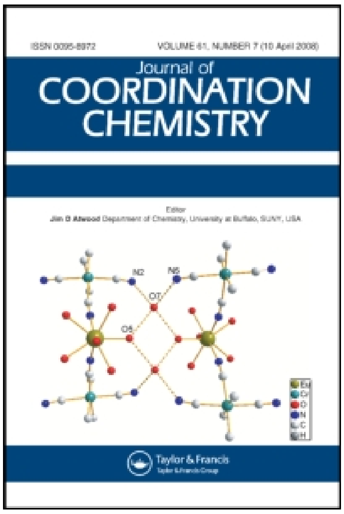

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Stabilization of tetrameric metavanadate ion by tris(1,10-phenanthroline)cobalt(III): synthesis, spectroscopic, and X-ray structural study of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$

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Stabilization of tetrameric metavanadate ion by tris(1,10-phenanthroline)cobalt(III): synthesis, spectroscopic, and X-ray structural study of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$

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A new complex salt of composition $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$ (phen = 1,10-phenanthroline and $[V_4O_{12}]^{4-}$ = tetrameric metavanadate, dodecaoxotetravanadate ion) was synthesized by the reaction of appropriate salts in aqueous medium. The complex salt has been characterized by elemental analyses, thermogravimetric analysis, cyclic voltammetry, FT-IR, and UV-Vis spectroscopies, solubility product and conductance measurements. Single crystal X-ray structure determination revealed ionic structure consisting of three complex cations, $[Co(phen)_3]^{3+}$, two $[V_4O_{12}]^{4-}$ anions, one chloride and 27 lattice water molecules. Detailed structural and spectroscopic analyses of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$ showed that the large anion is stabilized by large cationic metal complex as there is preferred shape compatibility that leads to a large number of lattice-stabilizing non-covalent interactions.

Keywords: Cobalt(III); Second sphere coordination chemistry; 1,10-Phenanthroline; Polyoxovanadate; X-ray crystallography

1. Introduction

Anions are essential to life with crucial roles in biological processes, industry, and agriculture [1–9]. Some anionic species exist only in solution but cannot be isolated as solid salts due to solvent stabilization or lattice inhibition. This lattice inhibition can be removed by selection of suitable counter ions. According to McDaniel [10], the counter ion affects the formation of complex in a number of ways, such as lattice-dominating effect, lattice-energy-limiting effect, insulating effects, polarization effect, shape and

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size [10]. It is also well known that "solid metal complexes are stabilized by large counter ions, preferably ions of the same but opposite charge". The importance of shape and size of cation in precipitating the desired complexes is well-illustrated by halocuprate and iodoplatinate(II) salts [10, 11]. Counter ions which can have non-covalent interactions with anions in addition to the electrostatic interaction are useful in the synthesis of new and unusual anionic species, such as $[Hg_2(SCN)_7]^{3-}$ and $[HgBr_5]^{3-}$ [12, 13]. In these complexes, in addition to the large counter anion, non-covalent interaction like N–H···X play crucial roles in lattice stabilization.

Anionic species containing polyoxotransition metals have been studied extensively due to their varied geometries and oxidation states. Vanadium, in the form of organic–inorganic metal hybrid vanadium oxides or complexes with polyoxovanadate, has shown ability to adopt a variety of coordination geometries and oxidation states [14] with potential utilization in catalysis and materials. These vanadates are good electron acceptors and electron relay stations [15], and some are used in photolytic water splitting [16, 17]. The formation of polyoxovanadates depends upon coordination preferences of the transition metal used and geometrical constraints of the polydentate ligands. Anhydrous alkali metal metavanadates are composed of infinite chains of corner-sharing VO_4 tetrahedra in MVO_3 $(M = NH_4, K, Rb, Cs)$; $KVO_3 \cdot H_2O$ and $Ca(VO_3)_2$ [18] contain chains of edge-linked VO_5 units while forming $M_2V_2O_6$ with metals like Mg, Zn, Pb, Cd, and Cu [19–23]. For transition metals with large organic ligands, oxovanadates $V_4O_{12}^{4-}$ have been reported, $[Co_4O_4(dpaH)_4(CH_3COO)_2]_2 \cdot V_4O_{12} \cdot 5H_2O$ [24] and $[M^{II}(phen)_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ $(M^{II} = Co, Ni)$ [25]. The majority of reported complexes containing polyoxovanadates have been prepared under isothermal conditions except a few like $Ni(C_8H_{22}N_4)](VO_3)_2$ and $[M^{II}(phen)_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ $(M^{II} = Co, Ni)$. In this study, we have utilized cationic tris(1,10-phenanthroline)cobalt(III) complex for the isolation of peroxovanadate $(V_4O_{12})^{4-}$ as there is no report in the literature of stabilization of $[V_4O_{12}]^{4-}$ by trivalent or complexed metal ion. It is also envisaged that oxygens bonded to vanadium(V) will form hydrogen bonds (through second sphere interactions) with C–H groups originating from 1,10-phenanthroline coordinated to cobalt(III) to generate an intricate network that would stabilize the crystal lattice. This study reports synthesis, spectroscopic and X-ray structural study of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$, the first report on stabilization of rare $[V_4O_{12}]^{4-}$ by $[Co(phen)_3]^{3+}$.

2. Experimental

2.1. *Materials*

Analytical grade reagents were used without purification. $[Co(phen)_3]Cl_3$ was prepared by reacting $[Co(NH_3)_5Cl]Cl_2$ and 1,10-phenanthroline monohydrate according to the method described in the literature [26].

2.2. *Instruments and measurements*

C, H, and N were estimated microanalytically by automatic Perkin-Elmer 2400 CHN elemental analyzer. Cobalt was estimated by volumetric method [27]. UV-Vis spectrum was recorded in water using a HITACHI 330 spectrophotometer. Infrared (IR) spectrum was recorded using a Perkin-Elmer spectrum RX FT-IR system using a KBr pellet. Conductance measurements were performed on a Pico Conductivity Meter (Model CNO4091201, Lab India) in an aqueous medium at 25°C using double distilled water.

Thermogravimetric analysis (TGA) was conducted with a Mettler Toledo TGA/SDTA 851 instrument calibrated using high-purity indium and high-purity zinc standards. The experiment was conducted under nitrogen flow between 308 and 873 K and under air flow between 873 and 1173 K. The flow was maintained at $70\,\mathrm{mL\,min^{-1}}$. The specimen, 10 mg, contained in a $70\,\mu\mathrm{L}$ alumina pan was carried from 308 to 1173 K at variable heating rate; the heating rate was $1\,\mathrm{K\,min^{-1}}$ when the weight loss was higher than $2\,\mu\mathrm{g\,s^{-1}}$ and $20\,\mathrm{K\,min^{-1}}$ when the weight loss was less than $1\,\mu\mathrm{g\,s^{-1}}$.

Electrochemical measurements were conducted on a potentiostat (CH Instruments 440a) with a glass-encased, 3-mm diameter glassy carbon electrode (Cypress Systems), Pt wire, and Ag/AgCl ($3\,\mathrm{mol\,L^{-1}}$ KCl) as the working, auxiliary, and reference electrodes, respectively. The working electrode was polished on a polishing pad with $0.05\,\mu\mathrm{m}$ alumina powder, rinsed and sonicated prior to use. All solutions were bubbled with N_2 for 5 min to remove O_2 prior to scanning.

2.3. *Synthesis of* $[Co(phen)_3]_3(V_4O_{12})_2Cl\cdot 27H_2O$

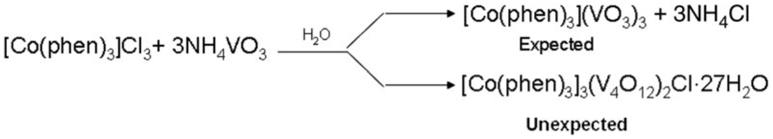
Tris(1,10-phenanthroline)cobalt(III) chloride (0.5 g, 0.7 mmol) was dissolved in water (10 mL) and in another beaker (0.248 g, 2.1 mmol) ammonium metavanadate was dissolved in water (30 mL). Upon mixing the two solutions, no color change or precipitation occurred. When it was allowed to evaporate slowly at room temperature, yellow single crystals appearing after a few hours were allowed to grow. The crystals were separated and dried in air. The yield was 0.487 g (66.25%). The composition was established by elemental analyses. $[Co(phen)_3]_3(V_4O_{12})_2Cl\cdot 27H_2O$ Found (%): C, 41.57; H, 4.02; N, 8.05; Co, 5.67; Cl, 1.09; Calcd (%): C, 41.67; H, 4.05; N, 8.10; Co, 5.70; Cl, 1.14.

2.4. *X-ray structure determination*

Single crystal X-ray diffraction data for the complex salt were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069\,\text{Å}$). All intensities were corrected for Lorentz-polarization and adsorption [28]. The structure was solved by direct methods with the SIR97 program [29] and refined by block-matrix least-squares (four blocks) using the SHELXL-97 program [30]. Non-hydrogen atoms were refined anisotropically. Hydrogens of phenanthroline were given calculated positions, while those belonging to water were not included in the refinement. All other calculations were performed using WinGX [31] and PARST [32]. Final *R*-values together with selected refinement details are given in table 1.

Table 1. Crystal data and refinement parameters of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$.

Chemical formula	$3(CoC_{36}H_{24}N_6) \cdot 2(V_4O_{12})Cl \cdot 27(H_2O)$
Formula weight	3112.03
Cell setting, space group	Triclinic, $P\bar{1}$
Temperature (K)	295
Unit cell dimensions (Å, °)	
a	15.4063(2)
b	18.8746(3)
c	25.1206(4)
α	97.7540(8)
β	103.5560(7)
γ	101.4310(7)
Volume ($Å^3$), Z	6833.14(18), 2
D_x ($mg\,m^{-3}$)	1.746
Radiation type	Mo-Kα
Absorption coefficient (mm^{-1})	0.99
Crystal form, color	Prismatic, orange
Crystal size (mm^3)	$0.29 \times 0.14 \times 0.09$
No. of measured, independent, and observed reflections	42,624, 28,163, 10,204
Criterion for observed reflections	$I > 2\sigma(I)$
θ_{max} (°)	27.0
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.101, 0.361, 0.98
No. of reflections/No. of parameters	28,163/1776
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.1928P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e\,Å^{-3}$)	0.99, −0.69



Scheme 1. Schematic representation of chemical reaction.

3. Results and discussion

3.1. *Synthesis*

The complex salt, $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$, was obtained by the reaction of tris(1,10-phenanthroline)cobalt(III) chloride and ammonium metavanadate in water in 1 : 3 molar ratio (scheme 1); metavanadate tetramerizes to form $[V_4O_{12}]^{4-}$ in the presence of $[Co(phen)_3]^{3+}$.

The newly formed complex salt has been characterized by elemental analyses, TGA, cyclic voltammetry (CV) studies, spectroscopies (UV-Vis and FT-IR), and conductance measurements. The presence of one chloride ion was confirmed by its gravimetric analysis using $AgNO_3$ solution. The complex salt is sparingly soluble in water and other common solvents. The crystal structure has been unambiguously established by single crystal X-ray crystallography.

3.2. *Thermogravimetric analysis*

TGA of the complex salt showed five weight loss steps. The first and second steps in TGA curve correspond to weight loss of 12.8 and 2.8% at 363 and 411 K, respectively (Supplementary material), which can be ascribed to loss of free water (calculated weight loss was 15.62% and observed weight loss was 15.60% in the first two steps). The third and fourth weight loss of 5.3 and 4.3%, respectively, take place between 425 and 873 K, corresponding to pyrolysis of organic matter. The fifth weight loss (41.3%) corresponds to oxidation of combustible material at 873 K, when the atmosphere changed from nitrogen to air. At the end of analysis 33.5% of ash remains in the pan.

3.3. *CV studies*

The electrochemical properties of $[Co(phen)_3]^{3+}$ have been studied [33], with CV reported to have an E_{pc} and E_{pa} of 0.114 and 0.179 V *versus* Ag/AgCl, respectively. CV of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$ showed a similar CV response at a glassy carbon electrode in 0.1 mol L^{-1} KCl aqueous solution with a scan rate of 100 mV s^{-1}. CV of the chloride salt showed similar behavior. $[Co(phen)_3]^{3+}$ undergoes a one-electron reduction to the 2+ form with a peak potential (E_{pc}) of 0.143 V *versus* Ag/AgCl as shown in Supplementary material. On the reverse scan, $Co(phen)_3^{2+}$ is re-oxidized at E_{pa} of 0.215 V. The peak potential separation (ΔE) of 72 mV indicates that this is the reversible one-electron couple as mentioned earlier. No electro-activity was seen for V^{5+} species in the potential range studied (0.6 to −0.9 V), even though the standard reduction potential (E^0) of VO^{2+} to V^{3+} species is 0.115 V *versus* Ag/AgCl. The ratio of I_{pa}/I_{pc} was close to 1 (0.988), further indicating that only the reversible couple contributes to I_{pc} as the irreversible reduction of V^{4+} species would be expected to contribute to I_{pc}.

3.4. *Measurement of solubility product*

The solubility product (Ksp) of the complex salt determined in water at 25°C was 8.08×10^{-22} as compared to that of $[Co(phen)_3]Cl_3$ (2.7×10^{-3}), showing affinity of the complex cation is greater for metavanadate than chloride ion. This increase in affinity may be due to the increased interactions between cations and anions.

3.5. *Molar conductance measurements*

Molar conductance of complex salt was measured in water in the concentration range 0–100×10^{-4} mol L^{-1} at 25°C. The limiting molar conductance at infinite dilution (Λ_o) was obtained by plotting the square root of concentration *versus* molar conductance, when extrapolated to zero. The Λ_o obtained is 882 S cm^2 mol^{-1}. The high value of molar conductance revealed that the complex salt consists of a large number of ions and unusual composition of complex salt.

3.6. *Spectroscopic characterization*

Vibrational spectrum of newly synthesized complex has been recorded in the region 400–4000 cm^{-1}. The peak assignments have been made in consultation with literature values [34–36]. IR spectral bands at 1634–1582, 3340, and 488 cm^{-1} were assigned to $\nu(C{=}C)/\nu(C{=}N)$, $\nu(O–H)$ of H_2O, and $\nu(Co–N)$, respectively. These peaks are characteristic for 1,10-phenanthroline coordinated to cobalt(III) and water of crystallization. The IR spectrum of individual polyoxovanadate is characteristic due to the relatively rigid structure of $V_4O_{12}^{4-}$ ion. IR bands at 942 and 905 cm^{-1} were assigned to symmetric and asymmetric vibrations of $V–O_t$ (terminal oxygens), while bands at 815 and 640 cm^{-1} were assigned to asymmetric and symmetric vibrations of the bridging $V–O_b–V$. Similar IR bands have been reported for $[Co(phen)_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ and $[Ni(phen)_3]_2V_4O_{12} \cdot phen \cdot 22H_2O$ [25]. For $[Co_4O_4(dpaH)_4(CH_3COO)_2]_2V_4O_{12} \cdot 5H_2O$ [24], bands due to V–O, V–O–V were reported at 950–770 cm^{-1}.

For Co(III) low-spin complexes, it is possible to observe d–d transitions in the visible region, because the transitions corresponding to $t_{2g}^6 \rightarrow t_{2g}^5\ e_g^1$ with promoted electron maintaining its spin are possible. Therefore, two electronic transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ reported, for familiar orange–yellow color for coordination compounds containing Co(III), around 340 and 470 nm. The electronic transitions for ligand 1,10-phenanthroline coordinated to Co(III) have been reported around 224, 264, and 290 nm [34, 37, 38]. The electronic spectrum of the title complex salt in water show absorption maxima (λ_{max}) at 219, 273, 280, 349, and 456 nm, close to reported values.

3.7. *Description of the structure*

3.7.1. Coordination geometry and bonding. The asymmetric unit is large, being constituted by three $[Co(phen)_3]^{3+}$, two dodecaoxotetravanadates, one chloride, and 27 co-crystallized water molecules. The high water content is confirmed by TGA, as reported above. The chloride ion is disordered over two equivalent positions, as well as a number of co-crystallized solvent molecules. A selection of relevant bond distances and angles is reported in table 2. The geometries around the cobalt(III) metal centers are slightly distorted octahedral, with N–Co–N angles involving nitrogen of the same 1,10-phenanthroline being $<90°$. The Co–N distances are consistent with those found in recently reviewed Co(III)-1,10-phenanthroline complexes [17–21]. The oxidation states of Co have been checked in the frame of the bond valence sum method [39] using the Co–N parameters reported in the byparm2009.cif table [40]. The calculated values are 3.5, 3.6, and 3.4 for Co1, Co2, and Co3, respectively. V–O distances are similar to the mean bond lengths obtained from a CSD search on compounds containing the oxovanadate anion, 1.779(6) and 1.632(6) Å for exocyclic and endocyclic bonds, respectively (values calculated on 16 hits). The eight-membered vanadate rings are almost planar, as shown by the total puckering amplitude index 0.16(9), according to Cremer & Pople [41] and by values of the endocyclic torsion angles, ranging from 0.7 to 38°. ORTEPIII [42] views of one cobalt complex and one oxovanadate are shown in figure 1.

3.7.2. Packing. The crystal packing, due to the high number of water molecules involved, is quite complicated. Table 3 reports short O···O contacts inside the crystal lattice ranging from 2.55(3) to 2.98(3) Å which are typical for hydrogen bonding of

Table 2. Selected bond lengths and angles (Å and °) for $[Co(phen)_3]_3(V_4O_{12})_2Cl\cdot 27H_2O$.

Co1–N1	1.931(8)	Co2–N10	1.950(9)
Co1–N2	1.936(8)	Co2–N11	1.938(9)
Co1–N3	1.952(8)	Co2–N12	1.922(8)
Co1–N4	1.960(9)	Co3–N13	1.951(9)
Co1–N5	1.959(9)	Co3–N14	1.955(9)
Co1–N6	1.935(8)	Co3–N15	1.937(9)
Co2–N7	1.932(9)	Co3–N16	1.961(9)
Co2–N8	1.954(9)	Co3–N17	1.955(9)
Co2–N9	1.930(8)	Co3–N18	1.971(9)
V1–O1	1.642(10)	V4–O12	1.604(7)
V1–O2	1.769(8)	V5–O13	1.623(8)
V1–O3	1.767(10)	V5–O14	1.628(10)
V1–O4	1.600(9)	V5–O15	1.774(8)
V2–O2	1.774(9)	V5–O16	1.786(11)
V2–O5	1.630(10)	V6–O16	1.762(11)
V2–O6	1.773(10)	V6–O17	1.643(9)
V2–O7	1.616(7)	V6–O18	1.624(8)
V4–O3	1.765(11)	V10–O19	1.599(12)
V3–O6	1.773(11)	V10–O20	1.773(10)
V3–O8	1.651(10)	V10–O21	1.731(1)
V3–O9	1.758(8)	V10–O24	1.619(12)
V3–O10	1.630(9)	V11–O20	1.758(10)
V4–O9	1.786(8)	V11–O22	1.628(12)
V4–O11	1.622(10)	V11–O23	1.595(11)
N1–Co1–N2	84.6(3)	N8–Co2–N12	87.9(4)
N1–Co1–N3	94.9(3)	N9–Co2–N10	84.2(4)
N1–Co1–N5	94.2(4)	N9–Co2–N11	91.5(4)
N1–Co1–N6	87.8(3)	N10–Co2–N11	88.9(4)
N2–Co1–N3	89.7(3)	N10–Co2–N12	93.7(4)
N2–Co1–N4	93.1(3)	N11–Co2–N12	85.1(4)
N2–Co1–N6	93.6(4)	N13–Co3–N14	84.1(3)
N3–Co1–N4	84.8(4)	N13–Co3–N16	92.5(4)
N4–Co1–N5	88.0(4)	N13–Co3–N18	89.7(3)
N4–Co1–N6	92.7(4)	N14–Co3–N15	92.6(4)
N5–Co1–N6	84.6(4)	N14–Co3–N16	88.9(4)
N7–Co2–N8	85.1(4)	N14–Co3–N18	93.6(4)
N7–Co2–N9	89.2(4)	N15–Co3–N16	83.9(4)
N7–Co2–N10	93.5(4)	N15–Co3–N17	89.1(4)
N7–Co2–N12	94.5(4)	N15–Co3–N18	94.0(4)
N8–Co2–N9	94.2(4)	N16–Co3–N17	94.1(4)
N8–Co2–N11	92.8(4)	N17–Co3–N18	83.4(4)

medium strength. In addition, phen C–H groups are involved in C–H···O/Cl type interactions [43–46] (as many as 32 significant hydrogen bonds have been observed which are given in table 4) defining the second-sphere coordination around the three cobalt complex cations. Three complex cations with C–H···O contacts are shown in figure 2. These C–H···O interactions (H···A distance ranging from 2.33–2.69 Å and A···H–D angles ranging from 132 to 160°) are of comparable strength to commonly employed N–H···O interaction (H···A distance ranging from 2.08 to 2.76 Å and A···H–D angles ranging from 130 to 179°) [47] in anion binding studies. These C–H···O interactions play a crucial role in binding of $[V_4O_{12}]^{4-}$, as 19 C–H···O interactions are between oxygens originating from $[V_4O_{12}]^{4-}$ and C–H of 1,10-phenanthroline. No significant π–π interactions have been observed, as the centroids of the stacked phenanthroline moieties are located more than 3.8 Å apart. The packing diagram of the complex salt is shown in figure 3.

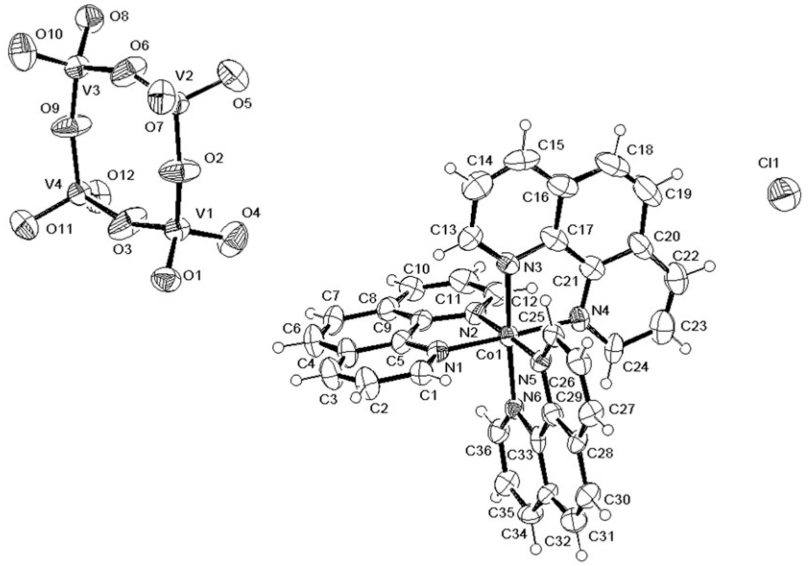


Figure 1. ORTEPIII view of one cobalt complex cation, one polyoxovanadate anion and one chloride in $[Co(phen)_3]_3(V_4O1_2)_2Cl\cdot27H_2O$. Ellipsoids are drawn at 40% probability. For the sake of clarity, the other ions and all lattice water molecules constituting the asymmetric unit are omitted.

Table 3. Short O···O/Cl contacts (Å) for $[Co(phen)_3]_3(V_4O_{12})_2Cl\cdot27H_2O$.

O14···O19W	2.768(17)	O8W···O22W	2.824(23)
O17···O5W	2.900(13)	O9W···O16W	2.755(16)
O17···O10W	2.775(15)	O9W···O17W	2.798(20)
O18···O27W	2.679(21)	O9W···O21W	2.844(21)
O24···O31W	2.818(22)	O10W···O16W	2.940(18)
O1W···O15W	2.892(16)	O16W···O27W	2.730(28)
O2W···O4W	2.777(15)	O18W···O20W	2.799(16)
O2W···O6W	2.868(16)	O18W···O32W	2.870(32)
O2W···O14W	2.787(20)	O19W···O20W	2.822(22)
O3W···O5W	2.698(13)	O26W···O29W	2.821(33)
O5W···O19W	2.780(19)	O26W···O31W	2.785(35)
O6W···O18W	2.816(17)	O27W···O34W	2.912(37)
O8W···O21W	2.897(18)		
O4···O24W$^{\mathrm{i}}$	2.737(18)	O33W···O22W$^{\mathrm{iv}}$	2.554(27)
O23W···O23$^{\mathrm{i}}$	2.728(26)	O3W···O22$^{\mathrm{v}}$	2.693(15)
O1W···O11$^{\mathrm{ii}}$	2.735(12)	O28W···O30W$^{\mathrm{vi}}$	2.778(40)
O8W···O8$^{\mathrm{ii}}$	2.776(14)	O23W···O11$^{\mathrm{vi}}$	2.810(23)
O15W···O10$^{\mathrm{ii}}$	2.690(16)	O25W···O32W$^{\mathrm{vi}}$	2.732(34)
O16W···O8$^{\mathrm{ii}}$	2.747(17)	O14W···O5$^{\mathrm{vii}}$	2.748(17)
O22W···O5$^{\mathrm{ii}}$	2.742(20)	O28W···O23$^{\mathrm{viii}}$	2.693(20)
O1W···O24$^{\mathrm{iii}}$	2.738(16)	O32W···O25W$^{\mathrm{ix}}$	2.732(34)
O6W···Cl1$^{\mathrm{iii}}$	2.781(13)	O1···O4W$^{\mathrm{x}}$	2.782(15)
O15W···O26W$^{\mathrm{iii}}$	2.801(23)	O4W···O24W$^{\mathrm{xi}}$	2.815(23)
O17W···O14$^{\mathrm{iii}}$	2.790(14)	O29W···O18W$^{\mathrm{xi}}$	2.989(25)
O25W···O22W$^{\mathrm{iv}}$	2.984(26)	O30W···O19$^{\mathrm{xi}}$	2.841(28)

Symmetry codes: ($^{\mathrm{i}}$) $1-x, -y, -z$; ($^{\mathrm{ii}}$) $x, y+1, z+1$; ($^{\mathrm{iii}}$) $1-x, -y, 1-z$; ($^{\mathrm{iv}}$) $x+1, y, z$; ($^{\mathrm{v}}$) $x, y, 1+z$; ($^{\mathrm{vi}}$) $x, y+1, z$; ($^{\mathrm{vii}}$) $x+1, y, z+1$; ($^{\mathrm{viii}}$) $x+1, y+1, z+1$; ($^{\mathrm{ix}}$) $x, y-1, z$; ($^{\mathrm{x}}$) $1-x, -y-1, 1-z$; ($^{\mathrm{xi}}$) $2-x, y, 1-z$.

Table 4. Hydrogen bonding parameters for CH···O/Cl contacts (Å and °) in $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$.

D–H···A	D–H	D···A	H···A	D–H···A
C11–H7···O21	0.930	3.55(1)	2.67	158
C22–H14···Cl1	0.930	3.54(2)	2.66	156
C43–H29···O7	0.930	3.23(2)	2.55	130
C73–H49···O15	0.930	3.15(1)	2.45	133
C85–H57···O33W	0.930	3.24(3)	2.51	136
C102–H68···O18	0.930	3.38(2)	2.69	132
C51–H35···O3^{i}	0.930	3.24(1)	2.39	151
C54–H36···O12^{i}	0.930	3.51(1)	2.63	158
C1–H1···O2^{i}	0.930	3.03(1)	2.33	132
C30–H20···O10^{i}	0.930	3.36(1)	2.60	139
C7–H5···O12^{ii}	0.930	3.20(1)	2.45	138
C12–H8···O22^{iii}	0.930	3.28(1)	2.51	141
C13–H9···O24W^{iii}	0.930	3.36(2)	2.67	131
C63–H43···O5W^{iv}	0.930	3.50(2)	2.67	149
C49–H33···O2W^{iv}	0.930	3.26(2)	2.47	143
C25–H17···Cl1^{v}	0.930	3.30(1)	2.54	138
C31–H21···O13^{vi}	0.930	3.41(1)	2.57	150
C36–H24···Cl2^{vi}	0.930	3.28(1)	2.49	144
C34–H22···O16^{vi}	0.930	3.25(1)	2.48	139
C97–H65···O5W^{vi}	0.930	3.26(1)	2.51	136
C62–H42···O22^{vii}	0.930	3.20(2)	2.38	147
C37–H25···O9^{vii}	0.930	3.19(1)	2.47	134
C55–H37···O4^{vii}	0.930	3.38(2)	2.66	135
C57–H38···O4^{vii}	0.930	3.40(2)	2.68	135
C59–H40···O8W^{viii}	0.930	3.40(1)	2.65	139
C79–H53···O13^{ix}	0.930	3.25(2)	2.52	136
C91–H61···O28W^{x}	0.930	3.42(3)	2.58	149
C84–H56···O25W^{x}	0.930	3.39(2)	2.61	142
C87–H59···O8W^{xi}	0.930	3.28(2)	2.39	158
C106–H70···O6^{xii}	0.930	3.30(1)	2.41	160
C103–H69···O7^{xii}	0.930	3.46(1)	2.58	158
C108–H72···O9W^{xiii}	0.930	3.29(2)	2.54	138

Symmetry codes: (^{i}) $-x, -y-1, -z$; (^{ii}) $1-x, -y-1, -z$; (^{iii}) $1-x, -y, -z$; (^{iv}) $x-1, y, z-1$; (^{v}) $-x, -y, -z$; (^{vi}) $1-x, -y, 1-z$; (^{vii}) $x-1, y, z$; (^{viii}) $x-1, y-1, z-1$; (^{ix}) $2-x, -y, 1-z$; (^{x}) $2-x, 1-y, 1-z$; (^{xi}) $1-x, 1-y, 1-z$; (^{xii}) $x+1, y+1, z+1$; (^{xiii}) $x+1, y, z$.

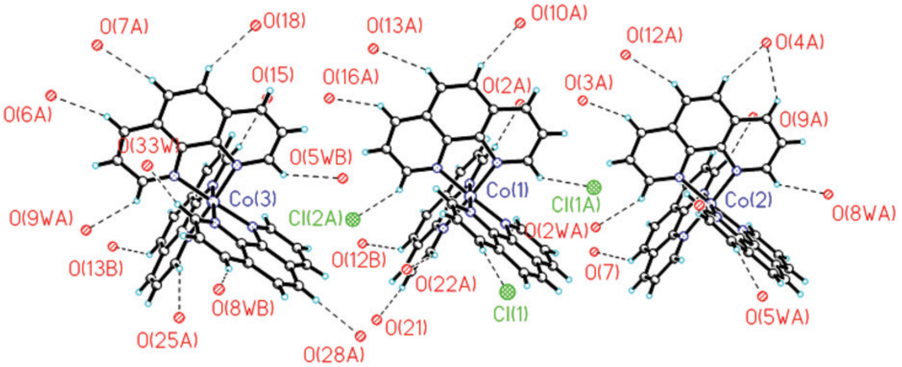


Figure 2. C–H···O interactions between complex cations and hydrogen bond acceptor groups from anions and lattice waters in $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$.

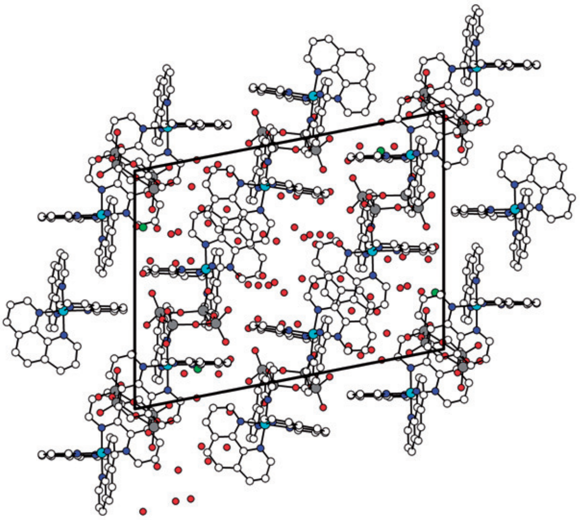


Figure 3. Packing diagram of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$ (viewed along *a*).

All related structures reported are characterized by high content of co-crystallized solvent with the number of water molecules ranging from 5 to 22. In particular, the reported [25] structure of Co(II) salt contains a free co-crystallized phenanthroline molecule besides 22 water molecules. A possible explanation is that two cumbersome objects (the cation and the anion), very different in shape, when put together in the crystal lattice leave large empty spaces that have to be occupied by the solvent of crystallization to assure efficient packing and thereby increasing stability of crystal lattice. Thus, O···O/Cl short contacts and C–H···O/Cl hydrogen bonds are driving forces for the stabilization of the crystal lattice and the formation of complex salt.

4. Conclusions

A new complex salt $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$ has been synthesized and characterized by physico-chemical, spectroscopic, and X-ray structural studies. Single crystal X-ray structure determination revealed an ionic structure consisting of three complex cations, two $V_4O_{12}^{4-}$ anions, one chloride and 27 lattice water molecules. The crystal lattice is stabilized by hydrogen bonding, C–H···O/Cl non-covalent interactions in addition to the electrostatic forces of attraction. Detailed structural and spectroscopic analyses of $[Co(phen)_3]_3(V_4O_{12})_2Cl \cdot 27H_2O$ showed that the large anion $[V_4O_{12}]^{4-}$ was stabilized by the large $[Co(phen)_3]^{3+}$.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 733583. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

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References

[1] L. Vieira, A. Lavan, F. Dragger, Z.I. Cabantchik. *J. Biol. Chem.*, **269**, 16254 (1994).
[2] P.D. Beer, P.A. Gale. *Angew. Chem. Int. Ed.*, **40**, 486 (2001).
[3] E. Bossi, S. Giovannardi, F. Binda, G. Forlani, A. Peres. *J. Physiol.*, **541**, 343 (2002).
[4] I. Stibor, P. Zlatušková. *Top. Curr. Chem.*, **255**, 31 (2005).
[5] S. Kubik, R. Goddard, S. Otto, S. Pohl, C. Reyheller, S. Stüwe. *Biosens. Bioelectron.*, **20**, 2364 (2005).
[6] F. Davis, S.D. Collyer, S.P. Higson. *Top. Curr. Chem.*, **255**, 97 (2005).
[7] P. Gale. *Coord. Chem. Rev.*, **250**, 2917 (2006).
[8] A. Goel, N. Brennan, N. Brady, P.T.M. Kenny. *Biosens. Bioelectron.*, **22**, 2047 (2007).
[9] T. Briza, Z. Kejik, I. Cisaova, J. Kralova, P. Martasek, V. Karl. *Chem. Commun.*, 1901 (2008).
[10] D.H. McDaniel, *Annual Reports in Inorganic and General Synthesis*, Vol. 1, p. 293 (1972).
[11] F. Basolo. *Coord. Chem. Rev.*, **3**, 213 (1968).
[12] R. Bala, R.P. Sharma, R. Sharma, B.M. Kariuki. *Inorg. Chem. Commun.*, **9**, 852 (2006).
[13] R.P. Sharma, R. Sharma, A. Kumar, P. Venugopalan, P. Brando, V. Felix. *Inorg. Chem. Commun.*, **12**, 945 (2009).
[14] G.H. Li, Z. Shi, Y.H. Xu, S.H. Feng. *Inorg. Chem.*, **34**, 1170 (2003).
[15] E. Coronado, C.J. Gomez-Garcia. *Chem. Rev.*, **98**, 273 (1998).
[16] A. Kudo, K. Omori, H. Kato. *J. Am. Chem. Soc.*, **121**, 11459 (1999).
[17] J. Ye, Z. Zou, H. Arakawa, M. Oshikiri, M. Shimoda, A. Matsushita, T. Shishido. *J. Photochem. Photobiol.*, **A148**, 79 (2002).
[18] H.T. Evans Jr. *Z. Kristallogr.*, **114**, 257 (1960).
[19] J.-C. Bouloux, J. Galy. *Bull. Soc. Chim. Fr.*, 739 (1969).
[20] H.N. Ng, C. Calvo. *Can. J. Chem.*, **50**, 3619 (1972).
[21] C. Calvo, D. Manolescu. *Acta Cryst.*, **B29**, 1743 (1973).
[22] J.-C. Bouloux, G. Prez, J. Galy. *Bull. Soc. Fr. Miner. Crist.*, **95**, 130 (1972).
[23] J. Angenault, A. Rimsky, C.R. Acad. *Sci. Peris Ser.C.*, **267**, 227 (1968).
[24] X. Zhang, W. You, Z. Zhu, L. Dang, Z. Sun, X. Zheng. *Inorg. Chem. Commun.*, **9**, 526 (2006).
[25] L. Zurkova, R. Kucsera, R. Gyepes, M. Sivak. *Monatsh. Chem.*, **134**, 1071 (2003).
[26] P. Pfeiffer, Br. Werdelmann. *Z. Anorg. Allg. Chem.*, **31**, 263 (1950).
[27] G.G. Schlessinger. *Inorg. Synth.*, **9**, 160 (1967).
[28] R.H. Blessing. *Acta Cryst.*, **A51**, 339 (1995).
[29] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Crystallogr.*, **32**, 115 (1999).
[30] G.M. Sheldrick. *SHELX-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[31] L.J. Farrugia. *J. Appl. Crystallogr.*, **32**, 837 (1999).
[32] M. Nardelli. *J. Appl. Crystallogr.*, **28**, 659 (1995).
[33] M.T. Carter, A.J. Bard. *J. Am. Chem. Soc.*, **109**, 7528 (1987).
[34] M.S. Atanassova, G.D. Dimitrov. *Spectrochim. Acta*, **A59**, 1655 (2003).
[35] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, John Wiley & Sons, New York (1997).
[36] R.A. Nyquist, R.O. Kagel. *Infrared Spectra of Inorganic Compounds*, Academic Press, London (1971).
[37] P. Hendry, A. Ludi. *Adv. Inorg. Chem.*, **35**, 117 (1990).
[38] C. Thomos, K. Pringle, G.B. Dsacon. *J. Chem. Edu.*, **68**, 516 (1989).
[39] D. Altermatt, I.D. Brown. *Acta Cryst.*, **B41**, 244 (1985).

[40] *Byparm2009.cif* table, Copyright: I.D. Brown, Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario Canada.

[41] D. Cremer, J.A. Pople. *J. Am. Chem. Soc.*, **97**, 1354 (1975).

[42] M.N. Burnett, C.K. Johnson. *ORTEP-III: Oak Ridge Thermal Ellipsoids Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, TN (1996).

[43] G.R. Desiraju. *Acc. Chem. Res.*, **35**, 565 (2002).

[44] P.K. Thallapally, A.K. Katz, H.L. Carell, G.R. Desiraju. *CrystEngComm.*, **5**, 87 (2003).

[45] G.R. Desiraju. *Acc. Chem. Res.*, **24**, 290 (1991).

[46] M. Czugler, N. Bathori. *CrystEngComm.*, **6**, 494 (2004).

[47] B. Wu, J. Liang, J. Yang, C. Jia, X.-J. Yang, H. Zhang, N. Tang, C. Janiak. *Chem. Commun.*, 1762 (2008).