

Published in final edited form as:

*J Coord Chem.* 2010 September 1; 63(17): 3016–3027. doi:10.1080/00958972.2010.504831.

## Stabilization of tetrameric metavanadate ion by tris(1,10-phenanthroline)cobalt(III): Synthesis, spectroscopic and X-ray structural study of $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$

RAJ PAL SHARMA<sup>\*,a</sup>, AJNESH SINGH<sup>a</sup>, PALOTH VENUGOPALAN<sup>a</sup>, ROYCE DANSBY-SPARKS<sup>b</sup>, ZI-LING XUE<sup>b</sup>, STEFANO ROSSETTI<sup>c</sup>, and VALERIA FERRETTI<sup>\*,d</sup>

<sup>a</sup>Department of Chemistry, Panjab University, Chandigarh-160014, India

<sup>b</sup>Department of Chemistry, The University of Tennessee, Knoxville, TN 37996, USA

<sup>c</sup>Istituto per la Sintesi Organica e la Fotoreattività (ISOF) -CNR sez. Ferrara, c/o Dipartimento di Chimica, University of Ferrara via L. Borsari 46, I-44100, Ferrara, Italy

<sup>d</sup>Centro di Strutturistica Diffraattometrica and Dipartimento di Chimica, University of Ferrara via L. Borsari 46, I-44100, Ferrara, Italy

### Abstract

A new complex salt of composition  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  (phen = 1,10-phenanthroline and  $[\text{V}_4\text{O}_{12}]^{4-}$  = tetrameric dodecaoxotetranavanadate ion) was synthesized by reacting appropriate salts in aqueous medium. The complex salt has been characterized by elemental analyses, thermogravimetric analysis (TGA), cyclic voltammetry (CV), 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,  $[\text{Co}(\text{phen})_3]^{3+}$ , two  $[\text{V}_4\text{O}_{12}]^{4-}$  anions, one chloride and twenty seven lattice waters. Detailed structural and spectroscopic analyses of  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  show that the large anion is stabilized by the 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 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 D.H. McDaniel, the counter ion affects the formation of complex in a number of ways like lattice dominating, lattice energy limiting, insulating effects, polarization effect, shape and size [10]. Solid metal complexes are stabilized by

\*Corresponding authors. rpsmapu@yahoo.co.in (RPS); frt@unife.it (VF).

**Supplementary data** 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; deposit@ccdc.cam.ac.uk.

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 synthesis of new and unusual anionic species like  $[\text{Hg}_2(\text{SCN})_7]^{3-}$  and  $[\text{HgBr}_5]^{3-}$  [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 have 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, 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  $\text{VO}_4$  tetrahedra in  $\text{MVO}_3$  ( $\text{M} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$ );  $\text{KVO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Ca}(\text{VO}_3)_2$  [18] contain chains of edge-linked  $\text{VO}_5$  units while forming  $\text{M}_2\text{V}_2\text{O}_6$  with metals like Mg, Zn, Pb, Cd and Cu [19-23]. For transition metals with large organic ligands, oxovanadates  $\text{V}_4\text{O}_{12}^{4-}$  have been reported,  $[\text{Co}_4\text{O}_4(\text{dpaH})_4(\text{CH}_3\text{COO})_2]_2 \cdot \text{V}_4\text{O}_{12} \cdot 5\text{H}_2\text{O}$  [24] and  $[\text{M}^{\text{II}}(\text{phen})_3]_2 \text{V}_4\text{O}_{12} \cdot \text{phen} \cdot 22\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Co}, \text{Ni}$ ) [25]. The majority of complexes containing polyoxovanadates reported have been prepared under isothermal conditions except a few like  $\text{Ni}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{VO}_3)_2$  and  $[\text{M}^{\text{II}}(\text{phen})_3]_2 \text{V}_4\text{O}_{12} \cdot \text{phen} \cdot 22\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Co}, \text{Ni}$ ). In the present study we have utilized cationic tris(1,10-phenanthroline)cobalt(III) complex for isolation of peroxovanadate ( $\text{V}_4\text{O}_{12}^{4-}$ ) as there is no report in the literature of stabilization of  $[\text{V}_4\text{O}_{12}]^{4-}$  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  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl} \cdot 27\text{H}_2\text{O}$ , the first report of a stabilization of rare  $[\text{V}_4\text{O}_{12}]^{4-}$  by  $[\text{Co}(\text{phen})_3]^{3+}$ .

## 2. Experimental

### 2.1. Materials

Analytical grade reagents were used without purification.  $[\text{Co}(\text{phen})_3]\text{Cl}_3$  was prepared by reacting  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  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/Visible spectra were recorded in water using a HITACHI 330 spectrophotometer. Infrared 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 aqueous medium at 25 °C using doubly-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 ml min<sup>-1</sup>. The specimen, about 10 mg, contained in a 70 µl alumina pan was carried from 308 to 1173 K at variable heating

rate: the heating rate was  $1 \text{ K min}^{-1}$  when the weight loss was higher than  $2 \mu\text{g s}^{-1}$ , and  $20 \text{ K min}^{-1}$  when the weight loss was less than  $1 \mu\text{g s}^{-1}$ .

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 M KCl) as the working, auxiliary, and reference electrodes, respectively. The working electrode was polished on a polishing pad with  $0.05 \mu\text{m}$  alumina powder, rinsed and sonicated prior to use. All solutions were bubbled with  $\text{N}_2$  for 5 min to remove  $\text{O}_2$  prior to scanning.

### 2.3. Synthesis of $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$

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.  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  Found (%): C, 41.57; H, 4.02; N, 8.05; Co, 5.67; Cl, 1.09; Calculated (%): 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  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). 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.

## 3. Results and discussion

### 3.1. Synthesis

The complex salt,  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  was obtained by 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  $[\text{V}_4\text{O}_{12}]^{4-}$  in the presence of  $[\text{Co}(\text{phen})_3]^{3+}$ .

The newly formed complex salt has been characterized by elemental analyses, TGA, cyclic voltammetry studies, spectroscopies (UV/Visible and FT-IR) and conductance measurements. The presence of one chloride ion was confirmed by its gravimetric analysis using  $\text{AgNO}_3$  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

Thermogravimetric analysis of the complex salt showed five weight loss steps. The first and second steps in the TGA curve correspond to weight loss of 12.8% and 2.8% at 363 K 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. In the pan, at the end of analysis, 33.5% of ash remains.

### 3.3. Cyclic voltammetry studies

The electrochemical properties of  $[\text{Co}(\text{phen})_3]^{3+}$  have been studied [33], with CV reported to have an  $E_{\text{pc}}$  and  $E_{\text{pa}}$  of 0.114 and 0.179 V vs. Ag/AgCl, respectively. CV of  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  showed a similar CV response at a glassy carbon electrode in 0.1 M KCl aqueous solution with a scan rate of 100 mV/s. A CV of the chloride salt showed similar behavior.  $[\text{Co}(\text{phen})_3]^{3+}$  undergoes a one-electron reduction to the 2+ form with a peak potential ( $E_{\text{pc}}$ ) of 0.143 V vs. Ag/AgCl as shown in Supplementary Material. On the reverse scan,  $\text{Co}(\text{phen})_3^{2+}$  is reoxidized at  $E_{\text{pa}}$  of 0.215 V. The peak potential separation ( $\Delta E$ ) of 72 mV indicates that this is the reversible one electron couple mentioned earlier. No electro-activity was seen for  $\text{V}^{5+}$  species in the potential range studied (0.6 to -0.9 V), even though the standard reduction potential ( $E^0$ ) of  $\text{VO}^{2+}$  to  $\text{V}^{3+}$  species is 0.115 V vs. Ag/AgCl. The ratio of  $I_{\text{pa}}/I_{\text{pc}}$  was close to 1 (0.988), further indicating that only the reversible couple contributes to  $I_{\text{pc}}$  as the irreversible reduction of  $\text{V}^{4+}$  species would be expected to contribute to  $I_{\text{pc}}$ .

### 3.4. Measurement of solubility product

The solubility product ( $K_{\text{sp}}$ ) of the complex salt determined in water at 25 °C was  $8.08 \times 10^{-22}$  as compared to that of  $[\text{Co}(\text{phen})_3]\text{Cl}_3$  ( $2.7 \times 10^{-3}$ ), showing affinity of the complex cation is greater for metavanadate than chloride. 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  $\times 10^{-4}$  M at 25 °C. The limiting molar conductance at infinite dilution ( $\Lambda_0$ ) was obtained by plotting the square root of concentration versus molar conductance, when extrapolated to zero. The  $\Lambda_0$  obtained is 882  $\text{Scm}^2\text{mol}^{-1}$ . 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  $\text{cm}^{-1}$ . The peak assignments have been made in consultation with literature values [34-36]. IR spectral bands at 1634-1582, 3340 and 488  $\text{cm}^{-1}$  were assigned to  $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{N})$ ,  $\nu(\text{O}-\text{H})$  of  $\text{H}_2\text{O}$  and  $\nu(\text{Co}-\text{N})$ . These peaks are characteristic for 1,10-phenanthroline attached to cobalt(III) and water of crystallization. The IR spectrum of individual polyoxovanadate is characteristic due to the relatively rigid structure of  $\text{V}_4\text{O}_{12}^{4-}$  ion. IR bands at 942 and 905  $\text{cm}^{-1}$  were assigned to symmetrical and asymmetric vibrations of V-O<sub>t</sub> (terminal oxygens) while bands at 815 and 640  $\text{cm}^{-1}$  were assigned to asymmetrical and symmetric vibrations of the bridging V-O<sub>b</sub>-V. Similar IR bands have been reported for  $[\text{Co}(\text{phen})_3]_2\text{V}_4\text{O}_{12}\cdot\text{phen}\cdot 22\text{H}_2\text{O}$  and  $[\text{Ni}(\text{phen})_3]_2\text{V}_4\text{O}_{12}\cdot\text{phen}\cdot 22\text{H}_2\text{O}$  [25]. For  $[\text{Co}_4\text{O}_4(\text{dpaH})_4(\text{CH}_3\text{COO})_2]_2\text{V}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$  [24] bands due to V-O, V-O-V were reported at 950-770  $\text{cm}^{-1}$ .

For Co(III) low spin complexes, it is possible to observe d-d transitions in the visible region because 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  $^1A_{1g} \rightarrow ^1T_{2g}$  are reported for familiar orange-yellow color for coordination compounds containing Co(III) which were observed around 340 and 470 nm. 1,10-Phenanthroline is also coordinated to

Co(III) and transitions around 224, 264, 290 nm arise from phen [34,37,38]. The electronic spectrum of the title complex salt in water show absorption maxima ( $\lambda_{\text{max}}$ ) 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  $[\text{Co}(\text{phen})_3]^{3+}$ , two dodecaoxotetranadates, one chloride and 27 co-crystallized waters. The high water content is confirmed by TGA analysis, as reported above. The chloride 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 geometry around the three cobalts is slightly distorted octahedral with N-Co-N angles involving nitrogen of the same 1,10-phenanthroline being  $< 90^\circ$ . 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  $38^\circ$ . 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  $\text{O}\cdots\text{O}$  contacts inside the crystal lattice, ranging from 2.55(3) to 2.98(3) Å, which are typical for hydrogen bonding of medium strength. In addition, *phen* C-H groups were involved in C-H $\cdots$ O/Cl type interactions [43-46] (as many as thirty two 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 $\cdots$ O contacts are shown in figure 2. These C-H $\cdots$ O interactions (H...A distance ranging from 2.33-2.69 Å and angles A...H-D ranging from  $132$ - $160^\circ$ ) are of comparable strength to commonly employed N-H $\cdots$ O interaction (H...A distance ranging from 2.08-2.76 Å angles A...H-D ranging from  $130$ - $179^\circ$ ) [47] in anion binding studies. These C-H $\cdots$ O interactions play a crucial role in binding  $[\text{V}_4\text{O}_{12}]^{4-}$  as nineteen C-H $\cdots$ O interactions are between oxygens originating from  $[\text{V}_4\text{O}_{12}]^{4-}$  and C-H of 1,10-phenanthroline. No significant  $\pi$ - $\pi$  interactions have been found, since 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.

All related structures reported are characterized by high content of co-crystallized solvent with the number of waters ranging from 5 to 22. In particular, the structure of the Co(II) salt contains, besides 22 water molecules, a free co-crystallized phenanthroline. A possible explanation is that two cumbersome objects (the cation and the anion), very different in shape, when put together in the crystal lattice leaves 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,  $\text{O}\cdots\text{O}/\text{Cl}$  short contacts and C-H $\cdots$ O/Cl hydrogen bonds are driving forces for stabilization of the crystal lattice and formation of the complex salt.

## 4. Conclusions

A new complex salt  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  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  $\text{V}_4\text{O}_{12}^{4-}$  anions, one chloride and twenty seven lattice waters. The crystal lattice is stabilized by hydrogen bonding,  $\text{C-H}\cdots\text{O}/\text{Cl}$  non-covalent interactions in addition to the electrostatic forces. Detailed structural and spectroscopic analyses of  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$  show the large anion  $[\text{V}_4\text{O}_{12}]^{4-}$  was stabilized by the large  $[\text{Co}(\text{phen})_3]^{3+}$ .

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

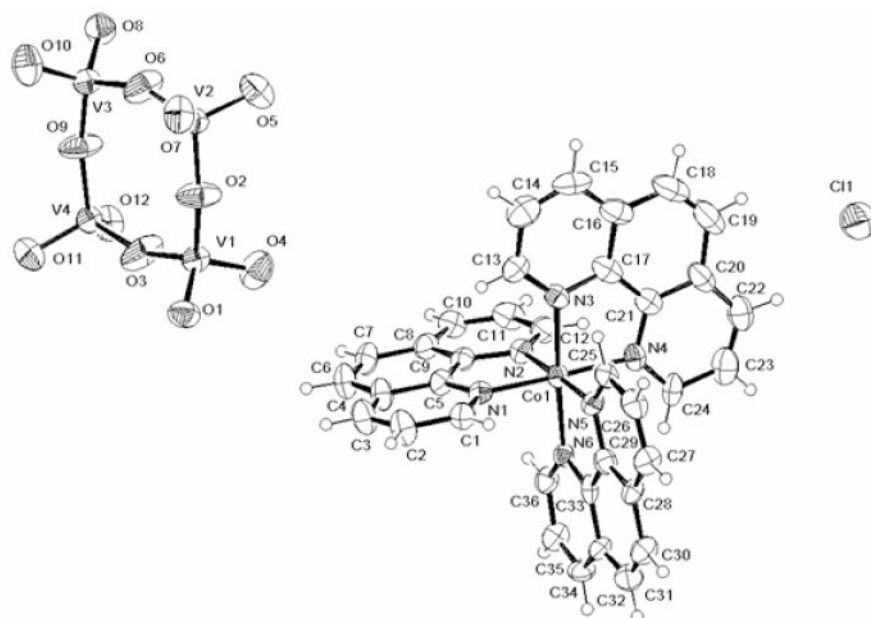
## Acknowledgments

The authors gratefully acknowledge the financial support of CSIR vide grant no- 01(2020) 2005/ EMR-II, the US National Science Foundation (CHE-0516928), and the US National Institute of Health (1R01DK078652-01A2).

## References

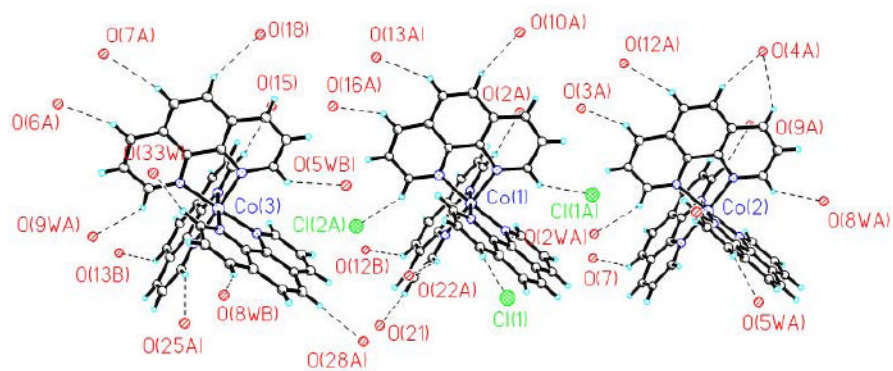
1. Vieira L, Lavan A, Dragger F, Cabantchik ZI. *J Biol Chem* 1994;269:16254. [PubMed: 8206930]
2. Beer PD, Gale PA. *Angew Chem Int Ed* 2001;40:486.
3. Bossi E, Giovannardi S, Binda F, Forlani G, Peres A. *J Physiol* 2002;541:343. [PubMed: 12042343]
4. Stibor I, Zlatušková P. *Top Curr Chem* 2005;255:31.
5. Kubik S, Goddard R, Otto S, Pohl S, Reyheller C, Stüwe S. *Biosens Bioelectron* 2005;20:2364. [PubMed: 15797340]
6. Davis F, Collyer SD, Higson SP. *Top Curr Chem* 2005;255:97.
7. Gale P. *Coord Chem Rev* 2006;250:2917.
8. Goel A, Brennan N, Brady N, Kenny PTM. *Biosens Bioelectron* 2007;22:2047. [PubMed: 17015010]
9. Briza T, Kejik Z, Cisaova I, Kralova J, Martasek P, Karl V. *Chem Commun* 2008:1901.
10. McDaniel DH. *Annual Reports in Inorganic and General Synthesis* 1972:1.
11. Basolo F. *Coord Chem Rev* 1968;3:213.
12. Bala R, Sharma RP, Sharma R, Kariuki BM. *Inorg Chem Commun* 2006;9:852.
13. Sharma RP, Sharma R, Kumar A, Venugopalan P, Brando P, Felix V. *Inorg Chem Commun* 2009;12:945.
14. Li GH, Shi Z, Xu YH, Feng SH. *Inorg Chem* 2003;34:1170. [PubMed: 12588154]
15. Coronado E, Gomez-Garcia CJ. *Chem Rev* 1998;98:273. [PubMed: 11851506]
16. Kudo A, Omori K, Kato H. *J Am Chem Soc* 1999;121:11459.
17. Ye J, Zou Z, Arakawa H, Oshikiri M, Shimoda M, Matsushita A, Shishido T. *J Photochem Photobiol* 2002;A148:79.
18. Evans HT Jr. *Z Kristallogr* 1960;114:257.
19. Bouloux J-C, Galy J. *Bull Soc Chim Fr* 1969:739.
20. Ng HN, Calvo C. *Can J Chem* 1972;50:3619.
21. Calvo C, Manolescu D. *Acta Cryst* 1973;B29:1743.
22. Bouloux J-C, Prez G, Galy J. *Bull Soc Fr Miner Cris t* 1972;95:130.
23. Angenault J, Rimsky A, Acad CR. *Sci Peris Ser C* 1968;267:227.
24. Zhang X, You W, Zhu Z, Dang L, Sun Z, Zheng X. *Inorg Chem Commun* 2006;9:526.
25. Zúrkova L, Kucsera R, Gyepes R, Sivak M. *Monatsh Chem* 2003;134:1071.
26. Pfeiffer P, Werdelmann Br. *Z Anorg Allg Chem* 1950;31:263.
27. Schlessinger GG. *Inorg Synth* 1967;9:160.

28. Blessing RH. *Acta Cryst* 1995;A51:339.
29. Altomare A, Burla MC, Camalli M, Cascarano GL, Giacovazzo C, Guagliardi A, Moliterni AGG, Polidori G, Spagna R. *J Appl Crystallogr* 1999;32:115.
30. Sheldrick, GM. SHELX97 Program for Crystal Structure Refinement. University of Göttingen; Germany: 1997.
31. Farrugia LJ. *J Appl Crystallogr* 1999;32:837.
32. Nardelli M. *J Appl Crystallogr* 1995;28:659.
33. Carter MT, Bard AJ. *J Am Chem Soc* 1987;109:7528.
34. Atanassova MS, Dimitrov GD. *Spectrochim Acta* 2003;A59:1655.
35. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 5. John Wiley & Sons; New York: 1997.
36. Nyquist, RA.; Kagel, RO. *Infrared Spectra of Inorganic Compounds*. Academic Press Inc; London: 1971.
37. Hendry P, Ludi A. *Adv Inorg Chem* 1990;35:117.
38. Thomos C, Pringle K, Dsacon GB. *J Chem Edu* 1989;68:516.
39. Altermatt D, Brown ID. *Acta Cryst* 1985;B41:244.
40. Brown, I David. Brockhouse Institute for Materials Research. McMaster University; Hamilton, Ontario Canada: Copyright
41. Cremer D, Pople JA. *J Am Chem Soc* 1975;97:1354.
42. Burnett, MN.; Johnson, CK. ORTEP-III: Oak Ridge Thermal Ellipsoids Plot Program for Crystal Structure Illustrations. Oak Ridge National Laboratory Report ORNL-6895; TN: 1996.
43. Desiraju GR. *Acc Chem Res* 2002;35:565. [PubMed: 12118996]
44. Thallapally PK, Katz AK, Carell HL, Desiraju GR. *CrystEngComm* 2003;5:87.
45. Desiraju GR. *Acc Chem Res* 1991;24:290.
46. Czugler M, Bathori N. *CrystEngComm* 2004;6:494.
47. Wu B, Liang J, Yang J, Jia C, Yang X-J, Zhang H, Tang N, Janiak C. *Chem Commun* 2008:1762.

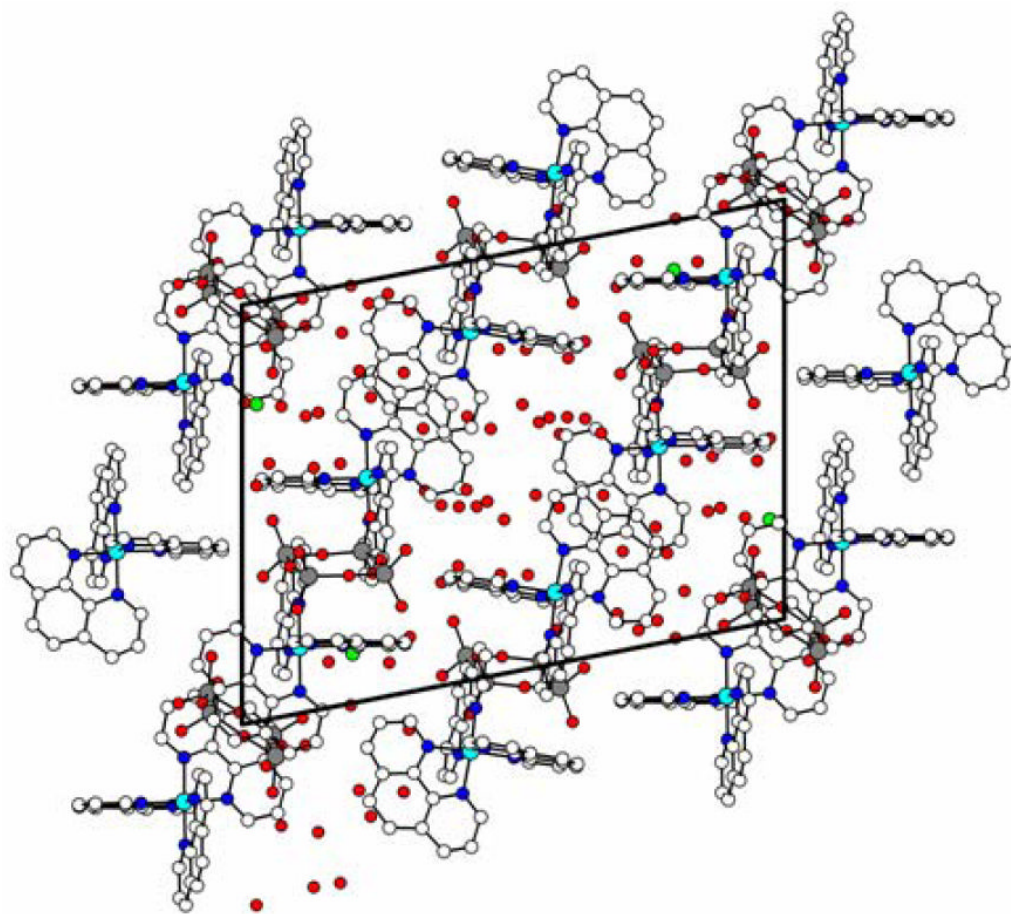


**Figure 1.** ORTEPIII view of one cobalt complex cation, one polyoxovanadate anion and one chloride. Ellipsoids are drawn at 40% probability. For the sake of clarity, the other ions and all lattice water molecules constituting the asymmetric unit are omitted.

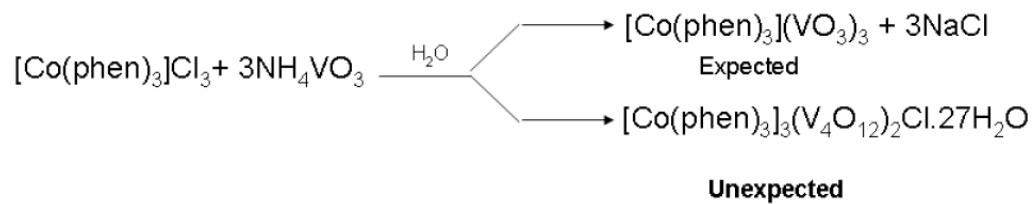




**Figure 2.** C-H...O interactions between complex cations and hydrogen bond acceptor groups from anions and lattice waters.



**Figure 3.**  
Packing diagram of the complex salt (viewed along *a*).



**Scheme 1.**  
Schematic representation of chemical reaction.

**Table 1**Crystal data and refinement parameters of  $[\text{Co}(\text{phen})_3]_3(\text{V}_4\text{O}_{12})_2\text{Cl}\cdot 27\text{H}_2\text{O}$ 

Chemical formula	$3(\text{CoC}_3\text{H}_{24}\text{N}_6)\cdot 2(\text{V}_4\text{O}_{12})\cdot \text{Cl}\cdot 27(\text{H}_2\text{O})$
$M_r$	3112.03
Cell setting, space group	Triclinic, $P-1$
Temperature (K)	295
$a, b, c$ (Å)	15.4063(2), 18.8746(3), 25.1206(4)
$\alpha, \beta, \gamma$ (°)	97.7540(8), 103.5560(7), 101.4310(7)
$V$ (Å <sup>3</sup> )	6833.14(18)
$Z$	2
$D_x$ (Mg m <sup>-3</sup> )	1.746
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.99
Crystal form, color	Prismatic, orange
Crystal size (mm)	0.29 × 0.14 × 0.09
No. of measured, independent and observed reflections	42624, 28163, 10204
Criterion for observed reflections	$I > 2\sigma(I)$
$\theta_{\text{max}}$ (°)	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	28163 / 1776
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.1928P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.99, -0.69

**Table 2**Selected bond lengths and angles (Å and °) for [Co(phen)<sub>3</sub>]<sub>3</sub>(V<sub>4</sub>O<sub>12</sub>)<sub>2</sub>Cl·27H<sub>2</sub>O.

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)
N3-Co1-N5	92.1(4)	N13-Co3-N17	94.4(3)
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)

Table 3

Short O...O/Cl contacts (Å) for [Co(phen)<sub>3</sub>]<sub>3</sub>(V<sub>4</sub>O<sub>12</sub>)<sub>2</sub>Cl·27H<sub>2</sub>O.

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 <sup>i</sup>	2.737(18)	O33W...O22W <sup>iv</sup>	2.554(27)
O23W...O23 <sup>i</sup>	2.728(26)	O3W...O22 <sup>v</sup>	2.693(15)
O1W...O11 <sup>ii</sup>	2.735(12)	O28W...O30W <sup>vi</sup>	2.778(40)
O8W...O8 <sup>ii</sup>	2.776(14)	O23W...O11 <sup>vi</sup>	2.810(23)
O15W...O10 <sup>ii</sup>	2.690(16)	O25W...O32W <sup>vi</sup>	2.732(34)
O16W...O8 <sup>ii</sup>	2.747(17)	O14W...O5 <sup>vii</sup>	2.748(17)
O22W...O5 <sup>ii</sup>	2.742(20)	O28W...O23 <sup>viii</sup>	2.693(20)
O1W...O24 <sup>iii</sup>	2.738(16)	O32W...O25W <sup>ix</sup>	2.732(34)
O6W...Cl1 <sup>iii</sup>	2.781(13)	O1...O4W <sup>x</sup>	2.782(15)
O15W...O26W <sup>iii</sup>	2.801(23)	O4W...O24W <sup>xi</sup>	2.815(23)
O17W...O14 <sup>iii</sup>	2.790(14)	O29W...O18W <sup>xi</sup>	2.989(25)
O25W...O22W <sup>iv</sup>	2.984(26)	O30W...O19 <sup>xi</sup>	2.841(28)

(i) Symmetry codes: 1-x,-y,-z;

(ii) <sub>x,y+1,z+1</sub>;(iii) <sub>1-x,-y,1-z</sub>;(iv) <sub>x+1,y,z</sub>;(v) <sub>x,y,1+z</sub>;(vi) <sub>x,y+1,z</sub>;(vii) <sub>x+1,y,z+1</sub>;(viii) <sub>x+1,y+1,z+1</sub>;

$$(ix)_{x,y-1,z};$$

$$(x)_{1-x,-y-1,1-z};$$

$$(xi)_{2-x,-y,1-z}$$



Table 4

Hydrogen bonding parameters for C–H...O/Cl contacts (Å and °).

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 <sup>i</sup>	0.930	3.24(1)	2.39	151
C54-H36...O12 <sup>i</sup>	0.930	3.51(1)	2.63	158
C1-H1...O2 <sup>i</sup>	0.930	3.03(1)	2.33	132
C30-H20...O10 <sup>i</sup>	0.930	3.36(1)	2.60	139
C7-H5...O12 <sup>ii</sup>	0.930	3.20(1)	2.45	138
C12-H8...O22 <sup>iii</sup>	0.930	3.28(1)	2.51	141
C13-H9...O24W <sup>iii</sup>	0.930	3.36(2)	2.67	131
C63-H43...O5W <sup>iv</sup>	0.930	3.50(2)	2.67	149
C49-H33...O2W <sup>iv</sup>	0.930	3.26(2)	2.47	143
C25-H17...Cl1 <sup>v</sup>	0.930	3.30(1)	2.54	138
C31-H21...O13 <sup>vi</sup>	0.930	3.41(1)	2.57	150
C36-H24...Cl2 <sup>vi</sup>	0.930	3.28(1)	2.49	144
C34-H22...O16 <sup>vi</sup>	0.930	3.25(1)	2.48	139
C97-H65...O5W <sup>vi</sup>	0.930	3.26(1)	2.51	136
C62-H42...O22 <sup>vii</sup>	0.930	3.20(2)	2.38	147
C37-H25...O9 <sup>vii</sup>	0.930	3.19(1)	2.47	134
C55-H37...O4 <sup>vii</sup>	0.930	3.38(2)	2.66	135
C57-H38...O4 <sup>vii</sup>	0.930	3.40(2)	2.68	135
C59-H40...O8W <sup>viii</sup>	0.930	3.40(1)	2.65	139
C79-H53...O13 <sup>ix</sup>	0.930	3.25(2)	2.52	136
C91-H61...O28W <sup>x</sup>	0.930	3.42(3)	2.58	149
C84-H56...O25W <sup>x</sup>	0.930	3.39(2)	2.61	142
C87-H59...O8W <sup>xi</sup>	0.930	3.28(2)	2.39	158
C106-H70...O6 <sup>xii</sup>	0.930	3.30(1)	2.41	160
C103-H69...O7 <sup>xii</sup>	0.930	3.46(1)	2.58	158
C108-H72...O9W <sup>xiii</sup>	0.930	3.29(2)	2.54	138

(i) Symmetry codes :  $-x,-y-1,-z$ ;

(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)  $x+1,y,z$