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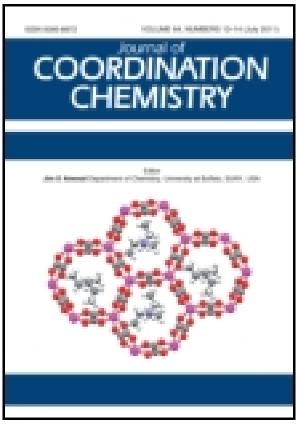

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Synthesis, structural, and spectral characterization of Keggin-type mono cobalt(II)-substituted phosphotungstate

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Keggin-type mono Co(II)-substituted phosphotungstate was synthesized from 12-tungstophosphoric acid and cobalt chloride tetrahydrate. The obtained complex was systematically characterized in solution as well as solid by various physicochemical techniques. A single-crystal X-ray analysis shows that the complex crystallizes in tetragonal system, $P4_2/ncm$ space group with $a = b = 20.9860(5)$ Å, $c = 10.4368(3)$ Å, and $Z = 4$. The crystal showed two types of disorders related by center of symmetry. Structural studies did not show the presence of Co, but the incorporation of the metal ion was proved by various spectral techniques. Spectral as well as electrochemical studies confirmed the presence of Co(II) into the lacunary position of the phosphotungstate moiety.

Keywords: Keggin-type phosphotungstate; Crystal structure; Cobalt; Electrochemistry

1. Introduction

Keggin-type lacunary polyoxometalates with formula $[XM_{11}O_{39}]^{n-}$, M = Mo, W; X = B, Si, Ge, P, As, represent a unique class of ligands, continuously studied due to their interesting properties and applications in various fields such as catalysis, materials science, and medicine [1–6]. They exhibit elaborate substitution chemistry in which one or more of the addenda ions can be substituted with other transition metal ions or even by organometallic groups. Transition metal substituted polyoxometalates (TMSPs) can be rationally modified on the molecular level, including shape, size, charge density, redox states, and stability [2–4]. They have several advantages over the general transition metal complexes, in that their physical properties, such as solubility, can be tuned by changing the counter cations and their redox properties can be adjusted by changing the central hetero atom and also by substituting the addenda atom.

Among the various TMSPs, Ru-substituted polyoxometalates have been well explored due to the unique redox properties of ruthenium [7–9]. Several reports are available on the synthesis, characterization, and oxidation reactions using

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mono-ruthenium-substituted polyoxometalates [10–24]. Even though cobalt-substituted polyoxometalates are of significant interest due to their magnetic and electronic properties, not much work have been carried out.

Baker and McCutcheon [25] reported the synthesis of alkali salts of $[Co^{2+}Co^{3+}W_{12}O_{42}]^{7-}$ from $NaWO_4 \cdot 2H_2O$ and cobaltous acetate tetrahydrate at neutral pH, characterized by elemental analysis, oxidation state, electrochemical properties, powder XRD, and single-crystal analysis [26]. In 1966, on the basis of crystal structure, the presence of Co ions was confirmed in the outer sphere of the polyoxotungstates rather than a central hetero atom by the same group.

Weakley and Malik [27] extended the work of Baker and McCutcheon by synthesizing a series of mono-cobalt-substituted polyoxotungstates, the cobalt-substituted silicotungstate was synthesized from 12-tungstosilicic acid and metal salt at pH 6. The obtained deep red crystal was analyzed by single-crystal X-ray pattern, powder XRD, and UV visible spectroscopy. In the 1970s Weakley *et al.* reported electronic properties of a series of cobalt-substituted polyoxotungstates by varying the hetero atom. Examples include $BCoW_{11}O_{40}H_2^{7-}$, $AsCoW_{11}O_{40}H_2^{5-}$, $PCo^{II}W_{11}O_{40}H_2^{5-}$, and $PCo^{III}W_{11}O_{40}H_2^{6-}$ [27–29]. In 1973, a detailed study on cobalt-substituted phospho and boro tungstates was reported by Weakley *et al.* Afterwards the crystal structure for $(Et_3H)_5[PW_{11}CoO_{40}H_2]$ was described by the same author [30], finding the mono-substituted Keggin groups assembled into straight chains through W–O–Co linkages.

Klevtsova *et al.* [31] discussed the crystal structure of the cesium salt of $[PW_{11}Co(H_2O)O_{39}]^{5-}$, synthesized from 11-phosphotungstate and the individual salt of the metal ion. The structure indicates that the cobalt substituted in the Keggin unit cannot be distinguished from W distributed over the 12 positions of the polyoxoanion. The presence of Co was confirmed by IR and Raman spectra.

Thus, all reported articles describe the two-step synthesis of cobalt-substituted phosphotungstate at almost neutral pH, starting either from undecaphosphotungstate ($PW_{11}O_{39}^{7-}$) [25–31] or from the individual salts (i.e., $Na_2WO_4 \cdot 2H_2O$).

In this article, we report the synthesis of cesium salt of mono-cobalt-substituted phosphotungstate ($PW_{11}O_{39}Co$) following a different synthetic route, starting from a commercially available Keggin polyanion. The synthesized complex was systematically characterized by various physicochemical techniques. The synthesized cesium salt was characterized in solid as well as in solution by elemental analysis, TGA, single crystal analysis, powder XRD, FT-IR, UV-Vis, ESR, and cyclic voltammetry. We are not able to find Co by single-crystal analysis; however, we have provided enough evidence for the presence of Co in the cavity of undecaphosphotungstate.

2. Experimental

2.1. *Materials*

All chemicals used were of A. R. grade. 12-Tungstophosphoric acid, $H_3PW_{12}O_{40} \cdot nH_2O$ (Loba Chemie, Mumbai), sodium hydroxide, acetone, and cobalt chloride tetrahydrate were obtained from Merck and used as received.

2.2. *Synthesis of $PW_{11}O_{39}Co$*

A total of 2.88 g of $H_3PW_{12}O_{40} \cdot nH_2O$ (PW_{12}) was dissolved in 10 mL of water and the pH of the solution adjusted to 4.8 using sodium hydroxide solution. 0.238 g of $CoCl_2 \cdot 4H_2O$ dissolved in minimum amount of water was mixed with the hot solution of PW_{12}. The solution was heated at 80° with stirring for 1 h and filtered hot. The final pH of the solution was maintained at 4.8 by using dilute NaOH solution. To the hot filtrate, 10 mL saturated solution of CsCl (~1 g) was added and allowed to stand overnight. The obtained dark red crystals (3.15 g; 76.6% yield) were filtered and air dried. The filtrate was used for the estimation of tungsten and cobalt.

2.3. *Characterization*

2.3.1. Single-crystal analysis. Dark red single crystals for $PW_{11}O_{39}Co$ were obtained by recrystallization from hot water. The compound crystallizes in the tetragonal system having $P4_2/ncm$ space group with $a = b = 20.9860(5)$ Å, $c = 10.4368(3)$ Å, and $\alpha = \beta = \gamma = 90°$.

The X-ray diffraction data were collected at 296°K with Mo-Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. Smart Apex II software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All non-H atoms were refined in the anisotropic approximation.

The final refinement of the crystal structure carried out for the atomic coordinates, anisotropic thermal parameters, and isotropic thermal parameters converged at $R = 0.0613$ ($R[I > 2\sigma(I)]$) and $R_w = 0.1841$.

2.3.2. Powder X-ray diffraction. The XRD pattern was obtained by using a PHILIPS PW-1830. The conditions were: Cu-Kα radiation (1.54 Å), scanning angle from 0° to 60°.

2.3.3. Analytical techniques. The filtrate was analyzed for tungsten gravimetrically and cobalt volumetrically. Elemental analysis was carried out using the JSM 5610 LV EDX-SEM analyzer. TGA was carried out on the Mettler Toledo Star SW 7.01°C to 600°C in air with heating rate of 5°C min^{-1}. FT-IR spectra of the sample were obtained by using KBr wafer on the Perkin Elmer instrument. The UV-Vis spectrum was recorded at room temperature on a Perkin Elmer 35 LAMDA instrument using the 1 cm quartz cell. ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer (room temperature scanned from 2000 to 4000 Gauss). Cyclic voltammetry was performed on the CHI 660 A system at room temperature. Cyclic voltammograms of 1 mm solutions of PW_{12}, PW_{11}, and $PW_{11}O_{39}Co$ were recorded in buffer of pH 4 (acetate buffer) with glassy carbon electrode as the working electrode, Ag/AgCl as the reference electrode, and Pt wire as the auxillary electrode.

3. Results and discussion

The complex was isolated as the cesium salt after completion of the reaction and the remaining solution was filtered. The filtrate was analyzed to estimate the amount of non-reacted materials, namely W and Co [32]. The observed % of W in the filtrate was 0.5%, which corresponds to the loss of one equivalent of tungsten from $H_3PW_{12}O_{40} \cdot nH_2O$ and the amount of Co in the filtrate was 20 mg which corresponds to unreacted excess of Co. The observed values for the elemental analysis are in good agreement with the theoretical values. Anal. Calcd: Cs, 18.7; W, 57.4; P, 0.88; Co, 1.67; O, 20.8. Found: Cs, 18.1; W, 57.2; P, 0.86; Co, 1.69; O, 21.0. The number of water molecules calculated from the TGA curve, based on total weight loss (3.9%) to 600°C, was eight.

3.1. *Crystal structure*

Dark red block-type single crystals were obtained by recrystallization from hot water having dimensions of 0.50 × 0.30 × 0.2 mm. The crystal was assigned to the tetragonal system with $a = b = 20.9860(5)$ Å, $c = 10.4368(3)$ Å, having space group $P4_2/ncm$ and $V = 4596.5(2)$ A^3, $D_{cal} = 5.323\ g\ cm^{-3}$, $D_{exp} = 4.940\ g\ cm^{-3}$. The number of reflections was 47,711 and the number of unique ones used for solving the structure was 2961. Direct methods were used to solve the crystal structure [33]. The structure is as expected (since Co, Ni, Mn are isostructural and crystallize within the same space group and phase) and is in agreement with the reported crystal structure of $Cs_5[PNi(H_2O)W_{11}O_{39}]$ [34]. The final cycle of refinement of the structure, including the atomic coordinates, anisotropic thermal parameters (Cs, P, and W) and isotropic thermal parameters (O) converged at 0.0582 $[I > 2\sigma(I)]$, and $R_w = 0.0816$. In the final difference map, the deepest hole was −3.212 located at 0.67 Å from W_1 and the highest peak was 3.71 Å located at 3.27 Å from O1.

The deepest hole at 0.67 from W_1 indicates the presence of disorder in the structure at W_1 position. The disorder at W_1 also indicates the probability for the occupancy of Co at W_1 position with different site occupancy ratio. The crystal structure analysis shows that cobalt ions are not present as counter cations. Cs was present as counter cations with Cs–P bond lengths of 5.799, 5.921, and 6.432 Å (figure 1), which is in agreement with the reported values [31]. Hence, the structural analysis confirms the presence of Cs as counter cations.

The crystallographic refinement of the complex suggests the presence of 5.50Cs counter cations, while the elemental analysis confirms the presence of 5Cs cations around the polyanion. So, based on the structural and elemental analysis, the final formula of $PW_{11}Co_{39}$ is proposed as

$$Cs_5[PCo(H_2O)W_{11}O_{39}] \cdot 6H_2O$$

The number of water molecules determined from the structural analysis shows the presence of one H_2O molecule in the coordination sphere, while the thermal analysis indicates the presence of seven water molecules. The difference in the value may be due to the loss of water in the process of single-crystal XRD data collection. The details of the recorded crystal data are presented in table 1.

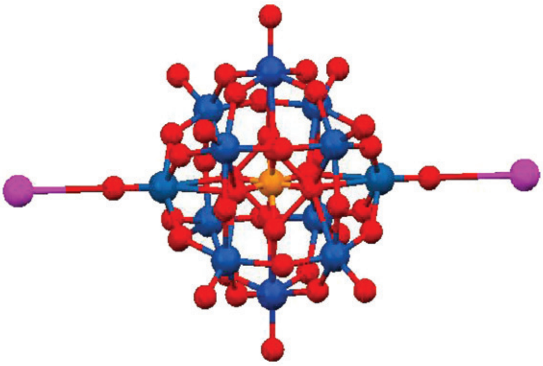


Figure 1. Disordered Keggin-type structure.

Table 1. Crystal data for $PW_{11}O_{39}Co$ and collection parameters.

Empirical formula	$H_2Cs_5CoO_{44}PW_{11}$
Formula weight	3418.82
Color	Red
Temperature (K)	296(2)
Crystal system	Tetragonal
Space group	$P4_2/ncm$
Unit cell dimensions (Å)	
$a=b$	20.9860(5)
c	10.4368(3)
Volume (Å^3), Z	4596.5(2), 4
Calculated density ($g\,cm^{-3}$)	4.940
Absorption coefficient (mm^{-1})	31.783
Final R indices $[I > 2\sigma(I)]^a$	0.0583
R indices (all data)^b	0.0816

$^aR = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $^bR_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$.

The structural analysis shows double disorder in the crystal; (i) the Co and W atoms were distributed over the 12 positions and the Co could not be distinguished from the 11W atoms distributed equally over the 12 addenda atoms in the Keggin structure; (ii) the Keggin polyanion is distributed over two orientations related by a center of symmetry. The observations are in agreement with a reported one [31].

The packing structure for the polyanion, along the *c* axis, indicates the presence of Cs in the voids created due to close packing. At the same time, H_2O is also expected to be present in the voids and interconnected via weak H-bonds. During the final refinement cycle, the isotropic thermal parameters for the atomic coordinates of O indicated the presence of 5 different oxygen atoms apart from oxygen atoms of the Keggin unit. These oxygen atoms are expected to originate from adsorbed water, but due to the large difference in electron densities of H and W, the presence of H could not be confirmed from structural data. The presence of seven water molecules was confirmed by thermal analysis (TGA). Crystallographically, unique two types of cesium are coordinated to terminal oxygen of the polyanion and also with H_2O, as seen in figure 2.

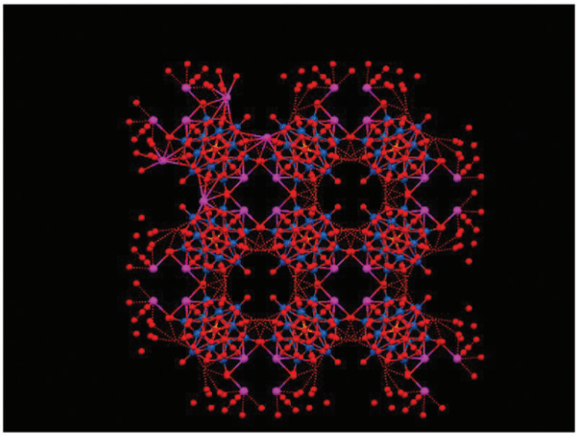


Figure 2. Packing structure of PW_{11} $O_{39}Co$.

The typical Keggin structure containing all W–W with equal distances (~3.57 Å) and different W–O distances was obtained. The three different types of W–O bond distances correspond to the terminal (1.67 Å), *cis* bridging (1.90 Å), and *trans* bridging (2.48 Å) oxygen atoms, respectively.

In Keggin-type POMs the central tetrahedral PO_4 is surrounded by twelve WO_6 octahedra in four groups of W_3O_{13} units. If the structure is totally symmetrical then PO_4 has Td symmetry with all P–O bond lengths (1.52 Å) being the same. In the present crystal structure, two different P–O bond lengths are obtained. Three P–O bonds have almost the same length of 1.52 Å while the fourth P–O has longer bond length of 1.61 Å, indicating distortion in the PO_4 Td symmetry. This may be due to the change in the environment around the corresponding W_3O_{13} unit. The oxygen for the P–O bond length (1.61 Å) is O_6. Hence, the change in the environment due to the substitution of Co around corresponding W_3O_{13}, $P–O_6–W_3O_{13}$, is expected. The three tungstens attached to O_6 are W_1, W_1 and W_2. The bond length of $W_1–O_6$ is 2.41 Å. The corresponding terminal oxygen attached to W_1 is O_1. As mentioned earlier in the discussion, the presence of disorder in the crystal structure is at O_1 and hence the probability of Co substitution is maximum at W_1. The observed data are in good agreement with the proposed explanation.

The XRD pattern of $PW_{11}O_{39}Co$ was totally different from PW_{12} while it resembled PW_{11}, confirming the presence of 11 tungstens instead of 12. Along with the characteristic peak of PW_{11}, additional peaks were found for $PW_{11}O_{39}Co$ due to the incorporation of Co into the lacunary position of phosphotungstate (figure 3). The presence of Co was confirmed by FT-IR, UV-Vis, ESR, and electrochemical studies.

The frequencies of FT-IR bands for PW_{12}, PW_{11}, and $PW_{11}O_{39}Co$ are shown in table 2. The P–O band at 1080 cm^{-1} of PW_{12} splits into bands at 1085 and 1043 cm^{-1} for PW_{11}. There is a splitting and shifting of the P–O vibrational band frequencies for PW_{11} compared to that of PW_{12}. Rocchiccioli-Deltcheff and Thouvenot [35, 36] reported the values of $\Delta\upsilon$ splitting for P–O bond for transition metals introduced into the octahedral lacuna of PW_{11}. In the present case the observed splitting value of 42 cm^{-1} indicates the formation of lacunary PW_{11}.

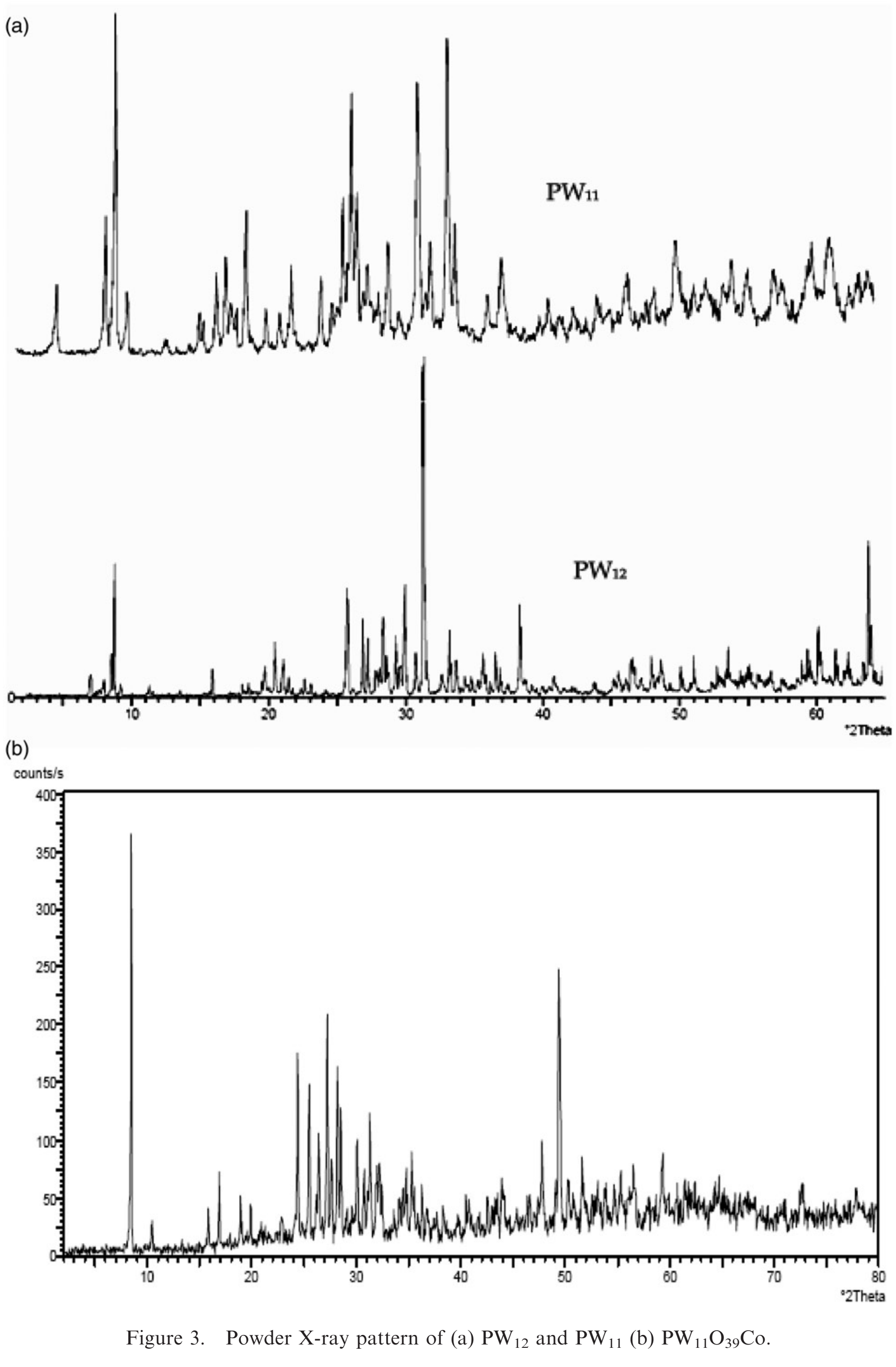


Figure 3. Powder X-ray pattern of (a) PW_{12} and PW_{11} (b) $PW_{11}O_{39}Co$.

Table 2. FT-IR frequency data.

	FT-IR band frequencies (cm^{-1})			
Polyoxometalate	P–O	W=O	W–O–W	Co–O–W
PW_{12}	1080	982	893 812	–
PW_{11}	1085 1043	952	863 808	–
$PW_{11}O_{39}Co$	1076 1057	959	884 810	512 438

The FT-IR spectrum of $PW_{11}O_{39}Co$ shows bands at 884 and 810 cm^{-1}, 959 cm^{-1}, and at 1076 and 1057 cm^{-1} corresponding to the symmetric stretch of W–O–W, W=O, and P–O bonds, respectively. The shift in the P–O stretching frequency is expected due to the complexation of Co as well as due to the change of environment around the central metal ion. The $\Delta\upsilon$ splitting for the vibrational stretch of P–O band was 19 cm^{-1}, which is in good agreement with the reported value [37] and indicating incorporation of Co into the O_h cavity created in the Keggin framework. The difference in the $\Delta\upsilon$ splitting from 42 to 19 cm^{-1} may be due to further lowering in symmetry around the P–O environment due to the exchange of terminal W(VI) with Co(II). There is also a shift in the stretching vibration of W=O from 952 to 959 and in the W–O–W vibration from 863 to 884, indicating the complexation of Co. The presence of additional vibrational bands at 512 and 438 are attributed to Co–O bands. Thus, FT-IR spectra clearly show incorporation of Co into the Keggin framework and not as a counter cation as not much shifting is expected when it acts as a counter cation.

The UV-Vis spectra for PW_{11} and $PW_{11}O_{39}Co$ were recorded in water. In the case of PW_{11} an intense peak at 291 nm was obtained corresponding to O→W charge transfer [1]. The $PW_{11}O_{39}Co$ spectrum shows two peaks, one at 293 nm and a broad peak in the visible region at 538 nm. The peak at 293 nm arises from PW_{11}, indicating the formation of lacunary species. The broad band in the visible region (538 nm) is typical of d–d transition for Co(II) species (figure 4). The observed broadening compared to that of PW_{11} may be due to the incorporation of Co into the vacant cavity of undecaphosphotungstate.

The absorption spectrum for $PW_{11}O_{39}Co$ resembles 11-tungstocobalto(II)phosphate species reported by Weakley *et al.* in 1976, indicating the formation of cobalt-substituted 11-tungstophosphate [27]. The spectrum of 11-tungstocobalto(II)phosphate differs distinctly from that of 12-tungstocobaltate(II) having Td symmetry, resembling that of the well-known cobalt(II) aqua-ion, except in intensity [27]. Weakley *et al.* reported a series of $PCo^{II}(L)W_{11}$ by replacing the aquo ligand and the absorption spectra were recorded for the resulting complexes. The values for the molar absorptivities are presented in table 3 [29]. The molar absorptivity for the present complex is 173 (mol L^{-1}) cm^{-1}, whereas the reported value for the molar absorptivity for the potassium salt of $PW_{11}O_{39}Co$ with aquo ligand was found to be 220 (mol L^{-1}) cm^{-1} [38]. The difference in the values is due to change in the counter cations as well as ligands. In the case of POM the change of counter cations and the replacement of ligands is known to influence the chemical as well as electronic

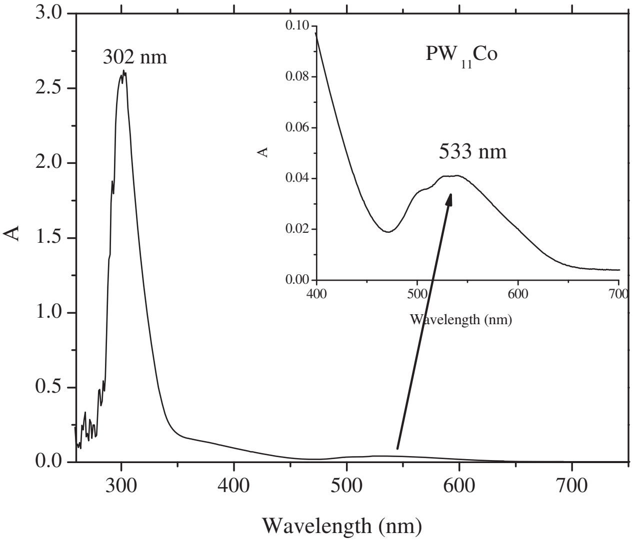


Figure 4. The UV-Vis spectra of 0.1% aqueous solution of $PW_{11}O_{39}Co$.

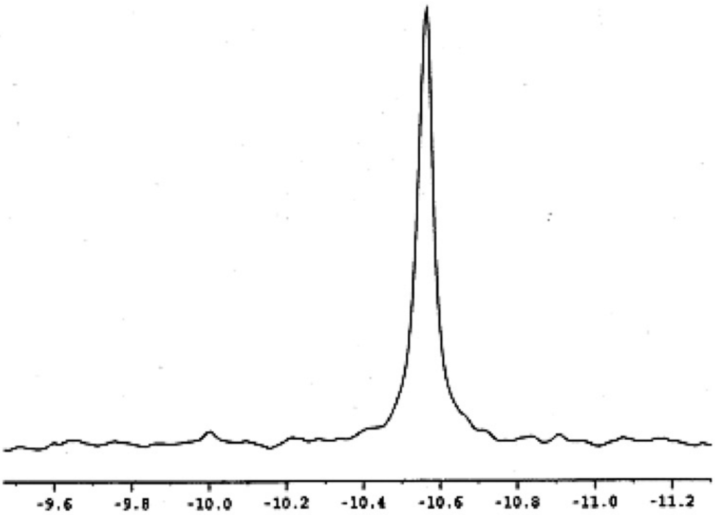
Table 3. Comparison of molar absorptivity values for $PCo^{II}(L)W_{11}$.

Ligands	ϵ Value ((mol L^{-1}) cm^{-1})	Reference
Pyridine	204	[29]
3-Cyano-pyridine	218	[29]
4-Methyl pyridine	230	[29]
2-Methyl pyridine	235	[29]
NCS^-	261	[29]
Thiourea	240	[29]
H_2O	220	[38]
Present study	173	–

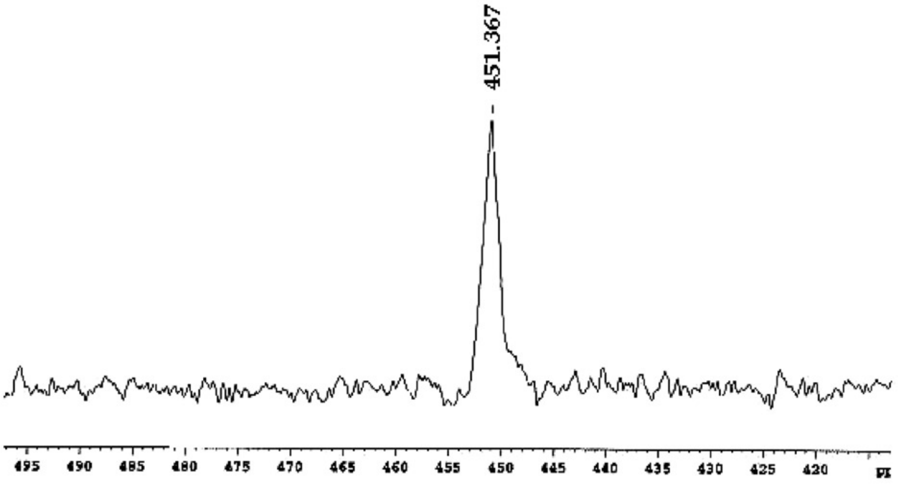
properties of the polyoxometalates. So the results are as expected. Thus, a comparison of the spectra confirms the presence of cobalt in the octahedral site.

The presence of paramagnetic Co^{II} is further confirmed by the ESR spectrum. Diamagnetic compounds result in giving ESR silent spectrum and Co(III) compounds are diamagnetic and do not give an ESR spectrum. In the present case, the room temperature ESR results in a single broad signal indicating flipping of a single unpaired electron giving an ESR signal, suggesting the presence of Co(II).

Solution ^{31}P NMR for PW_{11} and $PW_{11}O_{39}Co$ are shown in figure 5 (full-range spectrum for $PW_{11}CoO_{39}$ is shown in Supplementary material; figure S1). Removal of one W=O from the PW_{12} Keggin unit leads to a decrease in the δ by 4.5 ppm (δ for PW_{12}, −14.99 ppm and for PW_{11}, −10.5 ppm) [38]. But in the present case, the chemical shift value was significantly different from that expected. This markedly different chemical shift for the phosphorus adjacent to the substitution site is due to the considerable nephelauxetic effects for d-electrons, spreading their density and influence throughout the W–O framework in the Keggin unit. Thus the chemical shift at +451 ppm results due to the pairing up of the d-electron spins from the paramagnetic



(i) PW_{11}



(ii) $PW_{11}O_{39}Co$

Figure 5. ^{31}P solution NMR of (a) PW_{11} (b) $PW_{11}O_{39}Co$ in D_2O.

tetrahedral center (i.e., P atom) of the Keggin unit with the d-electrons of the paramagnetic Co center. The obtained chemical shift value is in agreement with the previously reported results [39].

3.2. *Electrochemistry*

All three electrochemical processes for PW_{12}, PW_{11}, and $PW_{11}O_{39}Co$ were diffusion controlled processes. Slow scan rate cyclic voltammograms were obtained for PW_{11} as

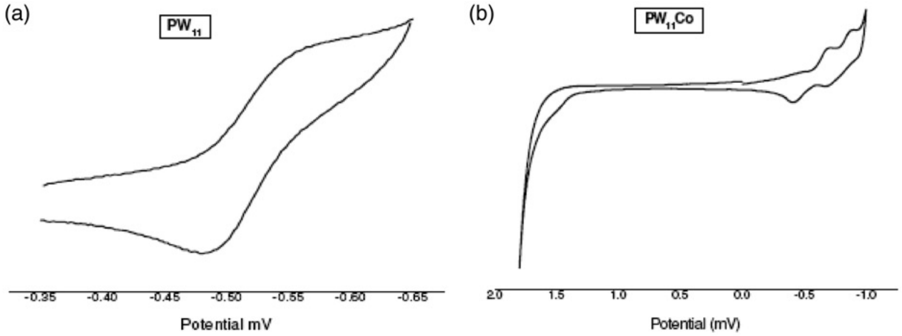


Figure 6. Cyclic voltammograms of (a) PW_{11} and (b) $PW_{11}O_{39}Co$ in buffer pH 4.

well as PW_{12} in buffered medium of pH 4. Reduction potentials for all three systems were independent of pH change. The lacunary anion having a formal charge of 7^-, features two processes in aqueous buffered media [40, 41]. The reversible redox couple corresponding to one electron reduction was observed for the PW_{11} species.

$$[PW_{11}O_{39}]^{7-} + e^- < \; = \; > [PW_{11}O_{39}]^{8-}$$

The value of the reduction potential for PW_{11} (−0.5 V) was lower than that obtained for PW_{12} species (−2.0 and −0.9 V). The obtained results are in agreement with the reported values. The cyclic voltammogram of $PW_{11}Co$ shows three redox couples, one in the positive potential is very weak corresponding to Co(II/III) (figure 6). The two reversible redox couples obtained at −0.4 and −0.7 V correspond to $2e^-$ reduction of W(VI), which is in agreement with the reported value [41]. The shift in the redox potential from the original value may be due to the incorporation of cobalt into the vacant cavity of phosphotungstate. The weak reduction potential obtained in the positive potential range between +0.97 and 1.1 V is attributed to one-step reduction of Co(II) to Co(III). The shift in the reduction potential from the literature [41] value indicates the complexation of cobalt with the electron-rich species (i.e., POM). The one-step electron reduction further confirms the presence of Co(II) in $PW_{11}O_{39}Co$.

4. Conclusions

In the present contribution, we report one-pot synthesis and crystal structure of Keggin-type mono-cobalt-substituted phosphotungstate starting from the commercially available Keggin polyanion. The crystal was characterized for elemental, spectral, thermal, as well as electrochemical analysis. From the above study we conclude that Cs ions, not Co ions, are present as counter cations. The structural analysis shows double disorder in the crystal: (i) the Co and W were distributed over the 12 positions and the Co could not be distinguished from the 11 tungstens distributed equally over the 12 addenda atoms in the Keggin structure; (ii) the Keggin polyanion is distributed over two orientations related by a center of symmetry. The presence of Co was confirmed by FT-IR, UV-visible, ESR, and cyclic voltammetric studies.

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