    |
| α /°                 | 90                                            | 90                                            | 90                                            | 90                                            |
| β /°                 | 126.1930(10)                                  | 126.360(7)                                    | 126.449(3)                                    | 90                                            |
| γ /°                 | 90                                            | 90                                            | 90                                            | 120                                           |
| V / Å³               | 4772.49(19)                                   | 4783.0(6)                                     | 4794.2(3)                                     | 7303.3(3)                                     |
| T / K                | 200                                           | 200                                           | 293                                           | 200                                           |
| Z                    | 2                                             | 2                                             | 2                                             | 3                                             |
| D_{calc} / Mg·m⁻³    | 2.114                                         | 2.115                                         | 2.110                                         | 1.9767                                        |
| μ / mm⁻¹             | 3.582                                         | 3.639                                         | 3.700                                         | 3.631                                         |
| θ_{max} /°           | 27.94                                         | 28.00                                         | 27.00                                         | 25.00                                         |
| measured refl.       | 37515                                         | 19592                                         | 14462                                         | 38040                                         |
| unique refl.         | 11411                                         | 10404                                         | 8392                                          | 8614                                          |
| R_{int}              | 0.0448                                        | 0.0647                                        | 0.0274                                        | 0.0717                                        |
| refl. with F/4σ(F0)  | 11411                                         | 10404                                         | 8392                                          | 8614                                          |
| Parameters           | 503                                           | 503                                           | 503                                           | 463                                           |
| R₁ [F > 4σ(F₀)]      | 0.0324                                        | 0.0453                                        | 0.0382                                        | 0.0580                                        |
| wR₂ (all refl.)      | 0.0768                                        | 0.1187                                        | 0.0941                                        | 0.1438                                        |
| GOF                  | 1.058                                         | 1.045                                         | 1.027                                         | 0.987                                         |
| Δρ_{max/min} / e·Å⁻³ | 1.169/-0.922                                  | 1.867/-1.609                                  | 1.249/-1.070                                  | 1.338/-0.862                                  |
Flack-x-parameter  -0.02(2)  -0.07(3)  -0.006(19)  -0.028(19)

Bond valence sum (BVS)\(^{[2]}\) yield following values:

Compound I: V 3.95 – 4.06, average: 4.00 and Sb 3.21 – 3.46, average: 3.37;

Compound II: V 3.90 – 4.06, average: 3.99 and Sb 3.21 – 3.48, average: 3.37;

Compound III: V 3.92 – 4.04, average 4.00 and Sb 3.38 – 3.61, average: 3.51;

Compound IV V 3.82 – 4.12, average: 4.01 and Sb 3.29 – 3.53, average: 3.45.

All values are in the typical range of antimonato-polyoxovanadates.\(^{[1b,c,d,e,h]}\)

The V-O bond lengths can be divided into four groups (Tables S3 – S6): Oa terminal V=O, Ob Sb-µ-O between two Sb atoms; Oc Sb/V-µ-O between two V and one Sb atom; Od V-µ-O with only V atoms are involved.

Table S3 Bond lengths of the four different oxygen atom types of I in Å.

| Type | Atom | V  | V  | V  | Sb  | Sb  |
|------|------|----|----|----|-----|-----|
| Oa   | O7   | 1.606(6) |    |    |     |     |
| Oa   | O9   | 1.596(8)  |    |    |     |     |
| Oa   | O11  | 1.619(5)  |    |    |     |     |
| Oa   | O13  | 1.620(6)  |    |    |     |     |
| Oa   | O16  | 1.611(6)  |    |    |     |     |
| Oa   | O19  | 1.609(5)  |    |    |     |     |
| Oa   | O20  | 1.615(6)  |    |    |     |     |
| Oa   | O21  | 1.600(5)  |    |    |     |     |
| Ob   | O1   | 1.933(6)  | 1.909(6) |    |     |
| Ob   | O22  | 1.926(4)  | 1.926(4) |    |     |
| Oc   | O2   | 1.967(6)  | 2.009(5) | 1.945(5) |     |
| Oc   | O3   | 1.966(5)  | 1.982(6) | 1.977(5) |     |
| Oc   | O4   | 1.980(5)  | 1.983(5) | 1.948(5) |     |
| Oc   | O5   | 1.975(6)  | 2.006(6) | 1.927(5) |     |
| Oc   | O14  | 1.987(5)  | 1.984(6) | 1.932(5) |     |
| Oc   | O17  | 2.011(6)  | 1.967(6) | 1.953(6) |     |
| Od   | O6   | 1.913(5)  | 1.950(5) | 1.930(5) |     |
| Od   | O8   | 1.955(5)  | 1.932(4) | 1.955(5) |     |
| Od   | O10  | 1.931(6)  | 1.916(5) | 1.927(6) |     |
| Od   | O12  | 1.941(6)  | 1.929(5) | 1.957(5) |     |
| Od   | O15  | 1.922(5)  | 1.937(5) | 1.946(5) |     |
| Od   | O18  | 1.912(6)  | 1.913(5) | 1.940(6) |     |
### Table S4 Bond lengths of the four different oxygen atom types of II in Å.

| Type | Atom | V | V | V | Sb | Sb |
|------|------|---|---|---|----|----|
| Oa   | O7   | 1.615(3) |   |   |   |    |
| Oa   | O9   | 1.597(7) |   |   |   |    |
| Oa   | O11  | 1.624(5) |   |   |   |    |
| Oa   | O13  | 1.628(5) |   |   |   |    |
| Oa   | O16  | 1.616(5) |   |   |   |    |
| Oa   | O19  | 1.621(5) |   |   |   |    |
| Oa   | O20  | 1.614(6) |   |   |   |    |
| Oa   | O21  | 1.600(6) |   |   |   |    |
| Ob   | O1   |   |   | 1.958(5) | 1.921(6) |    |
| Ob   | O22  |   |   | 1.939(3) | 1.939(3) |    |
| Oc   | O2   | 1.969(5) | 2.007(5) |   | 1.953(5) |    |
| Oc   | O3   | 1.960(5) | 1.975(5) |   | 2.007(5) |    |
| Oc   | O4   | 1.979(5) | 1.981(5) |   | 1.963(5) |    |
| Oc   | O5   | 1.969(5) | 2.003(6) |   | 1.942(6) |    |
| Oc   | O14  | 1.971(6) | 1.986(6) |   | 1.956(6) |    |
| Oc   | O17  | 2.012(6) | 1.981(6) |   | 1.953(6) |    |
| Od   | O6   | 1.927(5) | 1.954(5) | 1.920(5) |   |    |
| Od   | O8   | 1.955(5) | 1.931(5) | 1.963(5) |   |    |
| Od   | O10  | 1.928(5) | 1.916(5) | 1.940(5) |   |    |
| Od   | O12  | 1.945(6) | 1.932(6) | 1.956(6) |   |    |
| Od   | O15  | 1.943(5) | 1.944(5) | 1.926(5) |   |    |
| Od   | O18  | 1.914(5) | 1.922(5) | 1.939(5) |   |    |

### Table S5 Bond lengths (Å) of the four different oxygen atom types of III in Å.

| Type | Atom | V | V | V | Sb | Sb |
|------|------|---|---|---|----|----|
| Oa   | O7   | 1.607(3) |   |   |   |    |
| Oa   | O9   | 1.612(5) |   |   |   |    |
| Oa   | O11  | 1.616(3) |   |   |   |    |
| Oa   | O13  | 1.628(4) |   |   |   |    |
| Oa   | O16  | 1.618(4) |   |   |   |    |
| Oa   | O19  | 1.619(4) |   |   |   |    |
| Oa   | O20  | 1.622(4) |   |   |   |    |
| Oa   | O21  | 1.598(4) |   |   |   |    |
| Ob   | O1   |   |   | 1.950(4) | 1.928(4) |    |
| Ob   | O22  |   |   | 1.942(3) | 1.942(3) |    |
| Oc   | O2   | 1.966(3) | 2.007(3) |   | 1.952(3) |    |
| Oc   | O3   | 1.960(3) | 1.966(3) |   | 2.005(3) |    |
| Oc   | O4   | 1.975(3) | 1.978(3) |   | 1.964(3) |    |
| Oc   | O5   | 1.967(4) | 2.001(4) |   | 1.941(3) |    |
| Oc   | O14  | 1.974(4) | 1.972(4) |   | 1.958(4) |    |
| Oc   | O17  | 2.007(4) | 1.982(4) |   | 1.950(4) |    |
| Od   | O6   | 1.913(3) | 1.946(3) | 1.929(3) |   |    |
| Od   | O8   | 1.951(3) | 1.937(3) | 1.960(3) |   |    |
| Od   | O10  | 1.933(4) | 1.907(4) | 1.929(4) |   |    |
| Od   | O12  | 1.942(4) | 1.930(4) | 1.959(4) |   |    |
| Od   | O15  | 1.950(4) | 1.942(4) | 1.916(4) |   |    |
| Od   | O18  | 1.914(4) | 1.918(4) | 1.938(4) |   |    |
Table S6 Bond lengths of the four different oxygen atom types in Å of IV.

| Type | Atom | V      | V      | Sb     | Sb     |
|------|------|--------|--------|--------|--------|
| Oa   | O16  | 1.608(12) |        |        |        |
| Oa   | O17  | 1.602(12) |        |        |        |
| Oa   | O20  | 1.605(12) |        |        |        |
| Oa   | O21  | 1.628(12) |        |        |        |
| Oa   | O22  | 1.653(11) |        |        |        |
| Ob   | O11  |        | 1.909(14) | 1.966(15) |        |
| Oc   | O12  | 1.981(13) | 2.013(14) |        | 1.942(13) |
| Oc   | O13  | 1.943(13) | 1.993(12) |        | 1.967(13) |
| Oc   | O14  | 1.966(12) | 1.956(13) |        | 1.984(12) |
| Oc   | O15  | 1.994(13) | 2.003(14) |        | 1.938(14) |
| Od   | O18  | 1.896(12) | 1.920(12) | 1.933(13) |        |
| Od   | O19  | 1.917(11) | 1.927(11) | 1.952(10) |        |
| Od   | O23  | 1.872(12) | 1.915(12) | 1.956(12) |        |
| Od   | O24  | 1.888(12) | 1.958(12) | 1.965(12) |        |

Figure S7 shows the arrangement of the (pseudo)polymorph compound IV with its discrete cluster anions and the Ni amine complexes as counter cations.

Table S7 shows the TM-N bond length and angles. All values are in typical ranges for known TM amine complex acting as counter cations in heteroatom incorporated POVs.
Figure S7. Arrangement of the cluster anions and transition metal complex cations of IV. Hydrogen atoms are not displayed for clarity.
Table S7 Selected bond lengths and bond angles of the Ni(en)$_3^{2+}$ cations in the crystal structure of compound I.

| Bond Lengths | Bond Angles          |
|--------------|----------------------|
| Ni(1)-N(2)   | 2.122(6)             | N(2)-Ni(1)-N(11) | 92.0(3) |
| Ni(1)-N(11)  | 2.124(9)             | N(2)-Ni(1)-N(22) | 92.1(3) |
| Ni(1)-N(22)  | 2.134(9)             | N(11)-Ni(1)-N(22) | 92.1(3) |
| Ni(1)-N(1)   | 2.139(8)             | N(2)-Ni(1)-N(1)  | 80.1(3) |
| Ni(1)-N(12)  | 2.140(7)             | N(11)-Ni(1)-N(1) | 96.7(3) |
| Ni(1)-N(21)  | 2.146(8)             | N(22)-Ni(1)-N(1) | 168.4(3) |
| Ni(2)-N(41)  | 2.119(8)             | N(2)-Ni(1)-N(12) | 170.1(3) |
| Ni(2)-N(32)  | 2.123(9)             | N(11)-Ni(1)-N(12) | 81.3(3) |
| Ni(2)-N(31)  | 2.131(8)             | N(41)-Ni(2)-N(32) | 171.5(4) |
|              |                      | N(41)-Ni(2)-N(31) | 93.4(4) |
|              |                      | N(32)-Ni(2)-N(31) | 81.1(4) |
|              |                      | N(22)-Ni(1)-N(12) | 95.3(3) |
|              |                      | N(1)-Ni(1)-N(12)  | 93.5(3) |
|              |                      | N(2)-Ni(1)-N(21)  | 94.4(3) |
|              |                      | N(11)-Ni(1)-N(21) | 170.5(3) |
|              |                      | N(22)-Ni(1)-N(21) | 80.6(3) |
|              |                      | N(1)-Ni(1)-N(21)  | 91.3(3) |
|              |                      | N(12)-Ni(1)-N(21) | 93.2(3) |
Table S8 Selected bond lengths and angles of the Co(en)$_3^{2+}$ cations in the crystal structure of compound II.

| Bond Lengths | Bond Angles          |
|--------------|----------------------|
| Co(1)-N(1)   | 2.201(7)             | N(11)-Co(1)-N(1) 97.7(3) |
| Co(1)-N(2)   | 2.162(7)             | N(12)-Co(1)-N(1) 92.4(3) |
| Co(1)-N(11)  | 2.169(7)             | N(22)-Co(1)-N(1) 166.9(3) |
| Co(1)-N(12)  | 2.172(7)             | N(21)-Co(1)-N(1) 90.9(3) |
| Co(1)-N(22)  | 2.184(7)             | N(32)-Co(2)-N(41) 171.4(3) |
| Co(1)-N(21)  | 2.186(8)             | N(32)-Co(2)-N(31) 80.1(3) |
| Co(2)-N(32)  | 2.168(8)             | N(41)-Co(2)-N(31) 93.6(3) |
| Co(2)-N(31)  | 2.180(8)             | N(2)-Co(1)-N(11) 91.5(3) |
|              |                      | N(2)-Co(1)-N(12) 168.4(3) |
|              |                      | N(11)-Co(1)-N(12) 80.7(3) |
|              |                      | N(2)-Co(1)-N(22) 91.6(3) |
|              |                      | N(11)-Co(1)-N(22) 92.6(3) |
|              |                      | N(12)-Co(1)-N(22) 97.3(3) |
|              |                      | N(2)-Co(1)-N(21) 95.3(3) |
|              |                      | N(11)-Co(1)-N(21) 169.8(3) |
|              |                      | N(12)-Co(1)-N(21) 93.6(3) |
|              |                      | N(22)-Co(1)-N(21) 79.7(3) |
|              |                      | N(2)-Co(1)-N(1) 80.1(3) |
**Table S9** Selected bond lengths and angles of the Fe(en)$_3^{2+}$ cations in the crystal structure of compound III.

| Bond Lengths | Bond Angles |
|--------------|-------------|
| Fe(1)-N(2)   | 2.193(5)    | N(2)-Fe(1)-N(21) 96.74(18) |
| Fe(1)-N(12)  | 2.210(5)    | N(12)-Fe(1)-N(21) 93.5(2) |
| Fe(1)-N(11)  | 2.211(5)    | N(11)-Fe(1)-N(21) 167.40(19) |
| Fe(1)-N(22)  | 2.223(5)    | N(22)-Fe(1)-N(21) 78.23(18) |
| Fe(1)-N(21)  | 2.234(5)    | N(31)-Fe(2)-N(32) 78.4(2) |
| Fe(1)-N(1)   | 2.237(5)    | N(31)-Fe(2)-N(41) 94.1(2) |
| Fe(2)-N(31)  | 2.208(5)    | N(32)-Fe(2)-N(41) 169.6(2) |
| Fe(2)-N(32)  | 2.210(5)    | N(2)-Fe(1)-N(12) 166.43(19) |
| Fe(2)-N(41)  | 2.215(5)    | N(2)-Fe(1)-N(11) 91.9(2) |
|              |             | N(12)-Fe(1)-N(11) 79.6(2) |
|              |             | N(2)-Fe(1)-N(22) 91.29(19) |
|              |             | N(12)-Fe(1)-N(22) 99.5(2) |
|              |             | N(11)-Fe(1)-N(22) 92.5(2) |
|              |             | N(2)-Fe(1)-N(1) 78.44(18) |
|              |             | N(12)-Fe(1)-N(1) 92.4(2) |
|              |             | N(11)-Fe(1)-N(1) 98.9(2) |
|              |             | N(22)-Fe(1)-N(1) 164.87(19) |
|              |             | N(21)-Fe(1)-N(1) 91.8(2) |
Table S10 Selected bond lengths and angles of the Ni(en)$_3^{2+}$ cations in the crystal structure of compound IV.

| Bond Lengths | Bond Angles |
|--------------|-------------|
| Ni(1)-N(1)#7 | 2.110(17)   | N(9)-Ni(3)-N(9)#4 | 92.6(12) |
| Ni(1)-N(1)#8 | 2.110(17)   | N(9)-Ni(3)-N(9)#9 | 79(2)    |
| Ni(1)-N(1)  | 2.110(17)   | N(9)#4-Ni(3)-N(9)#9 | 167(3) |
| Ni(1)-N(2)#7 | 2.119(17)   | N(9)-Ni(3)-N(9)#10 | 167(3)  |
| Ni(1)-N(2)  | 2.119(17)   | N(9)#4-Ni(3)-N(9)#10 | 98(2)  |
| Ni(1)-N(2)#8 | 2.119(17)   | N(9)#9-Ni(3)-N(9)#10 | 92.6(12) |
| Ni(11)-N(3) | 2.110(13)   | N(9)-Ni(3)-N(9)#11 | 98(2)   |
| Ni(11)-N(6) | 2.112(19)   | N(9)#4-Ni(3)-N(9)#11 | 79(2)  |
| Ni(11)-N(8) | 2.12(2)     | N(9)#9-Ni(3)-N(9)#11 | 92.6(12) |
| Ni(11)-N(5) | 2.121(16)   | N(9)#10-Ni(3)-N(9)#11 | 92.6(12) |
| Ni(11)-N(4) | 2.12(2)     | N(9)-Ni(3)-N(9)#3  | 92.6(12) |
| Ni(11)-N(7) | 2.14(2)     | N(9)#4-Ni(3)-N(9)#3  | 92.6(12) |
| Ni(3)-N(9)#4 | 2.10(3)     | N(9)#9-Ni(3)-N(9)#3  | 98(2)   |
| Ni(3)-N(9)#9 | 2.10(3)     | N(9)#10-Ni(3)-N(9)#3  | 79(2)  |
| Ni(3)-N(9)#10 | 2.10(3)   | N(1)#7-Ni(1)-N(1)#8  | 92.0(6) |
| Ni(3)-N(9)#11 | 2.10(3)  | N(1)#7-Ni(1)-N(1)  | 92.0(6) |
| Ni(3)-N(9)#3 | 2.10(3)     | N(1)#8-Ni(1)-N(1)  | 92.0(6) |
|              |             | N(1)#7-Ni(1)-N(2)#7  | 173.6(7) |
|              |             | N(1)#8-Ni(1)-N(2)#7  | 91.7(7)  |
|              |             | N(1)-Ni(1)-N(2)#7  | 82.7(6)  |
|              |             | N(1)#7-Ni(1)-N(2)  | 91.7(7)  |
|              |             | N(1)#8-Ni(1)-N(2)  | 82.7(6)  |
|              |             | N(1)-Ni(1)-N(2)  | 173.6(7) |
|              |             | N(2)#7-Ni(1)-N(2)  | 94.0(6)  |
|              |             | N(1)#7-Ni(1)-N(2)#8  | 82.7(6)  |
|              |             | N(1)#8-Ni(1)-N(2)#8  | 173.6(7) |
|              |             | N(1)-Ni(1)-N(2)#8  | 91.7(7)  |
|              |             | N(2)#7-Ni(1)-N(2)#8  | 94.0(6)  |
|              |             | N(2)-Ni(1)-N(2)#8  | 94.0(6)  |
|              |             | N(3)-Ni(11)-N(6)  | 170.5(7) |
|              |             | N(3)-Ni(11)-N(8)  | 93.6(7)  |
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| N(6)-Ni(11)-N(8)           | 94.8(8)   |
| N(3)-Ni(11)-N(5)           | 91.4(6)   |
| N(6)-Ni(11)-N(5)           | 81.0(8)   |
| N(8)-Ni(11)-N(5)           | 170.6(7)  |
| N(3)-Ni(11)-N(4)           | 82.7(7)   |
| N(6)-Ni(11)-N(4)           | 92.6(8)   |
| N(8)-Ni(11)-N(4)           | 91.4(7)   |
| N(5)-Ni(11)-N(4)           | 97.2(8)   |
| N(3)-Ni(11)-N(7)           | 90.2(8)   |
| N(6)-Ni(11)-N(7)           | 95.6(8)   |
| N(8)-Ni(11)-N(7)           | 80.0(8)   |
| N(5)-Ni(11)-N(7)           | 92.0(8)   |
| N(4)-Ni(11)-N(7)           | 168.6(7)  |
| N(9)#11-Ni(3)-N(9)#3       | 167(3)    |

Table S10 continued
The discrete cluster anions and the discrete M(en)$_3$$_{2+}$ cations form a complex hydrogen network. The hydrogen bond lengths and the corresponding interacting atoms for all four compounds are listed in Tables S8 – S11.

**Table S11.** Hydrogen bonds with H-A < r(A) + 2.000 Å and °DHA > 110 ° of compound I.

| D-H     | d(D-H) | d(H-A) | °DHA   | d(D-A) | A            |
|---------|--------|--------|--------|--------|--------------|
| N1-H1N  | 0.920  | 2.357  | 141.34 | 3.128  | O21 [ x, y, z+1 ] |
| N2-H3N  | 0.920  | 2.022  | 164.17 | 2.918  | O16          |
| N2-H4N  | 0.920  | 2.283  | 167.58 | 3.188  | O32 [-x+2, y, -z+2 ] |
| N11-H5N | 0.920  | 2.206  | 154.72 | 3.063  | O20 [ x, y, z+1 ] |
| N11-H6N | 0.920  | 2.212  | 153.73 | 3.064  | O7 [-x+3/2, y+1/2, -z+1 ] |
| N12-H7N | 0.920  | 2.093  | 155.43 | 2.954  | O9 [ x-1/2, y+1/2, z ] |
| N12-H8N | 0.920  | 2.172  | 152.56 | 3.019  | O31 [-x+1, y, -z+1 ] |
| N21-H9N | 0.920  | 2.535  | 140.58 | 3.298  | O16          |
| N22-H11N| 0.920  | 2.361  | 150.53 | 3.194  | O8 [-x+3/2, y+1/2, -z+1 ] |
| N31-H13N| 0.920  | 2.188  | 163.43 | 3.081  | O11 [-x+1, y, -z ] |
| N31-H14N| 0.920  | 2.360  | 148.09 | 3.179  | O31 [-x+1, y, -z ] |
| N32-H15N| 0.920  | 2.245  | 158.72 | 3.121  | O6           |
| N32-H16N| 0.920  | 2.566  | 118.50 | 3.112  | O11          |
| N41-H17N| 0.920  | 2.425  | 130.19 | 3.099  | O18 [-x+1, y, -z ] |
| N41-H17N| 0.920  | 2.492  | 148.45 | 3.311  | O19 [-x+1, y, -z ] |
| N41-H18N| 0.920  | 2.220  | 149.86 | 3.050  | O21 [-x+1, y, -z ] |

**Table S12.** Hydrogen bonds with H-A < r(A) + 2.000 Å and °DHA > 110 ° of compound II.

| D-H     | d(D-H) | d(H-A) | °DHA   | d(D-A) | A            |
|---------|--------|--------|--------|--------|--------------|
| N1-H1N  | 0.920  | 2.353  | 139.09 | 3.107  | O21 [ x, y, z+1 ] |
| N2-H3N  | 0.920  | 2.021  | 165.98 | 2.922  | O16          |
| N2-H4N  | 0.920  | 2.302  | 164.36 | 3.197  | O32 [-x+2, y, -z+2 ] |
| N11-H5N | 0.920  | 2.202  | 152.22 | 3.046  | O20 [ x, y, z+1 ] |
| N11-H6N | 0.920  | 2.245  | 152.02 | 3.088  | O7 [-x+3/2, y+1/2, -z+1 ] |
| N12-H7N | 0.920  | 2.098  | 156.55 | 2.964  | O9 [ x-1/2, y+1/2, z ] |
| N12-H8N | 0.920  | 2.248  | 150.48 | 3.082  | O31 [-x+1, y, -z+1 ] |
| N21-H9N | 0.920  | 2.482  | 142.36 | 3.259  | O16          |
| N22-H11N| 0.920  | 2.389  | 147.98 | 3.206  | O8 [-x+3/2, y+1/2, -z+1 ] |
| N31-H13N| 0.920  | 2.196  | 161.51 | 3.083  | O11 [-x+1, y, -z ] |
| N31-H14N| 0.920  | 2.362  | 147.25 | 3.175  | O31 [-x+1, y, -z ] |
| N32-H15N| 0.920  | 2.242  | 160.50 | 3.124  | O6           |
| N32-H16N| 0.920  | 2.538  | 118.68 | 3.087  | O11          |
| N41-H17N| 0.920  | 2.429  | 130.14 | 3.103  | O18 [-x+1, y, -z ] |
| N41-H17N| 0.920  | 2.492  | 148.81 | 3.314  | O19 [-x+1, y, -z ] |
| N41-H18N| 0.920  | 2.214  | 150.98 | 3.051  | O21 [-x+1, y, -z ] |
### Table S13. Hydrogen bonds with H-A < r(A) + 2.000 Å and *DHA > 110 ° of compound III.

| D-H     | d(D-H) | d(H..A) | °DHA    | d(D..A) | A               |
|---------|--------|---------|---------|---------|-----------------|
| N1-H2N  | 0.900  | 2.383   | 138.19  | 3.112   | O21 [ x, y, z-1 ] |
| N2-H3N  | 0.900  | 2.386   | 164.69  | 3.262   | O32 [ -x, y, -z ] |
| N2-H4N  | 0.900  | 2.040   | 165.97  | 2.921   | O16             |
| N11-H5N | 0.900  | 2.313   | 150.79  | 3.130   | O7 [ -x+1/2, y-1/2, -z+1 ] |
| N11-H6N | 0.900  | 2.219   | 152.64  | 3.046   | O20 [ x, y, z-1 ] |
| N12-H7N | 0.900  | 2.274   | 151.69  | 3.096   | O31 [ -x+1, y, -z+1 ] |
| N12-H8N | 0.900  | 2.109   | 154.88  | 2.949   | O9 [ x+1/2, y-1/2, z ] |
| N21-H10N| 0.900  | 2.489   | 143.94  | 3.260   | O16             |
| N22-H12N| 0.900  | 2.458   | 144.75  | 3.235   | O8 [ -x+1/2, y-1/2, -x+1 ] |
| N31-H13N| 0.900  | 2.442   | 143.57  | 3.211   | O31 [ -x+1, y, -z+2 ] |
| N31-H14N| 0.900  | 2.246   | 161.54  | 3.113   | O11 [ -x+1, y, -z+2 ] |
| N32-H15N| 0.900  | 2.539   | 122.39  | 3.115   | O11             |
| N32-H16N| 0.900  | 2.276   | 156.25  | 3.121   | O6              |
| N41-H17N| 0.900  | 2.248   | 149.94  | 3.060   | O21 [ -x+1, y, -z+2 ] |
| N41-H18N| 0.900  | 2.477   | 132.08  | 3.151   | O18 [ -x+1, y, -z+2 ] |
| N41-H18N| 0.900  | 2.546   | 148.99  | 3.349   | O19 [ -x+1, y, -z+2 ] |

### Table S14. Hydrogen bonds with H..A < r(A) + 2.000 Å and <DHA > 110 ° of compound IV.

| D-H     | d(D-H) | d(H..A) | °DHA    | d(D..A) | A               |
|---------|--------|---------|---------|---------|-----------------|
| N1-H1N1 | 0.990  | 2.359   | 146.28  | 3.230   | O22 [ y, x, -z+2 ] |
| N1-H1N1 | 0.990  | 2.316   | 135.82  | 3.104   | O23 [ x-y+1, -y+1, -z+2 ] |
| N2-H2N1 | 0.990  | 2.307   | 142.40  | 3.150   | O22 [ x-y+1, -y+1, -z+2 ] |
| N2-H1N2 | 0.990  | 2.334   | 144.61  | 3.192   | O17 [ -x+1, -x+y, -z+1 ] |
| N2-H1N2 | 0.990  | 2.321   | 138.51  | 3.132   | O18 [ x-y+1, -y+1, -z+1 ] |
| N2-H2N2 | 0.990  | 2.397   | 133.80  | 3.164   | O17 [ x-y+1, -y+1, -z+1 ] |
| N3-H1N3 | 0.990  | 1.996   | 164.95  | 2.963   | O20 [ -x+y, -x+1, z ] |
| N4-H1N4 | 0.990  | 2.401   | 133.90  | 3.169   | O17 [ -x+1, -x+y, -z+1 ] |
| N5-H1N5 | 0.990  | 2.183   | 149.08  | 3.075   | O16 [ y, x, -z+1 ] |
| N5-H2N5 | 0.990  | 2.297   | 148.78  | 3.185   | O4 [ y, x, -z+2 ] |
| N6-H1N6 | 0.990  | 1.972   | 154.28  | 2.895   | O5              |
| N7-H1N7 | 0.990  | 2.414   | 147.12  | 3.290   | O6              |
| N8-H1N8 | 0.990  | 2.378   | 145.14  | 3.240   | O20 [ -x+y, -x+1, z ] |
| N9-H1N9 | 0.990  | 2.195   | 159.46  | 3.141   | O7              |
| N9-H1N9 | 0.990  | 2.477   | 123.67  | 3.136   | O8              |
| N9-H2N9 | 0.990  | 2.414   | 149.25  | 3.304   | O7 [ -x+y+1, -x+2, z ] |
7. Magnetic Properties

Figure S8. Molar magnetization $M_m$ as a function of the applied field $B$: $M_m(\text{exp}) - M_m([\text{V}_{12}\text{Sb}_6\text{O}_{42}]^{6-})$ for compound I (a), II (b), III (c), shown as blue open circles; best fits: red lines.
Table S15. Parameters of the “full model” simulations of I – III.

| Parameter | I (M = Ni) | II (M = Co) | III (M = Fe) |
|-----------|------------|-------------|--------------|
| Racah B a) / cm⁻¹ | 1084 | 1115 | 1058 |
| Racah C a) / cm⁻¹ | 4831 | 4366 | 3901 |
| ζ₃d a) / cm⁻¹ | 649 | 533 | 410 |
| BError b) / cm⁻¹ | -24307 ± 484 | -842 ± 80 | 13426 ± 43 |
| BError b) / cm⁻¹ | 26213 ± 98 | 43382 ± 50 | 39262 ± 15 |
| BError b) / cm⁻¹ | 13898 ± 167 | 25154 ± 16 | 10064 ± 35 |
| zJ c) / cm⁻¹ | -0.01 ± 0.01 | +0.01 ± 0.01 | -0.53 ± 0.01 |
| SQ d) | 2.1% | 2.6% | 1.6% |

a) Griffith, J.S. The Theory of Transition-Metal Ions, Cambridge University Press, Cambridge, 1971; b) ligand field parameter in Wybourne notation; c) mean field parameter (“−2J” notation); d) goodness of fit.
8. Electrospray ionization mass spectrometry

Besides the known signals of $[\text{M}]^3^+/[\text{M}\cdot\text{H}]^3^+$, $[\text{M}\cdot\text{H}_2\text{O}]^3^+/[\text{M}\cdot\text{H}\cdot\text{H}_2\text{O}]^3^+$, $[\text{M}\cdot\text{Ni(en)}]^2^+/ [\text{M}\cdot\text{H}\cdot\text{Ni(en)}]^2^+$, $[\text{M}\cdot\text{Ni(en)}\cdot\text{H}_2\text{O}]^2^+/ [\text{M}\cdot\text{H}\cdot\text{Ni(en)}\cdot\text{H}_2\text{O}]^2^+$ and $[\text{N}\cdot\text{H}_2\text{O}]^3^+/ [\text{N}\cdot\text{H}\cdot\text{H}_2\text{O}]^3^+$ at $m/z$ 722, 728, 1142, 1151 and 792, respectively, in the ESI-Q-TOF-HRMS spectra of $\{\text{Ni(en)}_3\}_{3}[\text{V}_{15}\text{Sb}_6\text{O}_{42}]$, a series of peaks exists for which no conclusive assignment could be made ($m/z$ 671, 677, 696, 702, 766, 1104, 1113).

In all experiments performed (ESI mass spectra at different ionization conditions, H/D- and $^{16}\text{O}/^{18}\text{O}$-exchange experiments, collision-induced fragmentation experiments), these ions behave in close analogy to the parent cluster. It can thus be assumed that they belong to structurally closely related cluster species, for which we were nevertheless unable to find a fully convincing elemental composition, which is in line with all experimental data.

As the powder diffraction patterns of a sample that was used for the mass spectrometric experiments clearly showed the sample not to contain significant amounts of impurities, we assume that these signals correspond to a marginal level of impurities, which are more easily ionized and thus appear with higher intensities in the mass spectra than expected from their abundance in the sample.
9. References

(1) (a) Y. Gao, Z. Han, Y. Xu, C. Hu, *J. Clust. Sci.*, 2010, **21**, 163; (b) E. Antonova C. Näther, P. Kögerler, W. Bensch, *Angew. Chem.*, 2011, **123**, 790; (c) R. Kiebach, C. Näther, P. Kögerler, W. Bensch, *Dalton Trans.*, 2007, **3221**; (d) E. Antonova, C. Näther, W. Bensch, *Dalton Trans.*, 2012, **41**, 1338; (e) E. Antonova, C. Näther, W. Bensch, *CrystEngComm.*, 2012, **14**, 6853; (f) E. Antonova, C. Näther, P. Kögerler, W. Bensch, *Dalton Trans.*, 2012, **41**, 6957; (g) L. Yu, J.-P. Liu, J.-P. Wang, J.-Y. Niu, *Chem. Res. Chinese Universities*, 2009, **25**, 426; (h) E. Antonova, C. Näther, P. Kögerler, W. Bensch, *Inorg. Chem.*, 2012, **51**, 2311.

(2) M. O’Keeffe, N. E. Brese, *J. Am. Chem. Soc.*, 1991, **113**, 3226.