

Supporting Information

**Heteroatomic molecular clusters derived from group 15 Zintl ion cages:
Synthesis and isolation of $[M_2(HP_7)_2]^{2-}$ (M = Ag, Au), two novel cluster
anions exhibiting metallophilic interactions.**

Caroline M. Knapp, Charlotte S. Jackson, Joseph S. Large, Amber L. Thompson and Jose M.

Goicoechea*

*Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield
Road, Oxford, OX1 3TA, U.K.*

Synthesis of $[Ag(nbe)_3][SbF_6]$

$[Ag(nbe)_3][SbF_6]$ was synthesized using a literature reported method similar to that detailed by Fianchini *et al.*^[1] $Ag[SbF_6]$ (1.20 g, 3.42 mmol) was placed in a medium-sized Schlenk tube with a magnetic stir bar. Norbornene (nbe), (1.50 g, 15.30 mmol) and dichloromethane (90 mL) were mixed at room temperature in a separate Schlenk tube and then transferred into the vessel containing the silver salt. The mixture was stirred overnight at room temperature. The resulting solution was concentrated to ~ 40 mL under a dynamic vacuum and 50 mL of hexane were added resulting in the production of a white precipitate which was separated by filtration. The white solid was redissolved in the minimum amount of dichloromethane, filtered into a clean, dry medium-sized Schlenk tube and layered with hexane. 540 mg (25.6% yield) of colourless, cube-like crystals formed after approximately one week. The crystals were indexed by single crystal X-ray diffraction and shown to be the correct product. Anal. Calcd. for $C_{21}H_{30}AgF_6Sb$: C 40.29%, H 4.83%. Found C 40.17%, H 4.74%. Once isolated $[Ag(nbe)_3][SbF_6]$ was stored under nitrogen in a low temperature freezer. ESI+ MS (DMF): m/z 483.07, $[Ag(nbe)_4]^+$. ESI- MS (DMF) m/z 1096.75, $\{[Ag(nbe)_3][SbF_6]_3\}^-$; 1485.82, $\{[Ag(nbe)_3]_2[SbF_6]_3\}^-$. ¹H NMR data (300.27 MHz, $CDCl_3$): δ (ppm) 6.32 (2H, s)

3.05 (2H, s), 1.67 (2H, m), 1.08 (1H, m), 0.96 (2H, m), 0.92 (1H, d).

Synthesis of [Au(nbe)₃][SbF₆]

[Au(nbe)₃][SbF₆] was synthesized using a similar method to that detailed by Russell and co-workers.^[2] AuCl(SMe₂) (0.118 g, 0.40 mmol) and Ag[SbF₆] (0.138 g, 0.40 mmol) were placed in a medium-sized Schlenk tube with a stir bar. A solution of norbornene (nbe), (0.452 g, 4.80 mmol) in dichloromethane (20 mL) was added and the reaction was stirred for 16 hours yielding a grey/cream coloured solution. The solvent was removed *in vacuo* and a further solution of nbe (0.226 g, 0.24 mmol) in dichloromethane (20 mL) was added to the resulting grey solid. The mixture was stirred for 2 hours. The solution was filtered through Celite to remove the grey precipitate, AgCl, and washed with dichloromethane (3 x 5 mL). The resulting solution was concentrated *in vacuo* to ~4 mL, filtered into a clean, dry Schlenk tube and layered with diethylether. After approximately a week, 280 mg (49.0% yield) of large colourless cube-like crystals were observed. The crystals were indexed to confirm the identity of the product. Anal. Calcd. for C₂₁H₃₀AuF₆Sb: C 35.25%, H 4.23%. Found C 35.17%, H 4.29%. Once isolated, [Au(nbe)₃][SbF₆] was stored under nitrogen in a low temperature freezer. ESI+ MS (DMF): *m/z* 573.02, [Au(nbe)₄]⁺; 667.13, [Au(nbe)₅]⁺. ¹H NMR data (300.27 MHz, CDCl₃): δ (ppm) 5.81 (2H, s) 3.15 (2H, s), 1.73 (2H, m), 1.00 (2H, m), 0.81 (1H, m), 0.76 (1H, m).

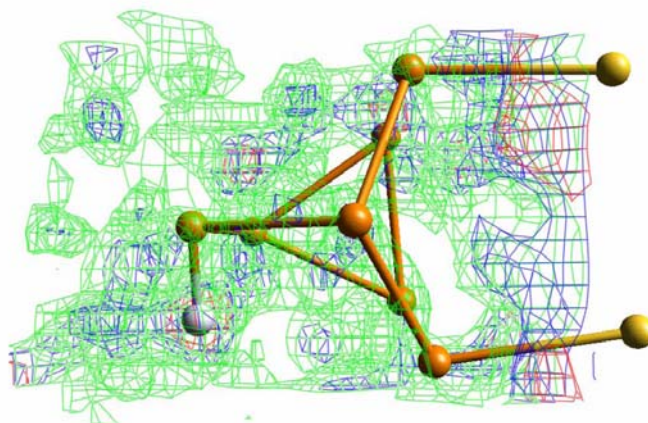
Additional crystallographic studies on 1 and 2.

1 and **2** are $[\text{K}(2,2,2\text{-crypt})]^+$ salts of the $[\text{Ag}_2(\text{HP}_7)_2]^{2-}$ and $[\text{Au}_2(\text{HP}_7)_2]^{2-}$, respectively.

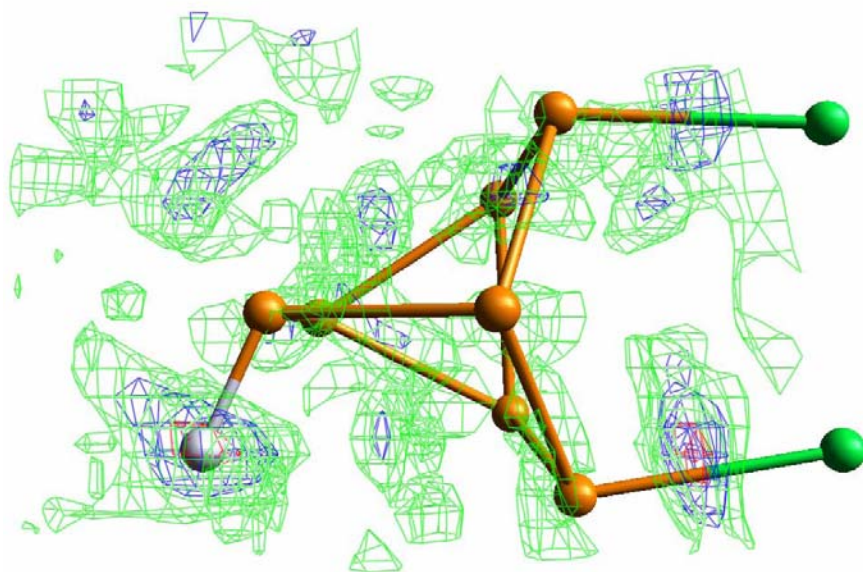
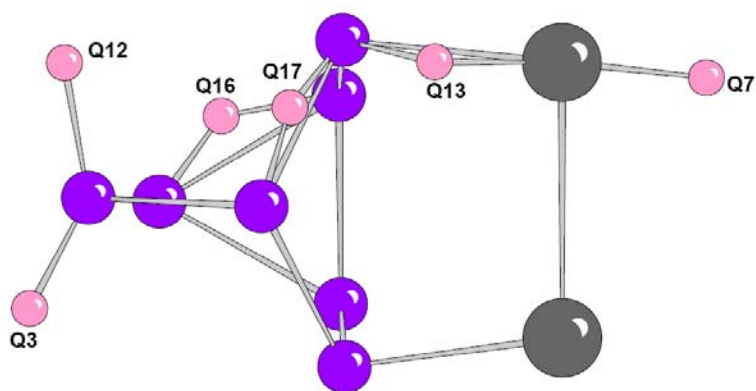
Determining protic positions by single crystal X-ray diffraction is often challenging and becomes increasingly difficult with poor quality data and in the presence of heavy atoms.

Both structures were refined with CRYSTALS and examined carefully.^[3] The first sample studied was **2**. After addition of hydrogen atoms to the 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ligand ([2.2.2]cryptand) and full matrix least-squares refinement, including positions and anisotropic displacement parameters (statistical weights), a Fourier difference map with all the data yielded 50 peaks between 1.2 and 2.0 electrons/Å³. No obvious structure was apparent in the peaks.

Recalculating the phases with the data truncated to $0.22 \text{ \AA}^{-2} (\sin \theta/\lambda)^2$, and recalculating the difference Fourier map (Cooper *et al.* 2010)^[4] gave 50 peaks between 0.35 and 1.0 electrons/Å³. The majority of these peaks were close to the cluster. For three of the four strongest peaks, the closest atom was the gold, but the second largest was 1.13 Å from P4 which formed an approximate trigonal pyramidal arrangement with the P-H bond parallel to the aurophilic interaction (below). On refinement either with all the data, or with only the low angle data, the hydrogen moved to a position away from the gold such that the P-H bond was no longer parallel with the aurophilic interaction and the coordination geometry of P4 was more pyramidal.



A similar study was carried out for **1**, for which the data were better. On examination of the difference map with all data, the 9th most intense peak was found 1.35 Å from P4, with the 10th and 14th most intense peaks 1.23 Å and 1.22 Å away, respectively. Q9 was found in a similar location to the refined position for the proton in structure **2**. On truncating to 0.22 \AA^{-2} ($\sin \theta/\lambda$)², the strongest peak (Q3) is 1.35 Å from P4 in the same location as described above with a second peak on the opposite side (c. 1.28 Å away, below). Given that there is no obvious steering interaction governing the location of the proton, it is not inconceivable that there is a small degree of disorder present. Indeed, reducing the occupancy slightly encourages the isotropic displacement parameter to adopt a more sensible value. However, refinement of a disorder model was unstable and therefore rejected.



The difference map is very noisy in both cases and there are a number of peaks of a suitable size to be a proton. The indications of the presence of a proton are in a similar location for both **1** and **2**. These structures are not isomorphous suggesting that it is not an artefact due to a systematic error like absorption as the effect would be expected to be different for different structures. In addition, the proposed positions are in chemically sensible locations, supporting the structural models reported.

Cartesian coordinates [\AA] for the optimized structure of ‘up-down’ $[\text{Ag}_2(\text{HP}_7)_2]^{2-}$ isomer

Atom	x	y	z
1. Ag	-1.378679	0.648146	0.126043
2. P	-1.350573	-2.639803	-1.445848
3. P	-2.434689	-0.712618	-1.599961
4. P	-0.769790	2.214291	1.894318
5. P	-2.066453	-3.282218	-3.457832
6. H	-1.037137	-4.245574	-3.724919
7. P	1.504170	0.108263	-3.431529
8. P	-0.553294	0.849529	3.600677
9. P	-1.197011	-1.691108	-4.774476
10. Ag	1.378679	-0.648146	-0.126043
11. P	1.350573	2.639803	1.445848
12. P	2.434689	0.712618	1.599961
13. P	0.769790	-2.214291	-1.894318
14. P	2.066453	3.282218	3.457832
15. H	1.037137	4.245574	3.724919
16. P	1.504170	-0.108263	3.431529
17. P	0.553294	-0.849529	-3.600677
18. P	1.197011	1.691108	4.774476

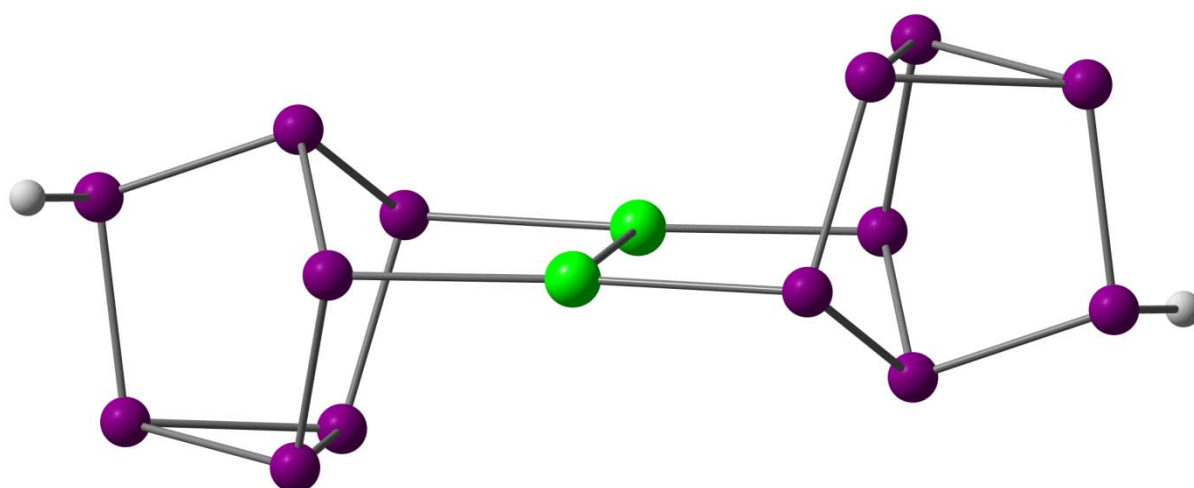


Figure S1. Optimized geometry of the ‘up-down’ isomer of the $[\text{Ag}_2(\text{HP}_7)_2]^{2-}$ cluster anion from DFT calculations.

Cartesian coordinates [Å] for the optimized structure of ‘up-up’ [Ag₂(HP₇)₂]²⁻ isomer

Atom	x	y	z
1. Ag	0.120763	-1.532375	-0.266116
2. P	-3.062009	-0.250867	-1.477789
3. P	-2.288049	-1.930422	-0.260579
4. P	2.559312	-1.605871	-0.389282
5. P	-5.142279	-0.596041	-0.743922
6. H	-5.659710	0.716453	-1.009683
7. P	-2.893983	-1.260892	1.760586
8. P	3.049868	-1.009507	1.666831
9. P	-4.910022	-0.272275	1.459862
10. Ag	-0.120763	1.532375	-0.266116
11. P	3.062009	0.250867	-1.477789
12. P	2.288049	1.930422	-0.260579
13. P	-2.559312	1.605871	-0.389282
14. P	5.142279	0.596041	-0.743922
15. H	5.659710	-0.716453	-1.009683
16. P	2.893983	1.260892	1.760586
17. P	-3.049868	1.009507	1.666831
18. P	4.910022	0.272275	1.459862

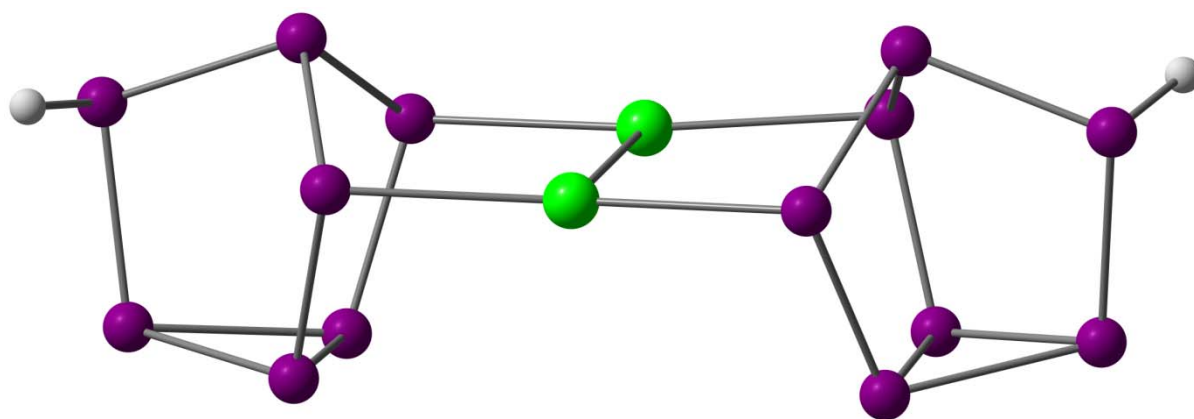


Figure S2. Optimized geometry of the ‘up-up’ isomer of the [Ag₂(HP₇)₂]²⁻ cluster anion from DFT calculations.

Table S1. Bond distances [Å] for the ‘up-down’ isomer of the $[\text{Ag}_2(\text{HP}_7)_2]^{2-}$ cluster anion crystallographically characterized in **1** and the optimized computed structure.

bond	1	1_{calc}
Ag1-Ag1A	2.947(1)	3.057
Ag1-P2	2.411(1)	2.438
Ag1A-P3	2.415(1)	2.440
P1-P2	2.177(1)	2.217
P1-P3	2.176(1)	2.209
P1-P4	2.181(1)	2.230
P2-P5	2.174(1)	2.212
P3-P6	2.164(1)	2.196
P4-P7	2.195(1)	2.241
P5-P6	2.236(1)	2.276
P5-P7	2.237(1)	2.266
P6-P7	2.230(1)	2.269
P4-H1	1.27(8)	1.43

Cartesian coordinates [\AA] for the optimized structure of ‘up-down’ $[\text{Au}_2(\text{HP}_7)_2]^{2-}$ isomer

Atom	x	y	z
1. Au	-0.376814	0.587702	1.460934
2. P	-2.353764	-2.179949	0.307400
3. P	-2.593986	-0.302712	1.457636
4. P	-1.760845	-1.605127	-1.756804
5. P	-4.459052	-2.514917	-0.325003
6. P	-3.625906	0.963083	-0.033312
7. P	-3.116616	0.131155	-2.083566
8. P	-5.039339	-0.469748	-1.061189
9. H	-5.063177	-2.361651	0.967720
10. Au	0.376814	-0.587702	-1.460934
11. P	2.353764	2.179949	-0.307400
12. P	2.593986	0.302712	-1.457636
13. P	1.760845	1.605127	1.756804
14. P	4.459052	2.514917	0.325003
15. P	3.625906	-0.963083	0.033312
16. P	3.116616	-0.131155	2.083566
17. P	5.039339	0.469748	1.061189
18. H	5.063177	2.361651	-0.967720

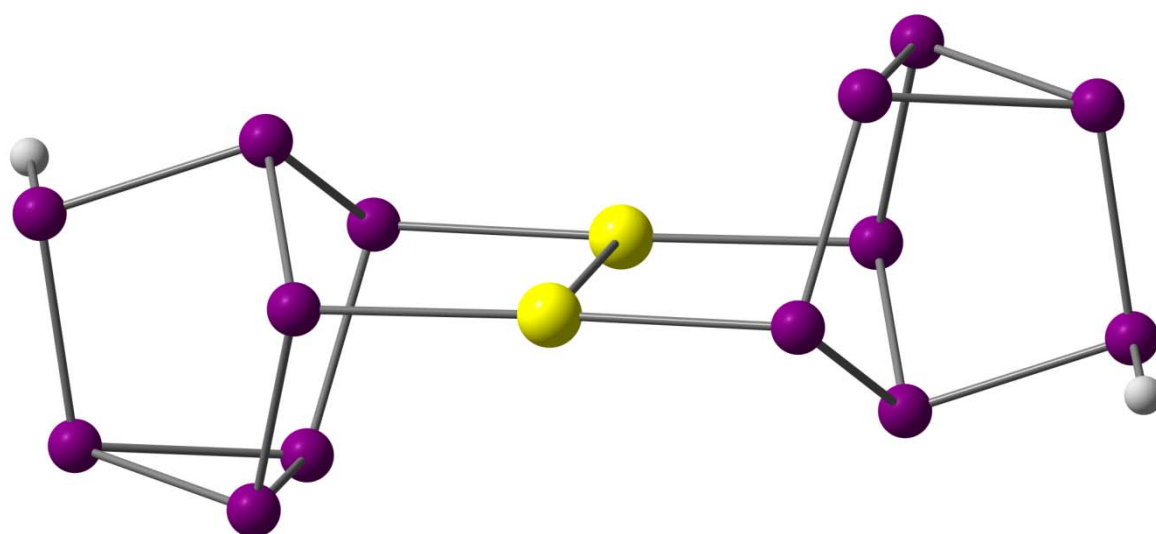


Figure S3. Optimized geometry of the ‘up-down’ isomer of the $[\text{Au}_2(\text{HP}_7)_2]^{2-}$ cluster anion from DFT calculations.

Cartesian coordinates [Å] for the optimized structure of ‘up-up’ $[\text{Au}_2(\text{HP}_7)_2]^{2-}$ isomer

Atom	x	y	z
1. Au	0.117544	-1.592243	-0.380708
2. P	-2.975568	-0.217404	-1.620515
3. P	-2.248494	-1.905386	-0.375365
4. P	2.503090	-1.615097	-0.520179
5. P	-5.065450	-0.550692	-0.938774
6. H	-5.565705	0.763513	-1.222617
7. P	-2.877502	-1.206671	1.643225
8. P	3.033465	-1.018040	1.539952
9. P	-4.879245	-0.220473	1.278440
10. Au	-0.116873	1.628554	-0.382161
11. P	2.977061	0.250673	-1.622280
12. P	2.250055	1.939240	-0.378516
13. P	-2.501986	1.651381	-0.521876
14. P	5.067863	0.581764	-0.942190
15. H	5.565220	-0.734280	-1.222853
16. P	2.878916	1.243024	1.641190
17. P	-3.031905	1.054763	1.538406
18. P	4.880641	0.257421	1.277081

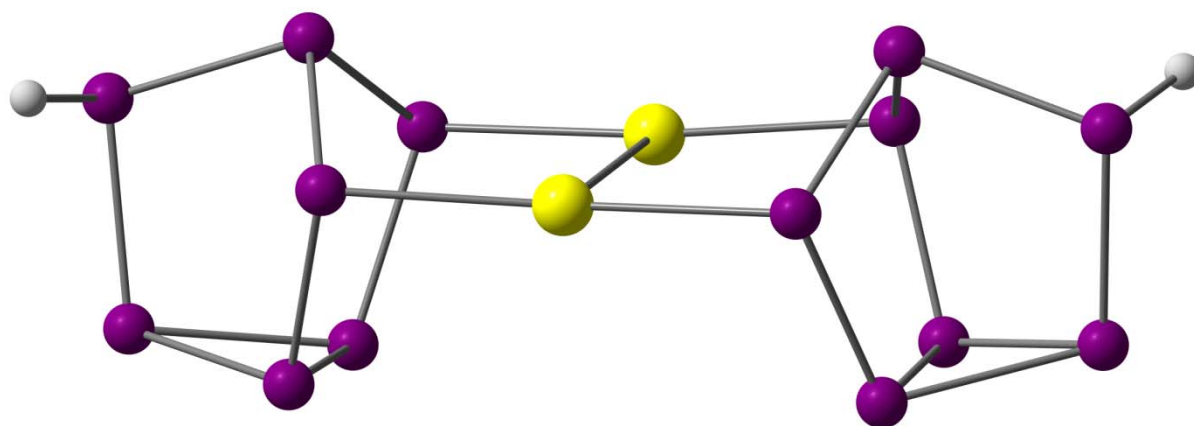


Figure S4. Optimized geometry of the ‘up-up’ isomer of the $[\text{Au}_2(\text{HP}_7)_2]^{2-}$ cluster anion from DFT calculations.

Table S2. Bond distances [\AA] of the ‘up-down’ isomer of the $[\text{Au}_2(\text{HP}_7)_2]^{2-}$ cluster anion crystallographically characterized in **2** and the optimized computed structure.

bond	2	2_{calc}
Au1-Au1A	3.047(1)	3.238
Au1-P2	2.357(2)	2.389
Au1A-P3	2.349(2)	2.383
P1-P2	2.184(3)	2.215
P1-P3	2.175(3)	2.223
P1-P4	2.185(3)	2.224
P2-P5	2.177(3)	2.211
P3-P6	2.175(3)	2.227
P4-P7	2.183(3)	2.250
P5-P6	2.224(3)	2.270
P5-P7	2.220(3)	2.260
P6-P7	2.217(3)	2.259
P4-H1	1.14(9)	1.44

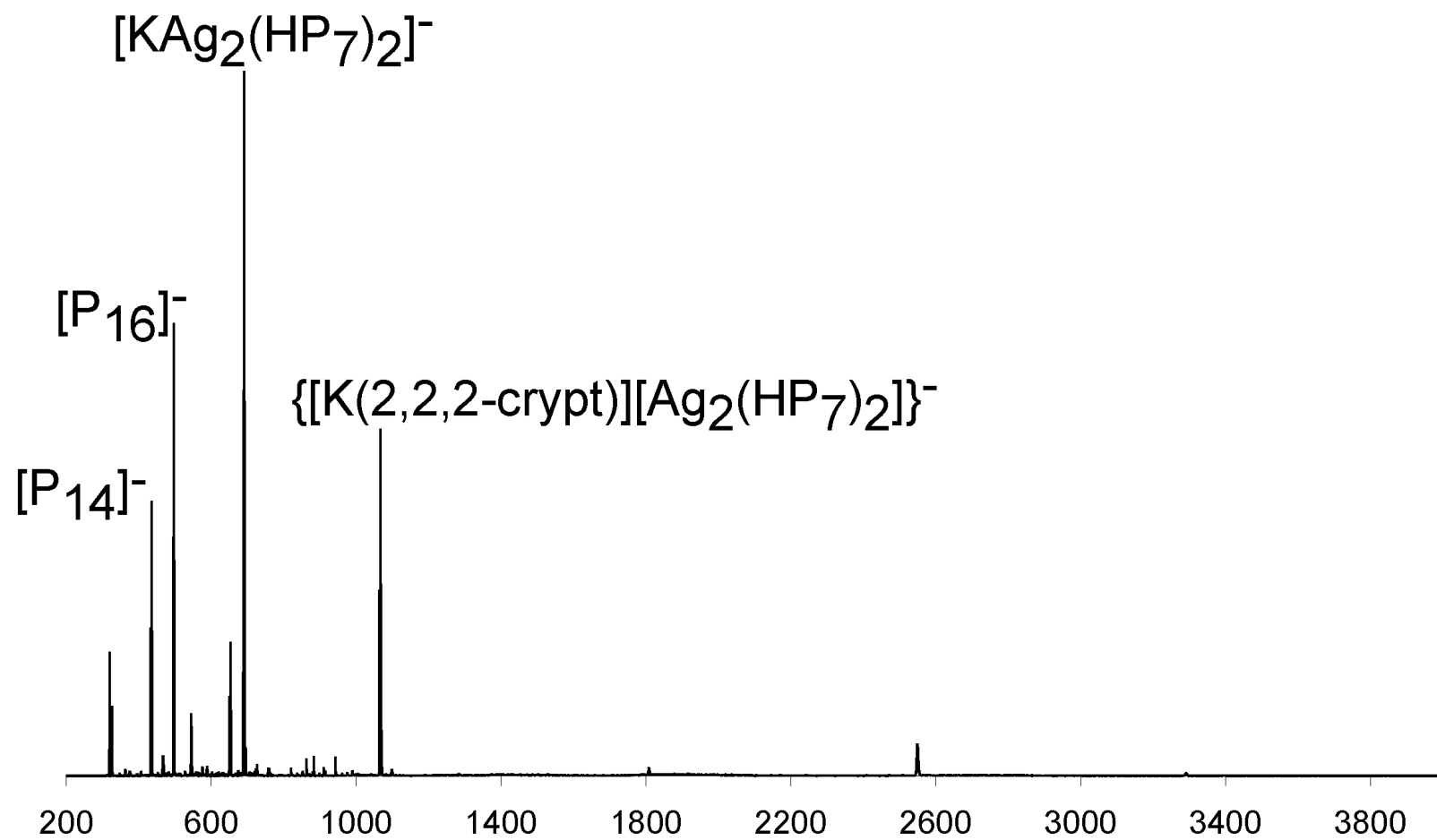


Figure S5. Negative ion mode mass spectrum of a DMF solution of **1**.

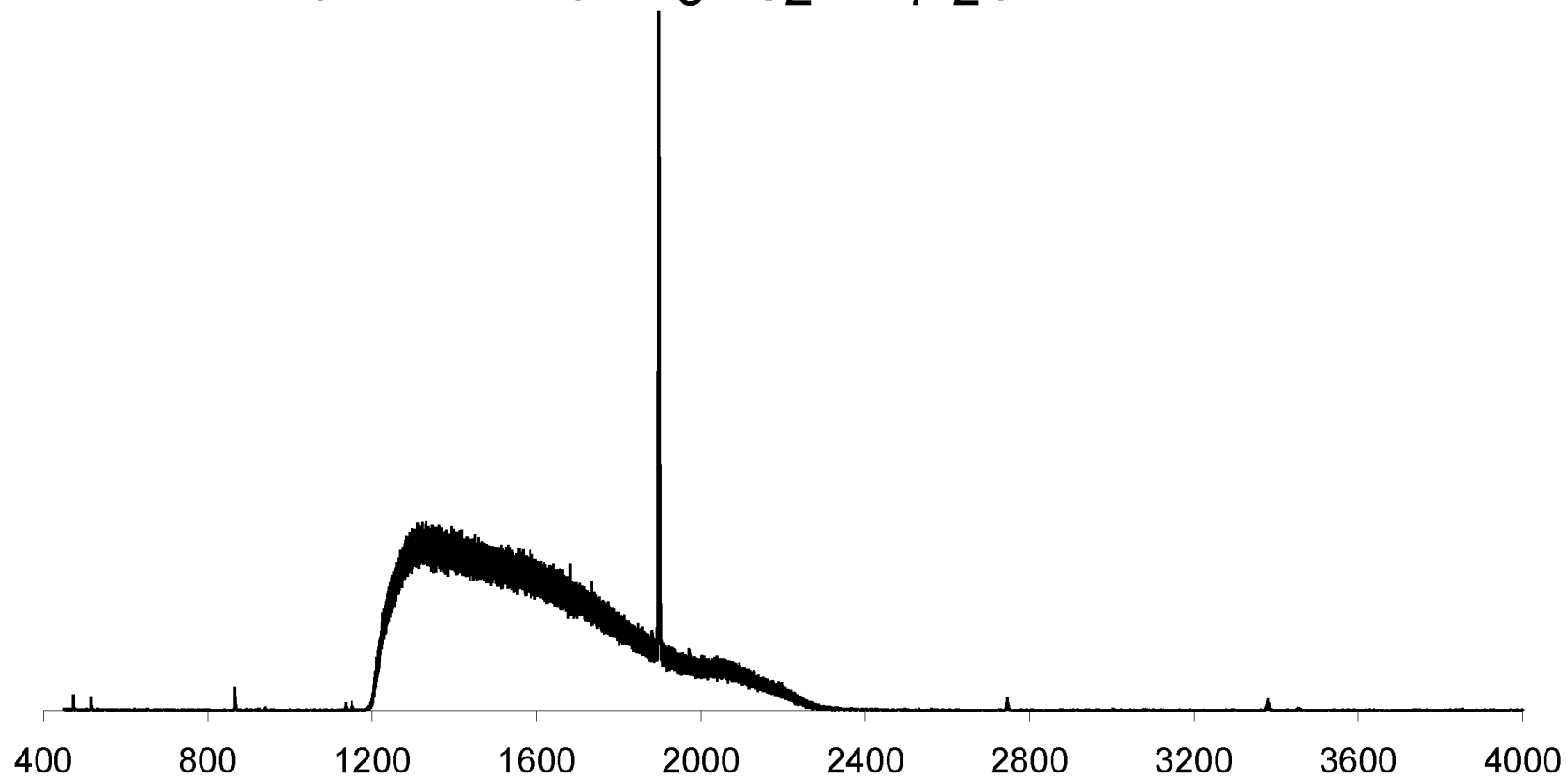
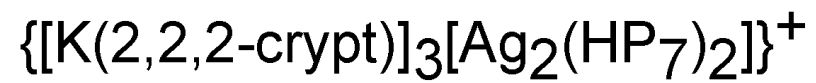


Figure S6. Positive ion mode mass spectrum of a DMF solution of **1**.

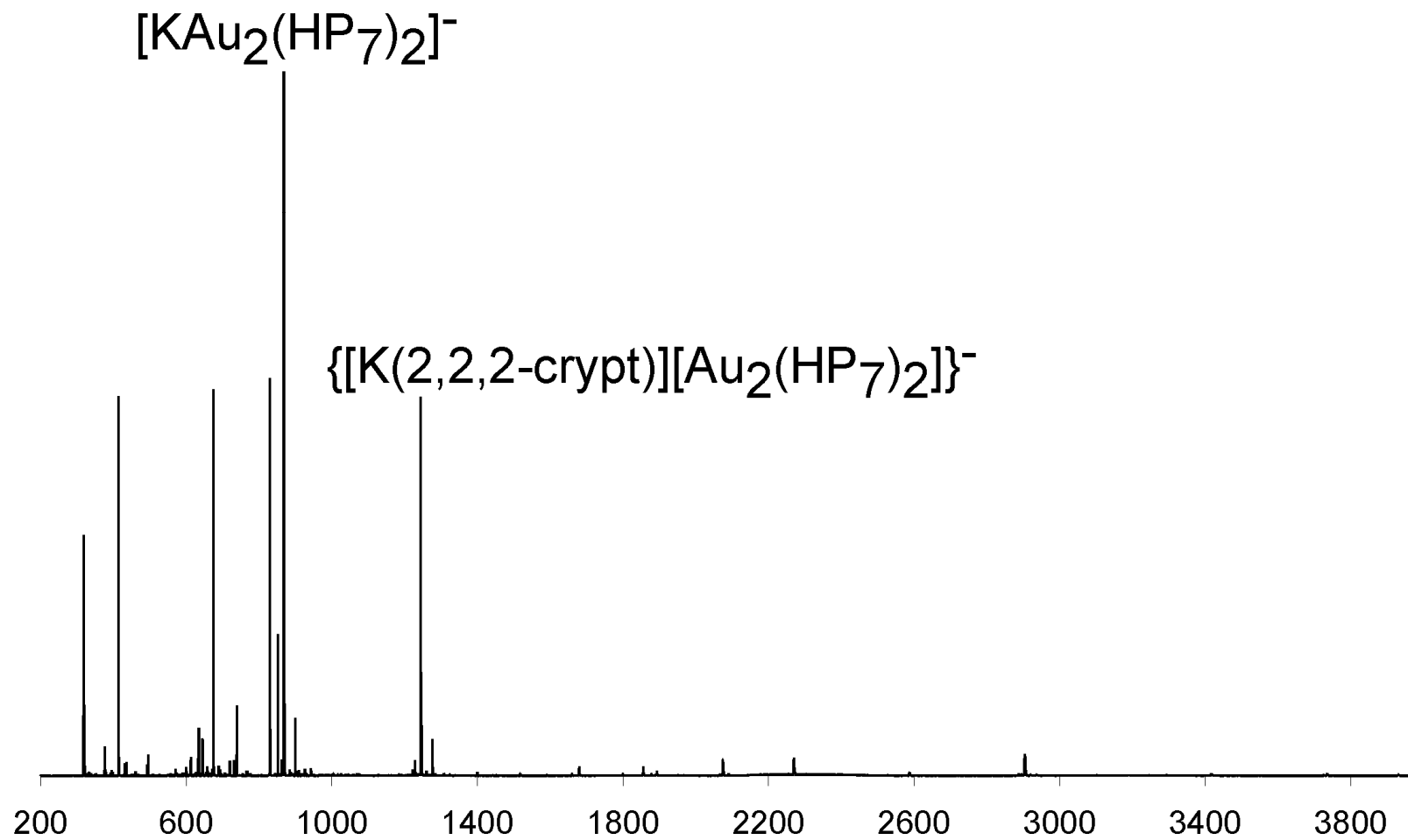


Figure S7. Negative ion mode mass spectrum of a DMF solution of **2**.

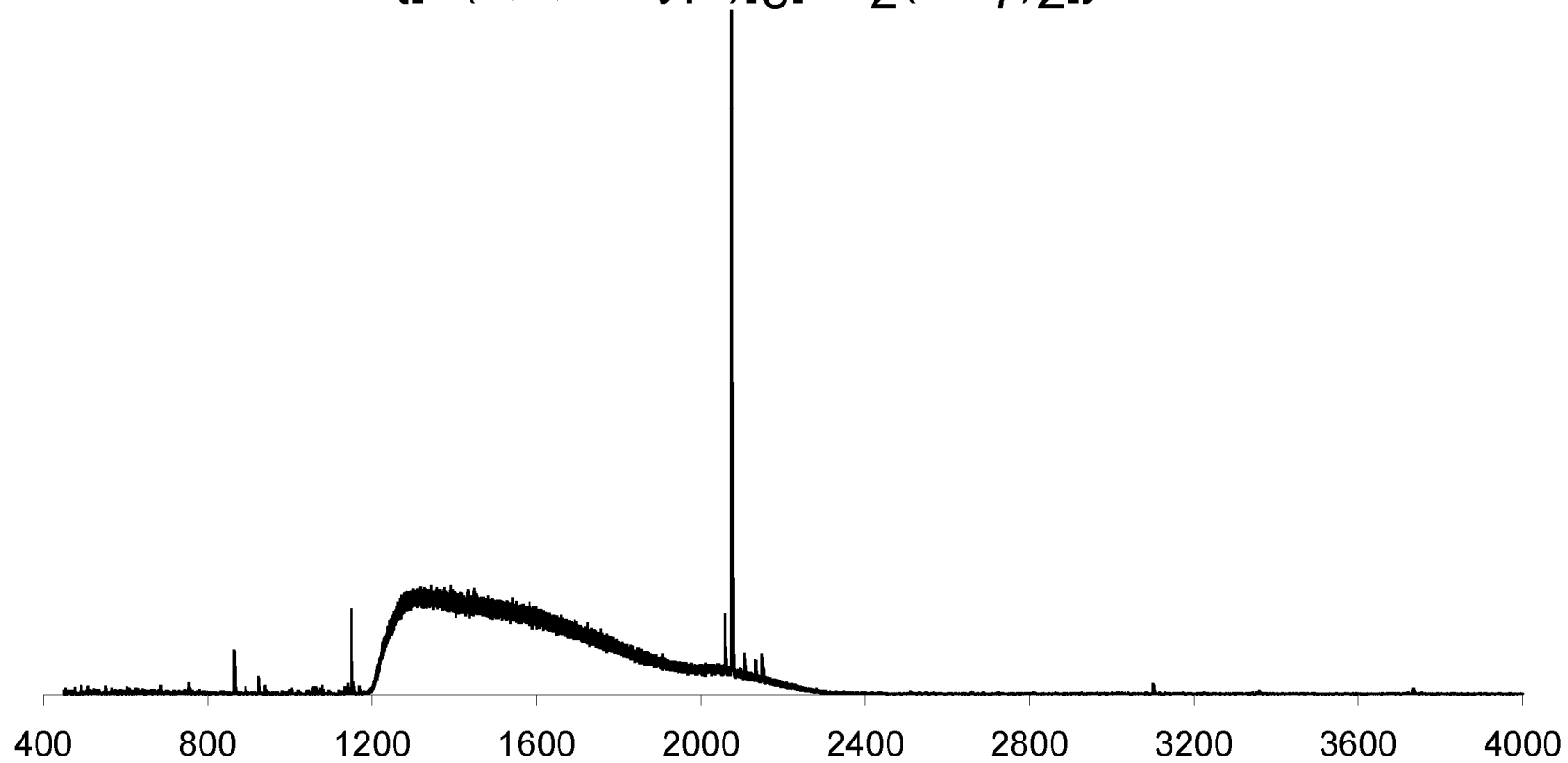
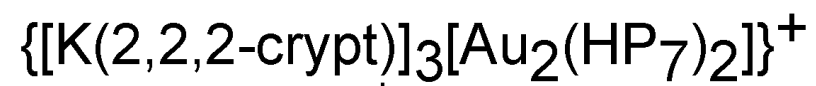


Figure S8. Positive ion mode mass spectrum of a DMF solution of **2**.

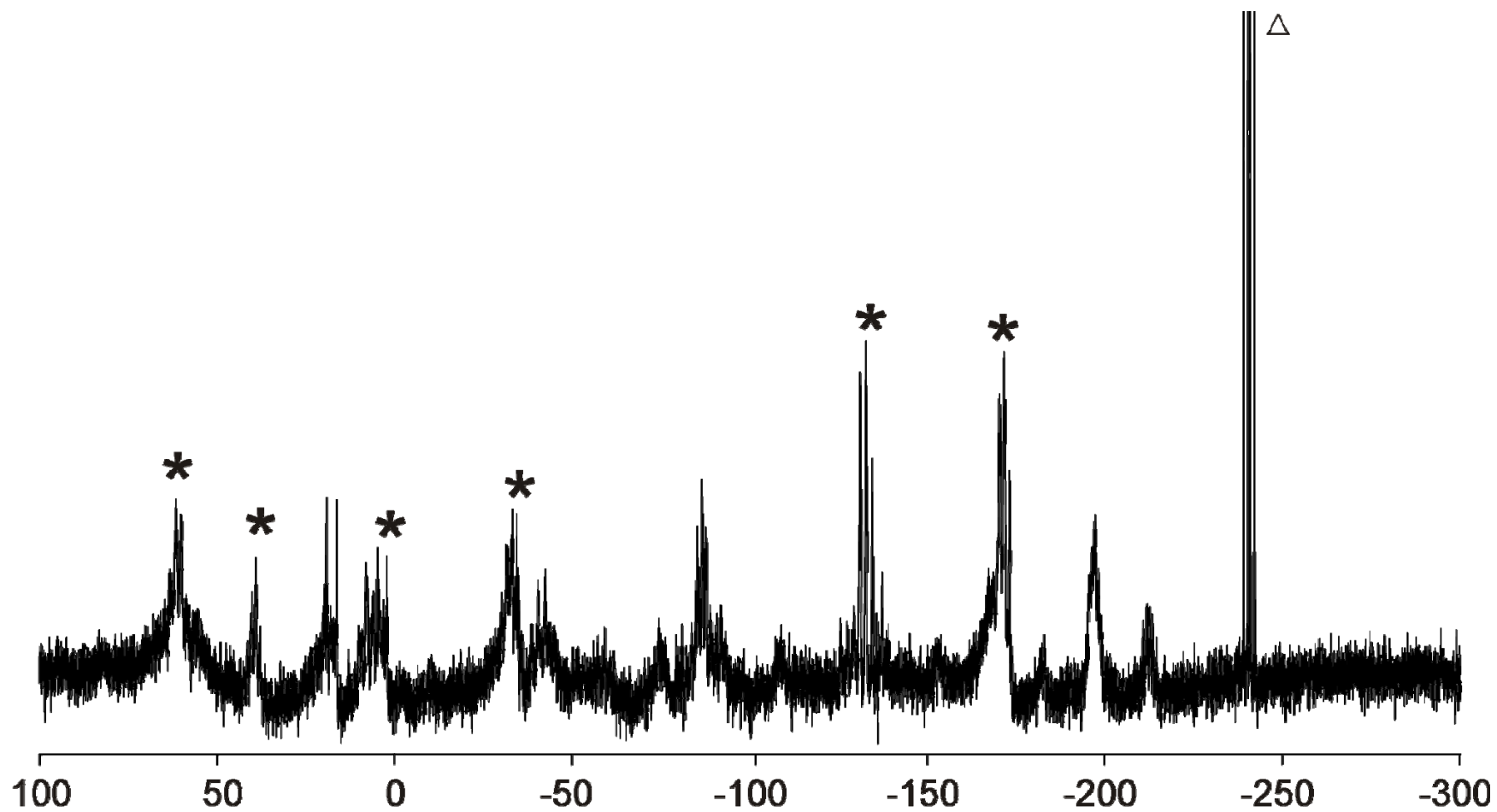


Figure S9. Room temperature ^{31}P NMR spectrum of a d_7 -DMF solution of sample **1**. Resonances highlighted with an asterisk correspond to some $[\text{P}_{16}]^{2-}$ impurity). The resonance marked with a triangle arises due to PH_3 .

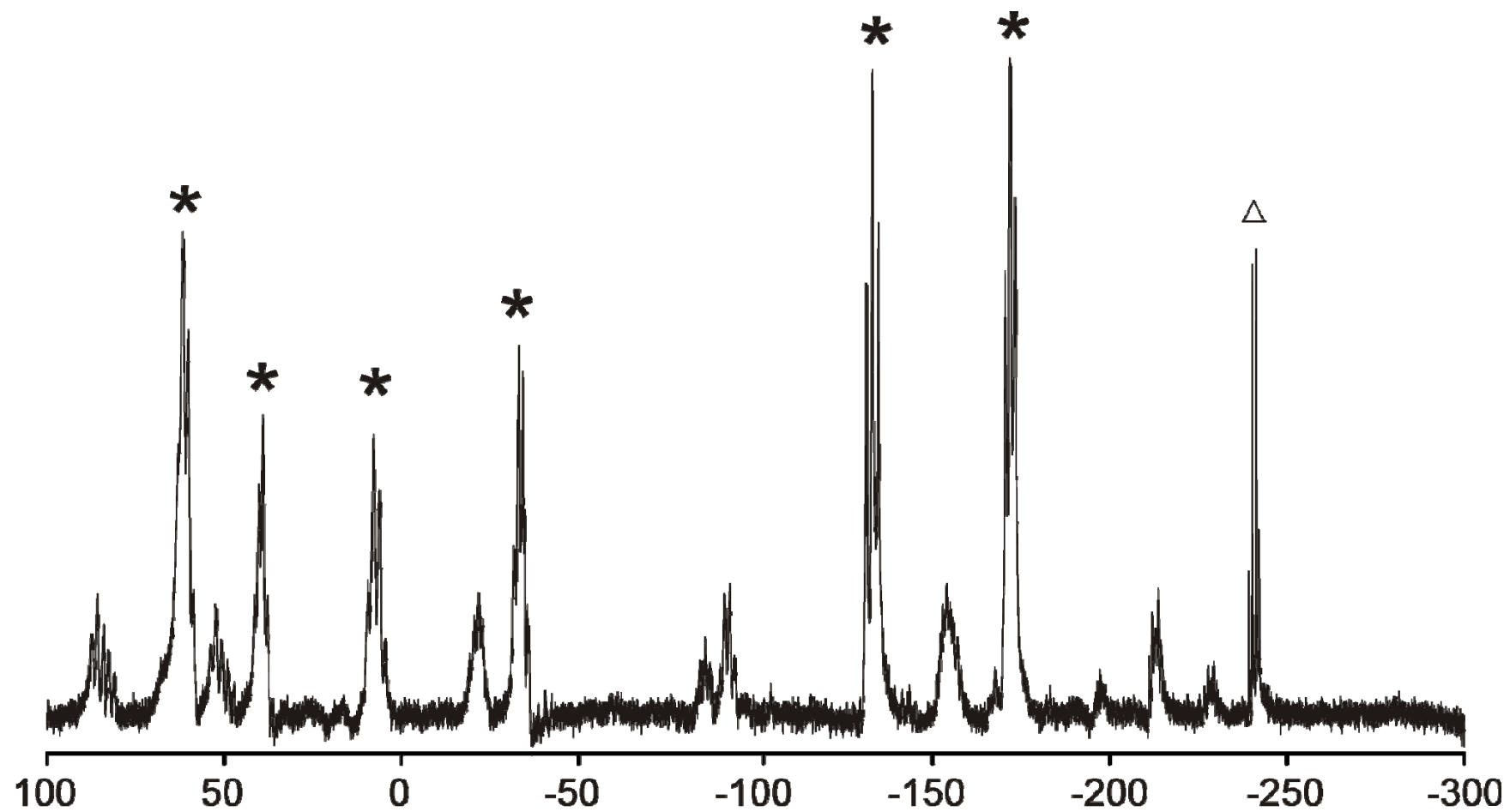


Figure S10. Room temperature ^{31}P NMR spectrum of a d_7 -DMF solution of sample **2**. Resonances highlighted with an asterisk correspond to some $[\text{P}_{16}]^{2-}$ impurity). The resonance marked with a triangle arises due to PH_3 .

- [1] Fianchini, M.; Dai H. X.; Dias, H. V. R. *Chem. Commun.* **2009**, 6373.
- [2] Hooper, T. N.; Butts, C. P.; Green, M.; Haddow, M. F.; McGrady J. E.; Russell, C. A. *Chem.-Eur. J.* **2009**, *15*, 12196.
- [3] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.
- [4] Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100.