

# $^{182}\text{W}$ Tungsten Mössbauer spectroscopy of heteropolytungstates†

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The tungsten-182 Mössbauer spectra of a series of Keggin structure heteropolytungstates,  $[\text{EW}_{12}\text{O}_{40}]^{n-}$  are reported. There is a very considerable variation in quadrupole coupling at the tungsten nucleus indicating considerable asymmetry in the electron distribution for the more electronegative elements E. The quadrupole coupling correlates well with the structural data, in particular with the distance between the tungsten and the oxygen atom of the  $\text{EO}_4$  group. These compounds may be regarded as rigid  $\text{W}_{12}\text{O}_{36}$  cages interacting more or less strongly with an  $\text{EO}_4^{n-}$  host. The spectra of salts of metatungstate  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  and  $[\text{W}_6\text{O}_{19}]^{2-}$  are also given.

## Introduction

The heteropolytungstates are one of the oldest families of self-assembled polynuclear species. Marignac<sup>1</sup> reported the preparation of silicotungstates in 1862 although the polyoxomolybdates were prepared even earlier. Despite their venerable age, polyoxotungstates have continued to be of interest to chemists, notably by virtue of their structural diversity, their rich redox chemistry, and their potential application in catalysis.<sup>2-6</sup>

Some years ago, in a preliminary investigation of the application of  $^{182}\text{W}$  Mössbauer spectroscopy to inorganic chemistry, we reported the spectrum of a sample of silicotungstic acid, which was remarkable in showing a large quadrupole coupling.<sup>7</sup> Since the tungsten atom, formally, has a  $5d^0$  electron configuration and lies in an octahedral environment, this was a surprising observation, and prompted us to investigate a series of these compounds. We report herein the somewhat surprising results of this study.

Mössbauer spectroscopy of tungsten<sup>8</sup> has a number of practical disadvantages, including the high  $\gamma$ -ray energy (100 keV), which requires source and absorber to be cooled to liquid helium temperature, and a very weak sensitivity of the isomer shift to changes in the chemical environment. However, the  $0 \rightarrow 2$  nuclear spin transition allows complete electric field gradient information (quadrupole coupling, sign and asymmetry parameter,  $\eta$ ) to be obtained.

We chose to concentrate our studies on heteropolytungstates of formula  $[\text{EW}_{12}\text{O}_{40}]^{n-}$  with the Keggin structure<sup>9</sup> (Fig. 1) although a few other compounds are included for comparison. The Keggin structure has high (432) symmetry such that all tungsten atoms are equivalent, and show a coordination number of six, formed by one terminal oxygen, four co-planar oxygen atoms bridging two

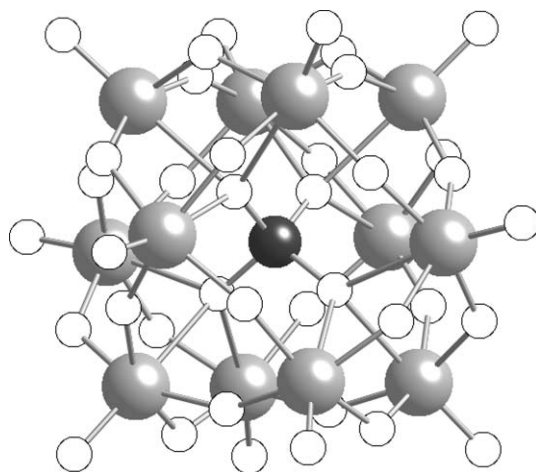


Fig. 1 The structure of the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  ion.<sup>10</sup>

tungsten atoms and finally a sixth oxygen, which is formally part of a  $[\text{EO}_4]^{n-}$  anion at the centre of the anion and which bridges three tungsten atoms. Thus, the coordination, although formally octahedral, is quite irregular.

## Experimental

Solvents and starting materials were purchased from Fluka and used without purification unless otherwise specified. Compounds were prepared according to literature methods and the references are given in Table 1. Caesium salts were obtained from the acids by precipitation with aqueous caesium chloride solution. Tetrabutylammonium salts were obtained by addition of saturated aqueous tetrabutylammonium chloride solution to an aqueous solution of the polytungstate. The resulting precipitate was filtered and recrystallised from acetonitrile. Full details of the characterisation of samples are given in the ESI.‡

## Physical measurements

The infrared spectra were recorded from KBr pellets with a Perkin-Elmer TR-850 or IR-883 spectrophotometer. Polarograms were recorded on a Metrohm Polarecord 626 in the DP10 mode (pulse amplitude of  $-10$  mV), with a sweep rate of  $-2$  mV  $\text{s}^{-1}$  from 0 to

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**Table 1** Mössbauer data

Sample	Quadrupole coupling, $e^2qQ/\text{mm s}^{-1}$	Asymmetry parameter, $\eta$	Linewidth $\Gamma/\text{mm s}^{-1}$	Synthesis Ref.
$\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 9\text{H}_2\text{O}$	-16.6	0.29	2.4	12
$\text{Cs}_3[\text{PW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	-16.4	0.20	2.2	"
$(\text{TBA})_3[\text{PW}_{12}\text{O}_{40}]$	-16.6	0.29	2.2	11
$\text{Na}_3[\text{PW}_{12}\text{O}_{40}] \cdot 9\text{H}_2\text{O}$	-16.3	0.29	2.5	12
$\text{Cs}_3[\text{AsW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$	-13.5	0.42	3.0	11
$(\text{TBA})_3[\text{AsW}_{12}\text{O}_{40}]$	-13.7	0.40	2.4	11
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$	-12.7	0.41	3.0	13
$\text{K}_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$	-12.0	0.22	3.0	11
$(\text{TBA})_4[\text{SiW}_{12}\text{O}_{40}]$	-12.8	0.39	2.4	11
$(\text{TBA})_4[\text{GeW}_{12}\text{O}_{40}]$	-10.0	0.58	2.3	11
$\text{K}_5[\text{BW}_{12}\text{O}_{40}] \cdot 11\text{H}_2\text{O}$	-13.1	0.33	2.8	11
$\text{H}_5[\text{BW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$	-12.5	0.41	2.5	11
$\text{Cs}_3\text{H}[\text{AlW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	-6.5	0.59	3.0	"
$(\text{TBA})_4\text{H}[\text{AlW}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$	-7.5	0.90	2.5	"
$\text{K}_5[\text{AlW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$	-7.4	0.51	2.7	14
$(\text{TBA})_4\text{H}[\text{FeW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$	-5.8	0.84	3.0	15
$\text{K}_5[\text{CoW}_{12}\text{O}_{40}] \cdot 11\text{H}_2\text{O}$	-6.2	0.80	2.4	16
$(\text{TBA})_4\text{H}_2[\text{CoW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	-6.7	0.69	2.8	17
$\text{K}_4\text{H}_2[\text{CoW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	6.1	0.76	2.5	16
$(\text{TBA})_4\text{H}_2[\text{ZnW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	-6.6	0.89	3.3	18
$\text{K}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$	6.4	1.0	3.1	19
$(\text{TBA})_2[\text{W}_6\text{O}_{19}]$	-9.4	0	2.3	20

" Prepared by metathesis from salt or acid.<sup>11</sup> TBA = tetrabutylammonium. Estimated errors: quadrupole coupling:  $\pm 0.5 \text{ mm s}^{-1}$ , asymmetry parameter  $\pm 0.1$ .

-1.5 V, at 20 °C. The half-wave potentials in aqueous solutions are referenced to Ag/AgCl/satd KCl and those in acetonitrile to Ag/AgNO<sub>3</sub>/HNO<sub>3</sub> and are corrected for the pulse amplitude; the potentials are expressed in mV, and the relative peak intensities are indicated in parentheses. For the tetrabutylammonium salts the polarograms were measured in acetonitrile solution (0.2M in LiClO<sub>4</sub>) against an Ag/AgNO<sub>3</sub>/HNO<sub>3</sub> electrode connected by an acetonitrile/LiClO<sub>4</sub> bridge). The potentials were calibrated against ruthenium(II)(tris-bipyridyl). The solutions were deoxygenated by bubbling N<sub>2</sub> for 15 min immediately before the measures. pH-dependent polarograms were obtained by progressive basification of a 1 M H<sub>2</sub>SO<sub>4</sub> solution with 5 M NaOH. The pH was measured with a Metrohm E500 pH-meter. TLC-plates (Merck 60, F254) were eluted with a 0.3 M ethanolic solution of LiClO<sub>4</sub> and the products were detected under a UV-lamp at 254 nm.

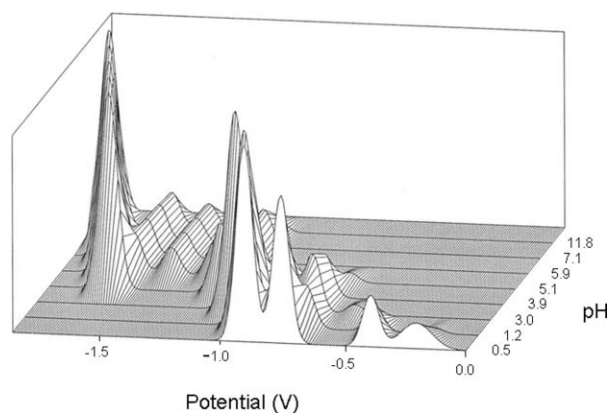
<sup>182</sup>W Mössbauer spectra were measured using a constant acceleration spectrometer with source and absorber cooled to liquid helium temperature in an Oxford Instruments cryostat. The source was <sup>182</sup>Ta obtained by neutron irradiation of a natural Ta foil. Because of the low recoil-free fractions relatively thick samples containing 110 mg tungsten cm<sup>-2</sup> were used. The spectra were fitted using the least square procedure of Stone using five lines of equal width whose positions are determined by the values of the isomer shift  $\delta$ , the quadrupole coupling  $e^2qQ$  and the asymmetry parameter  $\eta$ . Isomer shifts were identical within experimental error and are not discussed here.

## Results

### Preparation and characterisation of compounds

The compounds were prepared using standard methods from the literature, and the references are given in Table 1. Considerable ef-

fort was taken in the characterisation of the compounds. The infrared spectra were used to confirm the presence of the polyanion, and compared with the detailed survey of Rocchiccioli-Deltcheff *et al.*<sup>11</sup> Water content, and in the case of tetrabutylammonium (TBA) salts, the cation content were obtained by thermogravimetric analysis. Following Rocchiccioli-Deltcheff *et al.* we also studied the electrochemical properties of the anions. The DC polarograms obtained corresponded to those in the literature, but in general we found that differential pulse polarography (DPP) gave a better appreciation of the purity of the sample since well resolved peaks were obtained for pure samples. We noted however that the peaks were very sensitive to the pH of the medium. Fig. 2 represents the changes in the peaks, represented as Gaussian curves, as the pH is raised. It will be noticed that the polarogram of  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  disappears as low as pH 3. For this reason we believe the acetic acid/acetate buffer used by Rocchiccioli-Deltcheff *et al.* is not



**Fig. 2** Overlay of the DPP polarograms of phosphotungstic acid as a function of pH.

suitable for the phosphotungstates. The polarograms also allowed us to exclude the presence of  $\beta$ -isomers.

Finally, we found that TLC on silica may be used to check the purity of the samples. The eluent used was either ethanol with lithium perchlorate 0.3M or acetone–10% hexane–lithium perchlorate 0.3M. The  $R_f$  values decreased with increasing charge: typical values in ethanol were 0.62 for 4- ions, 0.58 for 5- ions and 0.38 for 6- ions. Phosphotungstates with a 3- charge showed a spot at an  $R_f$  value of 0.66, but other spots were also present suggesting decomposition in the solution. Paratungstate, a frequent impurity in the preparations, does not migrate under these conditions. An unsatisfactory TLC was inevitably confirmed by other measurements such as polarography or infrared spectroscopy.

### Mössbauer spectra

The data are summarised in Table 1. Isomer shifts showed no significant variation and we shall concentrate our discussion on the quadrupole coupling and asymmetry parameters. The first observation is the very large range of values. The phosphotungstates (around  $-16 \text{ mm s}^{-1}$ ) show the largest couplings, with values among the largest reported for tungsten compounds. There is a steady drop as the electronegativity of the central heteroatom falls to values around  $6 \text{ mm s}^{-1}$  for the systems where the heteroatom is a metallic cation. We may note that a value of  $6 \text{ mm s}^{-1}$  results in a spectrum which appears as a slightly broadened line, and consequently such couplings are not particularly precise. For couplings of  $10 \text{ mm s}^{-1}$  or more the peaks are well separated, and may be fitted with precision (Fig. 3). The value initially reported for silicotungstic acid is anomalously high,<sup>7</sup> and we believe this is due to a calibration error; it should be ignored in favour of the value reported here.

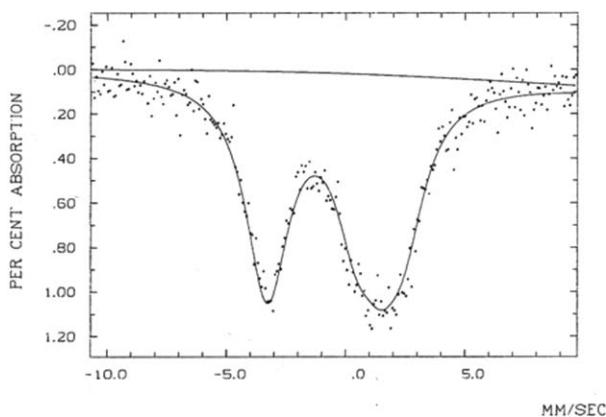


Fig. 3  $^{182}\text{W}$  Mössbauer spectrum of  $\text{K}_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$ .

The asymmetry parameters increase as the quadrupole coupling falls, to values close to 1 for couplings around  $6 \text{ mm s}^{-1}$ . In such systems, the sign of the coupling is not well defined, and the apparent change in sign of the gradient is not particularly significant.

The examination of the results leads to two questions. Firstly, why is the quadrupole coupling so large in the phosphotungstates, and why does it fall so sharply as the heteroatom changes? This change is remarkable in that the change of the central atom, from phosphorus to aluminium, for example, drops the quadrupole coupling by a factor of 2 for all twelve tungsten atoms. Secondly,

can we explain the variation in the asymmetry parameter? We will discuss the two non-Keggin systems,  $\text{K}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$  and  $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$  later.

As mentioned in the introduction, the tungsten coordination, although it is usually described as octahedral, is in fact highly distorted, as is often the case for the earlier transition metals.<sup>21</sup> Fig. 4 shows the coordination sphere for two examples,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  and  $[\text{FeW}_{12}\text{O}_{40}]^{5-}$  which correspond to the two extremes of the quadrupole coupling range.

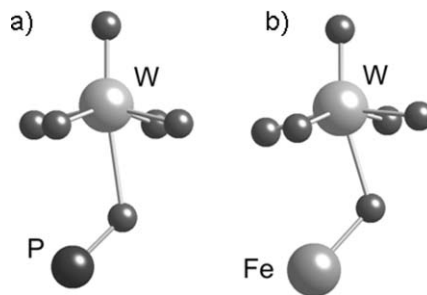


Fig. 4 The coordination sphere of tungsten in: (a)  $[\text{PW}_{12}\text{O}_{40}]^{3-10}$  and (b)  $[\text{FeW}_{12}\text{O}_{40}]^{5-}$ .

The coordination sphere consists of one oxygen atom at a distance of approximately  $1.7 \text{ \AA}$ , the distance corresponding to a tungsten-oxygen double bond,<sup>21</sup> and four at roughly  $1.9 \text{ \AA}$ , corresponding to a single bond distance. The sixth site of the octahedron, *trans* to the  $\text{W}=\text{O}$  double bond, is occupied by an oxygen of the  $\text{EO}_4$  tetrahedron, and the bond distance is much greater,  $2.437 \text{ \AA}$  for the phosphotungstate and  $2.229 \text{ \AA}$  for the ferrotungstate. This corresponds to a very low bond valence, perhaps not altogether surprisingly given that the bond valence sum for the first five bonds is close to 6 and the sixth oxygen is shared between three tungsten atoms. We may therefore consider the structure to be a  $\text{W}_{12}\text{O}_{36}$  cage which interacts more or less strongly with the central  $\text{EO}_4$  unit. Each tungsten is part of a square pyramidal (SP)  $\text{WO}_5$  unit, which interacts weakly with an oxygen bound to the heteroatom. This structure would be expected to give rise to a large negative quadrupole coupling as observed since the square pyramid may be considered as an octahedron from which electron density has been removed along the  $z$ -axis, giving a positive electric field gradient,  $q$ , and the quadrupole moment,  $Q$ , of the excited state is negative.<sup>23</sup>

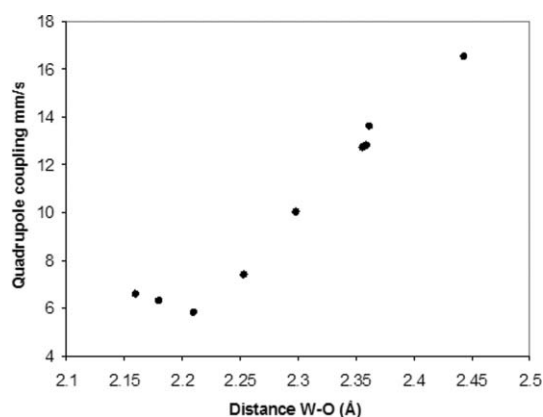
The quadrupole coupling will decrease as the interaction of the tungsten atom with the  $\text{EO}_4$  oxygen increases and charge is donated. The interaction with the  $\text{EO}_4$  unit can increase for two reasons: (1) an increased basicity of the  $\text{EO}_4^{n-}$  ion; and (2) an increase in the size of E, which will lengthen the E–O bonds, and for simple geometric reasons approach the oxygen to the tungsten.

Examination of the data supports this argument. As the formal positive charge on the central E atom falls, the basicity of the  $\text{EO}_4^{n-}$  increases, and quadrupole coupling drops, as shown in the series  $\text{P} > \text{Si} > \text{Al}$ . The size effect is shown by comparing two elements in the same column of the periodic table where we see  $\text{P} > \text{As}$ ,  $\text{Si} > \text{Ge}$ , and  $\text{B} > \text{Al}$ . The strength of the interaction between tungsten and  $\text{EO}_4$  oxygen may also be measured by the W–O bond distance. Table 2 gives the average W–OEO<sub>3</sub> distance for the heteropolytungstate anions extracted from the data in the

**Table 2** Mean distances between tungsten and the  $\text{EO}_4$  oxygen, the related bond order, and E–W distances as a function of E

Atom E	EO–W/Å	Bond order <sup>21</sup>	E–W/Å
P	2.443	0.195	3.556
As	2.362	0.249	3.567
Si	2.356	0.253	3.520
Ge	2.298	0.302	3.539
B	2.359	0.251	3.482
Al	2.253	0.346	3.504
Co	2.180	0.432	3.496
Fe	2.210	0.394	3.515
Zn	2.160	0.459	3.499

Cambridge Structural Database (version 5.29, update of January 2009). Fig. 5 shows that the average distances correlate very well with the observed quadrupole couplings for distances greater than 2.25 Å. For shorter distances the quadrupole coupling is both rather small and the environment is distinctly non-axial.



**Fig. 5** Correlation between quadrupole coupling and W–O bond distance.

The behaviour of the asymmetry parameter is also consistent with this explanation. Fig. 4 shows that the  $\text{EO}_4$  oxygen is displaced from the axis of the  $\text{W}=\text{O}$  double bond, giving non-axial symmetry. This is the origin of the small but non-zero asymmetry parameter in the phosphotungstate. As the size of the hetero atom increases the  $\text{EO}_4$  oxygen is moved progressively further away from the axis, and the asymmetry parameter increases. As can be seen from Fig. 4b in the ferrotungstate, the  $\text{EO}_4$  oxygen is much further from the  $\text{W}=\text{O}$  axis.

If we consider these compounds as containing  $\text{W}_{12}\text{O}_{36}$  cages encapsulating  $[\text{EO}_4]^{n-}$  anions, we may ask to what extent the  $\text{W}_{12}\text{O}_{36}$  cage can shrink or expand to fit in the anion. We may estimate the size of the cage from the mean E–W distance in  $[\text{EW}_{12}\text{O}_{40}]^{n-}$  and the averaged values extracted from the Cambridge Structural Data base are shown in Table 2. Although the values do vary as a function of E, the variation is much less than that of the O–W distances, which would tend to suggest that the cage is rather rigid. A similar conclusion was obtained from recent theoretical calculations on these systems.<sup>24</sup>

Finally, we may look at the two non-Keggin systems in Table 1. Both are similar to the Keggin systems in that they contain a  $\text{WO}_5$  square pyramidal unit with a sixth oxygen weakly bound. The metatungstate  $\text{K}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$  may be regarded as a Keggin system in which the central heteroatom is missing. The four oxygen

atoms that remain of the  $\text{EO}_4$  tetrahedron are thus formally oxide ions and are quite basic. The two hydrogen atoms are located inside the  $\text{O}_4$  cavity but cannot be observed by X-ray crystallography. The interaction with the tungsten atoms is thus strong, with a low quadrupole coupling. The average O–W distance is 2.212 Å in agreement with the correlation shown in Fig. 5. As for the Keggin systems a high asymmetry parameter is predicted and observed.

The  $[\text{W}_6\text{O}_{19}]^{2-}$  ion in  $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$  has a central oxygen atom octahedrally coordinated by six  $\text{WO}_5$  units composed of one terminal oxygen and four oxygen atoms shared with neighbouring tungsten atoms. The coordination is thus similar to the polytungstate except for the fact that the tungsten atom lies on a four-fold axis. We observe the expected zero asymmetry parameter with a negative coupling of  $-9.4 \text{ mm s}^{-1}$ . The average W–O distance for the central oxygen is 2.323 Å, and this lies close to the correlation in Fig. 5.

## Conclusions

The wide variation in quadrupole coupling observed in these systems was surprising for compounds which are often regarded as isostructural. The very large quadrupole coupling for the phosphotungstates is particularly remarkable, and lies among the highest values reported for tungsten compounds. The spectra are consistent with a very variable interaction of the central  $\text{EO}_4$  unit with the  $\text{W}_{12}\text{O}_{36}$  cage, and this is supported by a survey of bond distances in these systems. If the experimental difficulties of Mössbauer spectroscopy of tungsten limit its widespread use, it is significant that these results show a correlation between electron distribution as measured by the quadrupole coupling and bond distance and bond order as measured by X-ray crystallography.

## Acknowledgements

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