Inorganica Chimica Acta, 181 (1991) 201-205

Heteropoly-tungstate derivatives: isomerisation of $PW_9O_{34}^{9-}$ and reaction with Co^{2+} and Mn^{2+}

B. Moore and **K. Foger***

CSIRO Division of Materials Science and Technology, Locked Bag 33, Clayton, Vic. 3168 (Australia)

(Received July 11, 1990)

Abstract

The isomerisation (thermalisation) process of the lacunary ion A-$Na_8HPW_9O_{34}\cdot xH_2O$ (unthermalised PW_9) as a function of temperature and predrying procedures has been followed by FT-IR spectroscopy. Excessive water content inhibited conversion to B-$Na_8HPW_9O_{34}$ (thermalised or Δ-PW_9) on heating to 140 °C in a static system, but complete conversion was obtained in a flow system. Contacting B-$Na_8HPW_9O_{34}$ with water reversed the process. This has implications for the preparation of transition metal containing phosphotungstate dimer compounds. Reactions of solutions of transition metal ions such as Co^{2+} and Mn^{2+} with A-$Na_8HPW_9O_{34}$ yields predominantly $(MOH_2)_3P_2W_{18}O_{68}^{12-}$ while B-$Na_8HPW_9O_{34}$ forms $M_4(H_2O)_2P_2W_{18}O_{68}^{10-}$. Good yields of the latter are only obtained whenever solid B-$Na_8HPW_9O_{34}$ is added to a solution of transition metal ions.

Introduction

Since Weakley *et al.* [1] reported the preparation of di-substituted heteropoly-tungstates ($M_4(H_2O)_2$-$P_2W_{18}O_{68}^{10-}$) from tri-vacant heteropolyoxoanion precursors ($PW_9O_{34}^{8-}$), several studies on the synthesis and characterisation of this class of compounds have appeared in the literature [2–5]. According to Finke *et al.* [3], high yields of $M_4(H_2O)_2P_2W_{18}O_{68}^{10-}$ were obtained whenever the PW_9 precursor was thermalised at 140 °C prior to reaction with transition metal salts. Unthermalised PW_9 yielded a different product, which Knoth *et al.* [4] characterised as $(MOH_2)_3P_2W_{18}O_{68}^{12-}$. This compound transformed on recrystallisation at 100 °C (boiling water) into $M_4(H_2O)_2P_2W_{18}O_{68}^{10-}$. Thermalised PW_9 (Δ-PW_9) was ascribed to be predominantly B-PW_9 while unthermalised PW_9 was assigned the A-PW_9 structure [6]. Both forms are distinguished by their IR and NMR spectra. The isomerisation of A-type anion to B-type depends strongly on conditions of dehydration and has been described as somewhat 'erratic'.

In our efforts to produce di-substituted manganese heteropoly-tungstates we encountered irreproducibilities in the nature of the initial product and therefore studied the system in more detail. This work reports on the thermalisation of PW_9 as a function of drying conditions and water content, on the stability of Δ-PW_9 in aqueous solution, and on the type of transition metal containing dimer as a function of preparation procedure.

Experimental

FT-IR spectra were recorded with a Mattson Cygnus 100 FT-IR spectrometer using KBr sampling discs; ^{31}P NMR spectra were recorded in the solid state with a Brukker 400 spectrometer; thermal analysis data (TGA/DTA) were obtained with a Stanton-Reelcroft STA-780 analyser (nitrogen atmosphere, ramp rate = 10 °C/min).

Preparations

$Na_8HPW_9O_{34}\cdot xH_2O$ was prepared according to Massart *et al.* [7]. To sodium tungstate dihydrate (120 g), dissolved in distilled water (148 ml) with stirring, was added 93% *ortho*-phosphoric acid (2.6 ml) followed by glacial acetic acid (22 ml). Gentle stirring led to a white precipitate of $Na_8HPW_9O_{34}\cdot xH_2O$, which was isolated by filtration and washed ready for drying. The isomer obtained depended on drying temperature (T). At $20 < T < 80$ °C, almost pure A-$Na_8HPW_9O_{34}$ (unthermalised PW_9) was obtained, while at $T > 80$ °C B-$Na_8HPW_9O_{34}$ (thermalised or Δ-PW_9) appeared in the product. Isomerisation to B was complete after drying at 140 °C for >2 h.

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

Transition metal containing dimers of PW$_9$-($M_4(H_2O)_2P_2W_{18}O_{68}{}^{10-}$ and ($MOH_2)_3P_2W_{18}O_{68}{}^{12-}$) were prepared by adding either isomer to a solution of the transition metal ion in stoichiometric amounts. The solution was stirred for 15 min, then excess KCl was added to precipitate the compounds. The precipitates were filtered and recrystallised from water at 50 °C. A temperature of 50 °C was chosen because Knoth *et al.* [4] reported that $M(OH_2)_3$-$P_2W_{18}O_{68}{}^{12-}$ was converted to $M_4(H_2O)_2P_2W_{18}$-$O_{68}{}^{10-}$ in solution at temperatures above 60 °C.

Results and discussion

Isomerisation of PW$_9$

The FT-IR spectrum of freshly prepared PW$_9$ (Fig. 1, trace a) shows two prominent bands at 1060 and 1030 cm^{-1} and a series of peaks in the range 950–700 cm^{-1}. Bands at and above 1000 cm^{-1} have been attributed to P–O vibrations whereas terminal and bridging W–O bands appear below 1000 cm^{-1} [3]. When PW$_9$ is heated to 140 °C new IR peaks appear at 1170 and 1000 cm^{-1} (P=O bands of the Δ-PW$_9$ species), and intensities change in the W–O region (traces b, c, Fig. 1). Only incomplete isomerisation is observed with freshly prepared PW$_9$ (trace b, Fig. 1), while samples dried in air for 24 h before thermal treatment transform completely (trace c, Fig. 1). This is in agreement with Finke *et al.* [3] and Knoth *et al.* [4] who have reported previously that drying of PW$_9$ prior to heat treatment has a profound effect on the thermolysis process. The thermal isomerisation process can be followed also by solid state ^{31}P NMR spectroscopy (Fig. 2). The traces a and c agree closely with spectra reported for PW$_9$ and Δ-PW$_9$ [3].

However, in a flow system, with nitrogen continuously purging the sample, complete thermalisation occurs at 140 °C (Fig. 3) irrespective of whether the sample was freshly prepared or dried for 24 h prior to heat treatment. This is a clear indication that water content and/or rate of water removal influence isomerisation. A series of controlled drying experiments, followed by thermalisation and characterisation of the dried precursor by TGA were expected to shed some light onto this problem. TGA traces of samples as isolated from the preparation solution were difficult to obtain, due to their extremely high water content. However, compounds dried in air for 24 h at ambient temperature gave TGA/DTA traces (in the temperature range 22–250 °C) which showed two main peaks for water loss, namely a low temperature peak (peak I) with a maximum between 90 and 100 °C and a high temperature peak (peak II) at 167 °C. The results are summarised in Table 1. Further drying (up to 170 h) in a desiccator over silica gel resulted in reduction of water found in the low temperature peak from previously around 40 molecules of water per lacunary ion down to 9 molecules. The high temperature peak, which represented about 8 molecules of water per lacunary

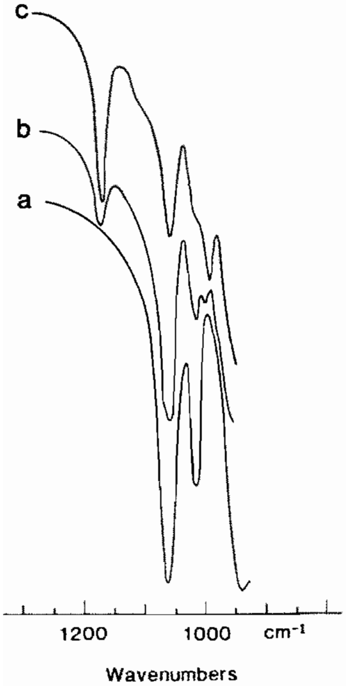

Fig. 1. FT-IR spectra of: a, PW$_9$ as prepared; b, PW$_9$ heated at 140 °C for 4 h; c, PW$_9$ dried at 22 °C for 24 h then heated at 140 °C for 2 h.

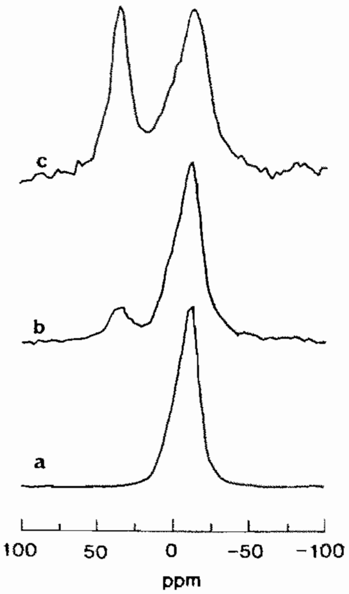

Fig. 2. Non-spinning solid state ^{31}P NMR of: a, PW$_9$; b, PW$_9$ heated at 140 °C for 0.5 h; c, PW$_9$ heated at 140 °C for 4 h.

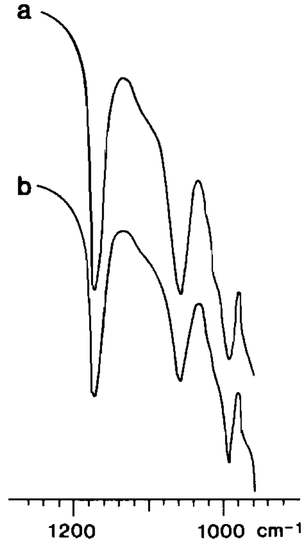

Fig. 3. FT-IR spectra of PW_9 thermalised by programmed (10 °C/min) heating in flowing nitrogen to 140 °C and held at that temperature for 1 h. Starting material: a, PW_9 immediately after filtration; b, PW_9 dried at ambient temperature for 24 h.

TABLE 1. TGA/DTA results (22–250 °C)

Drying time[a] (h)	Maxima of DTA peaks (°C)			H_2O content[b] (molecules)	
	Ia[c]	Ib	II	I	II
24	85	108	165	38	8
96	79	92	167	18	8
144	75	91	167	13	8
170		88	167	9	8

[a] In desiccator over silica gel at ambient temperature. [b] Calculated from weight loss. [c] Peak Ia appears as shoulder on Ib.

ion, was not reduced by drying at ambient temperature. If samples dried at ambient temperature for 24–170 h were heated to 140 °C, they completely isomerised to Δ-PW_9 as was evident from FT-IR spectra (spectra identical to trace a in Fig. 1). It appears that once the large quantities of water which are initially present after filtration are removed by drying in air at ambient temperature for 24 h, further drying has no influence on the thermalisation process.

Reversal of isomerisation by dissolution

The thermalised lacunary ion Δ-PW_9 (FT-IR trace 1, Fig. 4) was placed in a filter funnel and some water was passed through it. The solid remaining in the filter showed the IR spectrum in trace 3 (spectrum of mixture of Δ-PW_9 and PW_9), and the solid recovered from the liquor exhibited trace 2 (spectrum of PW_9). Thus, isomerisation is reversible according to

$$PW_9 \underset{140\ °C}{\overset{H_2O,\ 25\ °C}{\rightleftharpoons}} \Delta\text{-}PW_9$$

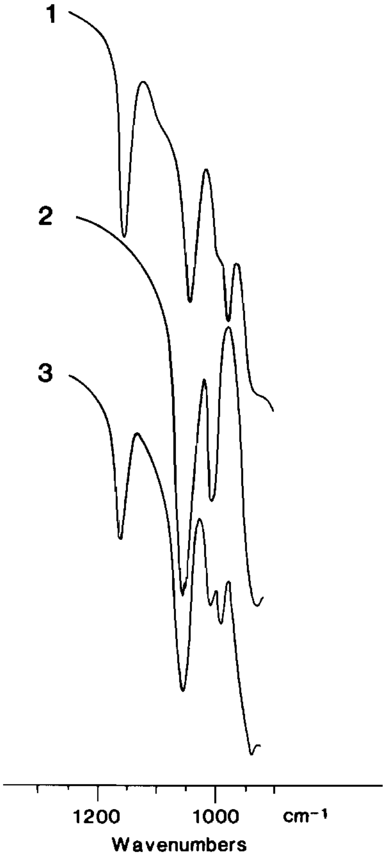

Fig. 4. FT-IR spectra of Δ-PW_9 washed with water: 1, starting material; 2, compound recovered from solution; 3, material remaining in filter funnel.

This reversibility of the isomerisation has strong implications for the preparation of transition metal containing phosphotungstate dimer compounds.

Preparation of $M_4(H_2O)_2P_2W_{18}O_{68}^{10-}$ and $(MOH_2)_3P_2W_{18}O_{68}^{12-}$ with M = cobalt, manganese

Figures 5 and 6 show the IR spectra of compounds obtained from thermalised PW_9 by different reaction sequences:

A: addition of solid Δ-PW_9 to an aqueous solution of metal halide (trace a, Figs. 5 and 6);

B: dissolution of Δ-PW_9 in water followed by addition to a solution of metal halide (traces b);

C: dissolution of Δ-PW_9 in water, followed by stirring at 22 °C for 16 h and subsequent addition to solution of metal halides (traces c).

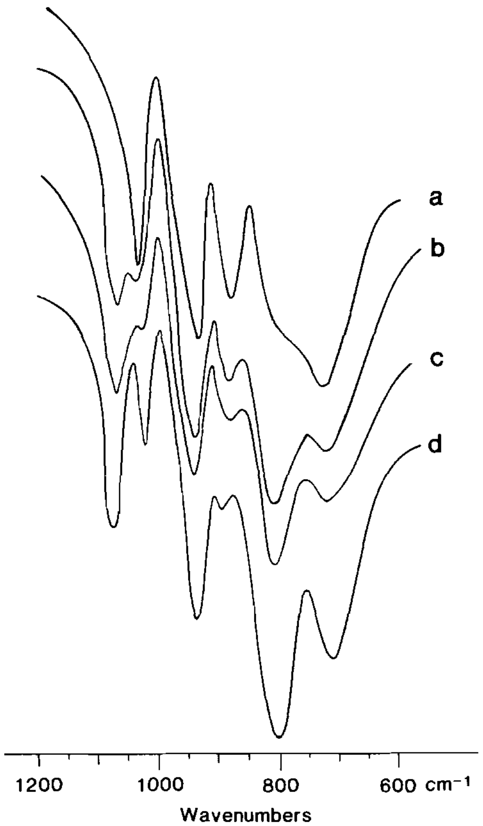

Fig. 5. FT-IR spectra of cobalt–$(PW_9)_2$ compounds prepared by adding to a Co^{2+} solution: a, solid Δ-PW_9; b, Δ-PW_9 in solution; c, Δ-PW_9 stirred in water for 16 h; d, solid PW_9 (unthermalised).

For comparison, the spectra obtained by reacting unthermalised PW_9 with solutions of metal halides are shown in traces d (Figs. 5 and 6). The spectra obtained by procedure A and from unthermalised PW_9 are identical to the spectra reported by Finke *et al.* [3] and Knoth *et al.* [4] for $M_4(H_2O)_2P_2W_{18}O_{68}{}^{10-}$ and $(MOH_2)_3P_2W_{18}O_{68}{}^{12-}$. When the starting material was Δ-PW_9, a change in the preparation sequence (procedures B and C) resulted predominantly in $M_4(H_2O)_2P_2W_{18}O_{68}{}^{10-}$ with manganese chloride solutions, but the quantities of $(MOH_2)_3P_2W_{18}O_{68}{}^{12-}$ among the product increased from B to C. The reaction of Δ-PW_9 with cobalt was substantially influenced by the procedure, with both B and C predominantly yielding $(MOH_2)_3P_2W_{18}O_{68}{}^{12-}$.

Conclusions

Reversible isomerisation reactions of tri-vacant heteropoly-tungstates upon heating and dissolution in water may lead to more than one product when reacting with M^{2+} solutions. Pure $M_4(H_2O)_2P_2W_{18}O_{68}{}^{10-}$ results only when Δ-PW_9 is added as a solid to solutions of transition metals. Pure $(MOH_2)_3P_2W_{18}O_{68}{}^{12-}$ is the product of unthermalised PW_9 with M^{2+} solutions irrespective of addition sequence. When Δ-PW_9 is contacted with water prior to addition to transition metal ion, solution induced isomerisation to PW_9 occurs, leading to mixtures of $M_4(H_2O)_2P_2W_{18}O_{68}{}^{10-}$ and $(MOH_2)_3P_2W_{18}O_{68}{}^{12-}$. Which product is dominant appears to depend on the type of metal ion, the effects being less pronounced with manganese than with cobalt.

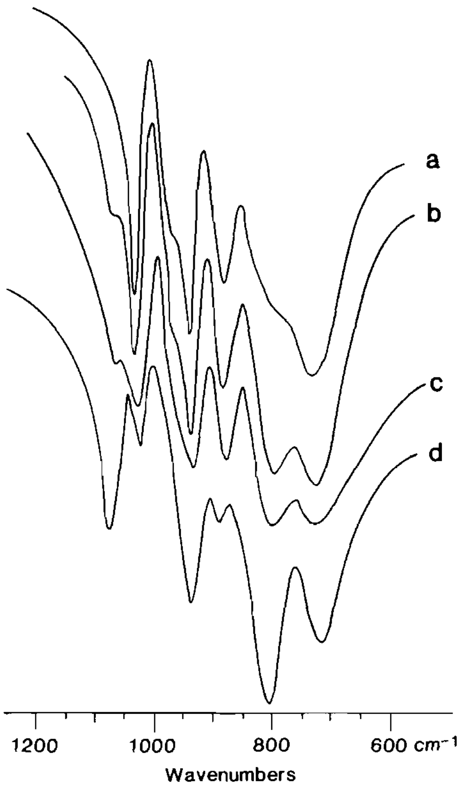

Fig. 6. FT-IR spectra of manganese–$(PW_9)_2$ compounds prepared by adding to a Mn^{2+} solution: a, solid Δ-PW_9; b, Δ-PW_9 in solution; c, Δ-PW_9 stirred in water for 16 h; d, solid PW_9 (unthermalised).

Acknowledgements

We thank G. West for recording NMR spectra and J. Newman for TGA/DTA data.

References

1 T. J. R. Weakley, H. T. Evans, J. S. Showell, G. F. Tourne and C. M. Tourne, *J. Chem. Soc., Chem. Commun.*, (1973) 139.

2 R. G. Finke and M. W. Droege, *J. Am. Chem. Soc., 103* (1981) 1587.

3 R. G. Finke, M. W. Droege and P. J. Domaille, *Inorg. Chem., 26* (1987) 3886.

4 W. H. Knoth, P. J. Domaille and R. D. Farlee, *Organometallics, 4* (1985) 62.

5 W. H. Knoth, P. J. Domaille and R. L. Harlow, *Inorg. Chem., 25* (1986) 1577.

6 M. T. Pope, in *Heteropoly and Isopoly Oxometalates,* Springer, Berlin, 1983, p. 56.

7 R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini and M. Fournier, *Inorg. Chem., 16* (1977) 2916.