Tungsten Mössbauer spectroscopy of heteropolytungstates

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Supplementary material
Characterisation of compounds:

**Infrared Spectroscopy (IR)**

The infrared spectra were recorded from KBr pellets with a Perkin-Elmer TR-850 or IR-883 spectrophotometer. Wavenumbers are given in cm⁻¹. Abbreviations for the intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

**H₄SiW₁₂O₴₀ 8 H₂O:** DPP (H₂O-AcONa/AcOH 1M): -310 (1), -530 (1), -985 (2). TLC: Rf=0.63. TGA: 5.79% (calcd for 8 H₂O: 5.89%). IR: 1018 (w), 980 (s), 923 (s), 882 (m), 784 (s), 560 (sh), 538 (m), 475 (w), 417 (w), 374 (s), 335 (s), 281 (w), 270 (w), 254 (m).

**K₄SiW₁₂O₴₀ 10 H₂O:** DPP (H₂O-AcONa/AcOH 1M): -345 (1), -580 (1), -1025 (2). TLC: Rf=0.64. TGA: 5.56% (calcd for 10 H₂O: 5.61%). IR: 1020 (w), 980 (s), 925 (s), 893 (w), 877 (m), 779 (vs), 555 (sh), 539 (m), 477 (w), 419 (w), 378 (s), 282 (m).

**[(C₄H₉)₄N]₄SiW₁₂O₴₀:** DPP (MeCN/LiClO₄ 0.2M): -700 (1), -960 (1), -1500 (3), -1620 (2). TLC: Rf=0.60. TGA: 26.0% (calcd for 0 H₂O: 26.1%). IR: 2952 (m), 2930 (sh), 2866 (m), 1478 (m), 1455 (m), 1375 (m), 1099 (m), 966 (s), 929 (s), 882 (m), 795 (vs), 552 (sh), 542 (m), 515 (sh), 481 (w), 415 (vw), 386 (s), 339 (m), 280 (w).

**H₃PW₁₂O₴₀ 8.5 H₂O:** DPP (EtOH/LiClO₄ 1M): -360 (1), -590 (1), -750 (3), -1120 (2). TGA: 7.46% (calcd for 8.5 H₂O 7.65%). IR: 1078 (s), 981 (s), 887 (s), 798 (vs), 595 (w), 523 (m), 480 (sh), 385 (s), 337 (m), 265 (m).

**[(C₄H₉)₄N]₃PW₁₂O₴₀:** DPP (MeCN/LiClO₄ 0.2M): -395 (1), -655 (1), -905 (2), -1315 (1). TLC: Rf=0.90. TGA: 24.0% (calcd for 0 H₂O 22.8%). IR: 2960 (m), 2940 (w), 2880 (m), 1470 (m), 1460 (m), 1380 (m), 1080 (s), 1025 (w), 987 (sh), 976 (s), 895 (s), 735 (sh), 657 (w), 596 (w), 522 (m), 387 (s), 375 (sh), 335 (m).

**Cs₃PW₁₂O₴₀ 6 H₂O:** TGA: 3.24% (calcd for 6 H₂O 3.19%). IR: 1080 (s), 1000 (sh), 980 (s), 890 (m), 790 (vs), 600 (w), 520 (m), 500 (sh), 380 (s), 330 (m), 268 (m).

**Na₃PW₁₂O₴₀ 9 H₂O:** DPP (H₂SO₄ 1M): -350 (2), -480 (1), -800 (2). TGA: 7.68% (calcd for 9 H₂O 7.50%). IR: 1080 (s), 980 (s), 920 (sh), 890 (m), 790 (vs), 600 (w), 530 (m), 380 (s), 330 (m), 340 (m).

**K₅AlW₁₂O₴₀ 15 H₂O:** DPP (H₂O-AcONa/AcOH 1M): -480 (1), -710 (1), -1010 (4). TLC: Rf=0.48. TGA: 8.22% (calcd for 15 H₂O: 8.09%). IR: 957 (s), 90 (s), 797 (s), 534 (m), 485 (m), 417 (w), 371 (m).

**Cs₅AlW₁₂O₴₀ 6 H₂O:** DPP (H₂SO₄ 0.1M/Na₂SO₄ 0.9M): -445 (1), -620 (1), -770 (1). TLC: Rf=0.58. TGA: 3.23% (calcd for 6 H₂O 2.96%). IR: 954 (s), 873 (s), 800 (s), 757, 537 (m), 485 (m), 472 (m), 374 (s).

**[(C₄H₉)₅N]₄HAlW₁₂O₄₀ 3 H₂O:** TLC: Rf=0.58. TGA: 27.3% (calcd for 3 H₂O: 27.3%). IR: 990 (sh), 956 (s), 910 (sh), 878 (s), 800 (vs), 750 (sh), 540 (w), 485 (w), 475 (sh), 400 (sh), 380 (m), 355 (sh), 328 (sh).

**H₅BW₁₂O₄₀ 15 H₂O:** DPP (H₂O AcOH/AcONa 1M): -380 (1), -595 (1), -1045 (2). TGA: 10.14% (calcd for 15 H₂O: 10.06%).
K$_2$BW$_{12}$O$_{40}$ 11 H$_2$O: DPP (H$_2$O - AcOH/AcONa 1M): -540 (1), -770 (1). TLC: Rf=0.63. TGA: 6.23% (calcd for 11 H$_2$O: 6.09%). IR: 1000 (m), 957 (s), 905 (s), 800 (vs), 520 (sh), 510 (m), 480 (sh), 423 (w), 380 (m), 335 (m), 285.

[(C$_4$H$_9$)$_4$N]$_3$AsW$_{12}$O$_{40}$: DPP (MeCN/LiClO$_4$ 0.2M): -425 (1), -680 (1), -950 (2), 1320 (1). TLC: Rf=0.66. TGA: 23.53% (calcd: 23.72%). IR: 2980 (m), 2930 (sh), 2870 (m), 1460 (m), 1380 (m), 983 (s), 912 (s), 873 (m), 793 (vs), 735 (sh), 680 (w), 525 (m), 470 (m), 420 (w), 381 (s), 358 (sh), 325 (w).

Cs$_3$AsW$_{12}$O$_{40}$ 10 H$_2$O: DPP (H$_2$O - AcOH/AcONa 1M): -540 (1), -840 (2), -910 (2). TGA: 5.32% (calcd for 10 H$_2$O: 5.15%). IR: 968 (s), 890 (s), 865 (sh), 792 (s), 740 (sh), 620 (sh), 520 (m), 472 (m), 466 (s), 418 (m), 322 (w), 301 (w).

[(C$_4$H$_9$)$_4$N]$_4$HFeW$_{12}$O$_{40}$ 4 H$_2$O: TLC: Rf=0.59. TGA: 27.6% (calcd for 4 H$_2$O: 27.5%). IR: 952 (s), 915 (sh), 872 (s), 775 (s), 725 (sh), 680 (vw), 580-500, 448 (s), 372 (s).

[(C$_4$H$_9$)$_4$N]$_4$H$_2$CoW$_{12}$O$_{40}$ 6 H$_2$O: DPP (MeCN/LiClO$_4$ 0.2M): -650 (1), -900 (1), -1350 (1). TLC: Rf=0.40. TGA: 28.2% (calcd for 6 H$_2$O: 28.3%). IR: 2960 (m), 2920 (m), 2860 (m), 1480 (m), 1455 (sh), 1380 (m), 943 (s), 887 (s), 786 (vs), 682 (sh), 565, 445 (s), 366 (s). UV-Vis (MeCN): 17718 (sh, 104.5), 16824 (sh, 183.6), 16000 (210.45), 15576 (sh, 194).

[(C$_4$H$_9$)$_4$N]$_4$GeW$_{12}$O$_{40}$: DPP (MeCN/LiClO$_4$ 0.2M): -675 (1), -900 (1), -1175 (1). TLC: Rf=0.61. TGA: 25.6% (calcd for 0 H$_2$O: 25.8%). IR: 2958 (m), 2930 (sh), 2863 (m), 1480 (m), 1455 (m), 1378 (m), 990 (sh), 962 (s), 880 (s), 830 (m), 780 (s), 530 (w), 464 (m), 410 (vw), 380 (s).

[(C$_4$H$_9$)$_4$N]$_4$H$_2$ZnW$_{12}$O$_{40}$ 3 H$_2$O: DPP: -470 (1), -650 (4), -980 (1). TLC: Rf=0.35. TGA: 27.3% (calcd for 3 H$_2$O: 27.3%). IR: 2960 (m), 2920 (sh), 2860 (m), 1460 (m), 1375 (m), 970 (sh), 943 (s), 875 (s), 760 (vs), 680 (w), 446 (m), 365 (m).

K$_2$H$_2$W$_{12}$O$_{40}$ 2 H$_2$O: DPP (H$_2$O - AcOH/AcONa 1M): -700 (1), -780 (1), -960 (2), -1140 (4). TLC: Rf=0.33. IR: 1396 (m), 1354 (w), 1252 (s), 969 (m), 950 (s), 876 (s), 762 (vs), 609 (m), 420 (s), 375 (s), 325 (w), 282 (m).