Electronic Supplementary Information for Dalton Transactions

Supporting Information.

Thermogravimetric analysis

Thermogravimetric analysis was undertaken on all Re (but not Tc) containing complexes under a constant stream of N_2 with the results shown below. At lower temperatures (< 250 ^oC) it was possible to confirm the loss of 4 H_2O molecules in **1** and one MeOH in **5**. At higher temperatures, the weight losses observed can be more difficult to assign due to the presence of volatile Re_2O_7 but in most cases, reasonable agreement is observed for loss of the P=O donor ligands.

Temp. Range (^{o} C)	**% wt. loss expt**	**% wt. loss calc**	**Assignment**
0 – 250	5.66	5.52	Loss of 4 eq. H_2O
540 – 640	71.87	74.32	Loss of 2 eq. Re_2O_7
			ThO_2 remains

TGA analysis for $[Th(ReO_4)_4].4H_2O$ (**1**)

Temp. Range (^{o} C)	**% wt. loss expt**	**% wt. loss calc**	**Assignment**
0 – 250	2.17	1.65	Loss of MeOH
300 – 700	39.31	41.99	Loss of 3 eq. TPPO and MeO^-
			Mixed Th & Re oxides remain

TGA analysis for $[Th(ReO_4)_4(TPPO)_3(OCH_3)(HOCH_3)]$ (**5**)

Temp. Range (^{o} C)	% wt. loss expt	% wt. loss calc	Assignment
260 – 550	43.36	41.44	Loss of 4 eq. TBPO
550 – 900	5.04	-	-
			Mixed Th & Re oxides remain

TGA analysis for $[Th(ReO_4)_4(TBPO)_4]$ (**4**)

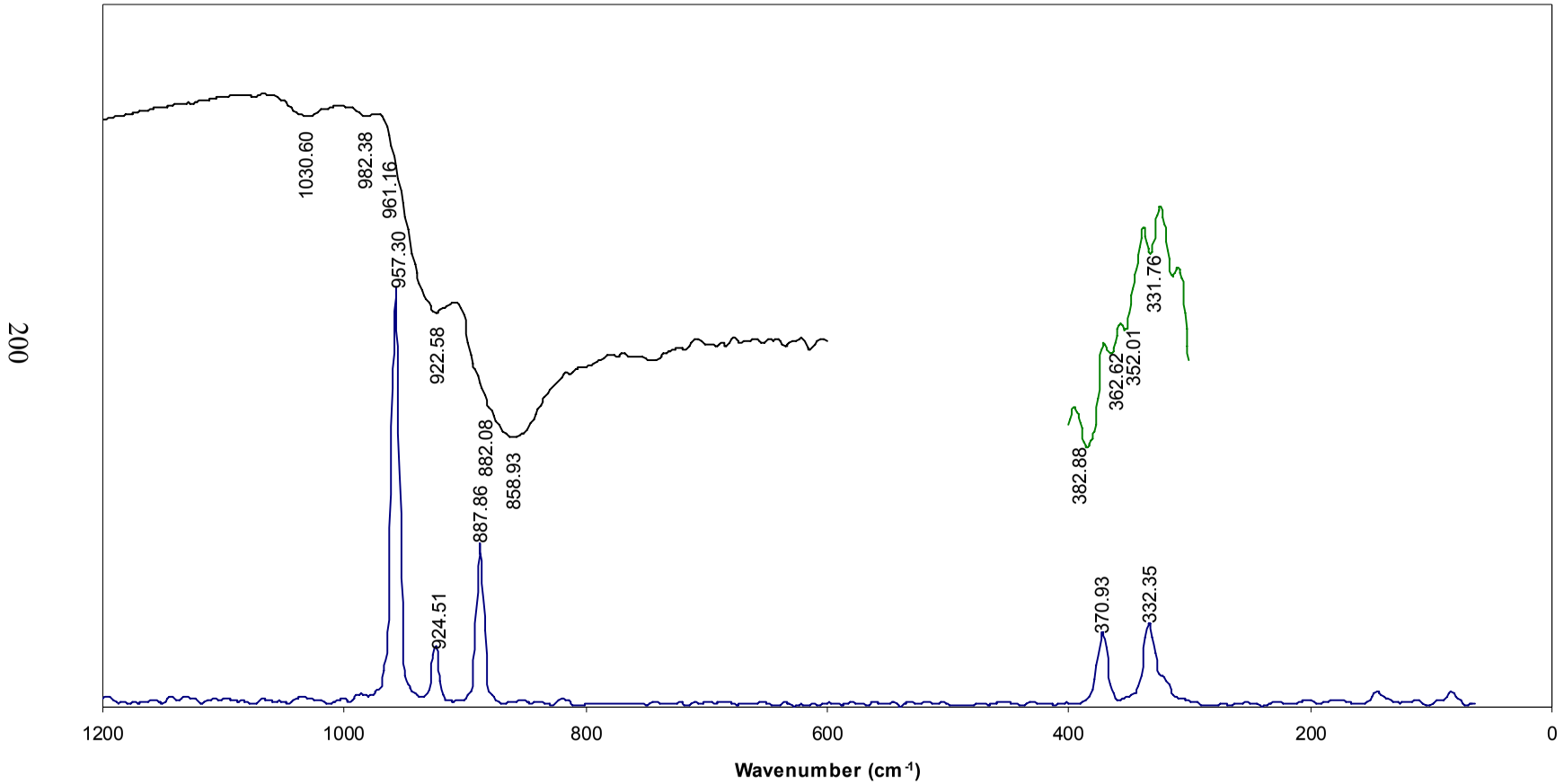
Temp. Range (^{o} C)	% wt. Loss expt	% wt. loss calc	Assignment
140 – 900	48.45	46.34	Loss of 4 eq. TiBP
			Mixed Th & Re oxides remain

TGA analysis for $[Th(ReO_4)_4(TiBP)_4]$ (**3**)

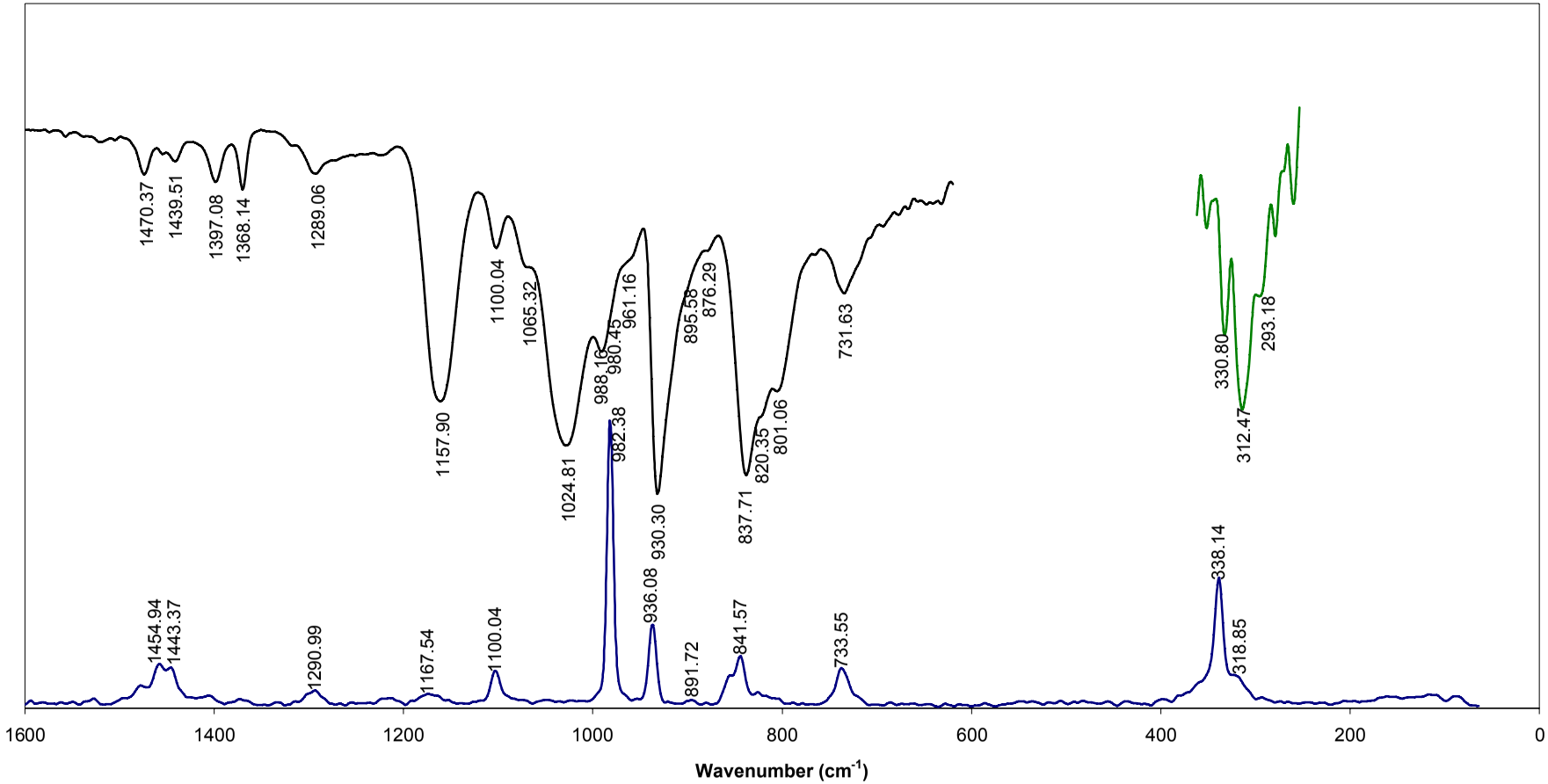
Temp. Range (^{o} C)	% wt. loss expt	% wt. Loss calc	Assignment
100- 900	35.54	34.60	Loss of 4 eq. TEP
			Mixed Th & Re oxides remain

TGA analysis for $[Th(ReO_4)_4(TEP)_4]$ (**2**)

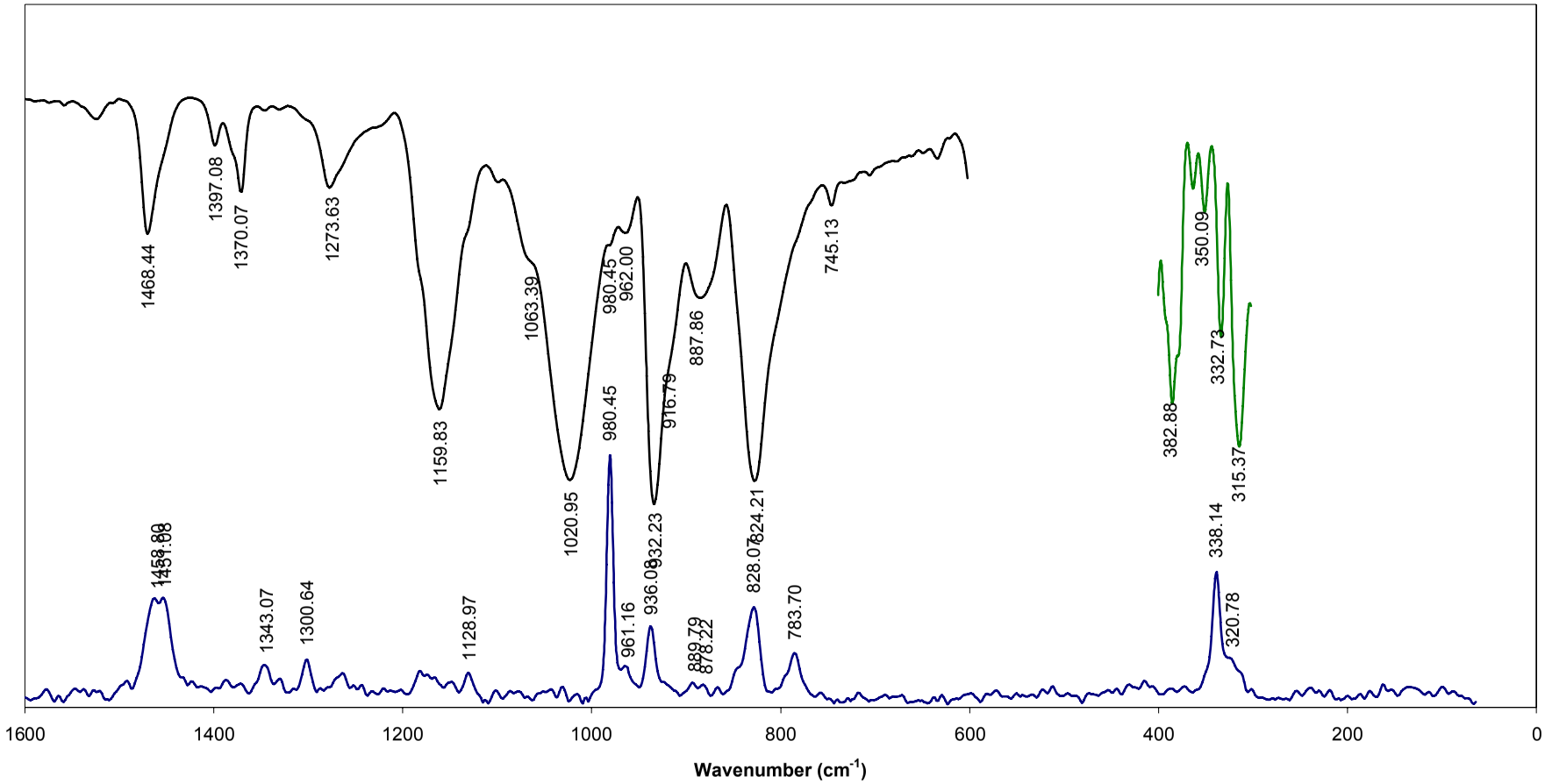
Vibrational Spectroscopy Data



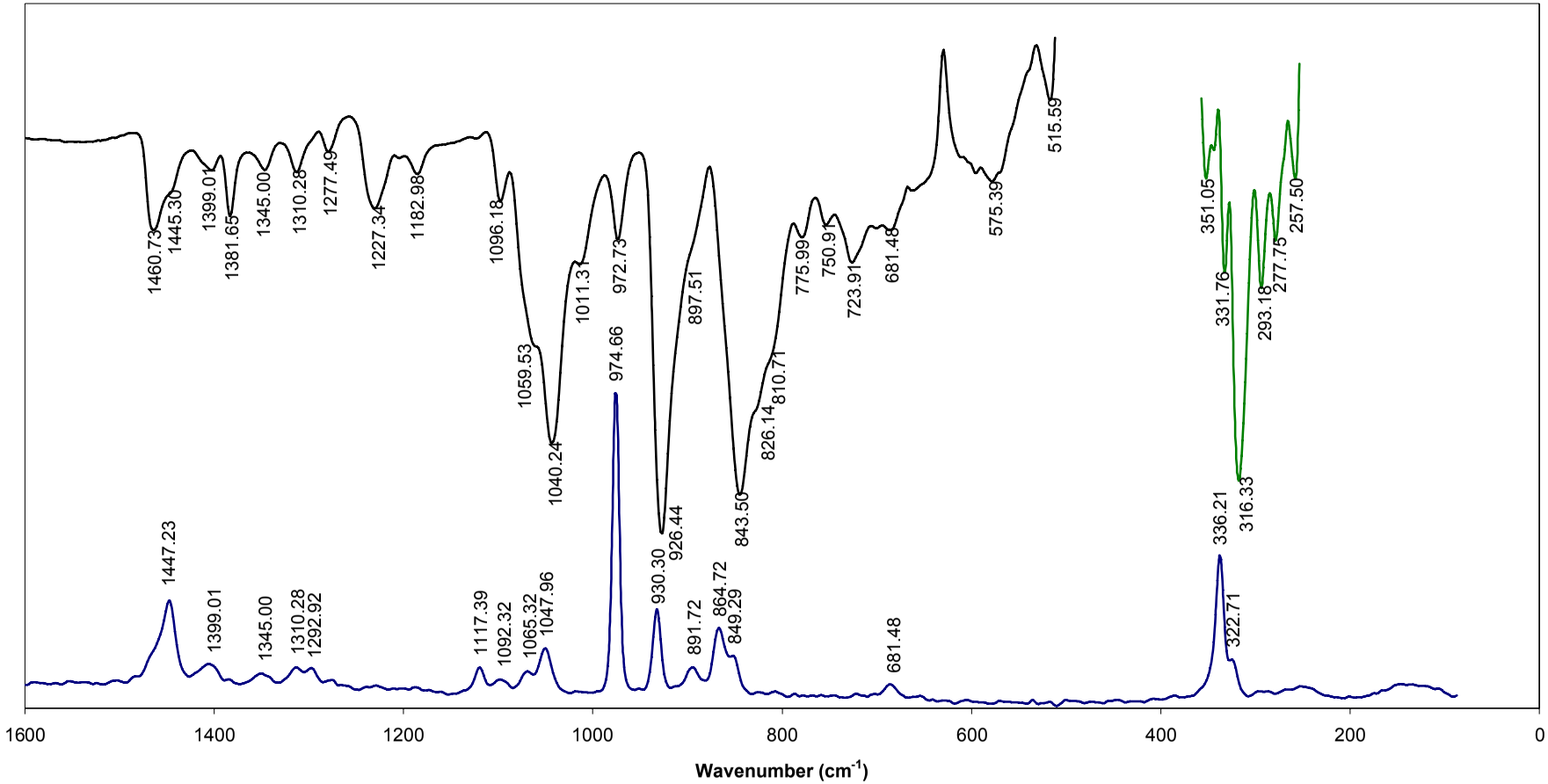
Mid- and far-infrared ATR (in transmission) and Raman (absorption) spectra of $[Th(ReO_4)_4].4H_2O$ (**1**)



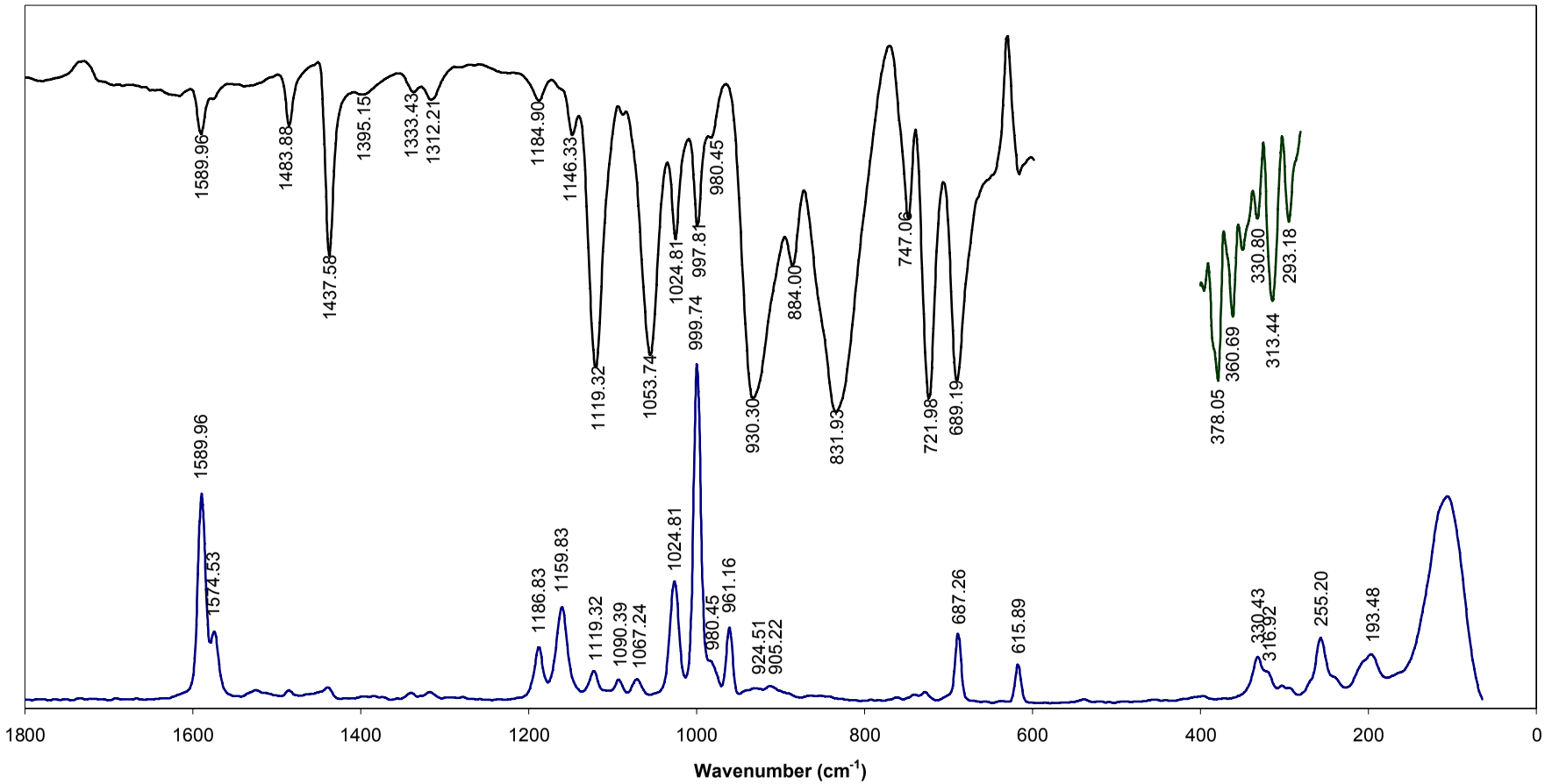
Mid- and far-infrared ATR (in transmission) and Raman (absorption) spectra of crystalline $[Th(ReO_4)_4(TEP)_4]$ (**2**)



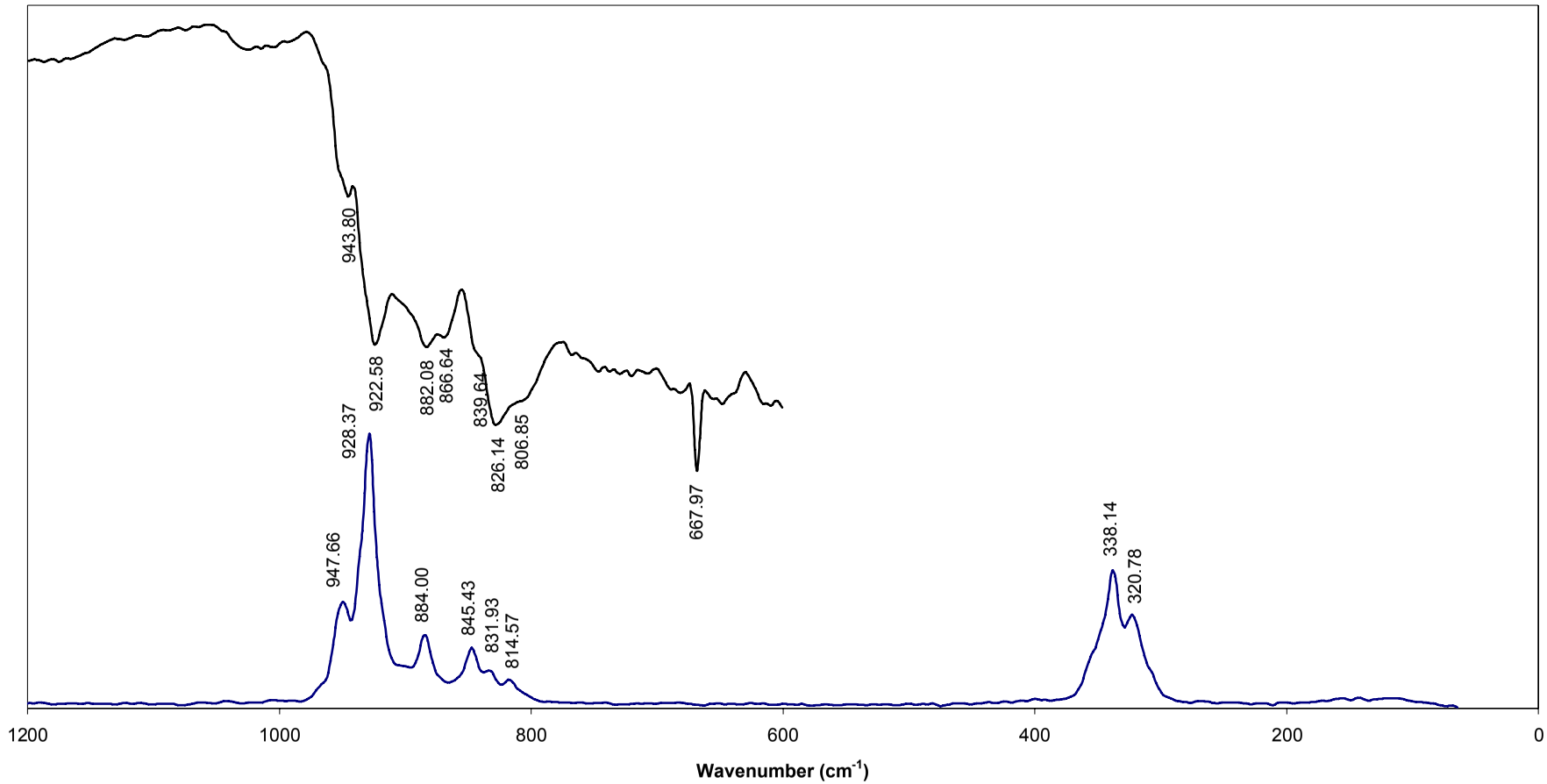
Mid- and far-infrared ATR (in transmission) and Raman (absorption) spectra of crystalline $[Th(ReO_4)_4(TiBP)_4]$ (**3**)



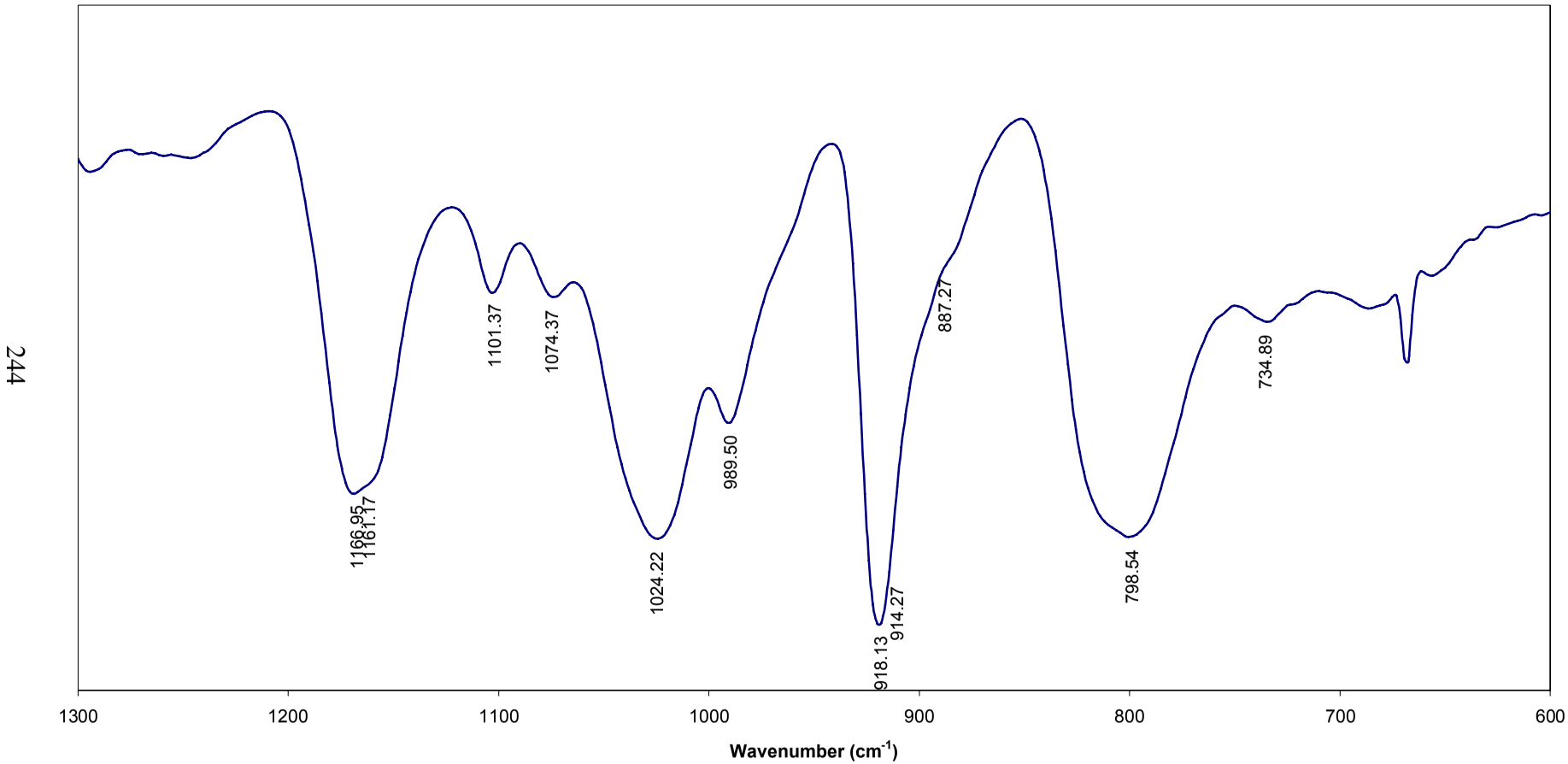
Mid- and far-infrared ATR (in transmission) and Raman (absorption) spectra of crystalline $[Th(ReO_4)_4(TBPO)_4]$ (**4**)



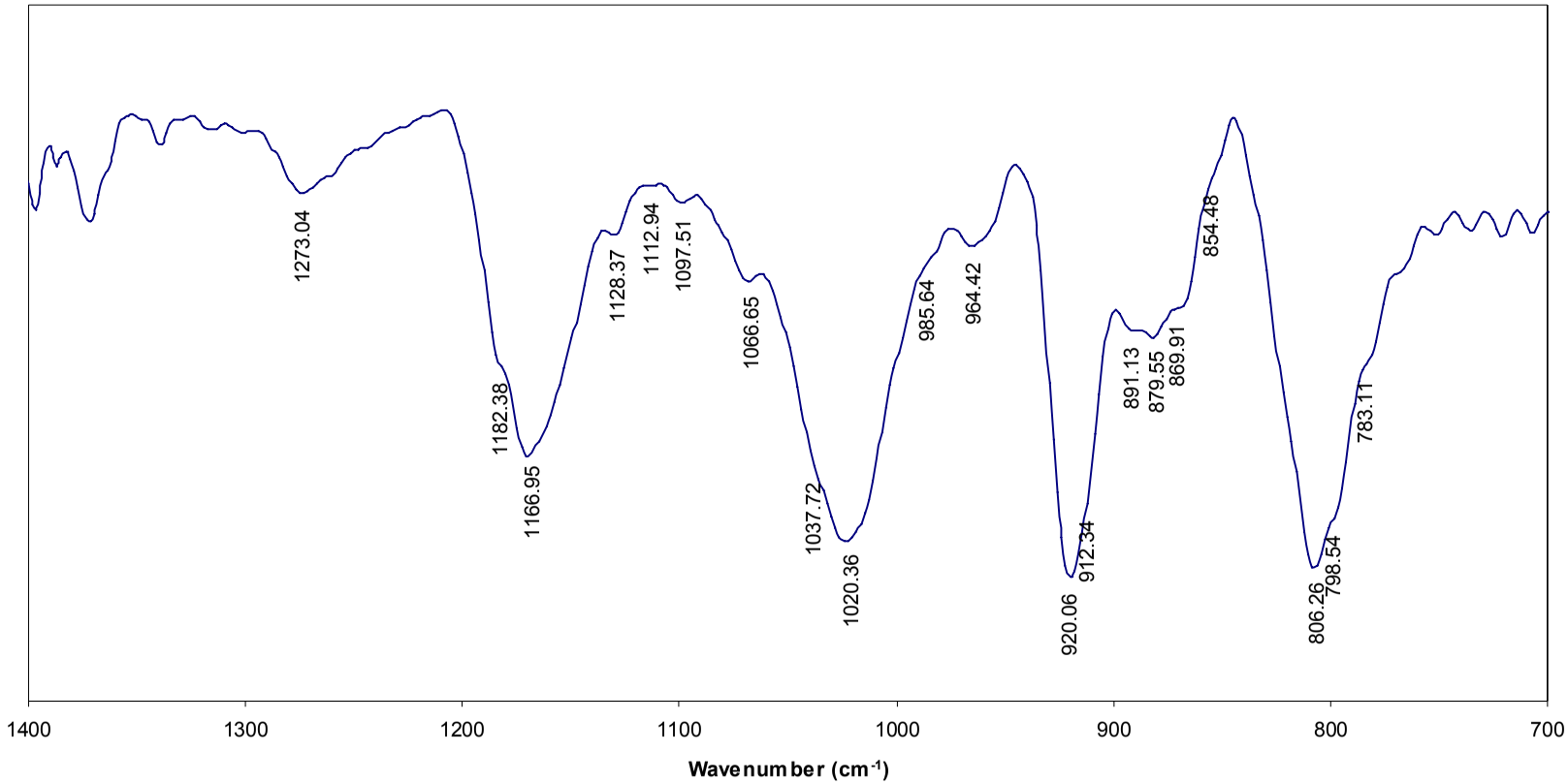
Mid- and far-infrared ATR (in transmission) and Raman (absorption) spectra of crystalline $[Th(ReO_4)_3(TPPO)_3(OCH_3)(HOCH_3)]$ (**5**)



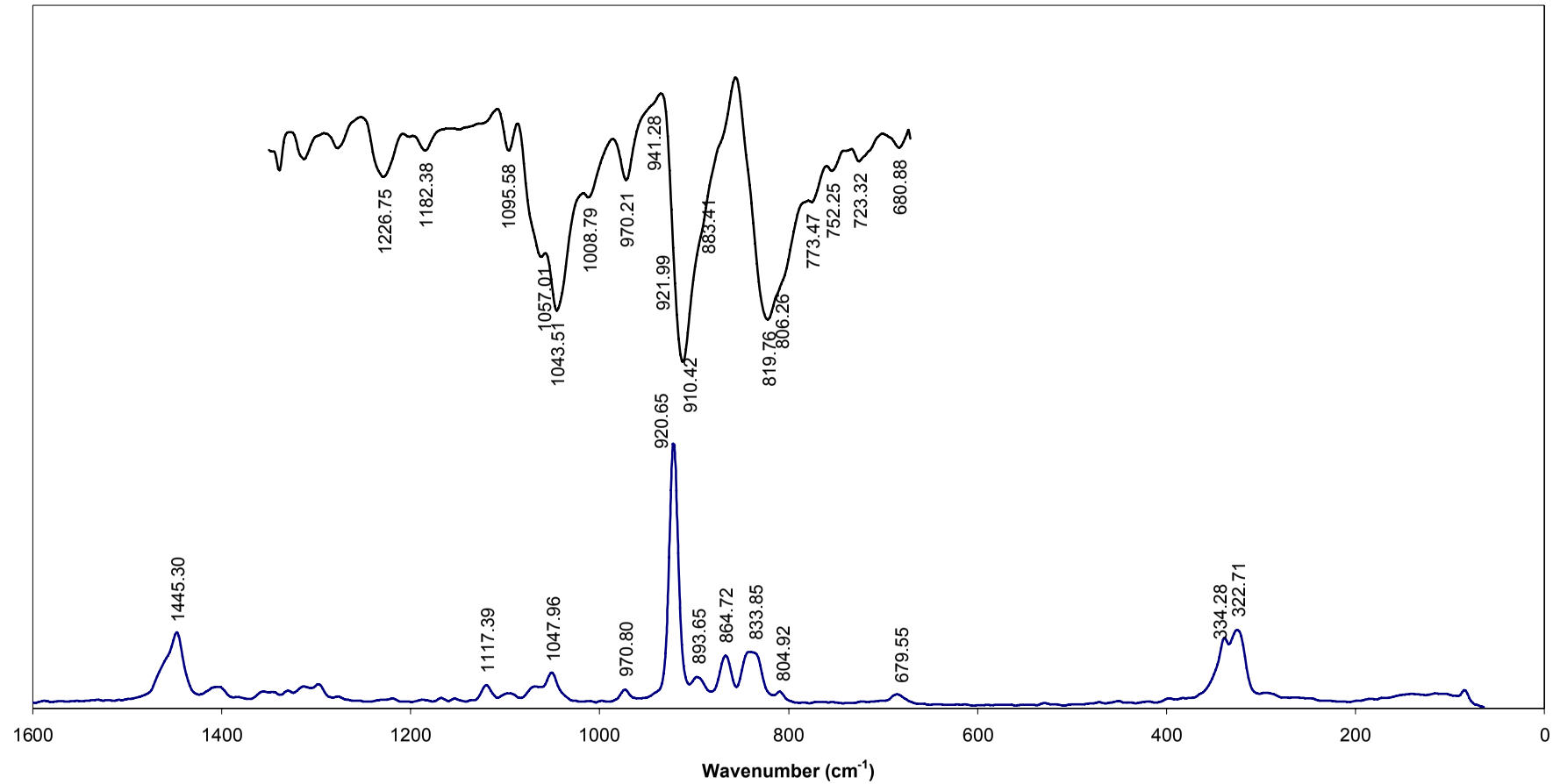
Mid-infrared ATR (in transmission) and Raman (absorption) spectra of $[Th(TcO_4)_4].4H_2O$ (**6**)



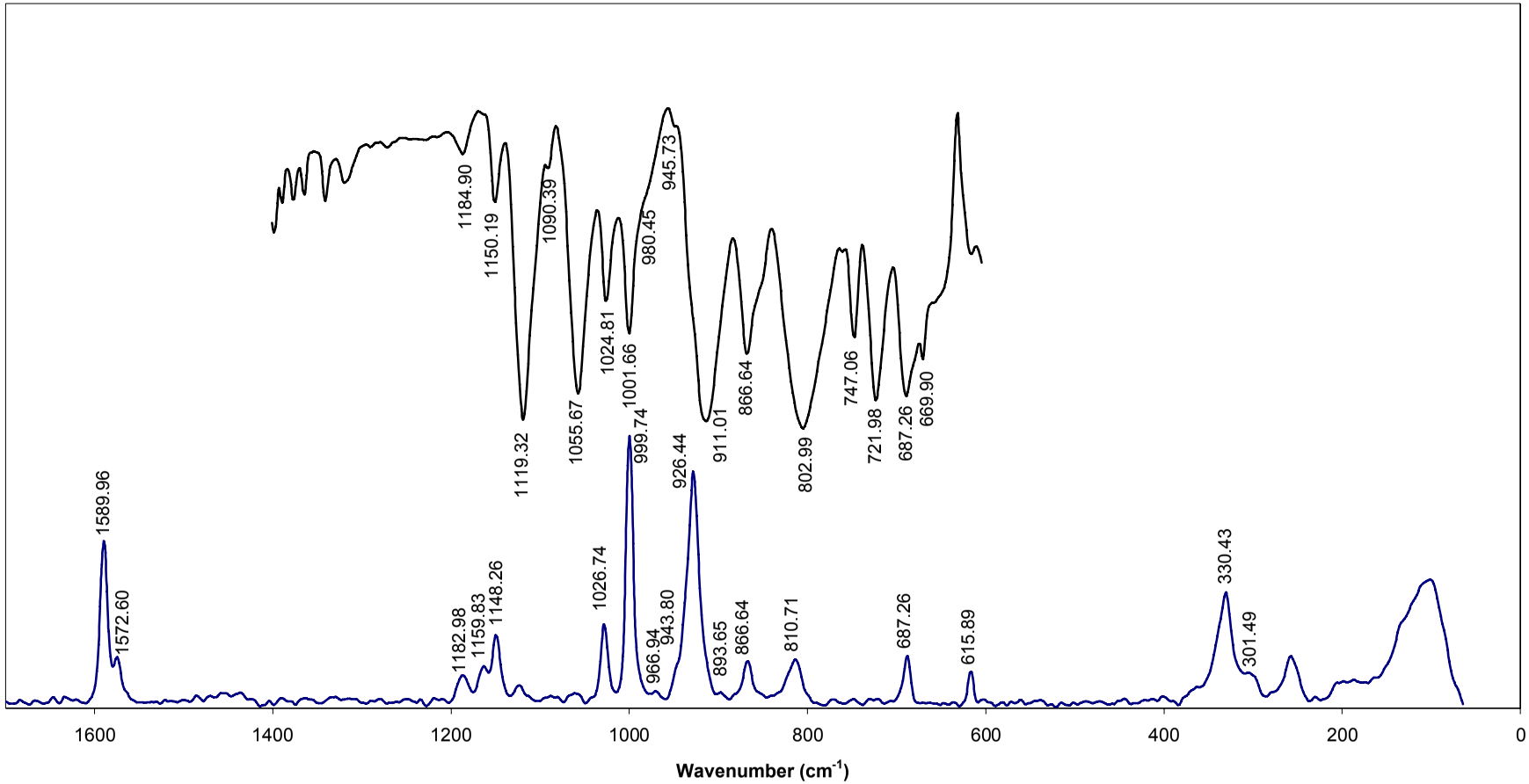
Mid-infrared ATR (in transmission) spectrum of $[Th(TcO_4)_4(TEP)_4]$ (**7**)



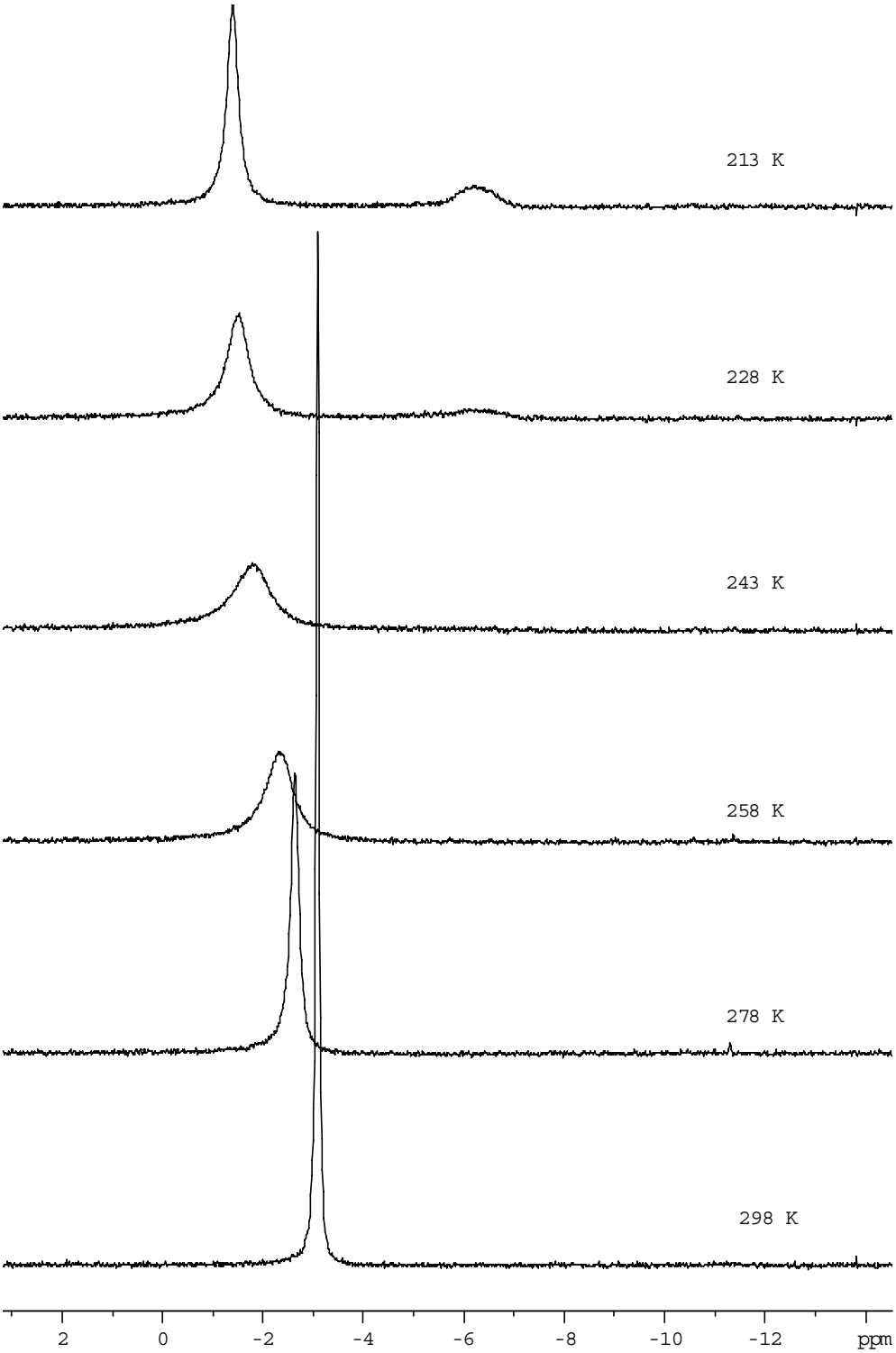
Mid-infrared ATR (in transmission) spectrum of $[Th(TcO_4)_4(TiBP)_4]$ (**8**)



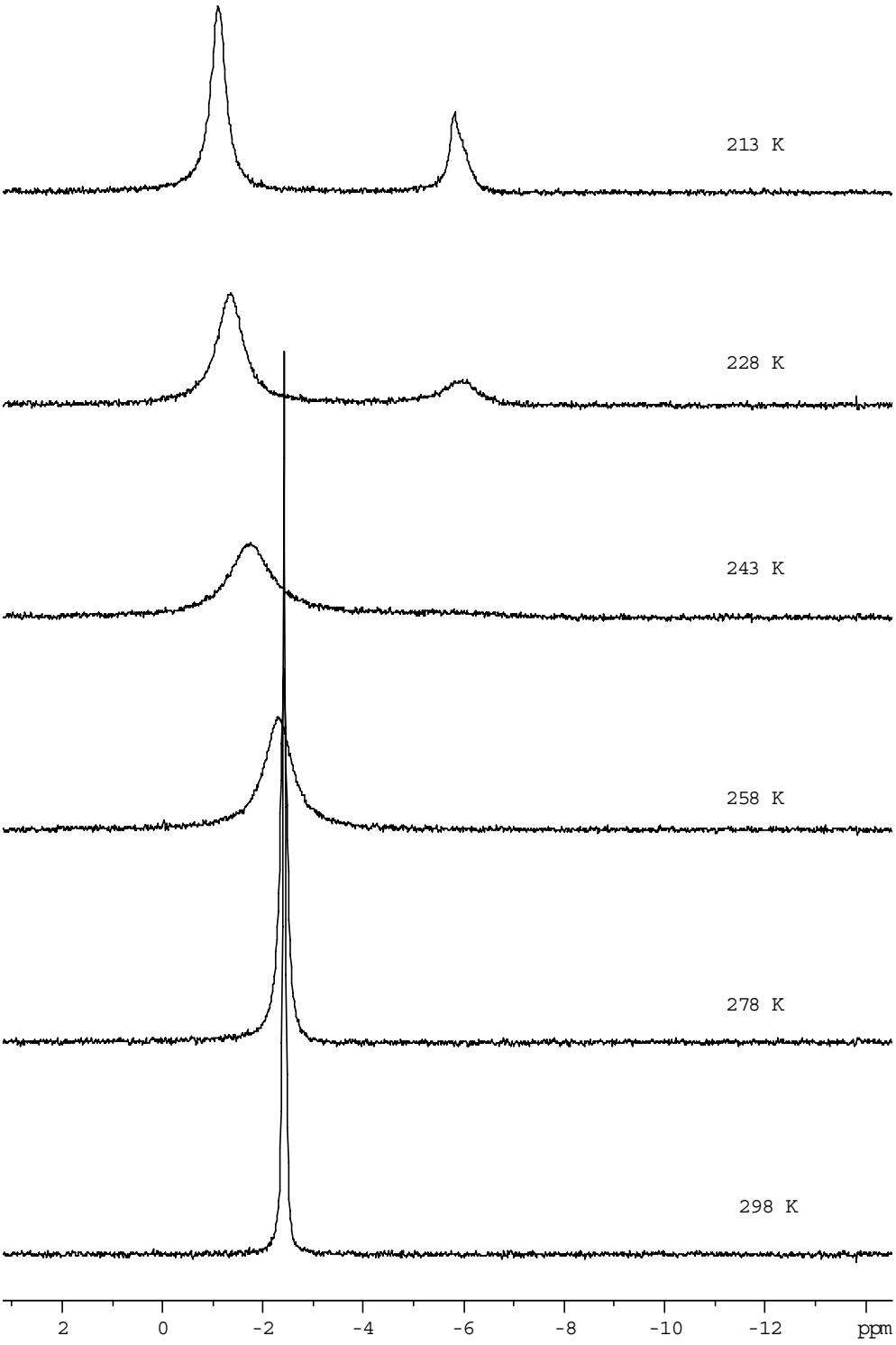
Mid-infrared ATR (in transmission) and Raman (absorption) spectra of $[Th(TcO_4)_4(TBPO)_4]$ (**9**)



Mid-infrared ATR (in transmission) and Raman (absorption) spectra of $[Th(TcO_4)_3(TPPO)_3(OCH_3)(HOCH_3)]$ (**10**)



Solution state variable temperature (213-298 K) ^{31}P NMR spectra (162 MHz, 16 scans) for $[Th(ReO_4)_4(TEP)_4]$ (**2**) in MeOD.



Solution state variable temperature (213-298 K) ^{31}P NMR spectra (162 MHz, 16 scans) for [Th(ReO_4)$_4$($TiBP$)$_4$] (**3**) in MeOD.

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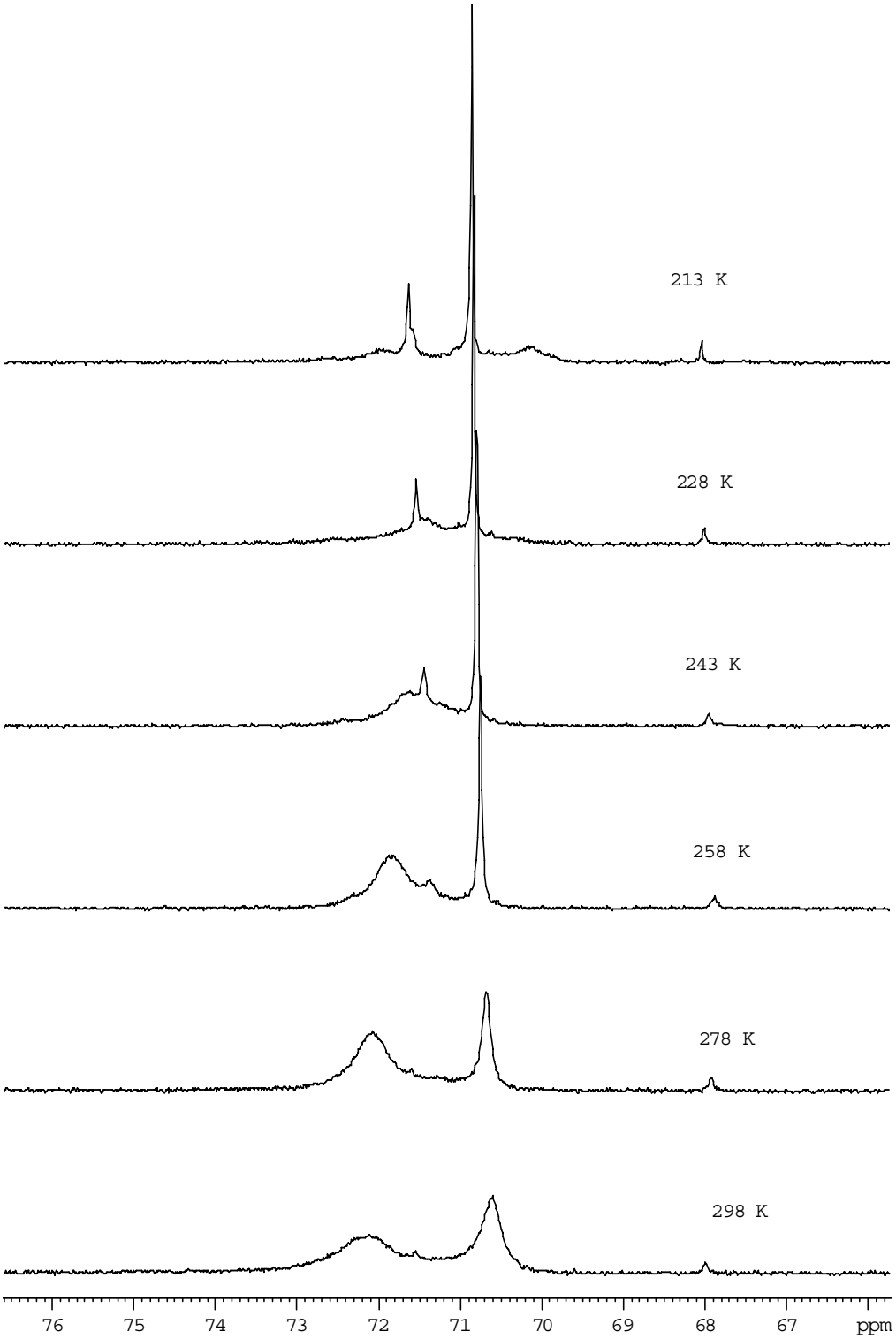
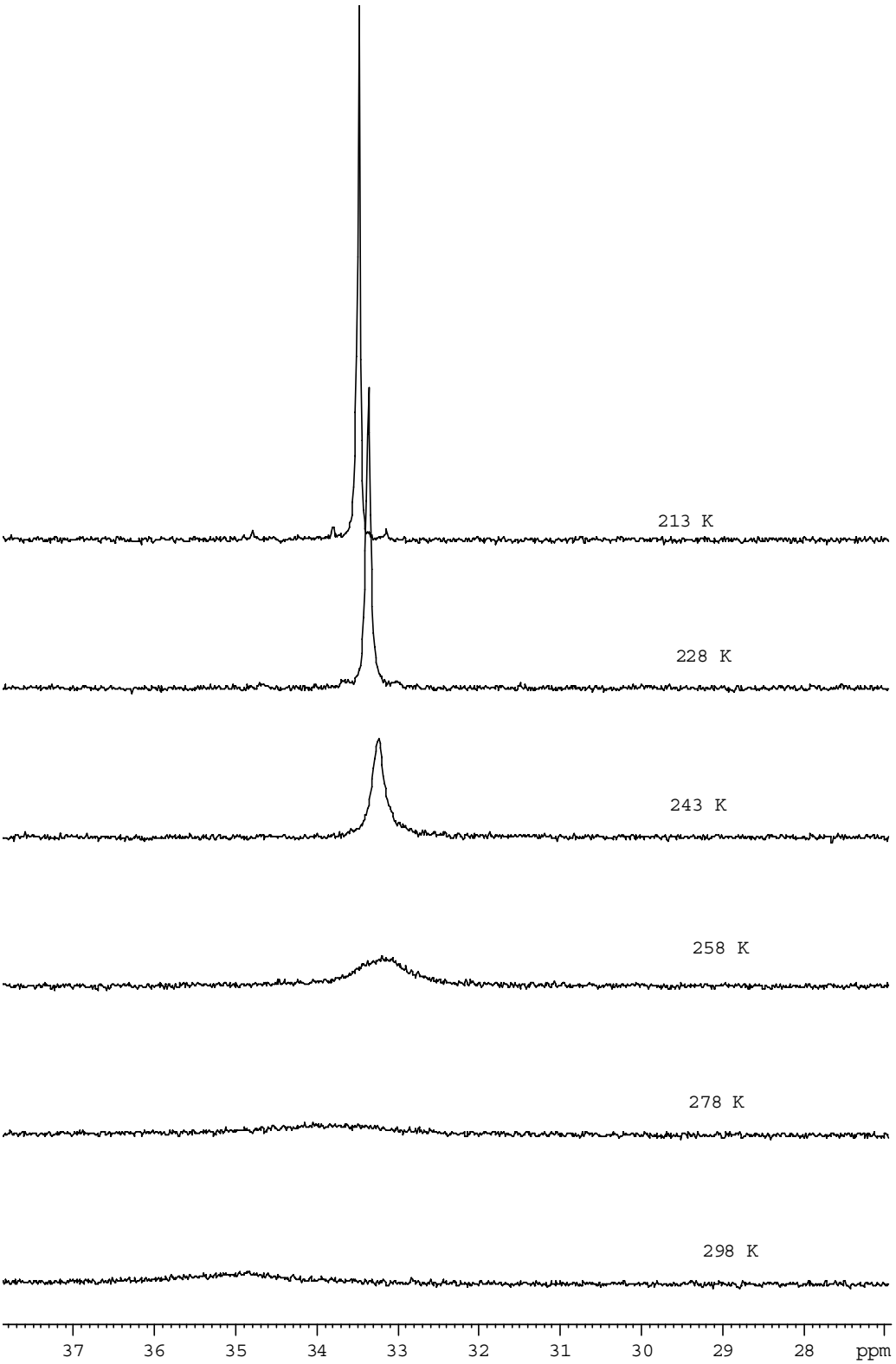
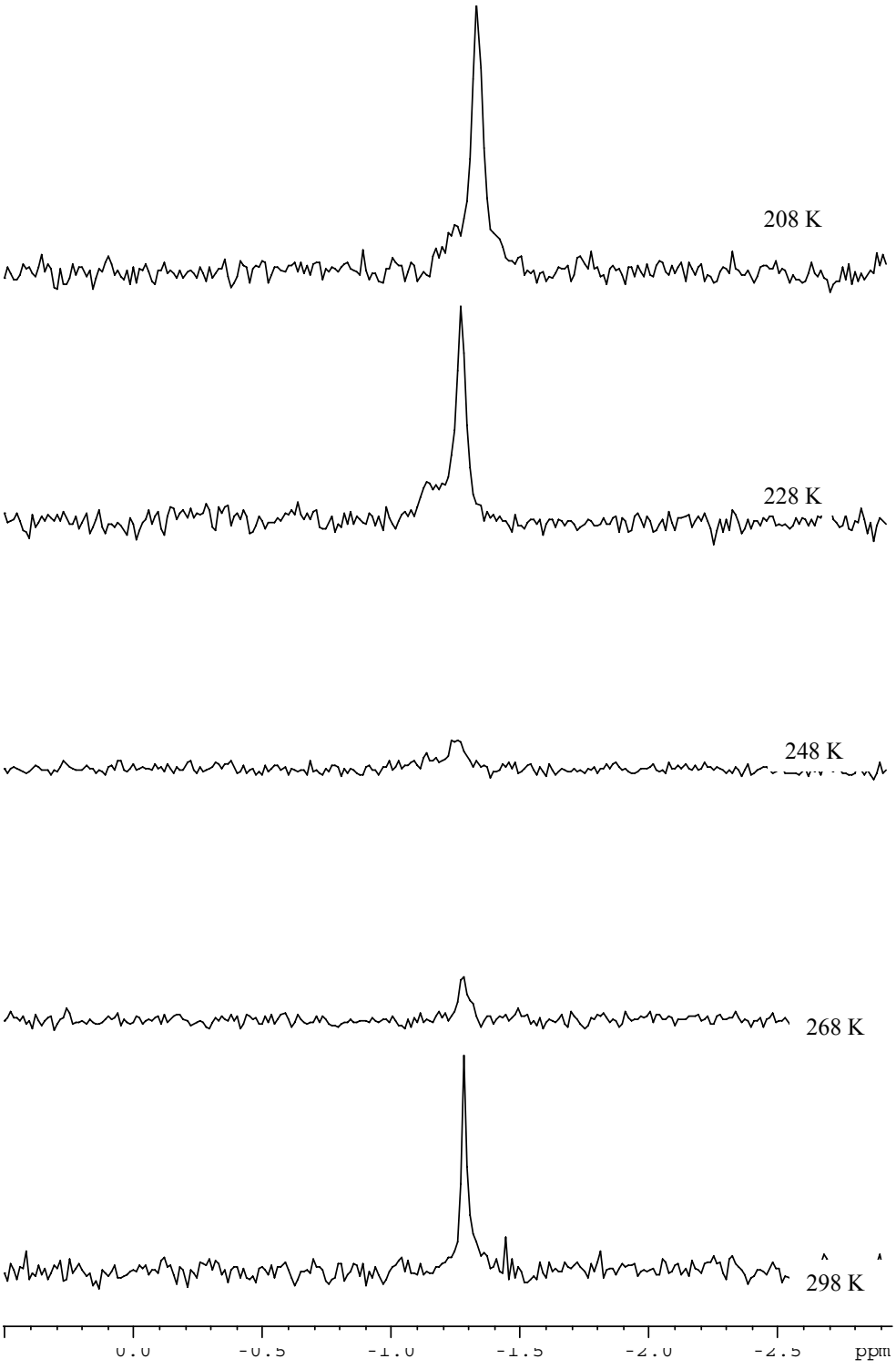


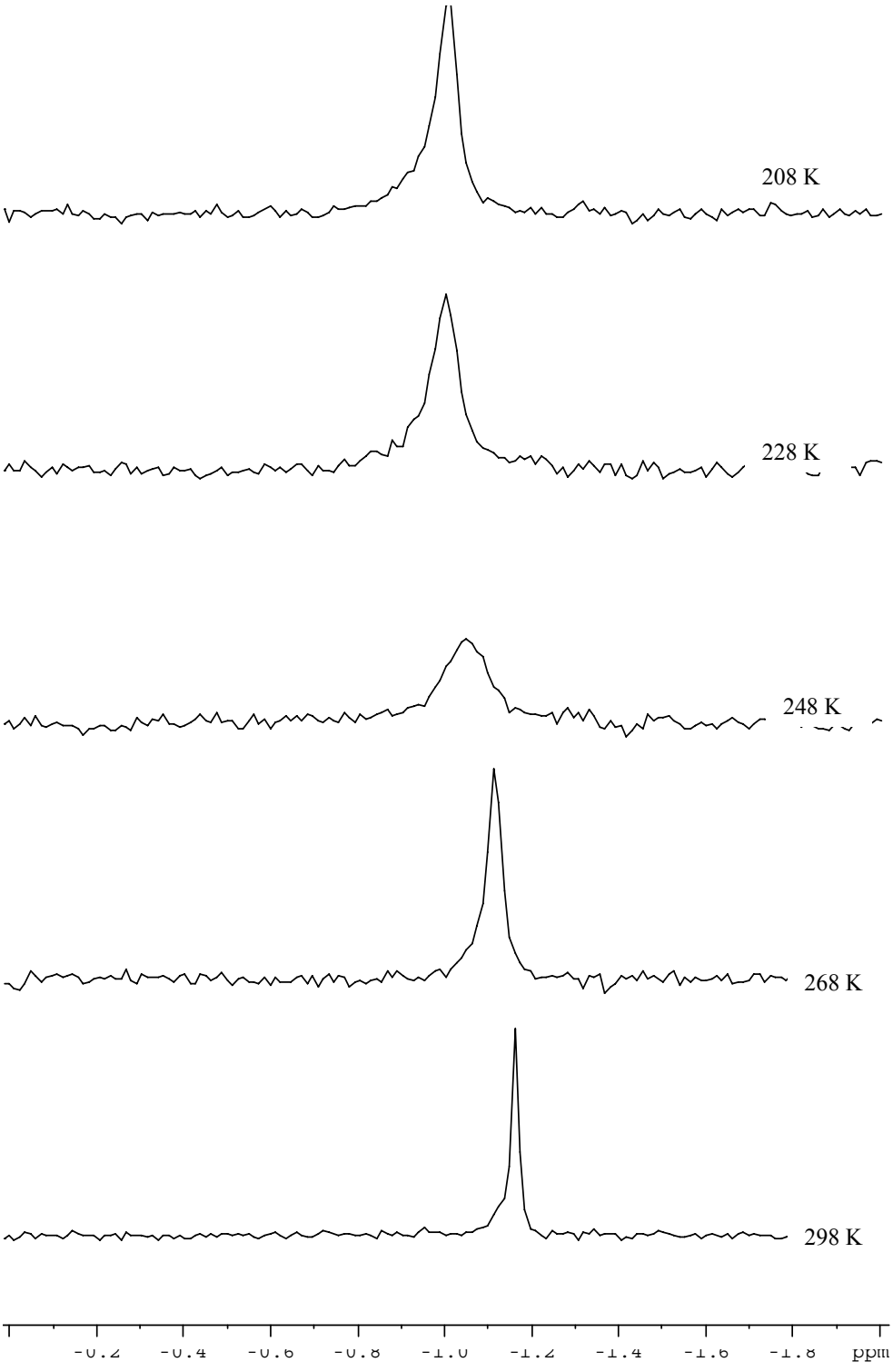
Solution state variable temperature (213-298 K) ^{31}P NMR spectra (162 MHz, 64 scans) for $[Th(ReO_4)_4(TBPO)_4]$ (**4**) in CD_2Cl_2.



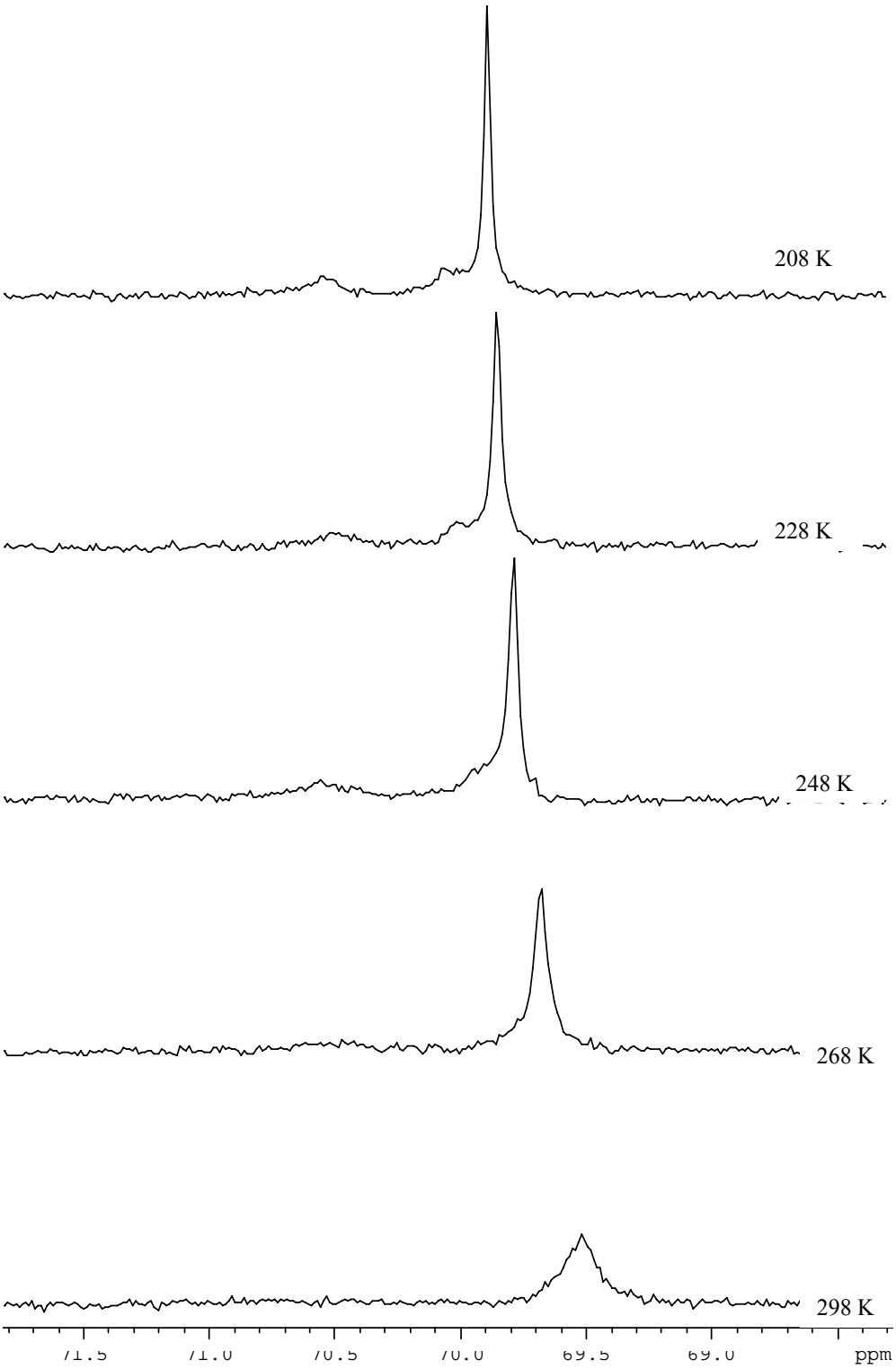
Solution state variable temperature (213-298 K) ^{31}P NMR spectra (162 MHz, 64 scans) for $[Th(ReO_4)_3(TPPO)_3(OCH_3)(HOCH_3)]$ (**5**) in MeOD.



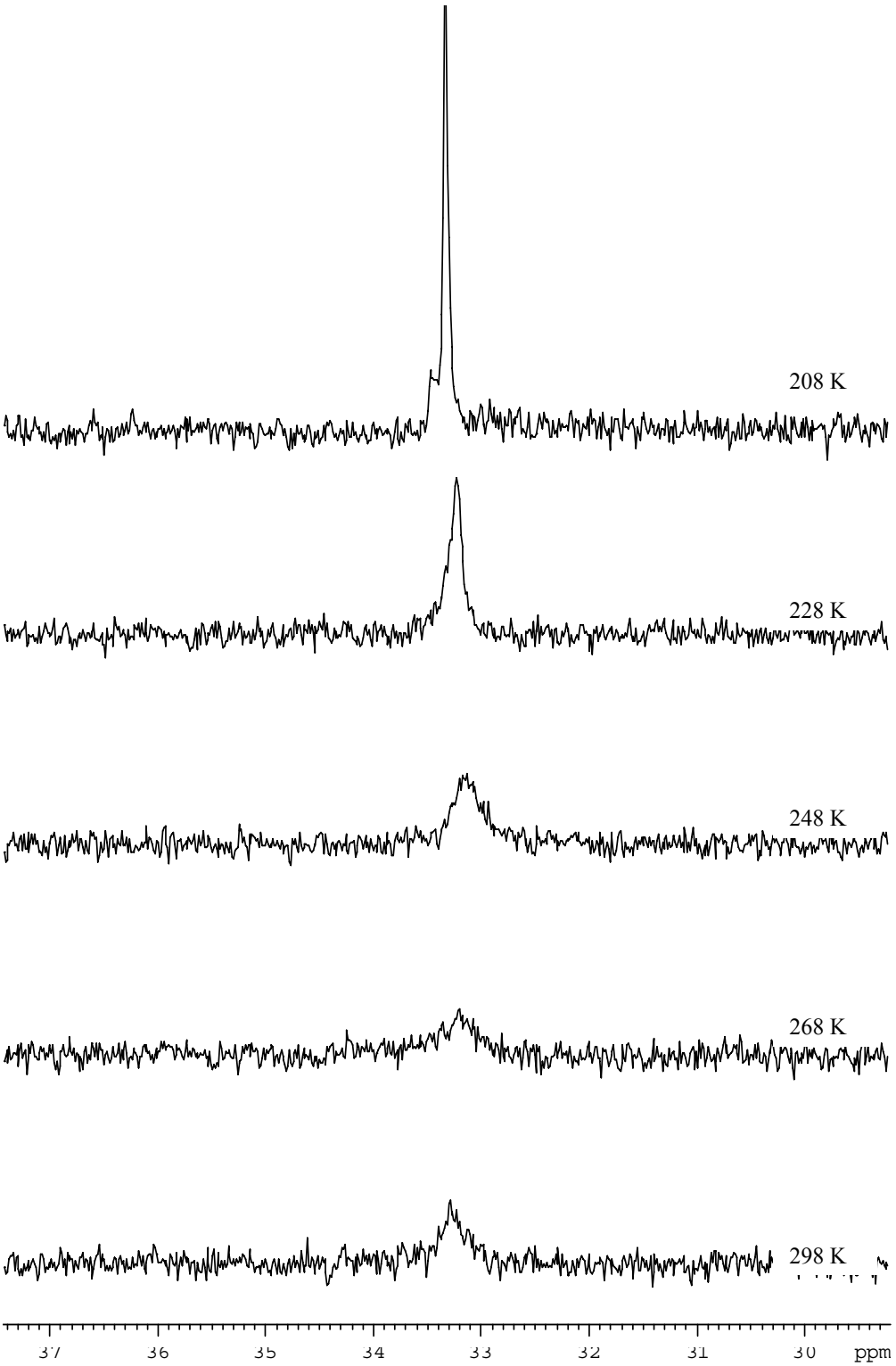
Solution state variable temperature (208-298 K) ^{31}P NMR spectra (162 MHz, 16 scans) for $[Th(TcO_4)_4(TEP)_4]$ (**7**) in MeOD.



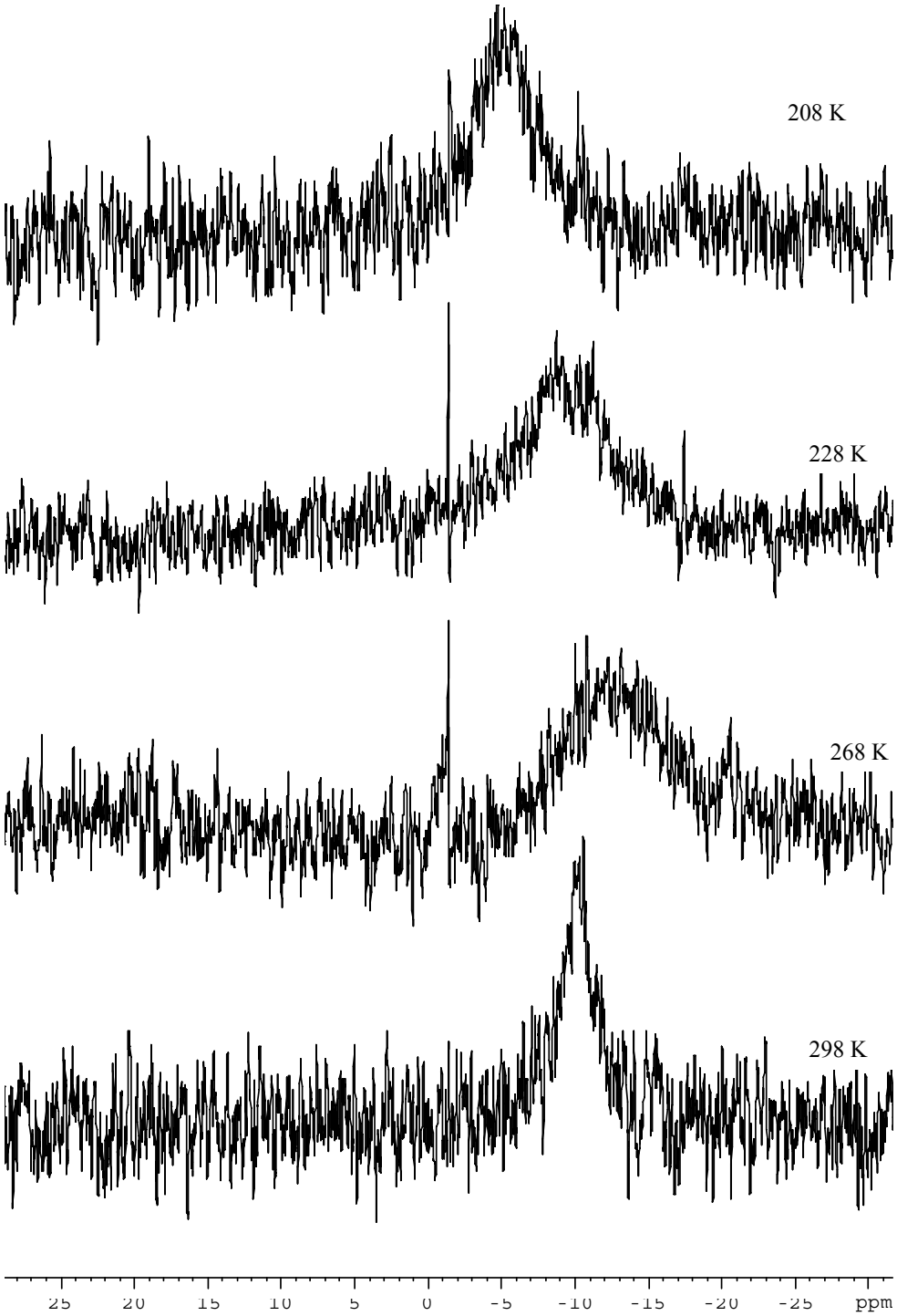
Solution state variable temperature (208-298 K) ^{31}P NMR spectra (162 MHz, 256 scans) for $[Th(TcO_4)_4(TiBP)_4]$ (**8**) in MeOD.



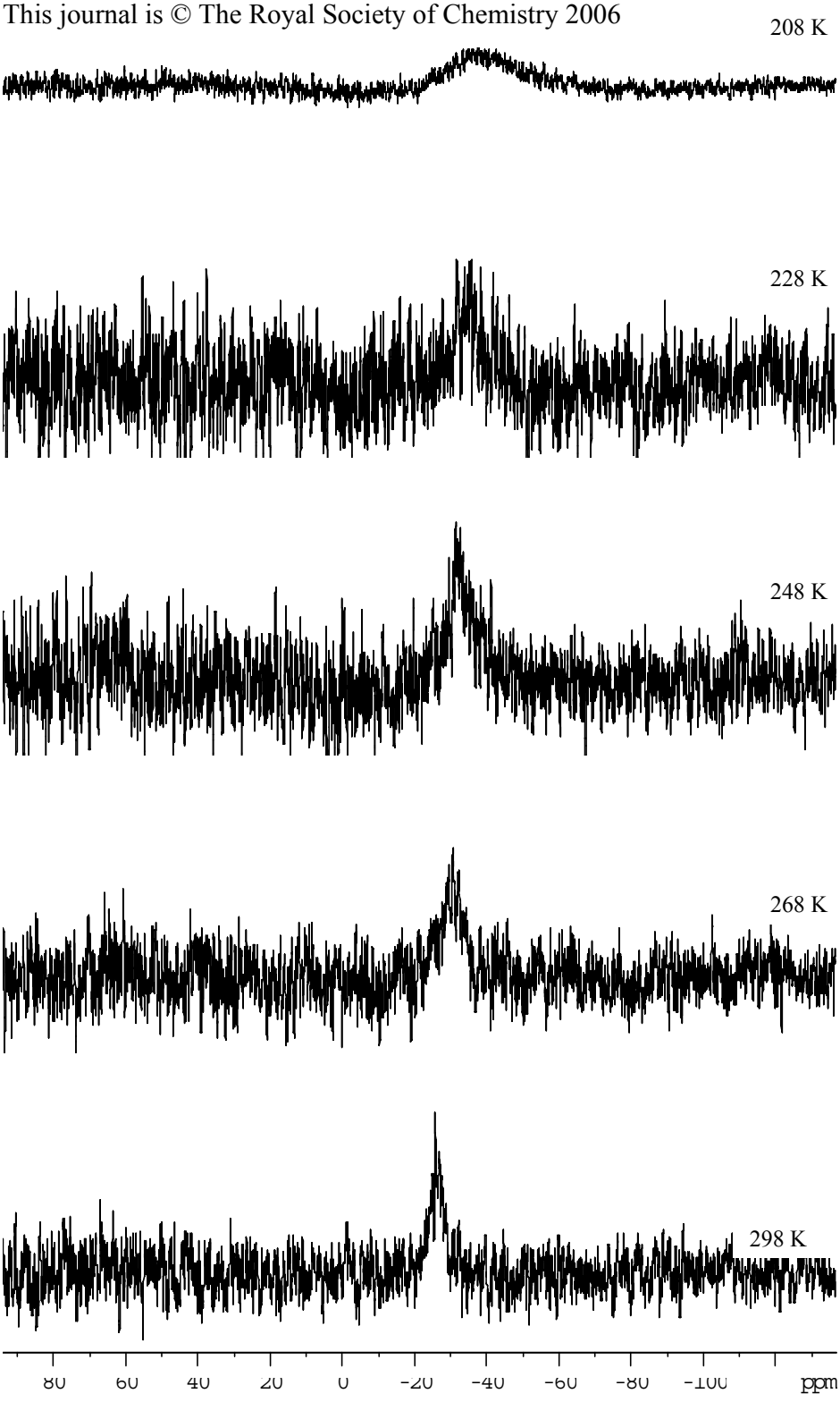
Solution state variable temperature (208-298 K) ^{31}P NMR spectra (162 MHz, 256 scans) for $[Th(TcO_4)_4(TBPO)_4]$ (**9**) in CD_2Cl_2.



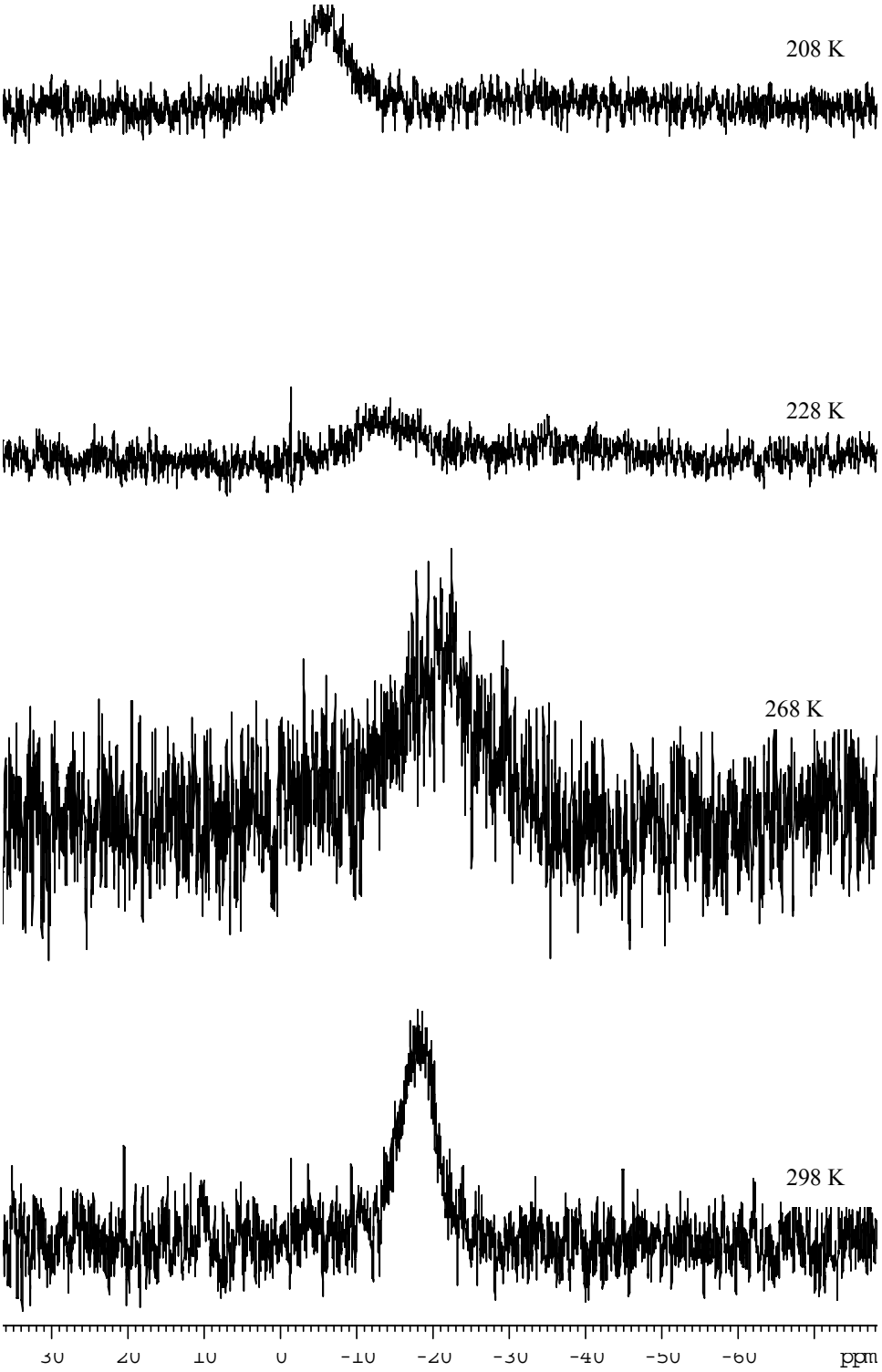
Solution state variable temperature (208-298 K) ^{31}P NMR spectra (162 MHz, 256 scans) for $[Th(TcO_4)_3(TPPO)_3(OCH_3)(HOCH_3)]$ (**10**) in MeOD.



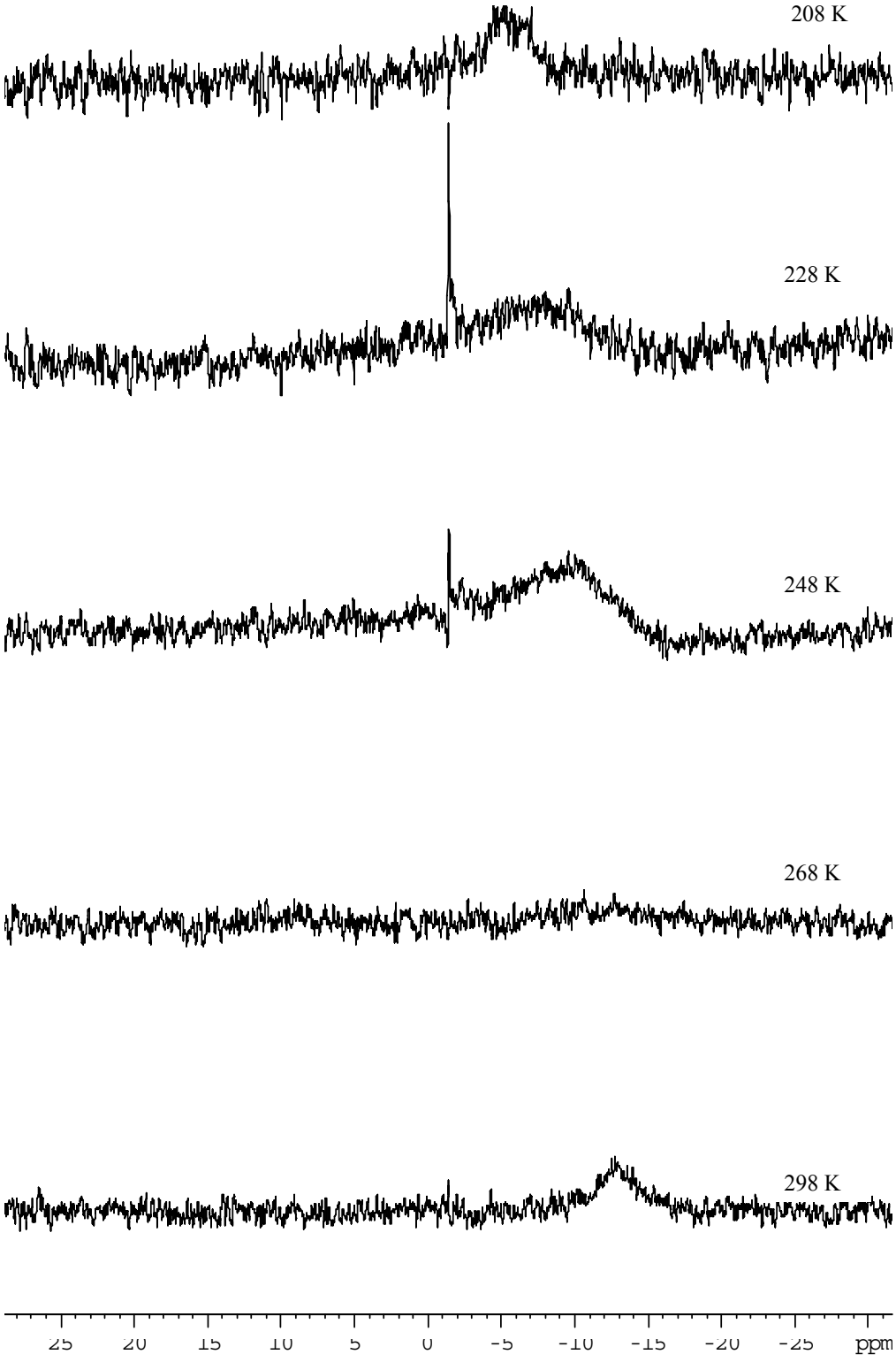
Solution state variable temperature (208-298 K) ^{99}Tc NMR spectra (90.08 MHz, 512 scans) for $[Th(TcO_4)_3(TPPO)_3(OCH_3)(HOCH_3)]$ (**10**) in MeOD.



Solution state variable temperature (208-298 K) ^{99}Tc NMR spectra (90.08 MHz, 512 scans) for $[Th(TcO_4)_4(TBPO)_4]$ (**9**) in CD_2Cl_2.



Solution state variable temperature (208-298 K) ^{99}Tc NMR spectra (90.08 MHz, 512 scans) for [Th(TcO_4)$_4$($TiBP$)$_4$] (**8**) in MeOD.



Solution state variable temperature (208-298 K) ^{99}Tc NMR spectra (90.08 MHz, 512 scans) for $[Th(TcO_4)_4(TEP)_4]$ (**7**) in MeOD.