Monatshefte für Chemie 134, 1071–1079 (2003)
DOI 10.1007/s00706-003-0030-4

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Synthesis and X-Ray Crystal Structure of Two Novel Complexes: $[M^{II}(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (M^{II} = Co, Ni; *phen* = phenanthroline)

L'udmila Žúrková[1,*], **Renáta Kucsera**[1], **Róbert Gyepes**[2],
and **Michal Sivák**[1]

[1] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, SK-84215, Bratislava, Slovak Republic
[2] Department of Inorganic Chemistry, Faculty of Natural Sciences, Charles University, CS-12800, Praha, Czech Republic

Received November 13, 2002; accepted (revised) February 3, 2003

Summary. Two novel compounds, $[Co(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (**1**) and $[Ni(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (**2**), were prepared from KVO_3–1,10-phenanthroline (*phen*)–$Co(NO_3)_2$, resp. $NiCl_2$–H_2O reaction systems. The compounds **1** and **2** are isomorphous and crystallize in triclinic system, space group P-1. Their crystal structures are formed by two types of layers parallel to 001: a cationic one consisting of $[M^{II}(phen)_3]^{2+}$ ions and an anionic one containing the cyclic $V_4O_{12}{}^{4-}$ anions. The solvate phenanthroline and crystal water molecules are located in the cationic and anionic layers, respectively. The IR spectra of **1** and **2** are consistent with the presence of the cyclic $V_4O_{12}{}^{4-}$ anions in the complexes.

Keywords. Inorganic–organic hybrid materials; X-ray structure determination.

Introduction

In recent times, the organic-inorganic hybrid vanadium oxides or complexes with polyoxovanadate anions have been extensively studied due to their structural variety and possible utilization in catalysis or material chemistry [1–5].

The structure of polyoxovanadates, with charge of the anion balanced by cationic complexes of other transition metals, is influenced by several factors, *e.g.* coordination preferences of the transition metal present (Cu, Co, Ni, or Mn), geometric constrains of the polydentate organic ligand usually providing a donor set of nitrogen atoms, and the substructure of the polyoxovanadate anion.

---

[*] Corresponding author. E-mail: zurkova@fns.uniba.sk

The secondary metal-ligand moiety, or its fragment, may form a variety of substructural motifs: isolated structural units as found in $[Zn(\mathit{bipy})_3]_2V_4O_{12} \cdot 11H_2O$ [2] (*bipy* = bipyridine), polynuclear bimetallic clusters involving covalent bonds with the V–O skeleton of the anion, *e.g.* in $[[Cu(\mathit{phen})_2]_4V_{10}O_{29}] \cdot 6H_2O$ [6], bridges in chain structures as observed in $[[Co(\mathit{phen})_2]_2V_6O_{17}]_n$ [6], layers as in $[Co(H\mathit{dpa})_2V_4O_{12}]$ [5] (*dpa* = dipyridylamine), or three-dimensional networks as in $[Ni(C_8H_{22}N_4](VO_3)_2 \cdot 3H_2O$ [7]. In the structures of such compounds, the polyoxovanadate anion may form isolated structural units [2], bridges between two coordination centers [2, 8], chains [4], or layers [9].

The majority of substances mentioned above were prepared under hydrothermal [2–6], but some of them also under laboratory conditions [7].

As one of the goals in our research on organic–inorganic hybrid compounds, we have synthesized in our laboratory vanadium(V) compounds with structures containing, besides the polyoxovanadate anion and another central atom of a transition metal, also an organic molecule bound both as coordinated ligand and uncoordinated solvate molecule. We report here the synthesis, spectral properties, and crystal structure of two new compounds with 1,10-phenanthroline: $[Co(\mathit{phen})_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ (**1**) and $[Ni(\mathit{phen})_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ (**2**).

Results and Discussion

The compounds **1** and **2** were prepared from aqueous KVO_3–1,10-phenanthroline–$Co(NO_3)_2 \cdot 6H_2O$, resp. $NiCl_2 \cdot 6H_2O$ reaction solutions, the molar ratio of reactants was 4:4:1. The molar ratio and the sequence of adding the reactants into the reaction solution were the main factors influencing the syntheses of **1** and **2.** At a lower phenanthroline content in the reaction solution, neither **1** and **2**, nor their corresponding compounds without a phenanthroline as solvate molecule were formed. From a reaction solution with the same molar ratio of reactants but performed under hydrothermal conditions, a mixture of at least two components was formed in each experiment. The number of components in the mixture increased with prolonged reaction time. It is noteworthy to mention that under hydrothermal conditions only **1** could be prepared.

In the region of symmetric and asymmetric V–O stretching vibrations, the IR spectra of the individual types of polyoxovanadates are characteristic due to the relatively rigid structure of the polyoxovanadate ions. IR Spectroscopy can thus be used as a method of identification of the type of polyvanadate ion which is present in the structure of the studied compound. The IR spectra (Fig. 1) confirm that **1** and **2** have similar structures containing the cyclic $V_4O_{12}{}^{4-}$ anions. We assign the bands at 940 and 905 cm^{-1} (for **1**) and at 940 and 899 cm^{-1} (for **2**) to the symmetric and asymmetric valence vibrations in $V(O_t)_2$ groups with terminal O_t oxygens, and the bands at 819, 804, and 642 cm^{-1} (for **1**) and at 816, 801, and 645 cm^{-1} (for **2**) to the asymmetric and symmetric valence vibrations of the bridging $V–O_b–V$ groups. The positions of the absorption bands in the region of stretching vibrations of the V–O bonds (500–1000 cm^{-1}) allow, with great certainty, to decide whether the structure of a compound studied is built up of cyclic $V_4O_{12}{}^{4-}$ anions or not. However, the assignment of these absorption bands made by individual authors differ. For example in the IR spectrum of $[(CH_3)_3CNH_3]_4[V_4O_{12}]$,

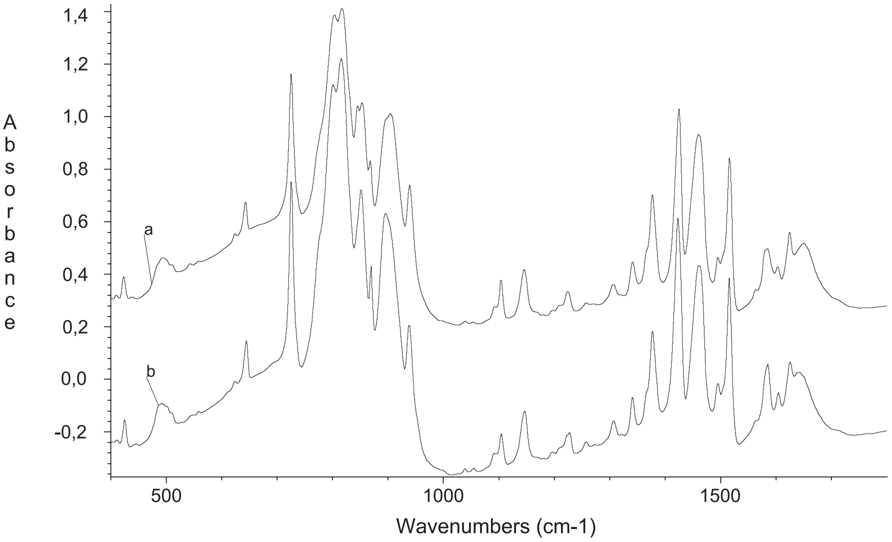

Fig. 1. IR spectra of **1** (a) and **2** (b)

Roman et al. [10] have assigned the bands at 935 (m, sh) and 890 (vs, br) cm^{-1} to $\bar{\nu}_s[V(O_t)_2]$, and the bands at 810 (vs, vbr) and 735 (w, sh) cm^{-1} to $\bar{\nu}_{as}[V(O_t)_2]$. To $\bar{\nu}_{as} + \bar{\nu}_s(V\text{–}O_b\text{–}V)$, they have assigned the bands at 660 (m), 500 (m), and 455 (s) cm^{-1}. It means that despite the known crystal structure, the exact assignment of IR bands for such a complicated system as the $V_4O_{12}{}^{4-}$ ion is not possible so far.

Crystal Structures

The crystal structure determination showed that **1** and **2** are isomorphous. Their structures are formed by two types of alternating layers: cationic, built up of $[M^{II}(phen)_3]^{2+}$ cations and phenanthroline solvate molecules occupying the interstices in this layer, and an anionic one, built up of $V_4O_{12}{}^{4-}$ anions and water molecules located between the anions (Fig. 2). The cationic layer is stabilized by π–π interactions between phenanthroline molecules, both coordinated to the central atom and uncoordinated solvate molecules. Such structure stabilization has been found in several compounds containing phenanthroline or other suitable organic molecules [11–13]. The anionic layer is stabilized by a network of hydrogen bonds between water molecules and the vanadate ions. The direct H–O···H hydrogen bonds have not been found as the hydrogen atoms of water molecules have not been determined, however, thirty oxygen–oxygen distances below 3.03 Å found in each structure confirm the existence of hydrogen bonds. These d(O–O) values are in the intervals: 2.9934–2.6069 Å for **1** and 3.0235–2.6226 Å for **2**. The M^{II} cations do not form M^{II}–O–V covalent bonds with oxygens of the tetravanadate ions, *i.e.* the layers are held together by electrostatic forces.

Cobalt and nickel atoms are six-coordinated in the $[M^{II}(phen)_3]^{2+}$ chelates, with a distorted octahedral arrangement of nitrogen atoms in the CoN_6 and NiN_6 polyhedra. In the independent positions there are two types of differently distorted octahedra (Fig. 3, Tables 1 and 2). As results from the average bond distances:

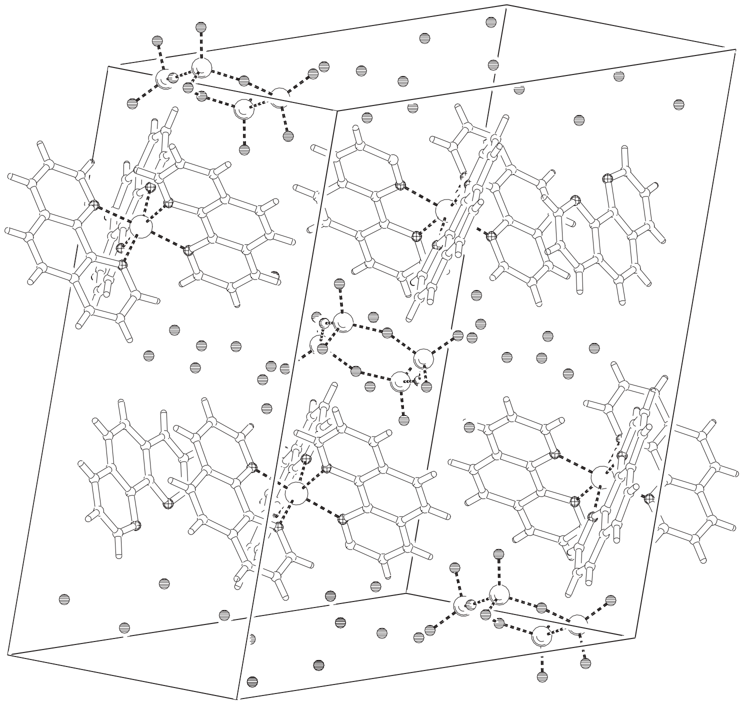

Fig. 2. Cell packing of **2**

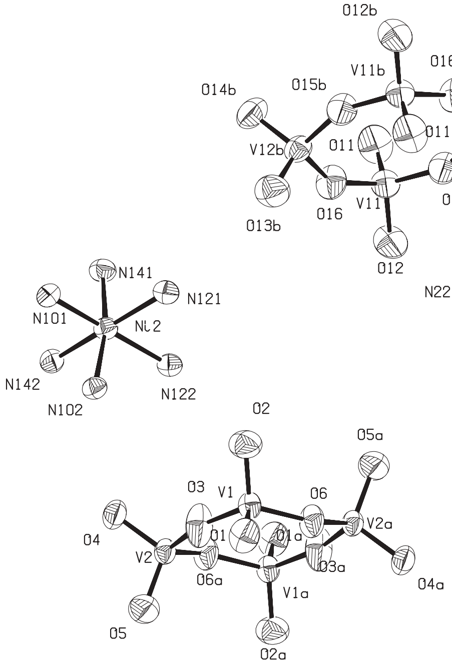

Fig. 3. Fragment of the structure of **2** with atomic labeling scheme (thermal ellipsoids at 50% probability)

Table 1. Selected bond lengths (Å) and angles (°) for **1**

in $[\mathrm{Co}(phen)_3]^{2+}$:			
Co(1)–N(2)	2.110(4)	Co(2)–N(112)	2.120(4)
Co(1)–N(41)	2.121(4)	Co(2)–N(101)	2.126(4)
Co(1)–N(1)	2.132(4)	Co(2)–N(102)	2.135(4)
Co(1)–N(21)	2.133(4)	Co(2)–N(142)	2.135(4)
Co(1)–N(22)	2.137(4)	Co(2)–N(142)	2.142(4)
Co(1)–N(42)	2.144(4)	Co(2)–N(141)	2.142(4)
N(2)–Co(1)–N(41)	169.02(15)	N(122)–Co(2)–N(101)	166.65(15)
N(2)–Co(1)–N(1)	78.89(15)	N(122)–Co(2)–N(102)	92.35(14)
N(41)–Co(1)–N(1)	95.19(16)	N(101)–Co(2)–N(102)	78.42(15)
N(2)–Co(1)–N(21)	94.51(14)	N(122)–Co(2)–N(121)	78.02(14)
N(41)–Co(1)–N(21)	94.96(15)	N(101)–Co(2)–N(121)	93.37(14)
N(1)–Co(1)–N(21)	92.35(15)	N(102)–Co(2)–N(121)	96.84(14)
N(2)–Co(1)–N(22)	95.31(15)	N(122)–Co(2)–N(142)	95.75(15)
N(41)–Co(1)–N(22)	92.08(15)	N(101)–Co(2)–N(142)	94.23(15)
N(1)–Co(1)–N(22)	168.37(15)	N(102)–Co(2)–N(142)	92.12(15)
N(21)–Co(1)–N(22)	77.96(14)	N(121)–Co(2)–N(142)	169.25(15)
N(2)–Co(1)–N(42)	93.45(15)	N(122)–Co(2)–N(141)	94.96(15)
N(41)–Co(1)–N(42)	77.97(15)	N(101)–Co(2)–N(141)	95.79(15)
N(1)–Co(1)–N(42)	96.87(15)	N(102)–Co(2)–N(141)	168.14(15)
N(21)–Co(1)–N(42)	168.82(15)	N(121)–Co(2)–N(141)	93.81(15)
N(22)–Co(1)–N(42)	93.51(15)	N(142)–Co(2)–N(141)	77.88(15)
in $\mathrm{V}_4\mathrm{O}_{12}{}^{4-}$:			
V(1)–O(2)	1.613(4)	V(11)–O(12)	1.605(4)
V(1)–O(1)	1.642(4)	V(11)–O(11)	1.647(5)
V(1)–O(3)#1	1.773(4)	V(11)–O(15)	1.780(4)
V(1)–O(6)	1.789(3)	V(11)–O(16)	1.793(4)
O(3)–V(2)	1.760(4)	V(12)–O(14)	1.635(4)
O(3)–V(1)#1	1.773(4)	V(12)–O(13)	1.638(4)
V(2)–O(5)	1.623(4)	V(12)–O(16)	1.768(4)
V(2)–O(4)	1.646(3)	V(12)–O(15)#2	1.773(4)
V(2)–O(6)	1.783(3)	O(15)–V(12)#2	1.773(4)
O(2)–V(1)–O(1)	107.8(2)	O(12)–V(11)–O(11)	109.3(2)
O(2)–V(1)–O(3)#1	109.5(2)	O(12)–V(11)–O(15)	108.4(2)
O(1)–V(1)–O(3)#1	110.1(2)	O(11)–V(11)–O(15)	111.4(2)
O(2)–V(1)–O(6)	110.46(19)	O(12)–V(11)–O(16)	108.0(2)
O(1)–V(1)–O(6)	107.69(19)	O(11)–V(11)–O(16)	109.2(2)
O(3)#1–V(1)–O(6)	111.22(17)	O(15)–V(11)–O(16)	110.45(18)
V(2)–O(3)–V(1)#1	162.5(2)	O(14)–V(12)–O(13)	109.6(2)
O(5)–V(2)–O(4)	107.86(19)	O(14)–V(12)–O(16)	109.7(2)
O(5)–V(2)–O(3)	111.3(2)	O(13)–V(12)–O(16)	109.6(2)
O(4)–V(2)–O(3)	108.9(2)	O(14)–V(12)–O(15)#2	109.8(2)
O(5)–V(2)–O(6)	109.9(2)	O(13)–V(12)–O(15)#2	108.1(2)
O(4)–V(2)–O(6)	109.26(19)	O(16)–V(12)–O(15)#2	110.03(18)
O(3)–V(2)–O(6)	109.66(18)	V(12)#2–O(15)–V(11)	156.2(3)
V(2)–O(6)–V(1)	148.3(2)	V(12)–O(16)–V(11)	148.2(2)

Table 2. Selected bond lenghts (Å) and angles (°) for **2**

in $[\mathrm{Ni}(\mathit{phen})_3]^{2+}$:			
Ni(1)–N(2)	2.080(4)	Ni(2)–N(122)	2.080(4)
Ni(1)–N(41)	2.084(4)	Ni(2)–N(101)	2.084(4)
Ni(1)–N(1)	2.092(4)	Ni(2)–N(102)	2.092(4)
Ni(1)–N(21)	2.095(4)	Ni(2)–N(121)	2.096(4)
Ni(1)–N(42)	2.105(4)	Ni(2)–N(141)	2.100(4)
Ni(1)–N(22)	2.105(4)	Ni(2)–N(142)	2.101(4)
N(2)–Ni(1)–N(41)	170.15(16)	N(122)–Ni(2)–N(101)	168.79(15)
N(2)–Ni(1)–N(1)	79.80(16)	N(122)–Ni(2)–N(102)	92.40(15)
N(41)–Ni(1)–N(1)	94.74(16)	N(101)–Ni(2)–N(102)	79.81(16)
N(2)–Ni(1)–N(21)	93.85(15)	N(122)–Ni(2)–N(121)	79.39(15)
N(41)–Ni(1)–N(21)	94.57(15)	N(101)–Ni(2)–N(121)	93.26(16)
N(1)–Ni(1)–N(21)	92.38(16)	N(102)–Ni(2)–N(121)	95.62(15)
N(2)–Ni(1)–N(42)	92.67(15)	N(122)–Ni(2)–N(141)	94.12(15)
N(41)–Ni(1)–N(42)	79.66(15)	N(101)–Ni(2)–N(141)	94.79(16)
N(1)–Ni(1)–N(42)	95.87(16)	N(102)–Ni(2)–N(141)	169.55(16)
N(21)–Ni(1)–N(42)	170.28(15)	N(121)–Ni(2)–N(141)	93.59(15)
N(2)–Ni(1)–N(22)	94.70(15)	N(122)–Ni(2)–N(142)	94.94(16)
N(41)–Ni(1)–N(22)	91.86(15)	N(101)–Ni(2)–N(142)	93.37(16)
N(1)–Ni(1)–N(22)	169.89(15)	N(102)–Ni(2)–N(142)	91.88(15)
N(21)–Ni(1)–N(22)	79.44(15)	N(121)–Ni(2)–N(142)	170.76(15)
N(42)–Ni(1)–N(22)	92.85(16)	N(141)–Ni(2)–N(142)	79.44(15)
in $\mathrm{V_4O_{12}}^{4-}$:			
V(1)–O(2)	1.612(4)	V(11)–O(12)	1.606(4)
V(1)–O(1)	1.646(4)	V(11)–O(11)	1.648(4)
V(1)–O(3)#1	1.776(4)	V(11)–O(15)	1.783(4)
V(1)–O(6)	1.788(3)	V(11)–O(16)	1.789(4)
O(3)–V(2)	1.759(4)	V(12)–O(14)	1.636(4)
O(3)–V(1)#1	1.776(4)	V(12)–O(13)	1.643(4)
V(2)–O(5)	1.619(4)	V(12)–O(16)	1.772(4)
V(2)–O(4)	1.649(4)	V(12)–O(15)#2	1.774(4)
V(2)–O(6)	1.786(3)	O(15)–V(12)#2	1.774(4)
O(2)–V(1)–O(1)	107.8(2)	O(12)–V(11)–O(11)	109.1(2)
O(2)–V(1)–O(3)#1	109.8(2)	O(12)–V(11)–O(15)	108.4(2)
O(1)–V(1)–O(3)#1	110.0(2)	O(11)–V(11)–O(15)	111.2(2)
O(2)–V(1)–O(6)	110.31(19)	O(12)–V(11)–O(16)	107.8(2)
O(1)–V(1)–O(6)	107.8(2)	O(11)–V(11)–O(16)	109.8(2)
O(3)#1–V(1)–O(6)	111.11(18)	O(15)–V(11)–O(16)	110.41(18)
V(2)–O(3)–V(1)#1	162.7(3)	O(14)–V(12)–O(13)	108.9(2)
O(5)–V(2)–O(4)	107.9(2)	O(14)–V(12)–O(16)	110.0(2)
O(5)–V(2)–O(3)	110.7(2)	O(13)–V(12)–O(16)	109.7(2)
O(4)–V(2)–O(3)	109.3(2)	O(14)–V(12)–O(15)#2	109.8(2)
O(5)–V(2)–O(6)	109.9(2)	O(13)–V(12)–O(15)#2	108.5(2)
O(4)–V(2)–O(6)	108.97(18)	O(16)–V(12)–O(15)#2	109.88(19)
V(12)–O(16)–V(11)	147.6(3)	V(12)#2–O(15)–V(11)	156.8(3)
V(2)–O(6)–V(1)	147.7(2)	O(3)–V(2)–O(6)	110.01(18)

$d(Co_1\text{–}N) = 2.129$ Å (2.110–2.144 Å, interval), $d(Co_2\text{–}N) = 2.133$ Å (2.120–2.144 Å, interval), $d(Ni_1\text{–}N) = 2.094$ Å (2.079–2.106 Å, interval), and $d(Ni_2\text{–}N) = 2.092$ Å (2.080–2.100 Å, interval), the differences in M^{II}–N distances for the individual cobalt and nickel octahedra are small. The shorter Ni–N bond lengths, when compared to Co–N distances, are caused by the difference in ionic radii for Ni^{2+} and Co^{2+} ions.

The structure of the tetravanadate ions in the crystal structures of **1** and **2** is approximately the same as found in $[Bu_4N]_3HV_4O_{12}$ [14] and $[Ni(C_{10}H_8N_2)_3]_2V_4O_{12} \cdot 11H_2O$ [15]: four VO_4 tetrahedra are linked to eight-membered rings by sharing oxygen atoms (Figs. 2 and 3). There are two types of differently distorted cyclic $V_4O_{12}{}^{4-}$ anions in the independent parts of the unit cells of **1** and **2**. The terminal V–O_t bond lengths range from 1.605 to 1.647 Å (1.631 Å, average) in **1** and from 1.606 to 1.649 Å (1.632 Å, average) in **2**. The V–O distances in the V–O_b–V bridges are within the intervals: 1.761–1.789 Å (1.775 Å, average) for **1** and 1.759–1.789 Å (1.777 Å, average) for **2** (Tables 1 and 2). It means that the different complex cations have no essential influence on the structure of the $V_4O_{12}{}^{4-}$ anions in **1** and **2**. Among the polyoxovanadates with $[M^{II}L_x]^{n+}$ complex cations which have been structurally characterized so far (M^{II} is Ni or Co, and L is a polydentate organic ligand with nitrogen donors), we can find two compounds with a structure built up of complex cations and cyclic $V_4O_{12}{}^{4-}$ anions, both as isolated structure units [15, 16]. In other structures, the polyoxovanadate anions form either chains [5, 6, 17] or layers [9, 18], whereas the complex cations, resp. their fragments, are covalently bound to the polyoxoanions *via* M^{II}–O–V bonds.

Experimental

Materials and Methods

KVO_3 was prepared according to Ref. [19], all other chemicals were supplied by Lachema or Aldrich. The vanadium content was estimated as follows: the weighted sample was annealed in Pt crucible to constant weight at 700°C, dissolved in hot water and titrated by 0.1 *M* $FeSO_4$ solution in the presence of H_3PO_4 and diphenylamine as indicator. The cobalt and nickel contents were calculated based on vanadium content, though the products obtained after annealing, as evidenced by their powder diffraction patterns, were $Co(VO_3)_2$ and $Ni(VO_3)_2$, respectively. Carbon, nitrogen, and hydrogen were estimated on a CHN analyzer (Carlo Erba). The IR spectra in Nujol mulls were measured on a FT IR Nicolet Magna 750 spectrophotometer. The powder diffraction patterns were registered on a Philips diffractograph equipped with a PW 1050 goniometer, CuK_α radiation was used.

$[Co(phen)_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ (**1**)

KVO_3 (0.5 g, 3.6 mmol), 1,10-phenanthroline (0.65 g, 3.6 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (0.25 g, 0.9 mmol) were subsequently added to 900 ml of water heated to 100°C. Yellow needle-like crystals of **1** were formed on free cooling of the solution. The crystals were washed with distilled water and air dried. Compound **1** crystallized also from more concentrated solutions (250 ml of water), however, the crystals formed were less suitable for X-ray analysis. **1** was prepared also by hydrothermal synthesis using the same mixture of reactants but in 25 ml of water. The reaction proceeded in a teflon crucible at 140°C, the reaction time was 2, resp. 24 h. In both hydrothermal syntheses, a mixture consisting of a major portion of **1** and a minor portion of red crystals of $[Co(phen)_4(\mu^4\text{-}V_4O_{12})]$ [8] was formed. In the mixture formed within 24 h, at least one additional unidentified phase was present. Anal. calcd (%) for

$Co_2C_{84}H_{100}N_{14}O_{34}V_4$: Co 5.43, V 9.38, C 46.46, H 4.64, N 9.03, found: Co 5.45, V 9.42, C 46.64, H 3.85, N 8.71; IR: $\bar{\nu}$ = 940 (m), 905 (s, br), 873* (w), 856* (m), 845* (sh), 819 (vs), 804 (vs), 723* (s), 642 (w), 495 (w, br), 426 (w) cm^{-1} (*phenanthroline bands).

$[Ni(phen)_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ (**2**)

KVO_3 (0.5 g, 3.6 mmol), 1,10-phenanthroline (0.65 g, 3.6 mmol), and $NiCl_2 \cdot 6H_2O$ (0.21 g, 0.9 mmol) were subsequently added to 250 ml of water heated to 100°C. In course of cooling, pink crystals of **2** were formed in the reaction solution. The crystals were washed with distilled water and air dried. Compound **2** was obtained also from more diluted reaction solutions (900 ml of water). Anal. calcd. (%) for $Ni_2C_{84}H_{100}N_{14}O_{34}V_4$: Ni 5.41, V 9.38, C 46.47, H 4.64, N 9.03, found: Ni 5.59, V 9.41, C 46.38, H 3.35, N 8.93; IR: $\bar{\nu}$ = 940 (m), 899 (s, br), 873* (w), 856* (w), 816 (vs), 801 (vs), 726* (s), 645 (w), 495 (w, br), 429 (w) cm^{-1} (*phenanthroline bands).

X-Ray Structure Determination

Single crystals of **1** and **2** were selected under a polarization microscope (Zeiss) and fixed on glass rods using epoxy glue. The data collection was carried out on a Nonius KappaCCD diffractometer using

Table 3. Crystallographic data for **1** and **2**

Compound	**1**	**2**
Formula	$Co_2C_{84}H_{100}N_{14}O_{34}V_4$	$Ni_2C_{84}H_{100}N_{14}O_{34}V_4$
Formula weight	2171.40	2170.96
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.9060(4)	12.8520(4)
b/Å	17.6390(6)	17.6290(7)
c/Å	23.3530(6)	23.3080(11)
α/°	106.4630(18)	106.619(2)
β/°	91.0950(19)	90.987(2)
γ/°	106.7130(17)	106.792(2)
V/Å^3, Z	4853.6(3), 2	4815.7(3), 2
D_{calcd}/g cm^{-3}	1.486	1.497
Absortion coefficicient/mm^{-1}	0.792	0.845
F(000)	2240	2244
θ range for data collection/°	2.38 to 25.30	1.81 to 25.07
Limiting indices	$0 < = h < = 15$	$0 < = h < 15$
	$-21 < = k < = 20$	$-21 < = k < = 20$
	$-27 < = l < = 27$	$-27 < = l < = 27$
Reflections collected/unique	17123/17123	16961/16961
	[R(int) = 0.0000]	[R(int) = 0.0000]
Completeness to θ/[%]	96.7%	99.2%
Data/restraints/parameters	17123/0/1243	16961/0/1243
Goodness-of-fit on F^2	1.088	1.043
R_1[a], wR_2[b]$[I > 2\sigma(I)]$	$R_1 = 0.0677$	$R_1 = 0.0607$
	$wR_2 = 0.1363$	$wR_2 = 0.1354$
R indices (all data)	$R_1 = 0.1187$	$R_1 = 0.1154$
	$wR_2 = 0.1623$	$wR_2 = 0.1692$
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.571, −0.318	0.618, −0.373

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Mo-K_α radiation at ambient temperature. No absorption correction was employed. The phase problem was solved by SIR-97 [20] and the structures were refined by full-matrix least-squares using the SHELXL-97 [21] program. All heavy atoms were found on the difference Fourier maps and were refined anisotropically. Hydrogen atoms were refined isotropically in their theoretical positions. Hydrogen atoms of the crystal water molecules could not be found and were neglected.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Center under the deposition numbers CCDC185904 (for **1**) and 185907 (for **2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 EZ, UK (Fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk, or www: http://ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Ministry of Education of the Slovak Republic (Grant No 1/8201/01) and by Grant No 160/202 based on Agreement between the Governments of Slovakia and Czech Republic on Cooperation in Science and Technology. We are grateful to Prof. *Schwendt* from our Department for useful discussions concerning the assignment of IR bands.

References

[1] Pope MT (1983) Heteropoly and Isopoly Oxometalates. Springer Verlag, New York
[2] Zhang Y, Zapf PJ, Meyer LM, Haushalter RC, Zubieta J (1977) Inorg Chem **36**: 2159
[3] Williams ID, Law TSC, Sung HHY, Wen GH, Zhang XX (2000) Solid State Sci **2**: 47
[4] Law TSC, Williams ID (2000) Chem Mater **12**: 2070
[5] La Duca RL, Rarig RS Jr, Zubieta J (2001) Inorg Chem **40**: 607
[6] Zhang XM, Tong ML, Chen XM (2000) Chem Commun, 1817
[7] Do J, Jacobson AJ (2001) Inorg Chem **40**: 2468
[8] Kucsera R, Gyepes R, Žúrková Ľ (2002) Cryst Res Techn **37**: 890
[9] Wang X, Liu L, Jacobson AJ, Ross K (1999) J Mater Chem **9**: 859
[10] Roman P, San José A, Luque A, Guttiérrez-Zorrilla JM (1993) Inorg Chem **32**: 775
[11] Chen W, Lo KM, Liu CM, Xiong RG, Li DG, You XZ (1998) J Coord Chem **43**: 227
[12] Xiong RG, Liu CM, Li DG, Wang H, You XZ (1997) Polyhedron **16**: 1263
[13] Yu XL, Tong YX, Chen XM, Mak TCW (1997) J Chem Cryst **27**: 441
[14] Fuchs J, Mahjour S, Pickardt S (1976) J Angew Chem **15**: 374
[15] Yang GY, Gao DW, Chen Y, Xu JG, Zeng GX, Sun HR, Pei ZW, Su Q, Xing Y, Ling YH, Jia HQ (1998) Acta Cryst C **54**: 616
[16] Kucsera R, Gyepes R, Žúrková Ľ (2003) Solid State Phen **90–91**: 329
[17] Zheng LM, Wang X, Wang Y, Jacobson AJ (2001) J Mater Chem **11**: 1100
[18] Liu CM, Hou YL, Zhang J, Gao S (2002) Inorg Chem **41**: 140
[19] Sivák M, Joniaková D, Schwendt P (1993) Transition Met Chem **18**: 304
[20] Altomare A, Cascarano G, Giacovazzo C, Guagliardi A, Burla MC, Polidori G, Camalli M (1994) J Appl Cryst **27**: 435
[21] Sheldrick GM (1997) SHELXL-97, Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Göttingen, Germany (1997)