Electronic Supplementary Information for Dalton Transactions

^{182}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.

$H_4SiW_{12}O_{40}$ 8 H_2O: DPP (H_2O-AcONa/AcOH 1M): -310 (1), -530 (1), -985 (2). TLC: Rf=0.63. TGA: 5.79% (calcd for 8 H_2O: 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).

$K_4SiW_{12}O_{40}$ 10 H_2O: DPP (H_2O-AcONa/AcOH 1M): -345 (1), -580 (1), -1025 (2). TLC: Rf=0.64. TGA: 5.56% (calcd for 10 H_2O: 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).

$[(C_4H_9)_4N]_4SiW_{12}O_{40}$: DPP ($MeCN/LiClO_4$ 0.2M): -700 (1), -960 (1), -1500 (3), -1620 (2). TLC: Rf=0,60. TGA: 26.0% (calcd for 0 H_2O: 26.1%). IR: 2952 (m), 2930 (sh), 2866 (m), 1478 (m), 1455 (m), 1375 (m), 1009 (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).

$H_3PW_{12}O_{40}$ 8.5 H_2O : DPP ($EtOH/LiClO_4$ 1M): -360 (1), -590 (1), -750 (3), -1120 (2). TGA: 7.46% (calcd for 8.5 H_2O 7.65% IR: 1078 (s), 981 (s), 887 (s), 798 (vs), 595 (w), 523 (m), 480 (sh), 385 (s), 337 (m), 265 (m).

$[(C_4H_9)_4N]_3PW_{12}O_{40}$: DPP ($MeCN/LiClO_4$ 0.2M): -395 (1), -655 (1), -905 (2), -1315 (1). TLC: Rf=0.66. TGA: 20.4% (calcd for 0 H_2O: 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).

$Cs_3PW_{12}O_{40}$ 6 H_2O: TGA: 3.24% (calcd for 6 H_2O: 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).

$Na_3PW_{12}O_{40}$ 9 H_2O: DPP (H_2SO_4 1M): -350 (2), -480 (1), -800 (2). TGA: 7.68% (calcd for 9 H_2O: 7.50%). IR**:** 1080 (s), 980 (s), 920 (sh), 890 (m), 790 (vs), 600 (w), 530 (m), 380 (s), 330（m)， 340 (m).

$K_5AlW_{12}O_{40}$15 H_2O: DPP (H_2O-AcONa/AcOH 1M): -480 (1), -710 (1), -1010 (4). TLC: Rf=0.48. TGA: 8.22% (calcd for 15 H_2O: 8.09%). IR: 957 (s), 90 (s), 797 (s), 534 (m), 485 (m), 417 (w), 371 (m).

$Cs_5AlW_{12}O_{40}$ 6 H_2O: DPP (H_2SO_4 0.1M/$Na2SO_4$ 0.9M): -445(1), -620 (1), -770 (1). TLC: Rf=0.58. TGA: 3.23% (calcd for 6 H_2O: 2.96%). IR: 954 (s), 873 (s), 800 (s), 757, 537 (m), 485 (m), 472 (m), 374 (s).

$[(C_4H_9)_4N]_4HAlW_{12}O_{40}$ 3 H_2O : TLC: Rf=0.58. TGA: 27.3% (calcd for 3 H_2O: 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).

$H_5BW_{12}O_{40}$ 15 H_2O: DPP (H_2O -AcOH/AcONa 1M): -380 (1), -595 (1), -1045 (2). TGA: 10.14% (calcd for 15 H_2O:10.06%).

$K_5BW_{12}O_{40}$ 11 H_2O : DPP (H_2O - AcOH/AcONa 1M): -540 (1), -770 (1). TLC: Rf=0.63. TGA: 6.23% (calcd for 11 H_2O: 6.09%). IR: 1000 (m), 957 (s), 905 (s), 800 (vs), 520 (sh), 510 (m), 480 (sh), 423 (w), 380 (m), 335 (m), 285.

$[(C_4H_9)_4N]_3AsW_{12}O_{40}$: DPP (MeCN/$LiC1O_4$ 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).

$Cs_3AsW_{12}O_{40}$ 10 H_2O: DPP (H_2O - AcOH/AcONa 1M): -540 (1), -840 (2), -910 (2). TGA: 5.32% (calcd for 10 H_2O: 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).

$[(C_4H_9)_4N]_4HFeW_{12}O_{40}$ 4 H_2O : TLC: Rf=0.59. TGA: 27.6% (calcd for 4 H_2O: 27.5%). IR: 952 (s), 915 (sh), 872 (s), 775 (s), 725 (sh), 680 (vw), 580-500, 448 (s), 372 (s).

$[(C_4H_9)_4N]_4H_2CoW_{12}O_{40}$6 H_2O : DPP (MeCN/$LiC1O_4$ 0.2M): -650 (1), -900 (1), -1350 (1). TLC: Rf=0.40. TGA: 28.2% (calcd for 6 H_2O: 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).

$[(C_4H_9)_4N]_4GeW_{12}O_{40}$: DPP (MeCN/$LiClO_4$ 0.2M): -675 (1), -900 (1), -1175 (1). TLC: Rf=0.61. TGA: 25.6% (calcd for 0 H_2O: 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).

$[(C_4H_9)_4N]_4H_2ZnW_{12}O_{40}$ 3 H_2O : DPP: -470 (1), -650 (4), -980 (1). TLC: Rf=0.35. TGA: 27.3% (calcd for 3 H_2O: 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).

$K_6H_2W_{12}O_{40}$ 2 H_2O: DPP (H_2O - 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).