

Spectral and voltammetric studies on titanium substituted Keggin-type heteropolyanions

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Abstract. Bonding and redox properties of mono- and dititanium substituted 12-heteropolytungsto-phosphates and their complexes with bivalent Mn, Co, Ni and Cu are studied by UV–Vis, ESR and cyclicvoltammetric techniques. The heteropoly blue analogue $[\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{W}_{10}\text{PO}_{40}]^{8-}$ is unstable and its presence in solution is proved by optical and ESR spectroscopy. ESR results reveal that the odd electron is trapped on the titanium atom at 77 K. The optical electronegativity of Ti(III) in this heteropoly blue is estimated to be 2.4 from the intervalence charge transfer (IVCT) bands. X-ray powder diffraction results show that the complexes $\text{K}_5\text{M}^{\text{II}}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot x\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Cu}$ or Mn) are isomorphous with $\text{K}_7[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$. Electronic spectroscopy indicates very high symmetry around the bivalent metal ion M in the $\text{K}_5\text{M}^{\text{II}}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot x\text{H}_2\text{O}$ complexes. This high symmetry is confirmed in $\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]$ by the observation of dynamic Jahn–Teller (JT) distortion at 300 K and static JT distortion at 77 K.

Keywords. Heteropolytungstates; heteropoly blues; cyclicvoltammetry; Jahn–Teller distortion.

1. Introduction

The heteropolyanions of transition elements of groups 5 and 6 attract large interest because of their similarities to their metal oxide lattices and their catalytic applications (Koshevnikov and Matveev 1982; Day and Klemperer 1985; Misono 1987). Of these the Keggin structure heteropolyanions containing more than one peripheral heteroatom with an oxidation state less than six are of special interest since such anions lead to increased total surface negative charge (Domaille and Knoth 1983). This increased negative charge enhances basicity and stability towards nucleophilic degradation. The mono- and divanadium substituted tungsto-phosphates and tungsto-silicates have been well characterised (Altenau *et al* 1975; Mossoba *et al* 1980). The reduction of these heteropolyanions gives mixed-valence heteropoly blues which are identified by the lowest energy IVCT bands (Pope 1980; So and Pope 1992). Both thermal and photo electron hopping mechanisms in these “semiconductor-like” lattices are studied by ESR and optical spectroscopy. On the contrary, studies on titanium substituted heteropolyanions, which are expected to be a better catalyst

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due to the enhanced negative charge, are limited. Hence in an attempt to make a systematic study of these titanium substituted heteropolyanions we report here the spectral and redox characteristics of $K_5[TiW_{11}PO_{40}] \cdot 5H_2O$, $K_7[Ti_2W_{10}PO_{40}] \cdot 6H_2O$, the heteropoly blue analogue $[Ti^{III}Ti^{IV}W_{10}PO_{40}]^{8-}$ and the electronic structure of the bivalent metal ion in the complexes $K_5M[Ti_2W_{10}PO_{40}] \cdot xH_2O$ ($M = Mn, Co, Ni$ or Cu).

2. Experimental

2.1 Materials

Chemicals used were of reagent grade and used as such without further purification. $K_5[TiW_{11}PO_{40}] \cdot 5H_2O$, $K_7[Ti_2W_{10}PO_{40}] \cdot 6H_2O$ and the metal complexes $K_5M[Ti_2W_{10}PO_{40}] \cdot xH_2O$, where M is bivalent Mn, Co, Ni or Cu , were prepared by literature methods (Domaille and Knoth 1983; Knoth *et al* 1983) and purified by repeated recrystallisation from conductivity water. The titanium, tungsten and phosphorus composition in these heteropolyanions were verified by standard methods (Bassett *et al* 1978). Further the heteropolyanions were identified also through their characteristic IR spectra (Domaille and Knoth 1983).

2.2 Physical measurements

UV-Vis spectra were recorded by using Hitachi model 200-20 and Shimadzu UV-Vis-NIR model UV-3100 spectrophotometers. IR spectra were recorded on Perkin-Elmer 783 spectrometer as KBr disks. Voltammetric studies were carried out on cyclicvoltammograph (CV-27), using a three-electrode system. The compounds were dissolved in proper buffer solution and the voltammograms were recorded under nitrogen atmosphere using glassy-carbon working electrode (GCE), platinum auxiliary electrode and silver-silver chloride reference electrode (RE1). ESR spectra were recorded on a Varian E-112 spectrometer, equipped with 100 kHz field modulation. DPPH was used as an internal field marker. The 77 K spectra were measured using an immersion type liquid nitrogen dewar whose tail fitted into the ESR cavity. For γ -irradiation a ^{60}Co source with dose rate of 0.2μ rad was used. SEIFERT X-ray powder diffractometer (3000 P) (Germany) was utilised to record the power patterns of the samples with $Cu K\alpha_1$ radiation.

3. Results and discussion

3.1 $K_5[TiW_{11}PO_{40}] \cdot 5H_2O$

The optical spectrum of this compound shows charge transfer (CT) band at $40,000 \text{ cm}^{-1}$ highly characteristic of 12-heteropolyanion with Keggin structure (Schouten and Cros 1982). The cyclicvoltammogram (CV) of this anion in 1 M sulphuric acid given in figure 1a shows only a single reduction process at a cathodic peak potential (E_{pc}) of -0.60 V. The corresponding anodic peak potential (E_{pa}) occurs at -0.50 V. ΔE value of 0.10 V shows the quasi-reversible nature of the redox process. Further the anodic wave height for the reduced anion is found to be diminished. Such effects have been observed and are correlated to a decrease in the extent of adsorption of reduced species in more acidic solution (Pope and Varga 1966).

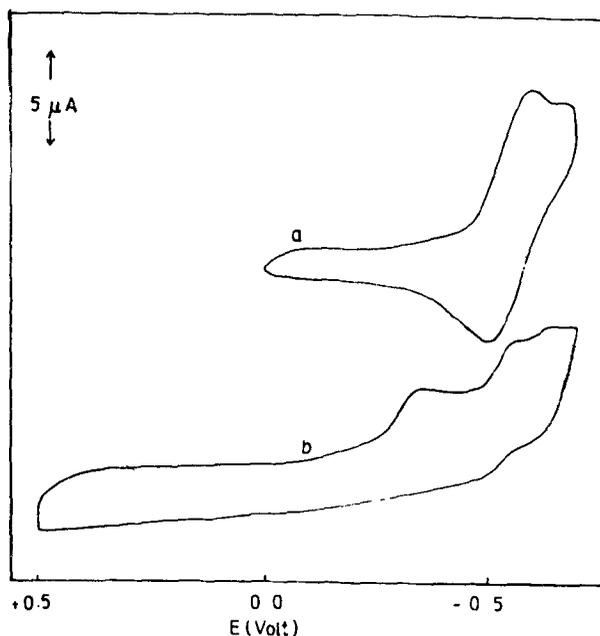


Figure 1. Cyclicvoltammogram of (a) $K_5[TiW_{11}PO_{40}].5H_2O$ and (b) $K_7[Ti_2W_{10}PO_{40}].6H_2O$ in 1 M sulphuric acid.

3.2 $K_7[Ti_2W_{10}PO_{40}].6H_2O$

This compound also shows CT band at $40,000\text{ cm}^{-1}$ confirming the Keggin structure. The CV of $K_7[Ti_2W_{10}PO_{40}].6H_2O$ (0.2 mmol) in 1 M sulphuric acid given in figure 1b shows two cathodic reductions corresponding to E_{pc} values of -0.37 V and -0.62 V . When compared with the CVs of the vanadium substituted heteropolytungsto-phosphates (Smith and Pope 1973) the CV of $[Ti_2W_{10}PO_{40}]^{7-}$ is not generally well resolved. Also the E_{pc} values of $[Ti_2W_{10}PO_{40}]^{7-}$ are more negative when compared with the E_{pc} values of $[W_{12}PO_{40}]^{3-}$ (Prados and Pope 1976). This indicates that the substitution of W(VI) by Ti(IV) enhances the hydrolytic stability of heteropolyanion (Ortega and Pope 1984). (Further this compound also shows diminished anodic peak heights like the $K_5[TiW_{11}PO_{40}].5H_2O$). The second E_{pc} at -0.62 V is assigned to W(VI) \rightarrow W(V) reduction. The E_{pc} at -0.37 V may be due to the titanium reduction (Jeske *et al* 1994) which can be conclusively assigned only by controlled potential electrolysis followed by identification of the products formed. However, due to the lack of such facilities we tried to prepare chemically the one electron reduced heteropoly blue of $[Ti_2W_{10}PO_{40}]^{7-}$ viz $[Ti^{III}Ti^{IV}W_{10}PO_{40}]^{8-}$, by using 1 mmol of $TiCl_4$ and 1 mmol of $TiCl_3$ in the place of 2 mmol of $TiCl_4$ in the original procedure (Domaille and Knoth 1983). The product formed is blue in colour, highly air sensitive and turns white on exposure to air. This made the analysis of the solid compound difficult and hence, the blue coloured refluxed solution was used for spectral studies without salting out the product.

The optical spectra of the blue coloured solution taken at various intervals of time are given (figures 2a, b, c and d) along with the spectrum of $TiCl_3$ (figure 2e) for the sake

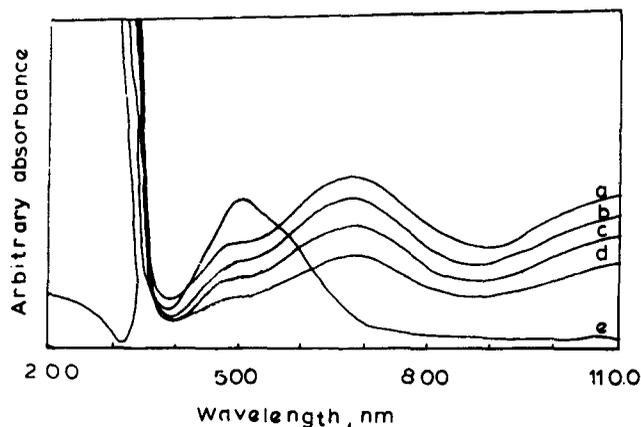


Figure 2. Optical spectra of the reaction mixture (1 mmol TiCl_4 + 1 mmol TiCl_3 + 11 mmol Na_2WO_4 + 5 mmol NaH_2PO_4 after 20 minutes refluxing) at various time intervals (a) just after refluxing, (b) after 10 minutes, (c) after 20 minutes, (d) after 40 minutes of 'a' and (e) the optical spectra of aqueous TiCl_3 .

of comparison. The refluxed solution was measured at longer wavelength also and the optical data are given in table 1.

The presence of IVCT bands in reduced heteropoly-molybdates, -tungstates and -vanadates is well known (Pope 1983). In most cases three bands are observed at 8,000, 14,000 and 20,000 cm^{-1} . The band at 8,000 cm^{-1} is due to IVCT between edge-shared MO_6 octahedra and is known as "intra" group transition, that is the transition within the " M_3O_{13} " triplets. The band around 14,000 cm^{-1} is the IVCT between corner-shared octahedra and it is called "extra" group transition, that is the transition between adjacent " M_3O_{13} " triplets through corner-shared oxygen (Sanchez *et al* 1982). From table 1 it is assigned that the band at 8,690 cm^{-1} is homonuclear IVCT $\text{Ti}^{\text{III}} \rightarrow \text{O} \rightarrow \text{Ti}^{\text{IV}}$ and band at 14,280 cm^{-1} is heteronuclear IVCT $\text{Ti}^{\text{III}} \rightarrow \text{O} \rightarrow \text{W}^{\text{VI}}$. These IVCT bands support the presence of the heteropoly blue analogue $[\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{W}_{10}\text{PO}_{40}]^{8-}$ in the refluxed solution. ESR data also support this formulation (*vide infra*).

IVCT band shown by the heteropoly blues can be calculated (So and Pope 1972) from the optical electronegativity χ_{opt} of the ligands and metals (Jorgensen 1959). Following this procedure the χ_{opt} of Ti(III) is computed to be 2.4. This calculated χ_{opt} of Ti(III) follows the general trend and nicely fits in the χ_{opt} table given by So and Pope (1972).

Table 1. Optical data of $[\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{W}_{10}\text{PO}_{40}]^{8-}$ with assignments.

Band position (cm^{-1})	Assignment
20,400	$d-d B_2 \rightarrow B_1$
14,280	IVCT $\text{Ti}^{\text{III}} \rightarrow \text{W}^{\text{VI}}$
11,760	$d-d B_2 \rightarrow E$
8,690	IVCT $\text{Ti}^{\text{III}} \rightarrow \text{Ti}^{\text{IV}}$

ESR spectra measured at 300 and 77 K of the blue coloured refluxed solution are given in figures 3a and b. There is no hyperfine features in the spectrum. This is not unexpected since the natural abundance of magnetic nuclei of ^{47}Ti and ^{49}Ti is very low viz 7.3 and 5.5% respectively. The g_{iso} value obtained (1.919) compares well with Ti(III) in oxo environments (Tkaeda and Watanabe 1967). If W(V) is formed the g_{iso} is expected in the range of 1.83 (Prados and Pope 1976). Another interesting feature of the ESR signal is the observed linewidth (14G) which is relatively low for a d^1 transition ion. However, if the odd electron is hopping between the two titanium atoms then a resonance narrowing is expected. Such a hopping process is well known in mixed-valence heteropoly blues (Pope *et al* 1975; Mossoba *et al* 1980; Harmalker *et al* 1983; So and Pope 1992). A ^{47}Ti enriched sample may unequivocally prove the hopping process by exhibiting hyperfine coupling from both the titanium atoms.

The 77 K spectrum shows axial symmetry (figure 3b). Although a metal ion in the Keggin structure has only rhombic symmetry, rhombic ESR spectra are observed only in the $5d^1$ species in the tungstates, an example being $[\text{Re}^{\text{V}}\text{W}_{11}\text{PO}_{40}]^{4-}$ (Ortega and

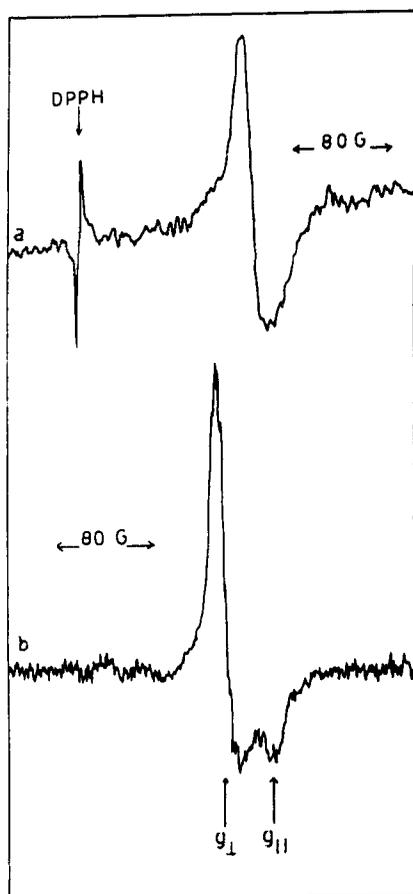


Figure 3. ESR spectra of the refluxed solution (1 mmol TiCl_4 + 1 mmol TiCl_3 + 11 mmol Na_2WO_4 + 5 mmol NaH_2PO_4 after 20 minutes refluxing) at (a) 300 K and (b) 77 K.

Pope 1984). In the $3d^1$ cases only axial symmetry is observed and a $4d^1$ species appears to be intermediate. These different types of spectra are traced to the large increase in spin orbit coupling constant (λ) and hence to larger ranges of g values.

The g values for a d^1 complex with the unpaired electron in the d_{xy} orbital are given (Launay et al 1980) by

$$g_{\parallel} = 2.0023 - 8\lambda/\Delta E(x^2 - y^2 \leftarrow xy)$$

$$g_{\perp} = 2.0023 - 2\lambda/\Delta E(xz, yz \leftarrow xy)$$

The fact that g_{\perp} (1.938) $>$ g_{\parallel} (1.907) reveals that the unpaired electron is present in the d_{xy} orbital (Samuel et al 1979). It is very interesting to note that there is no TiCl_3 left in the reaction mixture as revealed by the ESR since TiCl_3 solution gives an ESR spectrum with $g_{\parallel} = 1.988$ and $g_{\perp} = 1.897$.

With an attempt to generate the heteropoly blue polycrystalline samples of $[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]^{7-}$ were γ -irradiated. The irradiated samples became blue coloured, but gave no observable ESR spectra down to 77 K. It is well known that the 'two-electron blues' are diamagnetic (Pope 1980) due to possible antiferromagnetic coupling of electrons localized on adjacent metal centres. Hence we propose that γ -irradiation leads to 2-electron blue resulting in the localisation of the electrons on the adjacent titanium atoms.

3.3 $\text{K}_5\text{M}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot x\text{H}_2\text{O}$ [$\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$ or Cu(II)]

The X-ray powder diffraction pattern shows that $\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$ and $\text{K}_5\text{Mn}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 9\text{H}_2\text{O}$ are isomorphous with $\text{K}_7[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$. By knowing the crystal structure of dititanodecatungstophosphate (orthorhombic, $a = 17.934$, $b = 18.699$, $c = 20.461$ Å) (Ozeki and Yamase 1991) the h, k, l values for $\text{K}_7[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$ were refined. Further, using these h, k, l values, the lattice parameters for $\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$ and $\text{K}_5\text{Mn}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 9\text{H}_2\text{O}$ were refined using the least squares program and the values are given in table 2.

The optical spectra of these complexes recorded in aqueous solution are identical with reflectance spectra taken in the solid form (pellets). The optical bands, their assignment and the 10 Dq and interelectronic repulsion parameter 'B' values calculated using Tanabe–Sugano diagram (Tanabe and Sugano 1954) are all collected in table 3. For comparison the values of free ions and aquo complexes are also included in table 3. The reduction in the B value is significant compared to the free ions indicating that the bonding is considerably covalent in these complexes. The electronic spectrum of $\text{K}_5\text{Co}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 7\text{H}_2\text{O}$ is given in figure 4. Co(II) being a d^7 system, its excited

Table 2. Lattice parameters for $\text{K}_5\text{M}^{\text{II}}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Cu}$ or Mn).

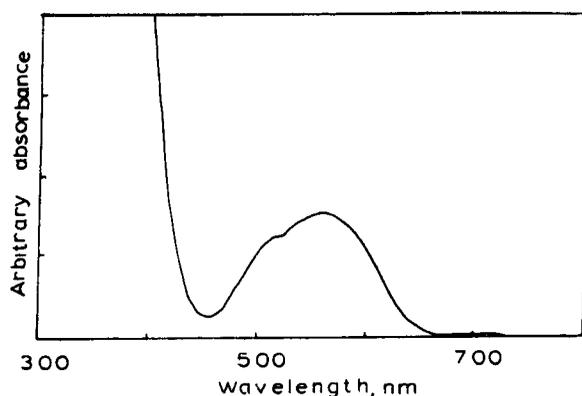
Compound	a (Å)	b (Å)	c (Å)
$\text{K}_7[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$	17.95	18.70	20.46
$\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$	18.04	18.76	20.52
$\text{K}_5\text{Mn}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 9\text{H}_2\text{O}$	18.06	18.77	20.46

Table 3. Optical data of $K_5M^{II}[Ti_2W_{10}PO_{40}] \cdot xH_2O$ ($M = Mn, Co, Ni$ or Cu) with assignments.

Compound	Band position (cm ⁻¹)	Assignment	10Dq (cm ⁻¹)	B* (cm ⁻¹)	B ⁺ Free ion (cm ⁻¹)
$K_5Mn[Ti_2W_{10}PO_{40}] \cdot 9H_2O$	17,900	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$	9,270	772(770)	960
	24,700	${}^4T_{2g}(P) \leftarrow {}^6A_{1g}$			
	33,300	${}^4T_{1g}(P) \leftarrow {}^6A_{1g}$			
	42,000	CT			
$K_5Co[Ti_2W_{10}PO_{40}] \cdot 7H_2O$	17,600	${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$	9,100	828(980)	1120
	19,400	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$			
	40,000	CT			
$K_5Ni[Ti_2W_{10}PO_{40}] \cdot 4H_2O$	13,500	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$	8,700	790(905)	1040
	24,500	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$			
	40,000	CT			
$K_5Cu[Ti_2W_{10}PO_{40}] \cdot 6H_2O$	11,400	${}^2T_{2g} \leftarrow {}^2E_g$	11,370	—	—
	34,600	CT			
	42,600	CT			

* Values in parentheses are for aqua complexes of type $[M(H_2O)_6]^{+2}$

+ Values collected from Figgis (1967)

**Figure 4.** Optical spectrum of $K_5Co[Ti_2W_{10}PO_{40}] \cdot 7H_2O$ in water.

state is susceptible to JT distortion. The two bands observed are the bands due to the spin allowed transitions from ${}^4T_{1g}(F)$ ground state to the excited quartet state which arises from JT splitting (Figgis 1967).

The ESR spectrum of a polycrystalline sample of $K_5Cu[Ti_2W_{10}PO_{40}] \cdot 6H_2O$ taken at X-band frequency and at 300 K is given (figure 5a). This spectrum does not show the usual anisotropic pattern expected for a powder sample (Kneubuhl 1960) rather it is close to an isotropic spectrum. The g value evaluated from this spectrum is 2.1241. Further the spectrum does not exhibit any hyperfine feature from ${}^{63}Cu(I = 3/2)$, indicating that the exchange interactions are sufficiently strong (> 1 GHz) to average out

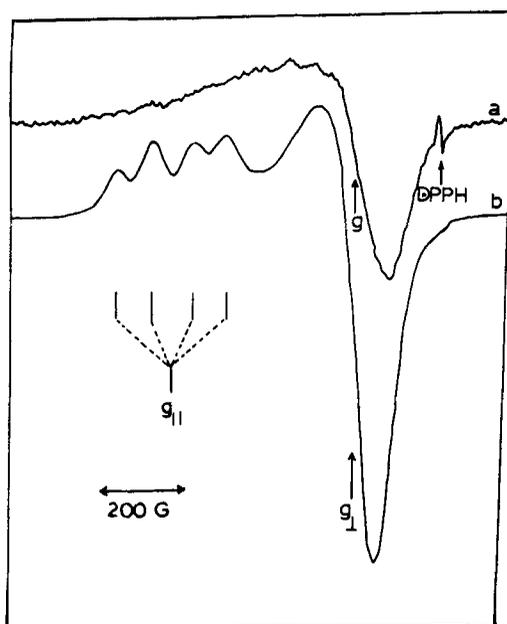


Figure 5. X-band ESR spectra of fresh polycrystalline sample of $\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$ at (a) 300 K and (b) 77 K.

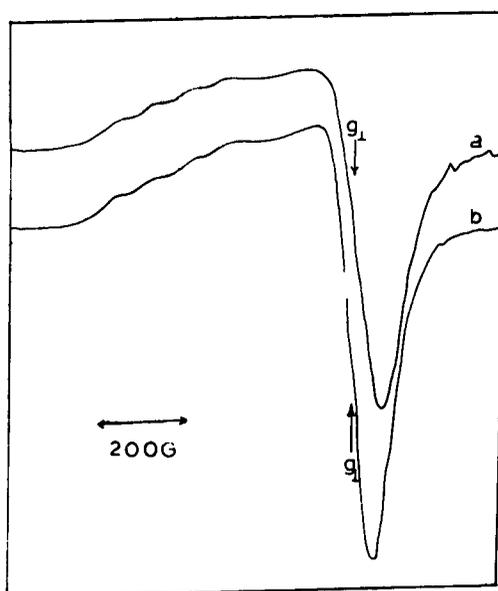
copper hyperfine interactions. Similar ESR spectra were observed in the case of undiluted polycrystalline samples of copper (*cis, cis*-1,3,5-triaminocyclohexane) $_2(\text{ClO}_4)_2$ at 300 K (Ammeter *et al* 1979). However, when $\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$ was cooled down to 77 K a typical spectrum expected for an axially elongated Cu^{2+} complex with the unpaired electron present in $d_{x^2-y^2}$ orbital (Kuska and Rogers 1968) was obtained (figure 5b). ESR parameters derived from this spectrum are given in table 4. The changeover of the spectrum from isotropic to anisotropic pattern by lowering the temperature can be interpreted in terms of a dynamic to static JT distortion (Murugesan and Subramanian 1984). When the JT active Cu(II) system is completely frozen in one of the three valleys the g and A tensors are given by the usual axially symmetric spin Hamiltonian. Using these expressions for g -tensors for a static JT distortion (Sambasiva Rao and Subramanian 1976) and a Δ value of $11,400\text{ cm}^{-1}$ from the optical spectrum we obtained $\lambda_{\parallel} = -652.7\text{ cm}^{-1}$ and $\lambda_{\perp} = -783.6\text{ cm}^{-1}$. This decrease in the values of λ_{\parallel} and λ_{\perp} from free ion value of -828 cm^{-1} reveals considerable “covalency effects” in the metal–ligand bonding (Hathaway and Billing 1970).

When polycrystalline $\text{K}_5\text{Cu}[\text{Ti}_2\text{W}_{10}\text{PO}_{40}]\cdot 6\text{H}_2\text{O}$ is ground and left aside, it slowly becomes amorphous powder by losing water. The ESR spectrum of this amorphous powder at 300 K (figure 6a) is no longer isotropic. It is the typical spectrum expected for tetragonally elongated Cu(II). The 77 K spectrum of this powder (figure 6b) is almost the same as that of the 300 K spectrum except that the A_{\parallel} features are slightly better resolved. The fact that no isotropic spectrum was obtained at 300 K for this powder indicates that the loss of water has led to the crumbling of the crystal leading to reduction in Cu(II) site symmetry.

Table 4. Cu(II) ESR parameters of $K_5Cu[Ti_2W_{10}PO_{40}] \cdot 6H_2O$.

$K_5Cu[Ti_2W_{10}PO_{40}] \cdot 6H_2O$	Temp. (K)	g tensor		$A_{\cdot, Cu} (G)$	
		g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}^*
Fresh polycrystalline	300	$g = 2.1241$		—	—
	77	2.4593	2.1378	81.7	43.3
Left in air for a day	300	2.4630	2.1399	78.3	56.7
	77	2.4501	2.1413	88.3	46.7

* Estimated values from linewidth

**Figure 6.** X-band ESR spectra at (a) 300 K and (b) 77 K after exposure of the polycrystalline $K_5Cu[Ti_2W_{10}PO_{40}] \cdot 6H_2O$ in air for a day.

4. Conclusion

The existence of heteropoly blue analogue $[Ti^{III}Ti^{IV}W_{10}PO_{40}]^{8-}$ is identified by optical and ESR studies. The JT effect noticed in the ESR spectrum of copper and in the optical spectrum of cobalt complexes of the $K_5M[Ti_2W_{10}PO_{40}] \cdot xH_2O$ series reveals the presence of high symmetry around M(II). The reduction in λ value of Cu(II) and B values of the others from free ion values support the covalent bonding in these complexes. Powder X-ray diffraction results reveal that these complexes are isomorphous.

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