STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LII, 4, 2007

In memoriam prof. dr. Ioan A. Silberg

SYNTHESIS AND CHARACTERIZATION OF A NEW BISMUTHO(III)POLYOXOMETALATE WITH MIXED ADDENDA

OANA BABAN[a], DAN RUSU[b], ADRIAN PATRUT[a],
CORA CRACIUN[C], MARIANA RUSU[a*]

ABSTRACT. A new bismutho(III)polyoxometalate cluster with mixed addenda, which corresponds to the formula $K_8[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]\cdot 23H_2O$, was synthesized. The cluster was investigated by FT-IR, UV-Vis-NIR and EPR spectroscopy. The FT-IR spectrum exhibits vibrations, which indicates the presence of Bi heteroatoms and of W and V addenda. The UV spectrum contains charge-transfer bands, which are specific to the polyoxometalate building. The Vis-NIR spectrum shows two heteronuclear intervalence charge-transfer bands 608 and 806 nm, due to the presence of V^{4+} metal centers. The EPR spectrum indicates non-interacting V^{4+} metal centers.

KEYWORDS: *polyoxometalate, metal cluster, FT-IR spectroscopy, UV-Vis-NIR spectroscopy; EPR spectroscopy.*

INTRODUCTION

Polyoxometalates, also called metal-oxygen clusters, are the most important representatives of the inorganic molecular nanoclusters. The continuous diversification of polyoxometalates through the synthesis of new substances, with interesting electronic structures, unexpected topologies, various electron-transfer processes and remarkable magnetic-exchange interactions, has triggered numerous applications, especially in catalysis, analysis, biochemistry, medicine and materials science [1-7].

---

[a] *"Babes-Bolyai" University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Str., 400028 Cluj-Napoca, Romania*

[b] *"Iuliu Hatieganu" University, Faculty of Pharmacy, 13 Iuliu Hatieganu Str., 400023 Cluj-Napoca, Romania*

[c] *"Babes-Bolyai" University, Faculty of Physics, 1 Kogalniceanu Str., 400084 Cluj-Napoca, Romania*

[*] Corresponding author: mrusu@chem.ubbcluj.ro

Polyoxometalates are polyoxoanions of the early transition elements, especially Mo, W and V, made up by linked MO_n units. The M metal centers, which may belong to one or several atomic species, are called addenda. In a simplified classification, polyoxometalates are divided into isopolyoxometalates and heteropolyoxometalates. For isopolyoxometalates one or more atomic species act as addenda, while in the case of heteropolyoxometalates, beside the addenda, there are also one or several atomic species playing the role of X heteroatom(s) [8, 9].

Heteropolyoxometalates in which the X heteroatom has an unshared electron pair are of particular importance, showing special structural characteristics and specific properties. Due to the stereochemical activity of the lone pair, the primary group adopts an unusual XO_3 trigonal pyramid shape. The role of the X heteroatom with an unshared electron pair is usually played by subvalent group 15 elements, *i.e.*, As (III), Sb (III) or Bi (III).

A very interesting heteropolyoxometalate series of this type contains 22 addenda metal centers. It consists of two trivacant *Bß*-XW_9O_{33} units (X = Sb^{3+}, Bi^{3+}), which are connected to each other by two WO_2 and by two additional *fac*-$WO_2(OH)$ or $M(H_2O)_3$ connector groups. Several such polyoxometalates with the general formula $[X_2W_{22}O_{74}(OH)_2]^{12-}$ and $[X_2W_{20}M^{(n+)}{}_2O_{70}(H_2O)_6]^{(14-2n)-}$ (M = Fe^{3+}, Co^{2+}, Ni^{2+}, Ni^{2+}, Mn^{2+}) have been reported [10-17]. The general structure of the respective polyoxometalates with mixed addenda is displayed in Fig. 1.

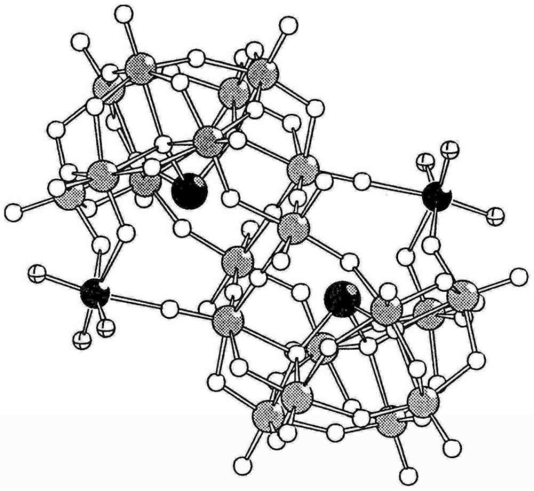

Figure 1. Ball-and-stick representation of the mixed addenda $[X_2W_{20}M^{(n+)}{}_2O_{70}(H_2O)_6]^{(14-2n)-}$ polyoxometalate structure (X large dark spheres, W large gray spheres, M medium-sized dark spheres, O small white spheres, H_2O small white spheres with crossing lines).

In this paper we describe the synthesis of (the potassium salt of) a new bismutho(III)heteropolyoxometalate with mixed addenda of this series, which corresponds to the formula $K_8[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]\cdot 23H_2O$. The substance is abbreviated as $K_8[Bi^{III}W_{20}V^{IV}_2]$ for the neutral salt and $[Bi^{III}W_{20}V^{IV}_2]^{8-}$ for the anion, respectively. The new cluster was investigated by vibrational (FT-IR), electronic (UV-Vis-NIR) and EPR spectroscopy.

RESULTS AND DISCUSSION

The new bismutho(III)heteropolyoxometalate with mixed addenda was prepared according to the following formal reaction of metal center/ addenda substitution:

$$[Bi^{III}_2W_{22}O_{74}(OH)_2]^{12-} + 2VO^{2+} + 6H_2O \longrightarrow$$
$$[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]^{8} + 2WO_4^{2-} + 4H^+$$

The elemental analysis is consistent with the proposed formula for the synthesized substance, *i.e.*, $K_8[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]\cdot 23H_2O$.

FT-IR spectra. The FT-IR spectra of $K_8[Bi_2W_{20}V_2]$ polyoxometalate with mixed addenda and of the parent $Na_{12}[Bi_2W_{22}]$ polyoxometalate with unique addenda are displayed in Fig. 2. The main vibration bands and their assignment are listed in Table 1.

The FT-IR spectra of $K_8[Bi_2W_{20}V_2]$ and $Na_{12}[Bi_2W_{22}]$ are quite similar, suggesting that the two polyoxometalates belong to the same series.

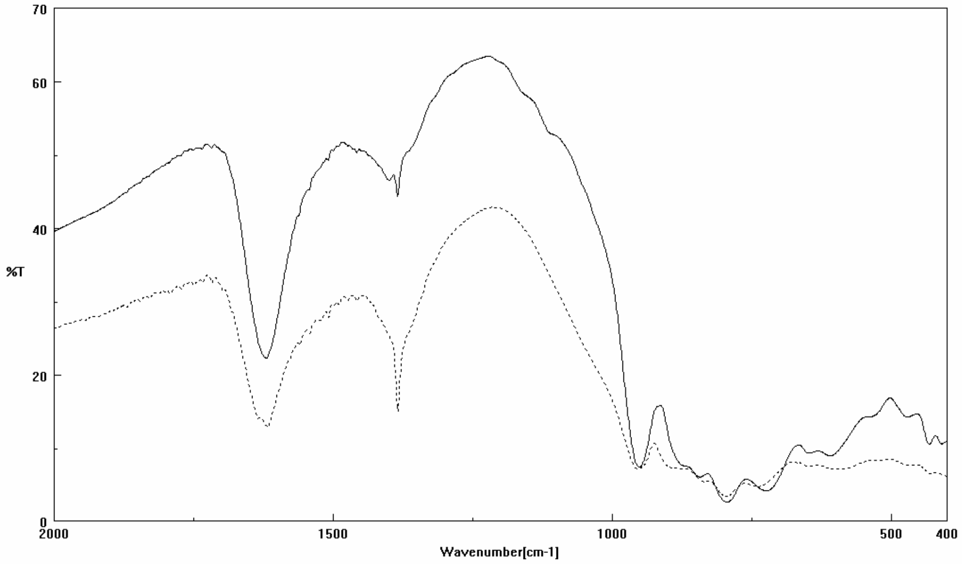

Figure 2. FT-IR spectra of $K_8[Bi_2W_{20}V_2]$ (solid line) and $Na_{12}[Bi_2W_{22}]$ (dashed line).

The stretching vibration of the terminal W=O_t bonds is recorded at about 950 cm^{-1} for both polyoxometalates. This indicates that terminal oxygen atoms are not involved in the coordination of V^{4+} metal centers.

The main stretching vibration of the Bi–O_i bonds is recorded at ca. 840 cm^{-1} for the two substances. This shows that also internal oxygens are not involved in the coordination of V^{4+}.

The vibrations of tricentric W-O_c-W bonds of the corner sharing WO_6 octahedra are recorded at 835, 796 and 738 cm^{-1} for Bi_2W_{22} and 842, 794 and 724 cm^{-1} for $Bi_2W_2V_2$, respectively. The three peaks demonstrates the non-equivalence of W-O_c-W bonds, when linking octahedra from equatorial and polar regions of the BiW_9 trilacunary fragments [18].

The vibration bands of tricentric W-O_e-W bonds of the edge-sharing WO_6 octahedra are also splitted, being revealed at 648 and 593 cm^{-1} for Bi_2W_{22} and 647 and 609 cm^{-1} for $Bi_2W_{20}V_2$, respectively. The splitting evinces the presence of two non-equivalent bonds of this type in the oxo-cage [19, 20].

As expected, the $Bi_2W_{20}V_2$ spectrum shows additional peaks, due to the new metal centers/addenda. These maxima are recorded at 1158 and 1105 cm^{-1} and can be attributed to the stretching vibration ν_{as}V-O, which is also splitted.

Table 1.

Main vibrations of the FT-IR spectra of $K_8[Bi_2W_{20}V_2]$ and $Na_{12}[Bi_2W_{22}O_{74}]$.

Vibration	ν (cm^{-1})	
	$Na_{12}[Bi_2W_{22}]$	$K_8[Bi_2W_{20}V_2]$
ν_{as}V-O	-	1158 1105
ν_sW=O_t	953	951
ν_{as}Bi-O_i+ ν_{as}W-O_c-W	835	842
ν_{as}W-O_c-W	796 738	794 724
ν_{as}W-O_e-W	648 593	647 609

UV spectra. The UV spectra of $Bi_2W_{20}V_2$ and Bi_2W_{22} polyoxometalates (Fig. 3) exhibit the two charge-transfer bands, characteristic to the polyoxometalate structure [21, 22]. The ν_2 band (~50,000 cm^{-1}), due to dπ-pπ transitions of the M=O_t bonds, is recorded at identical frequencies (195 nm/ 51,165 cm^{-1}) in both spectra, which indicates that the terminal O_t atoms are not involved in the coordination of the V^{4+} metal centers. The ν_1 band (~40,000 cm^{-1}), due to dπ-pπ-dπ transitions from the tricentric M-$O_{c,e}$-M bonds, is also recorded practically at same frequencies in both spectra (254 nm/39,370 cm^{-1} for $Bi_2W_{20}V_2$ *vs.* 255 nm/39,215 cm^{-1} for Bi_2W_{22}).

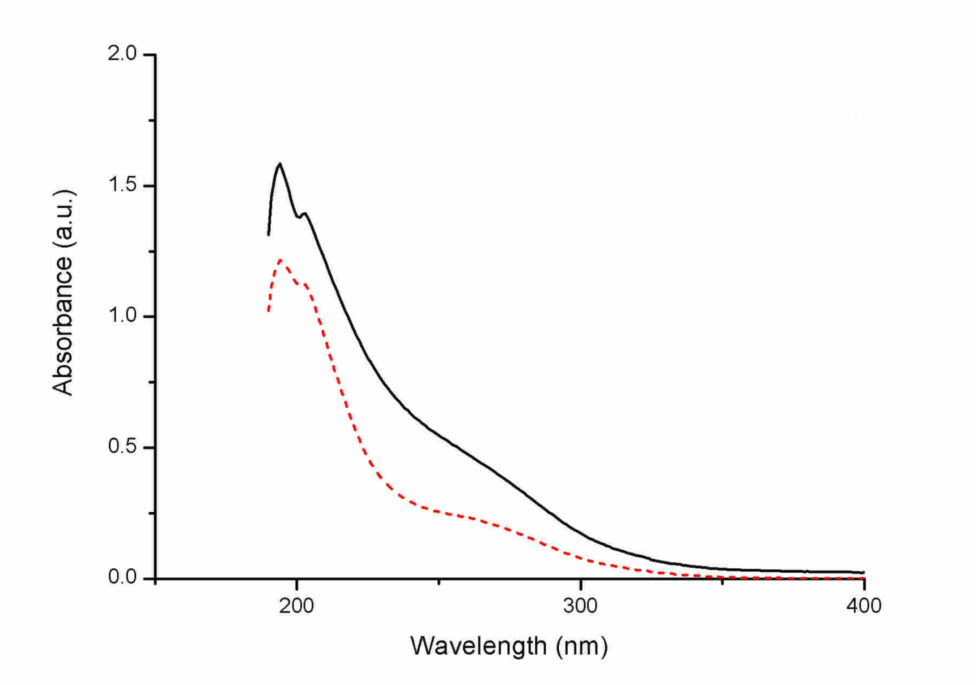

Figure 3. UV absorption spectra of $Bi_2W_{20}V_2$ (solid line) and Bi_2W_{22} (dashed line) in aqueous solution ($c = 5 \cdot 10^{-5}$ mol dm^{-3}).

The higher intensity of $Bi_2W_{20}V_2$ bands, when compared to Bi_2W_{22}, indicates a higher distortion and decrease in symmetry, due to the presence of two different types of metal centers/addenda.

Vis-NIR spectrum. In polyoxometalates with one or several reduced addenda, new intervalence charge-transfer (IVCT) bands arise in the visible and NIR. In most cases, three IVCT bands are observed, marked by A, B and C [23].

For $Sb_2W_{20}V^{IV}_2$ polyoxometalate, the reduced addendum is the V^{4+} metal center, which determines the presence of heteronuclear IVCT V^{IV}-W^{VI} (more precisely, V^{IV}-O-W^{VI}) bands. The recorded spectrum (Fig. 4) exhibits a strong absorption over the entire visible range, which extends in NIR and accounts for the brown color of the substance, in both solid state and solution.

The A IVCT band, located in NIR at 806 nm (12,410 cm^{-1}), as well as the B IVCT band, recorded at 628 nm (15,915 cm^{-1}), are each reduced to a shoulder. The two bands are related to the $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ (for A) and $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$ (for B) transitions in the Ballhausen and Gray molecular orbital theory for V^{4+} in a C_{4v} local symmetry [24]. On the other hand, the broad C IVCT band is not recorded.

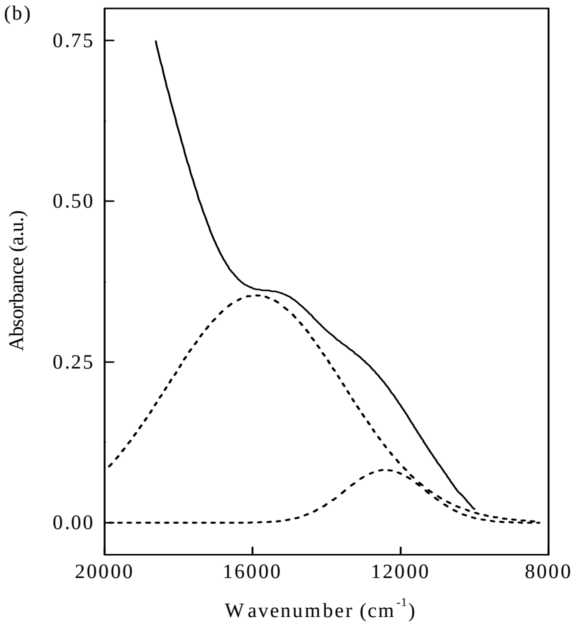

Figure 4. Vis-NIR absorption spectrum of $Bi_2W_{20}V^{IV}_2$ in aqueous solution (c = 10^{-4} mol dm^{-3}). The Guassian components are shown with dashed lines.

EPR Spectrum. Powder EPR spectrum of $K_8[Bi_2W_{20}V^{IV}_2]$, recorded at room temperature in the X band contains 8 components, both in the perpendicular and in the parallel bands, due to the hyperfine coupling of the spin of one unpaired electron with the nuclear spin of the ^{51}V isotope (I = 7/2) (Fig. 5). The spectrum can be described by an axial spin Hamiltonian, characteristic for the S = 1/2 system with C_{4v} local symmetry [25, 26]:

$$H = \mu_B[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1),$$

where $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$, $A_{\perp}$ are the axial principal values of the ***g*** and hyperfine tensors, μ_B is the Bohr magneton, B_x, B_y, B_z are the components of the applied magnetic field in direction of the principal ***g*** axes, S_x, S_y, S_z and I_x, I_y, I_z are the components of the electronic and nuclear spin angular momentum operators. This behavior suggests the equivalence of the two paramagnetic V^{4+} ions in the investigated substance.

Parameters were estimated by using a DPPH standard as g-marker (g = 2.0037), $g_{\parallel}$ = 1.908, $g_{\perp}$ = 1.974, $A_{\parallel}$ = 202.1 G, $A_{\perp}$ = 71.6 G for $K_8[Bi^{III}_2W_{20}V^{IV}_2]$. The simulated EPR spectrum indicates no V-V coupling.

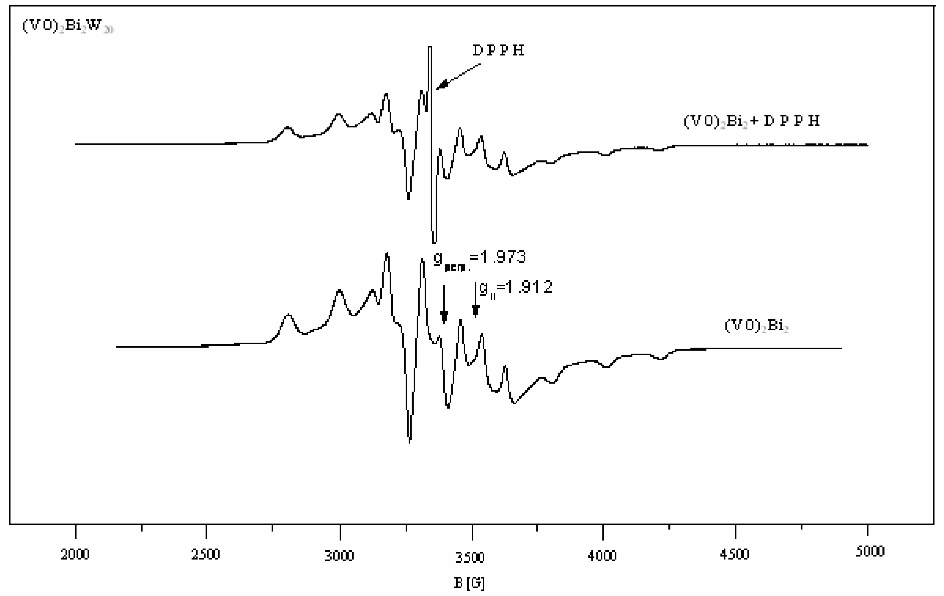

Figure 5. Simulated powder EPR spectrum of $K_8[Bi_2W_{20}V^{IV}_2]$.

EXPERIMENTAL SECTION

Synthesis. An amount of 6.76 g (1 mmol) $Na_{12}[Bi_2W_{22}O_{74}(OH)_2]\cdot 44H_2O$, prepared according to the procedure described in the literature [13], was dissolved in 100 mL AcONa/AcOH acetate buffer (pH 4) and heated at 70°C. Then, 0.50 g (2.5 mmol) $VOSO_4\cdot 2H_2O$ were added slowly and under continuous stirring to the solution. The mixture was heated again for 1 h, at 70°C, after which 0.90 g (12 mmol) of finely ground KCl were added. The brown solution was purified by filtration and stored at room temperature. Brown-gray microcrystals of $K_8[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]\cdot 23H_2O$ precipitated after 3-4 days. The crystals were filtered off, washed with distilled water and dried. Eventually, they were recrystallized twice from hot distilled water. Yield: 4.95 g (0.885 mmol; 88.5 % based on W).

Analysis. The synthesized substance was characterized by elemental and thermogravimetric analysis, as follows:

K was determined by FEP with an Eppendorf flame photometer.

Bi, W and V were determined by OES-ICP with a Bird 2070 spectrophotometer.

Water content was determined by dehydration at 350 ^{0}C.

Results (wt %): found (calculated for $K_8[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]\cdot 23H_2O$; M = 6149.81) K 5.05 (5.09); Bi 6.91 (6.80); W 59.02 (59.79); V 1.61 (1.66); H_2O 7.95 (7.91).

Investigation. FT-IR spectra were recorded in the 4000-400 cm^{-1} range by means of a Jasco FT/ IR 610 spectrophotometer, using KBr pellets.

Electronic spectra in aqueous solution were acquired in the 190-1300 nm range on an ATI Unicam-UV-Visible spectrophotometer, by means of a Vision Software V 3.20.

EPR spectra were obtained at room temperature and 9.6 GHz (X-band), with a Bruker ESP 380 spectrometer.

CONCLUSION

The paper reports the synthesis and investigation of a new polyoxometalate cluster, with the formula $K_8[Bi^{III}_2W_{20}V^{IV}_2O_{70}(OH)_2(H_2O)_4]\cdot 23H_2O$. The substance is the neutral salt of a heteropolyoxometalate, which contains two Bi^{3+} heteroatoms with an unshared electron pair and mixed addenda, namely W^{6+} and V^{4+}.

The main vibration of the FT-IR spectrum, ν_{as}Bi-O, registered at 835 cm^{-1}, reveals the presence of Bi as a heteroatom. The ν_{as}V-O vibration, recorded at 1158 and 1105 cm^{-1}, indicates the presence of the V^{4+} metal centers/addenda.

The UV spectrum exhibits two chage-transfer (CT) bands, recorded at 195 and 254 nm, specific to the polyoxometalate edifice.

The Vis-NIR spectrum contains two heteronuclear intervalence charge-transfer (IVCT) bands, owing to the presence of the V^{4+} metal centers, as reduced addenda. The V^{IV}-W^{VI} IVCT bands are registered at 608 and 806 nm.

The EPR spectrum suggests the presence of non-interacting V^{4+} metal centers.

REFERENCES

1. M.T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl*. **1991**, *30*, 34.
2. M.T. Pope, A. Müller, in *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (eds. M.T. Pope, A. Müller), Kluwer, Dordrecht, Boston, London, **1994,** 1.
3. M.T. Pope, A. Müller, in *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications* (eds. M.T. Pope, A. Müller), Kluwer, Dordrecht, Boston, London, **2001**, 3.
4. A. Müller, M. Luban, M. Schröder, R. Modler, P. Kögerler, M. Axenovich, M. Schmack, J. Canfield, S. Bud'ko, N. Harrison, *ChemPhysChem.*, **2001**, *2*, 517.

5. T. Yamase, M.T. Pope, in *Polyoxometalate Chemistry for Nano-Composite Design* (eds. T. Yamase, M.T. Pope), Kluwer, New York, Boston, Dordrecht, London, Moscow, **2002**, 1.

6. A. Müller, *Science*, **2003**, *300*, 749.

7. A. Müller, S. Roy, *Eur. J. Inorg. Chem.*, **2005**, 3561.

8. M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, Heidelberg, New York, Tokyo, **1983**, 3.

9. L.C.W. Baker, D.C. Glick, *Chem. Rev.*, **1998**, *98*, 3.

10. B. Krebs, R. Klein, in *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (eds. M.T.Pope, A. Müller), Kluwer, Dordrecht, Boston, London, **1994**, 41.

11. M. Bösing, I. Loose, H. Pohlmann, B. Krebs, *Chem. Eur. J.,* **1997**, *3*, 1232.

12. D. Rodewald, Y. Jeannin, *C. R. Acad. Sci. Paris, Ser. II c,* **1998**, *1*, 175.

13. M. Bösing, A. Nöh, I. Loose, B. Krebs, *J. Am. Chem. Soc.,* **1998**, *120*, 7252.

14. I. Loose, E. Droste, M. Bösing, H. Pohlmann, M.H. Dickman, C. Rosu, M.T. Pope, B. Krebs, *Inorg. Chem.,* **1999**, *38*, 2688.

15. D. Drewes, E.M. Limanski, M. Piepenbrink, B. Krebs, *Z. Anorg. Allg. Chem.*, **2004**, *630*, 58.

16. Y. Jeannin, *C. R. (Chimie)*, **2004**, *7*, 1235.

17. D. Laurencin, R. Villanneau, P. Herson, R. Thouvenot, Y. Jeannin, A. Proust, *Chem.Commun.*, **2005**, 5524.

18. R.Thouvenot, M. Fournier, R.Franck, C. Rocchiccioli-Deltcheff, *Inorg. Chem.*, **1984**, *23*, 598.

19. C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Frank, *Spectrochim. Acta A*, **1976**, *32*, 587.

20.C. Roccchiccioli-Deltcheff, R. Thouvenot, R., *C. R. Acad. Paris, Ser. C*, **1974**, *278*, 857.

21. S. Hyunsoo, M.T. Pope, *Inorg. Chem.*, **1972**, *11*, 1441.

22. X. Zhang, G. Chen, D.C. Duncan, R.J. Lachicotte, C.L.Hill, *Inorg. Chem.*, **1997**, *36*, 4381.

23. M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, Heidelberg, New York, Tokyo, **1983**, 109.

24. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, New York, **1984**, 385.

25. C.W. Lee, H. So, *Bull. Korean Chem. Soc.*, **1986**, *7*, 318.

26. J. Park, H. So, *Bull. Korean Chem. Soc.*, **1994**, *15*, 752.