| Complex | Formula | Conquest | CCDC | Reference |
|---|---|---|---|---|
| **1** | $[RNH_3][V^V_2O_2(H_1TBC[8])]$ | - | - | 8 |
| **2** | $[V^V_2(p\text{-tolylN})_2(H_2TBC[8])]$ | XENCOI | 155489 | 9 |
| **3** | $[PPh_4][V^V_2O_2(H_1TBC[8])]$ | HEQJIX | 610228 | 10 |
| **4** | $[Li(MeCN)_4][V^V_2O_2(H_1TBC[8])]$ | KUGJIH | 1017371 | 11 |
| **5** | $[Na(MeCN)_5][V^V_2O_2(H_1TBC[8])]$ | KUGHIF | 895365 | 11 |
| **6** | $[^tBuNH_3][V^V_2(p\text{-tolylN})_2(H_1TBC[8])]$ | KUGJOL | 895369 | 11 |
| **7** | $[Na(MeCN)_6][V^V_8Na_7O_{16}(TBC[8])_2(MeCN)_6]$ | KUGHOL | 895366 | 11 |
| **8** | $[V^V_4O_6(TBC[8])]$ | KUGHUR | 895367 | 11 |
| **9** | $[V^V_4Li_6O_8(TBC[8])(O^tBu)_2(THF)_2(Et_2O)_2]$ | KUGJED | 1017370 | 11 |
| **10** | $[V^V_2Nb^V_2O_5(O^iPr)_2(TBC[8])(MeCN)_2]$ | YEKNAH | 2156671 | 12 |
| **11** | $[V^V_2Ta^V_2O_5(O^iPr)_2(TBC[8])(MeCN)_2]$ | YEKMUA | 2156670 | 12 |
| **12** | $[V^V_3V^{IV}_1Nb^V_2O_9(O^nPr)_3(TBC[8])(MeCN)_2]$ | YEKNEL | 2156672 | 12 |
| **13** | $[HNEt_3]_2[V^VO_2(H_5TBC[8])]$ | MIPXIV | 1574244 | 13 |
| **14** | $[HNEt_3]_2[Co^{II}_2(H_5TBC[8])_2]$ | TIQFOP | 631678 | 14 |
| **15a** | $[Sm^{III}_6Co^{II}_8(TBC[8])_2O_2(OH)_4(CO_3)_2(OAc)_4(HCOO)_2(dmf)_8(H_2O)_6]$ | NEWCEZ | 876031 | 15 |
| **15b** | $[Gd^{III}_6Co^{II}_8(TBC[8])_2O_2(OH)_4(CO_3)_2(OAc)_4(HCOO)_2(dmf)_{10}(H_2O)_4]$ | DICZIA | 876032 | 15 |
| **15c** | $[Dy^{III}_6Co^{II}_8(TBC[8])_2O_2(OH)_4(CO_3)_2(OAc)_4(HCOO)_2(dmf)_{10}(H_2O)_4]$ | DICZEW | 876033 | 15 |
| **16a** | $[Dy^{III}_4Co^{II}_4(TBC[8])_2O_2(def)_8(H_2O)_4]$ | PIBXUW | 1548028 | 16 |
| **16b** | $[Er^{III}_4Co^{II}_4(TBC[8])_2O_2(def)_8(H_2O)_4]$ | PIBXOQ | 1548027 | 16 |
| **16c** | $[Y^{III}_4Co^{II}_4(TBC[8])_2O_2(def)_6(H_2O)_6]$ | PIBYEH | 1568708 | 16 |
| **17a** | $[HNEt_3][Y^{III}_6Co^{II}_6(H_1TBC[8])_3(OMe)_6(OAc)_2(CO_3)(dmf)_6(MeOH)]$ | CABBEQ | 2013507 | 17 |
| **17b** | $[HNEt_3][Eu^{III}_6Co^{II}_6(H_1TBC[8])_3(OMe)_6(OAc)_2(CO_3)(dmf)_6(MeOH)]$ | CUZXAZ | 2013506 | 17 |
| **17c** | $[HNEt_3][Dy^{III}_6Co^{II}_6(H_1TBC[8])_3(OMe)_6(OAc)_2(CO_3)(dmf)_6(MeOH)]$ | CUZXED | 2013508 | 17 |
| **18** | $[Co^{II}_2Th^{IV}_4O_2(OH)_2(H_1TBC[8])_2(dmf)_6]$ | JIYSIV | 948469 | 18 |
| **19** | $[Co^{II}_2Li_8(OH)_2(TBC[8])Br_2(MeCN)_4(THF)_6]$ | GAZHUO | 2090098 | 19 |
| **20** | $[Co^{II}_2Li_6(OH)_2(TBC[8])Br_2(MeCN)_4]$ | GAZJAW | 2090100 | 19 |
| **21** | $[Co^{II}_4Na(H_4TBC[8])_2Br(MeCN)_6]$ | GAZCUJ | 2152002 | 19 |
| **22** | $[Ge^{II}_4(TBC[8])][Fe^0_2(CO)_8]$ | XUGKOA | 709989 | 20 |
| **23** | $[Ge^{IV}_4(C[8])][Fe^{-I}_2(CO)_8]_4$ | LIPHAU | 665344 | 21 |
| **24** | $[Fe^{III}_4K_4O_2(H_2O)_2(H_2TBC[8])_2(MeCN)_6]$ | GUQZOI | 749033 | 22 |
| **25** | $[Mn^{III}_2Na_4(H_5TBC[8])_2(CO_3)_2(dmf)_6]$ | BAKDIC | 824374 | 23 |
| **26** | $[Mn^{III}Mn^{IV}(H_4TBC[8])(Ph\text{-}sao)(\mu\text{-}OMe)(dmf)_2]$ | BEYHOE | 914769 | 24 |
| **27** | $[Mn^{II}_5(H_4TBC[8])(OH)_2(OMe)_{1.5}(HCOO)(OAc)_{0.5}(O_2CNMe_2)(dmf)_5]$ | XIPHOV | 888020 | 25 |
| **28** | $[Ni^{II}_2Th^{IV}_5O_4(OH)_2(H_1TBC[8])_2(dmf)_5(MeOH)_2]$ | JIYSOB | 948470 | 18 |
| **29a** | $[Cr^{III}Gd^{III}_6O_2(OH)(TBC[8])_2(H_2O)_4(dmf)_5(MeOH)_2]$ | HANWAX | 1517454 | 27 |
| **29b** | $[Cr^{III}Tb^{III}_6O_2(OH)(TBC[8])_2(H_2O)_4(dmf)_5(MeOH)_2]$ | HANWOL | 1517457 | 27 |
| **29c** | $[Cr^{III}Dy^{III}_6O_2(OH)(TBC[8])_2(H_2O)_4(dmf)_5(MeOH)_2]$ | HANWIF | 1517456 | 27 |
| **29d** | $[Cr^{III}Tm^{III}_6O_2(OH)(TBC[8])_2(H_2O)_4(dmf)_5(MeOH)_2]$ | HANWEB | 1517455 | 27 |
| **30** | $[Eu^{III}_2(H_2TBC[8])(dmf)_5]$ | FUVVEX | 1161880 | 28 |
| **31** | $[Eu^{III}(H_6TBC[8])(NO_3)(dmf)_4]$ | SOGDOH | 1261238 | 33 |
| **32** | $[Gd^{III}(H_6TBC[8])Cl(dmso)_4]$ | VESVEW | 892672 | 34 |
| **33** | $[Ce^{IV}_4O_2(H_2TBC[8])_2(dmf)_4]$ | VESVIA | 892673 | 34 |
| **34** | $[Tb^{III}_5O(OH)_4(H_3TBC[8])Cl(dmso)_8(H_2O)_3]Cl_3$ | VESVOG | 892674 | 34 |
| **35** | $[Ce^{IV}_6O_4(H_2TBC[8])_2(OMe)_4(dmf)_6]$ | VESVUM | 892675 | 34 |
| **36** | $[Dy^{III}_7O_2(OH)_4(H_1TBC[8])(H_2TBC[8])(dmf)_9]$ | VESWAT | 892676 | 34 |
| **37** | $[NaDy^{III}(H_6TBC[8])(OAc)_2(dmf)_3]$ | JOJJAW | 1902422 | 35 |
| **38** | $[Gd^{III}_8(H_1TBC[8])_2(CO_3)_4(HCOO)_2(dmf)_8]$ | VESWEX | 892677 | 34 |
| **39a** | $[La^{III}_{18}O_3(OH)_{12}(TBC[8])_3(CO_3)_2Cl_6(H_2O)_6(dmf)_{18}Cl]OH$ | KOFWEL | 2299004 | 37 |
| **39b** | $[Nd^{III}_{18}O_3(OH)_{12}(TBC[8])_3(CO_3)_2Cl_6(H_2O)_6(dmf)_{18}Cl]OH$ | - | - | 37 |
| **39c** | $[Gd^{III}_{18}O_3(OH)_{12}(TBC[8])_3(CO_3)_2Cl_6(H_2O)_6(dmf)_{18}Cl]OH$ | - | - | 37 |

**Table S1**. A list of all known *p*-tert-butylcalix[8]arene-supported transition (3d limited to V – Cu) and lanthanide metal complexes in the literature. The table provides the number of the complex in this review, the formula of each complex, the relevant Conquest code, CCDC number and reference in the main text.

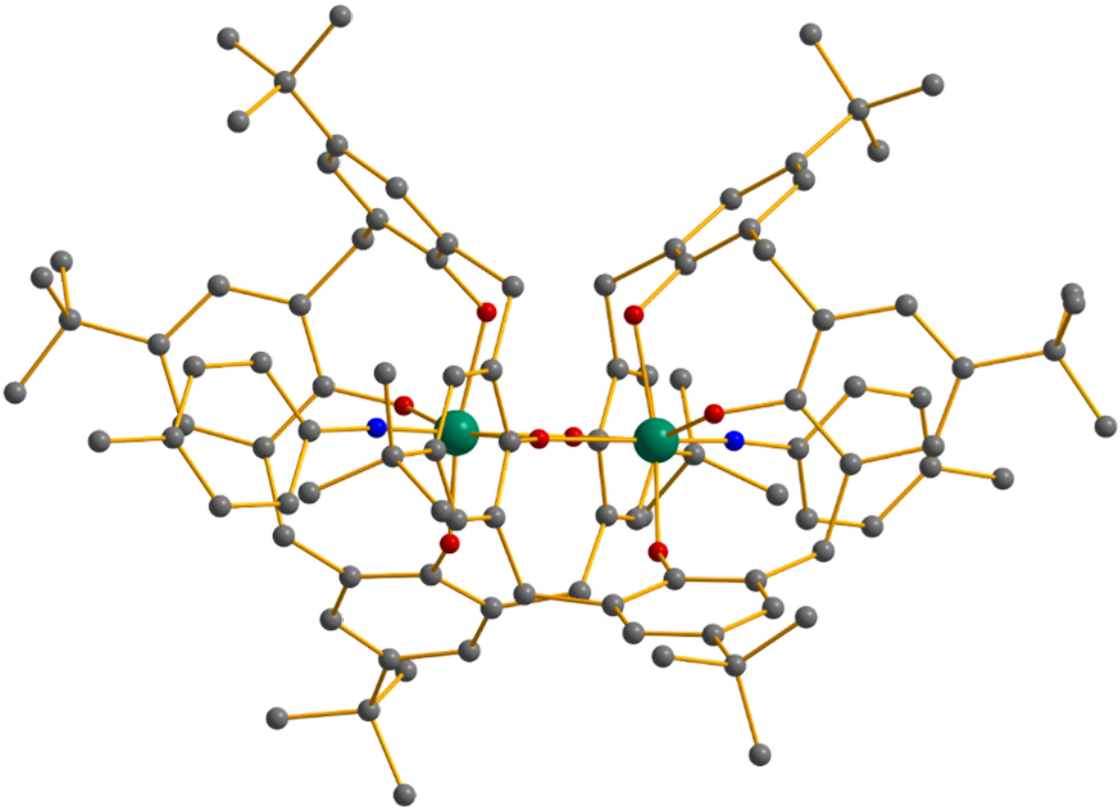


**Figure S1**. Structure of the [$V_2$] dimer in **2**. Colour code: V = dark green, O = red, N = blue, C = grey. H atoms, counter ions omitted for clarity.

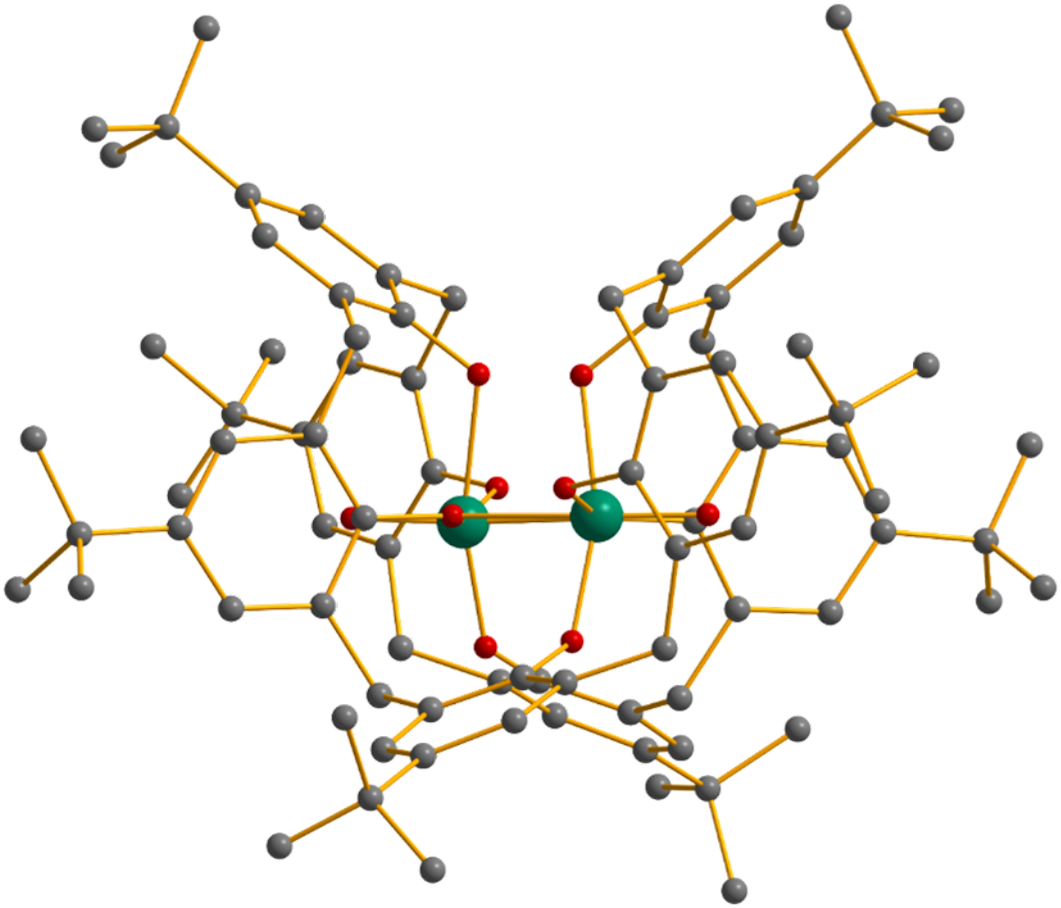


**Figure S2**. Structure of the [$V_2$] dimer present in **3**-**5**. Colour code: V = dark green, O = red, C = grey. H atoms, counter ions omitted for clarity.

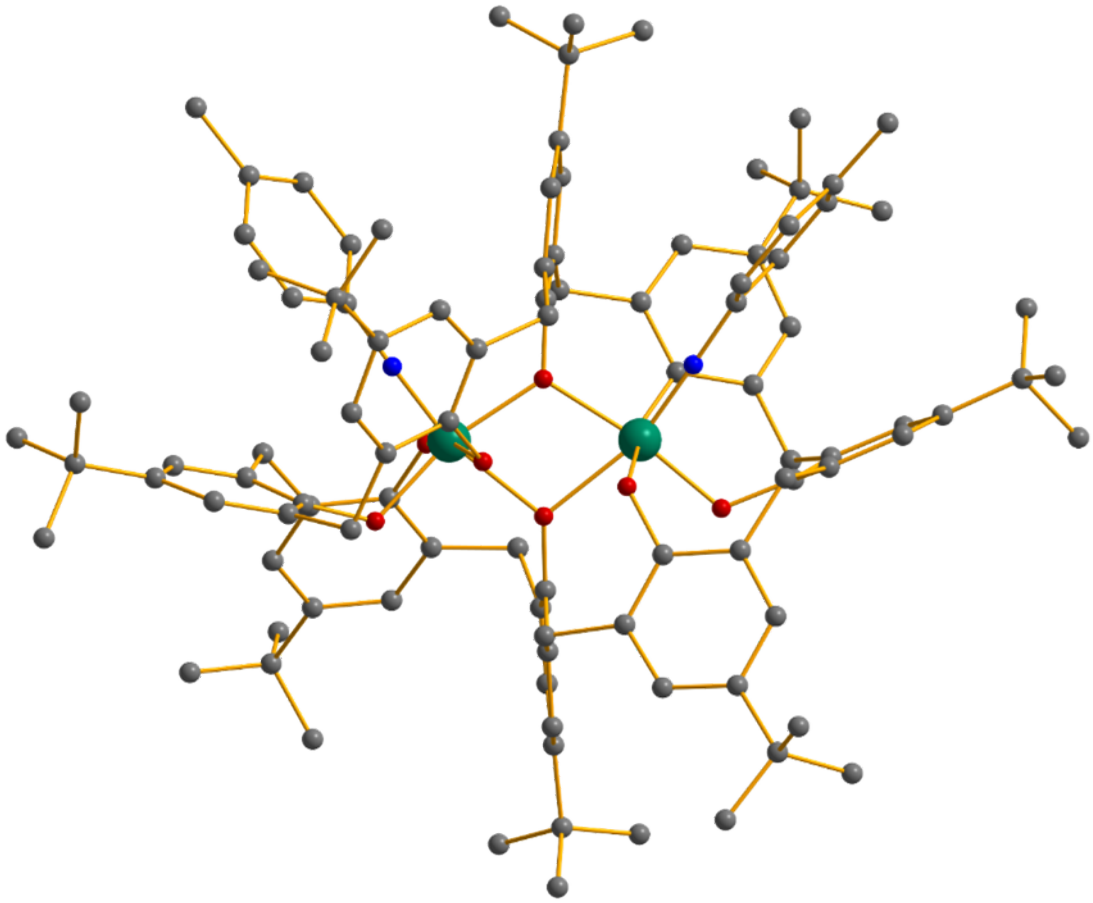


**Figure S3**. Structure of the [$V_2$] dimer present in **6**. Colour code: V = dark green, O = red, N = blue, C = grey. H atoms, counter ions omitted for clarity.

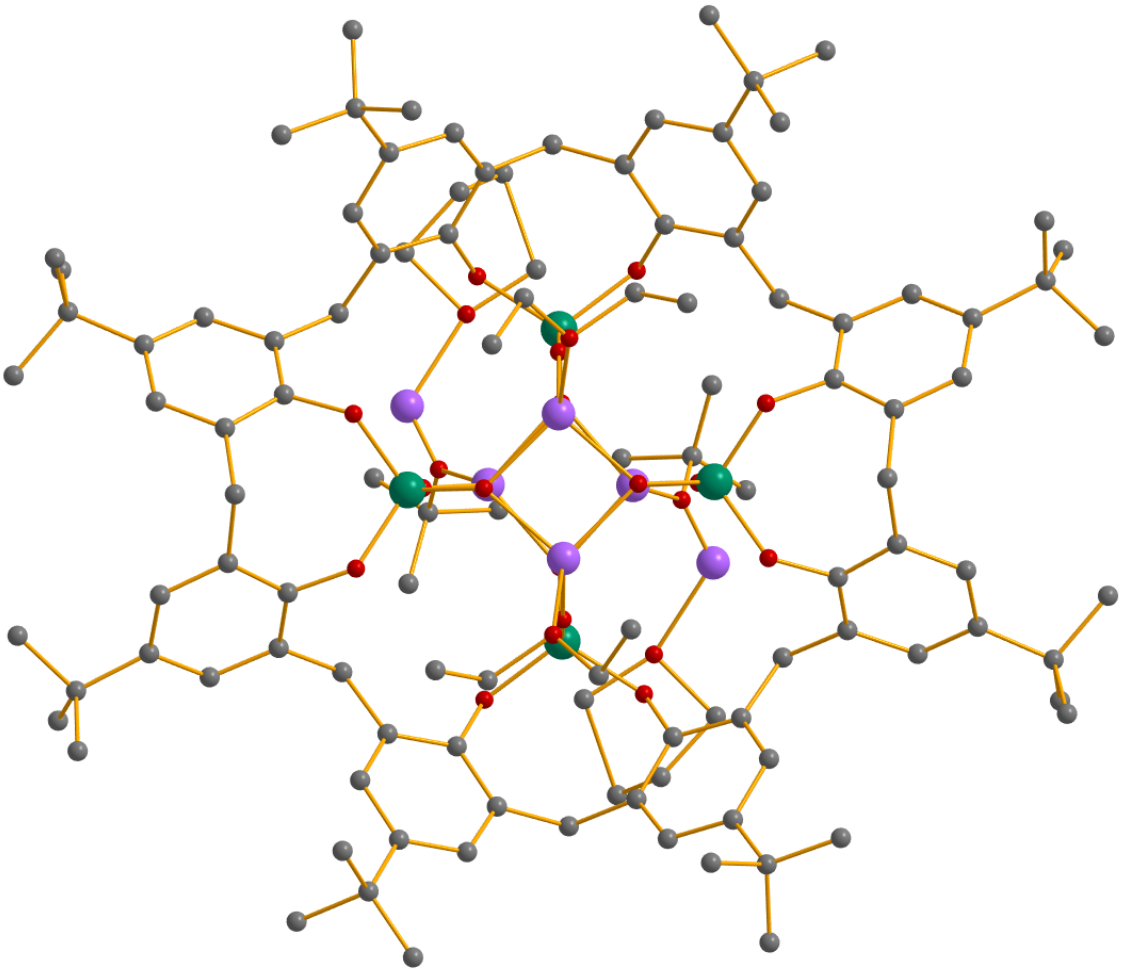


**Figure S4**. Structure of the [$V_4Li_6$] cluster in **9**. Colour code: V = dark green, Li = light purple, O = red, C = grey. H atoms omitted for clarity.

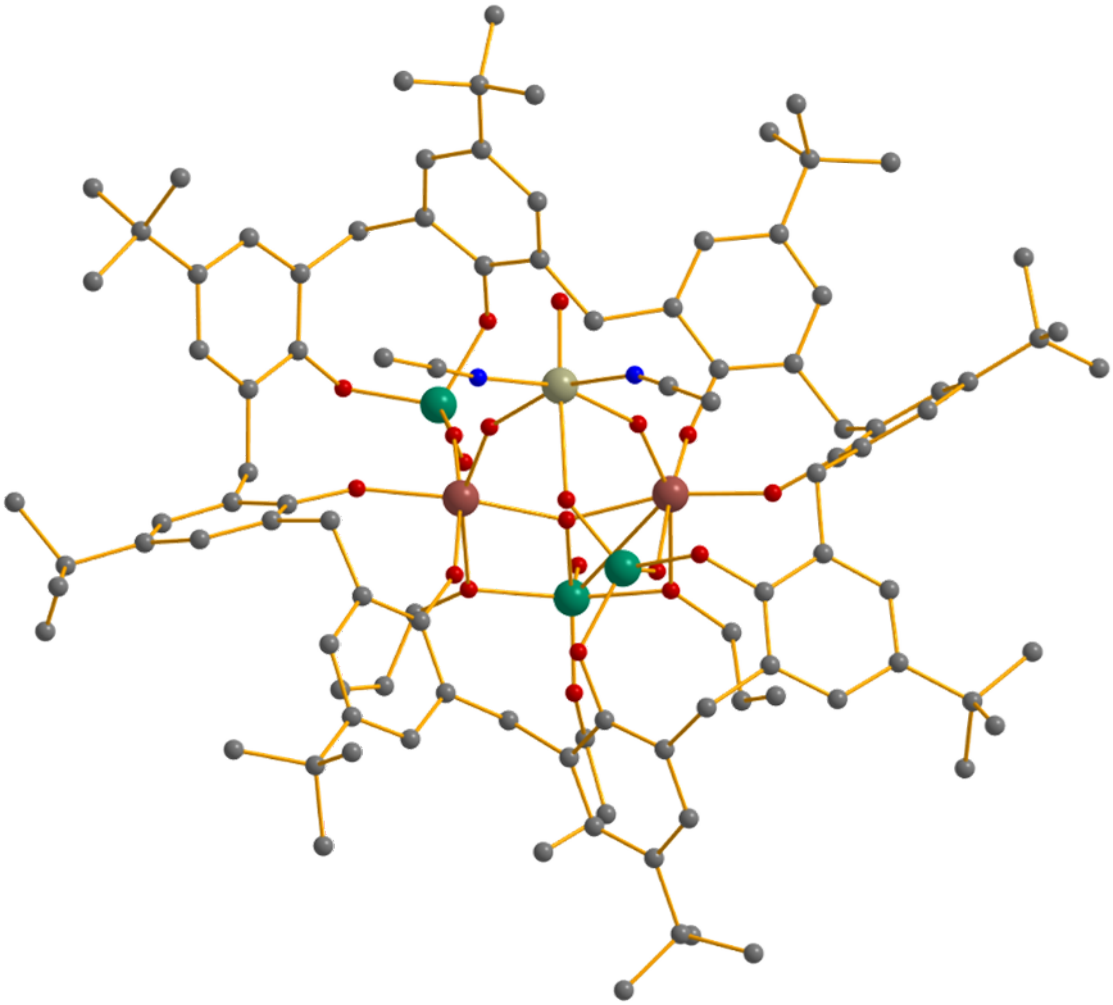


**Figure S5**. Structure of compound **12**. Colour code: $V^{V}$ = dark green, $V^{IV}$ = sage green, Nb = maroon, O = red, N = blue, C = grey. H atoms omitted for clarity.

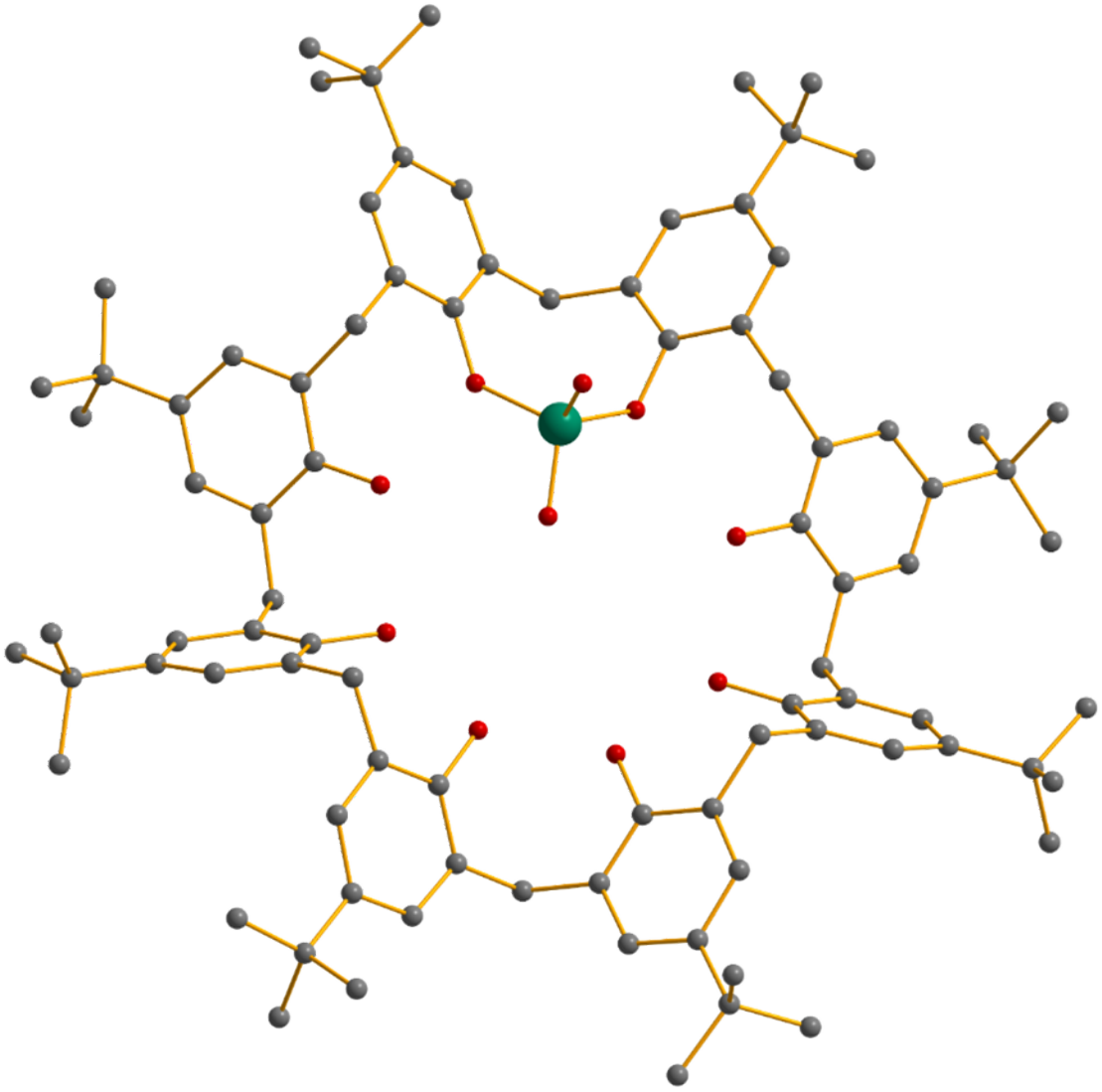


**Figure S6**. Structure of compound **13**. Colour code: V = dark green, O = red, C = grey. H atoms, counter ions omitted for clarity.

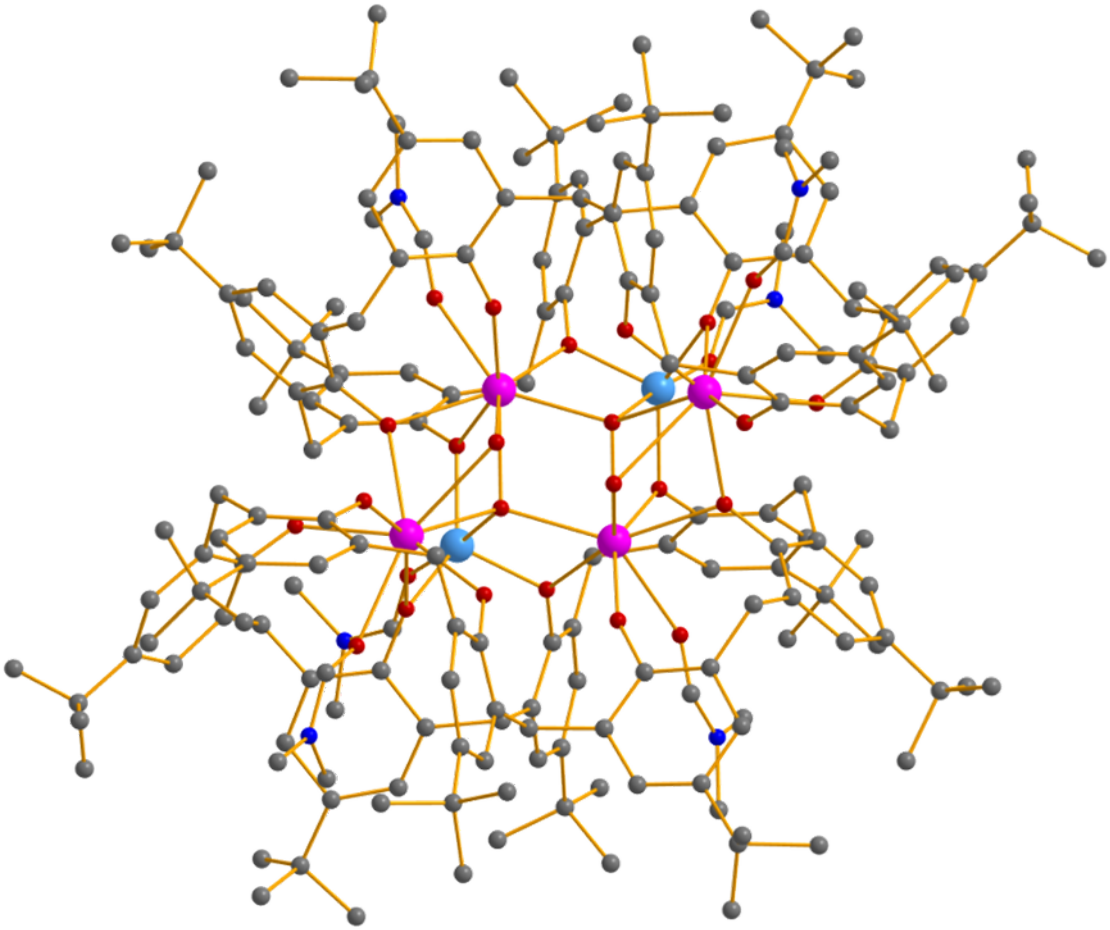


**Figure S7**. Structure of compound **18**. Colour code: Co = sky blue, Th = deep pink, O = red, N = blue, C = grey. H atoms omitted for clarity.

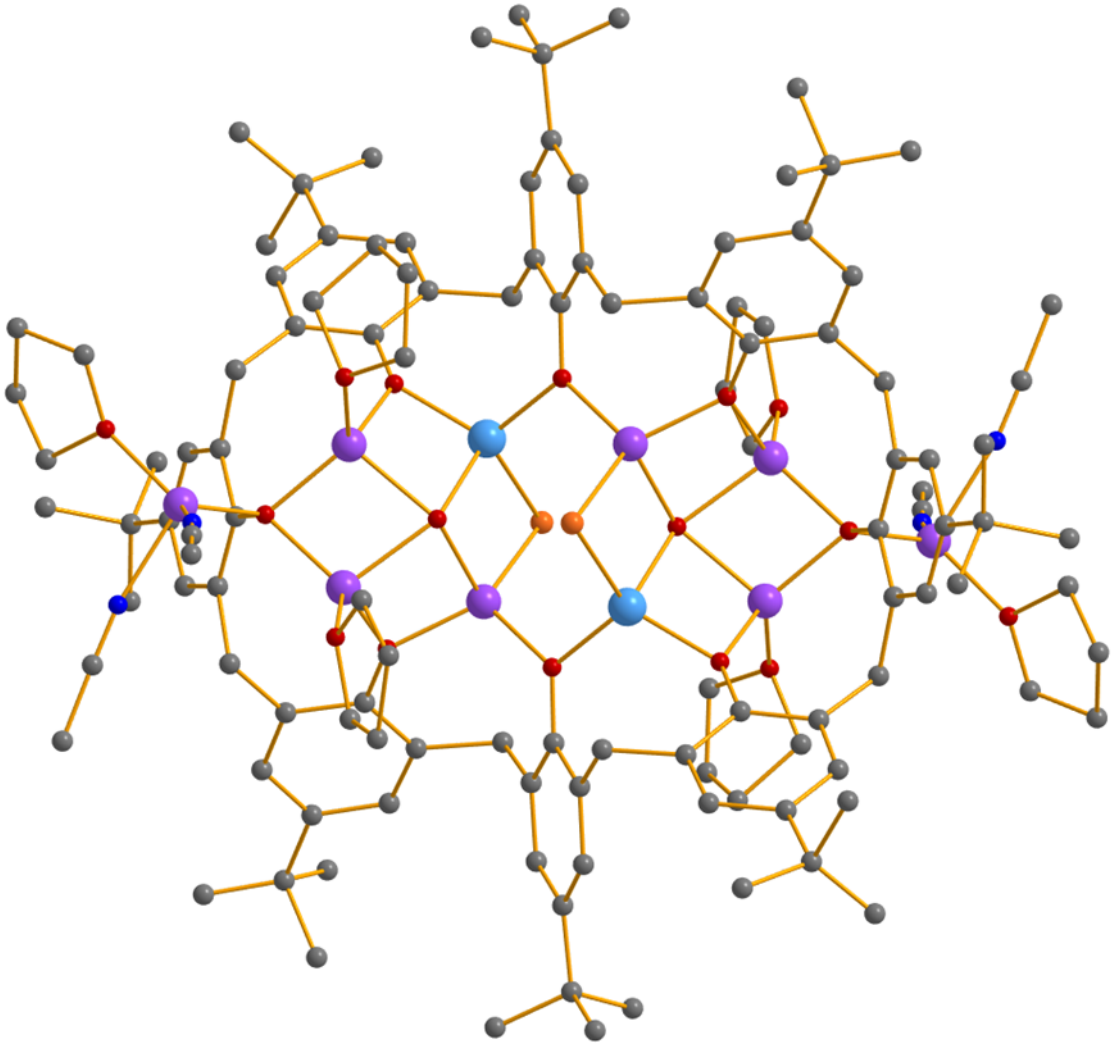


**Figure S8**. Structure of compound **19**. Colour code: Co = sky blue, Li = light purple, O = red, N = blue, C = grey, Br = orange. H atoms omitted for clarity.

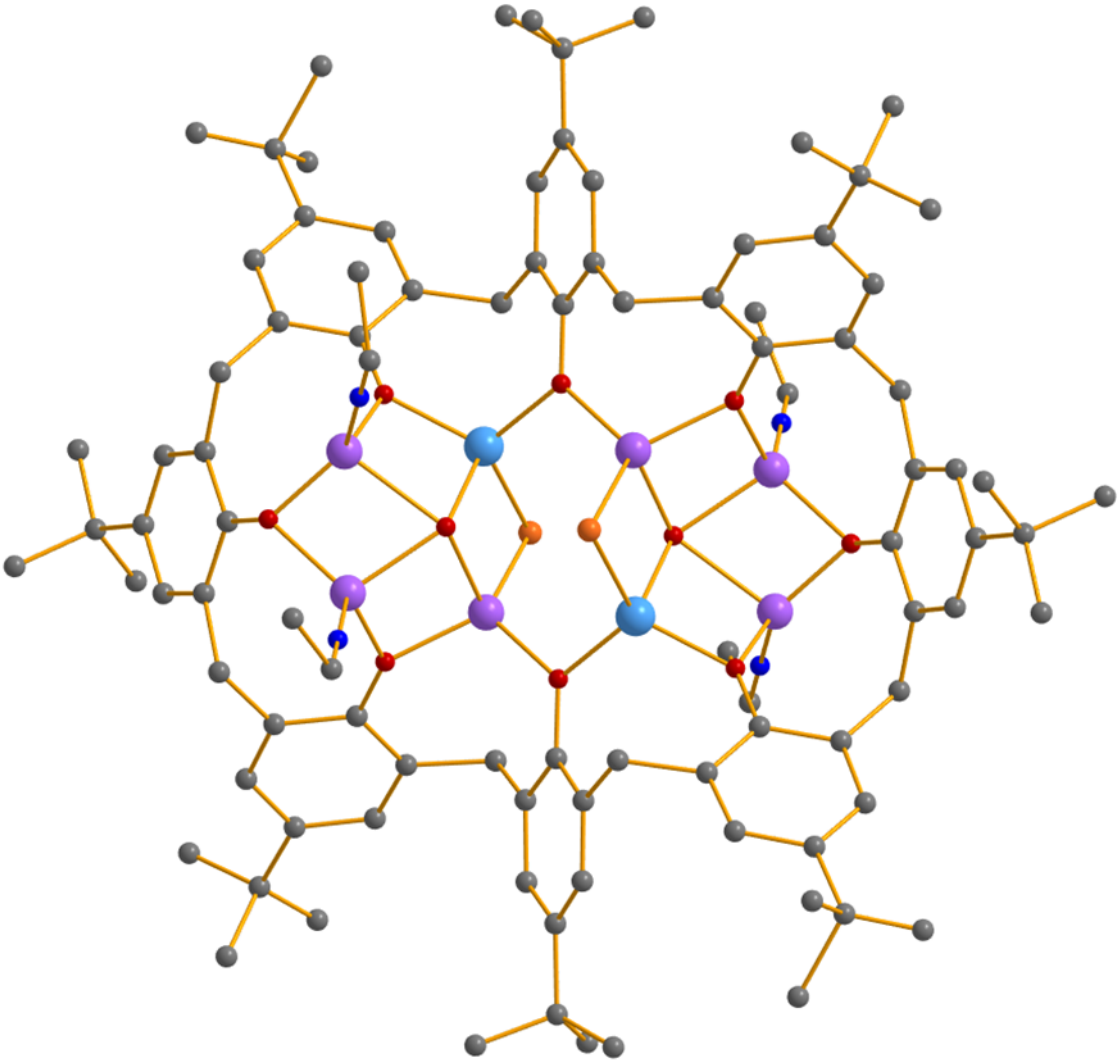


**Figure S9**. Structure of compound **20**. Colour code: Co = sky blue, Li = light purple, O = red, N = blue, C = grey, Br = orange. H atoms omitted for clarity.

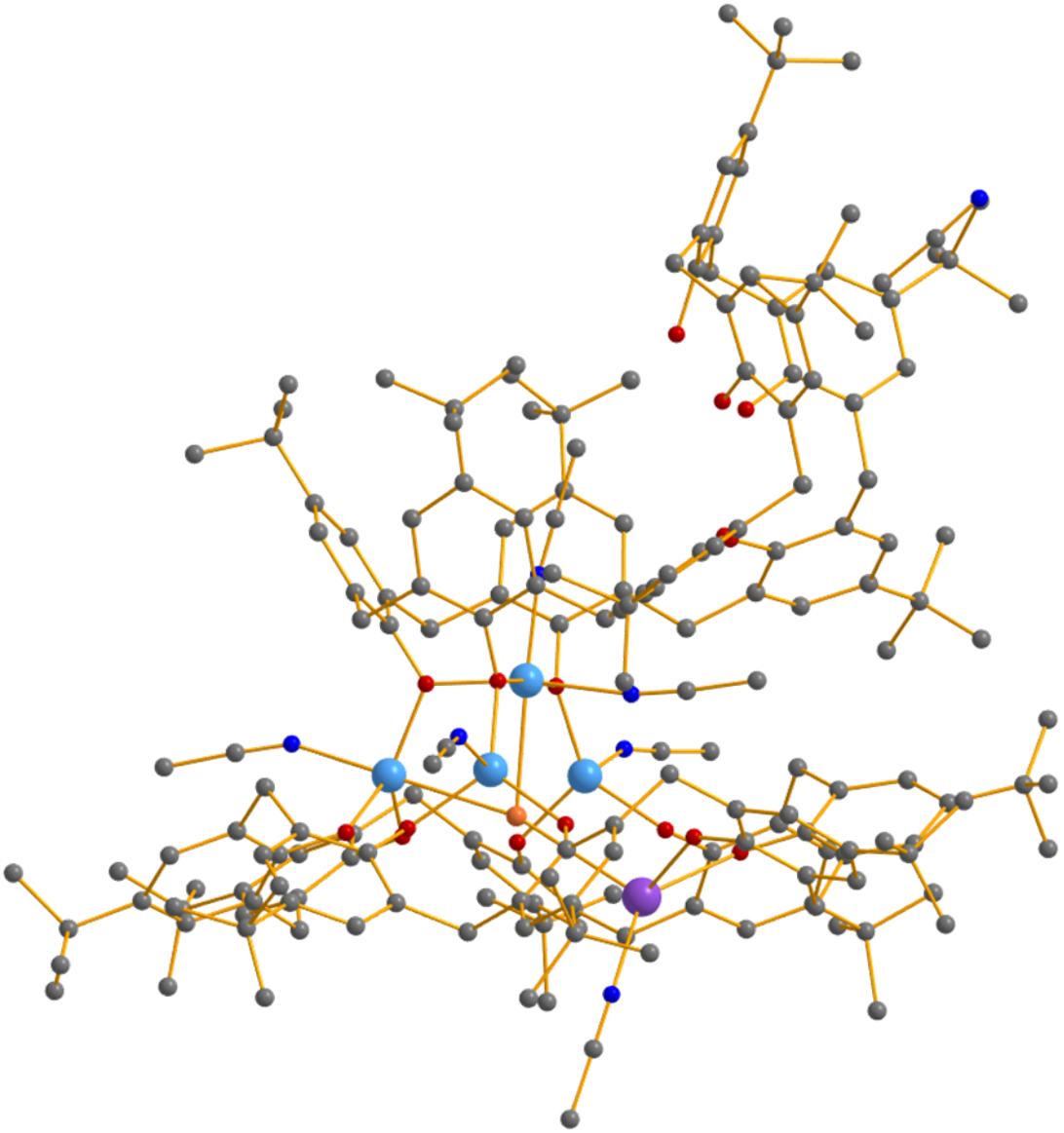


**Figure S10**. Structure of compound **21**. Colour code: Co = sky blue, Na = purple, O = red, N = blue, C = grey, Br = orange. H atoms omitted for clarity.

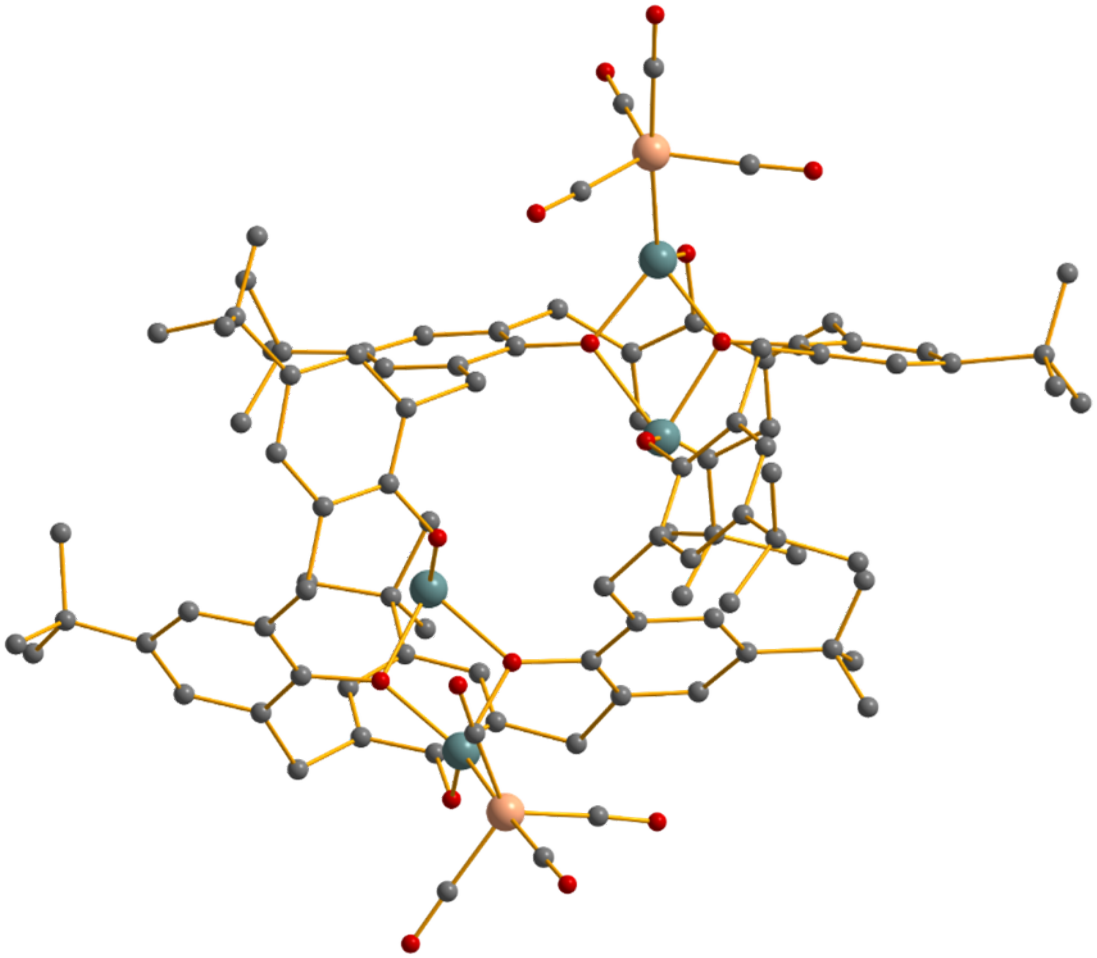


**Figure S11**. Structure of compound **22**. Colour code: Fe = pale orange, Ge = teal, O = red, C = grey. H atoms omitted for clarity.

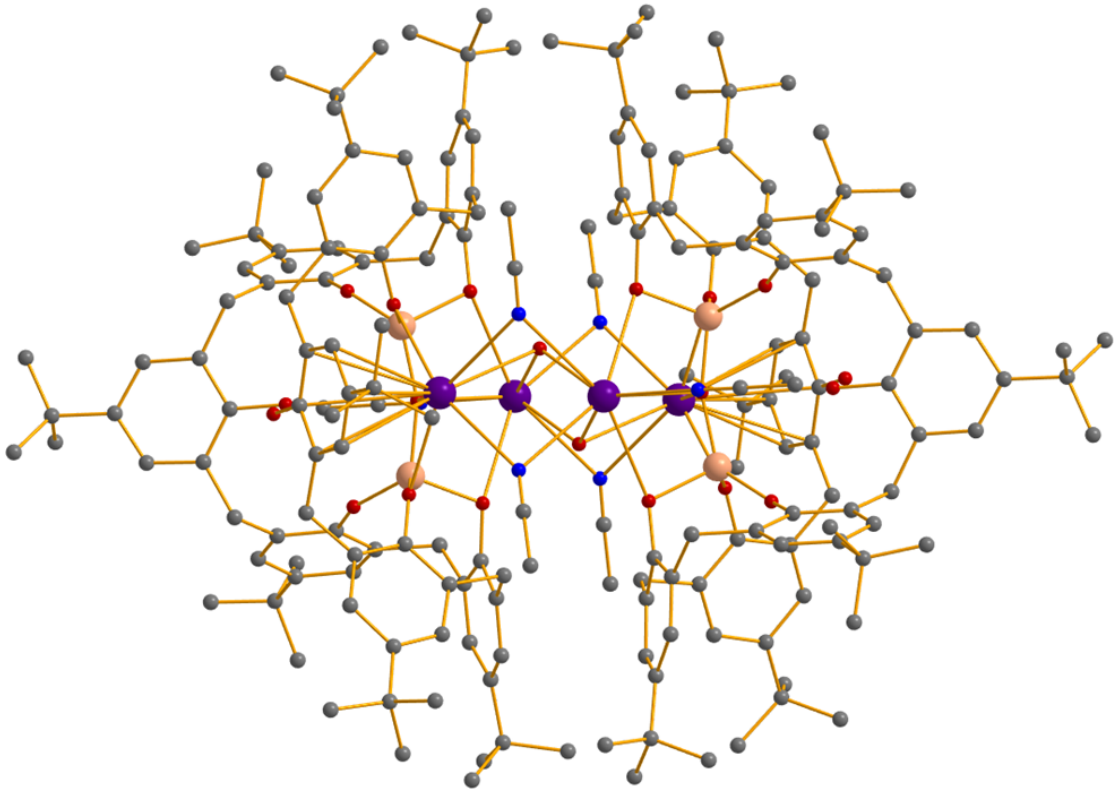


**Figure S12**. Structure of compound **24**. Colour code: Fe = pale orange, K = deep purple, O = red, N = blue, C = grey. H atoms omitted for clarity.

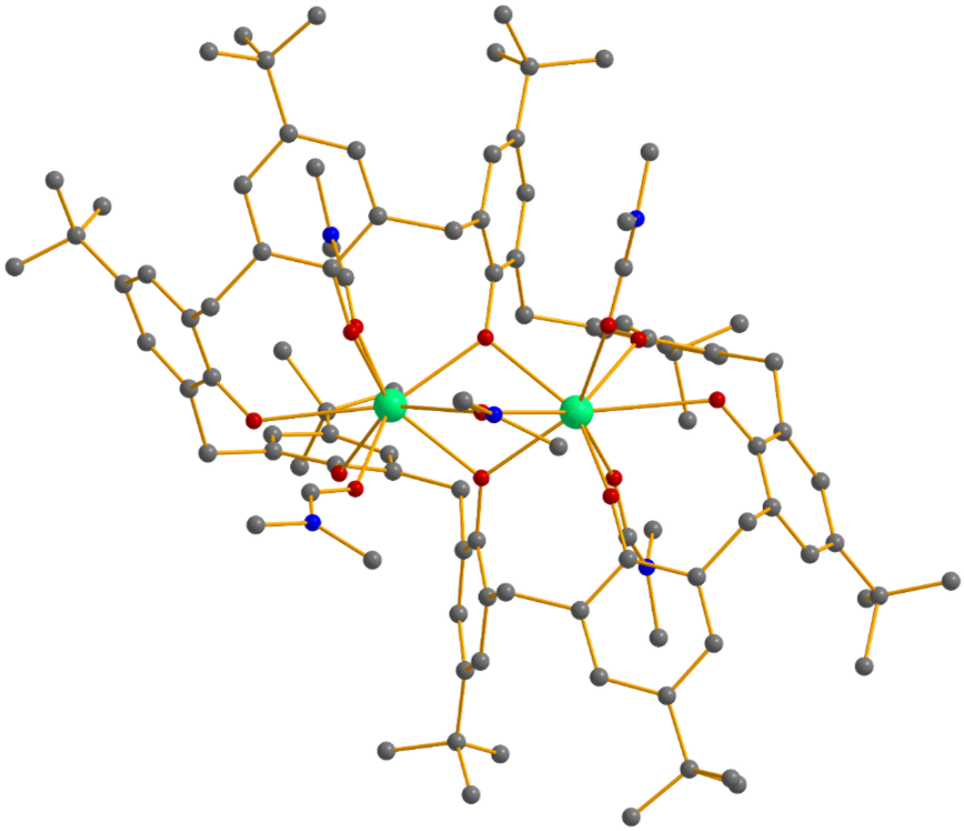


**Figure S13**. Structure of compound **30**. Colour code: Ln = light green, O = red, N = blue, C = grey. H atoms omitted for clarity.

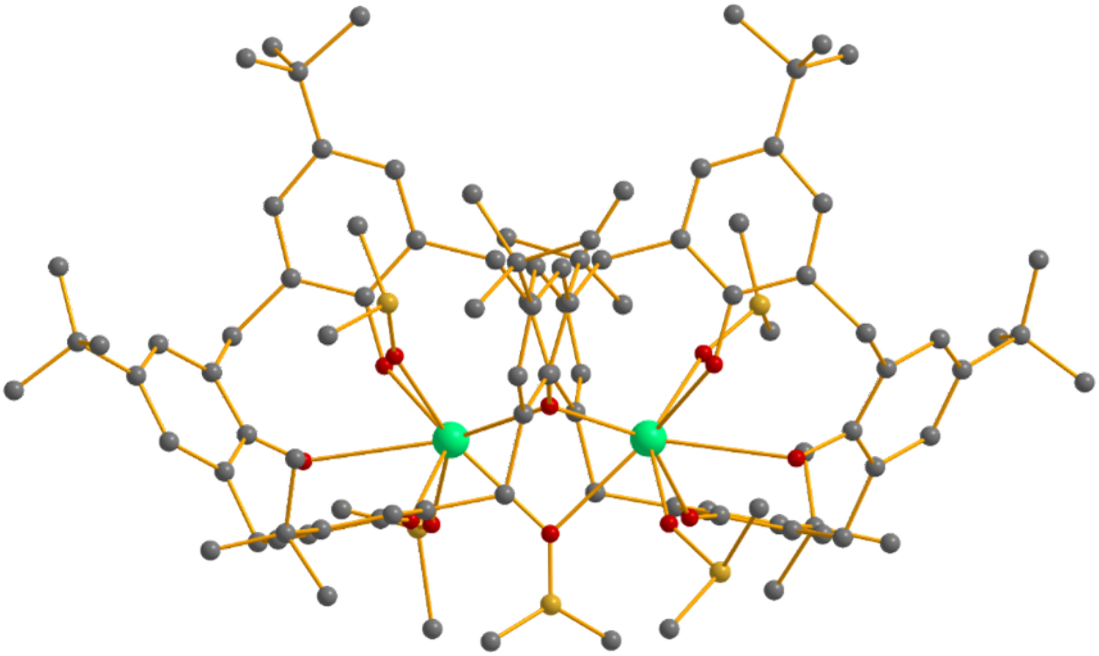


**Figure S14**. Structure of compound **30** with dmso replacing dmf. Colour code: Ln = light green, O = red, C = grey, S = dark yellow. H atoms omitted for clarity.

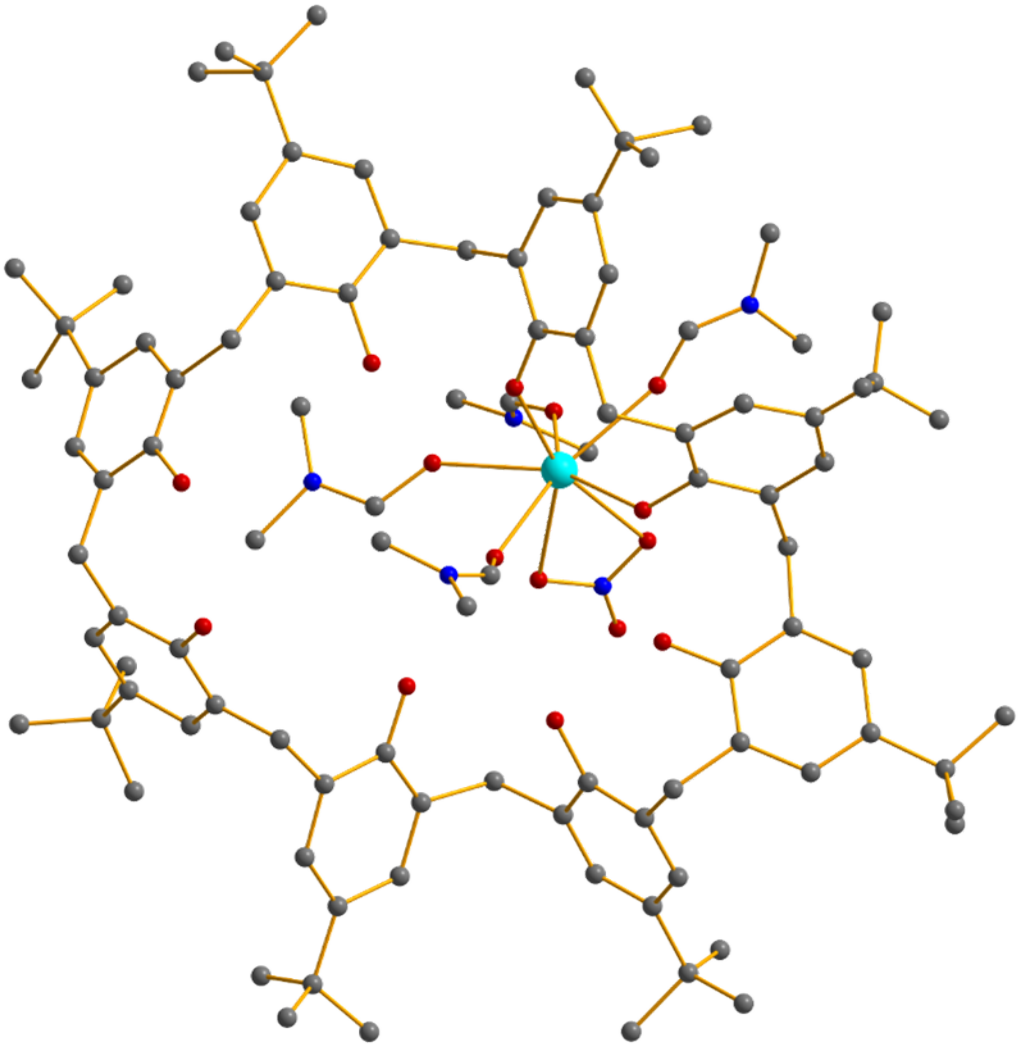


**Figure S15**. Structure of compound **31**. Colour code: Eu = light blue, O = red, N = blue, C = grey. H atoms omitted for clarity.

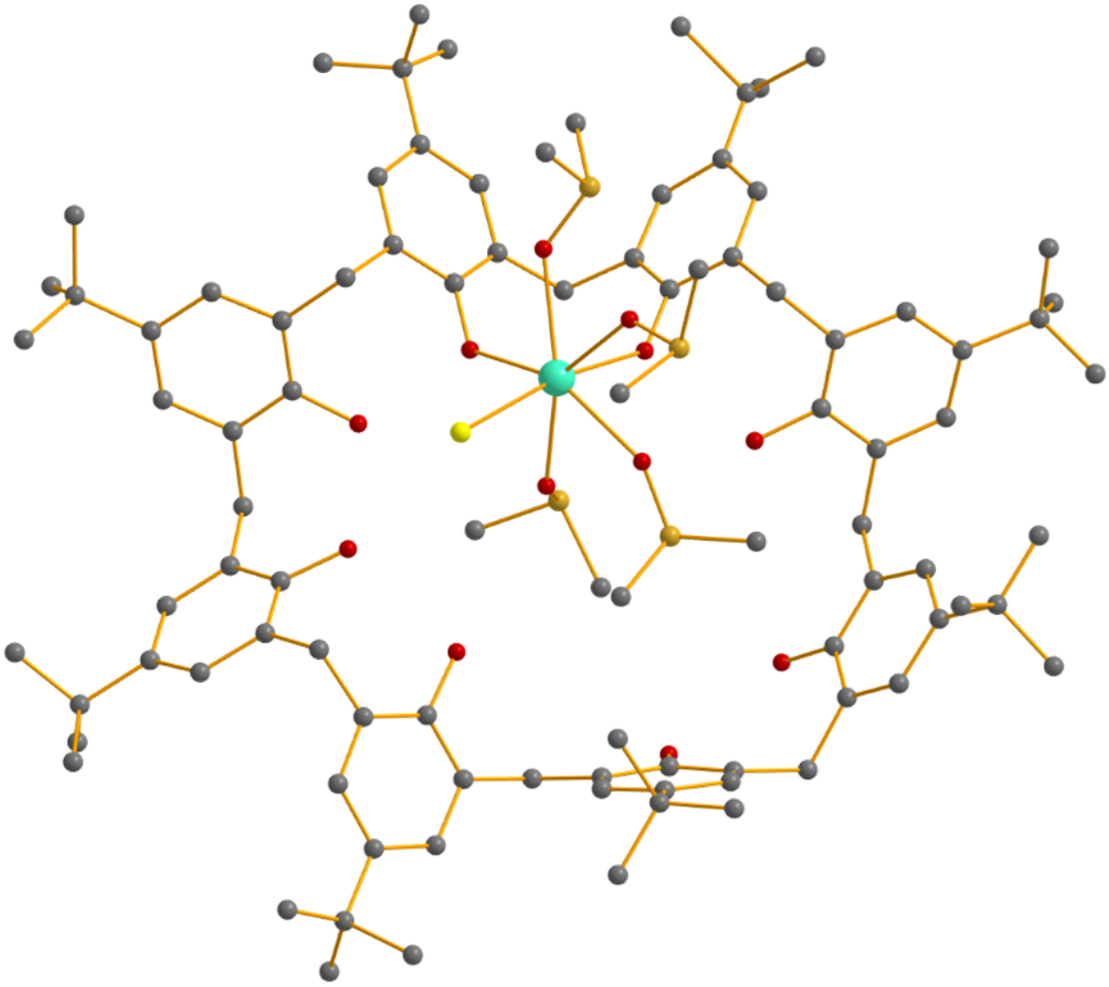


**Figure S16**. Structure of compound **32**. Colour code: Gd = cyan, O = red, C = grey, S = dark yellow, Cl = yellow. H atoms omitted for clarity.

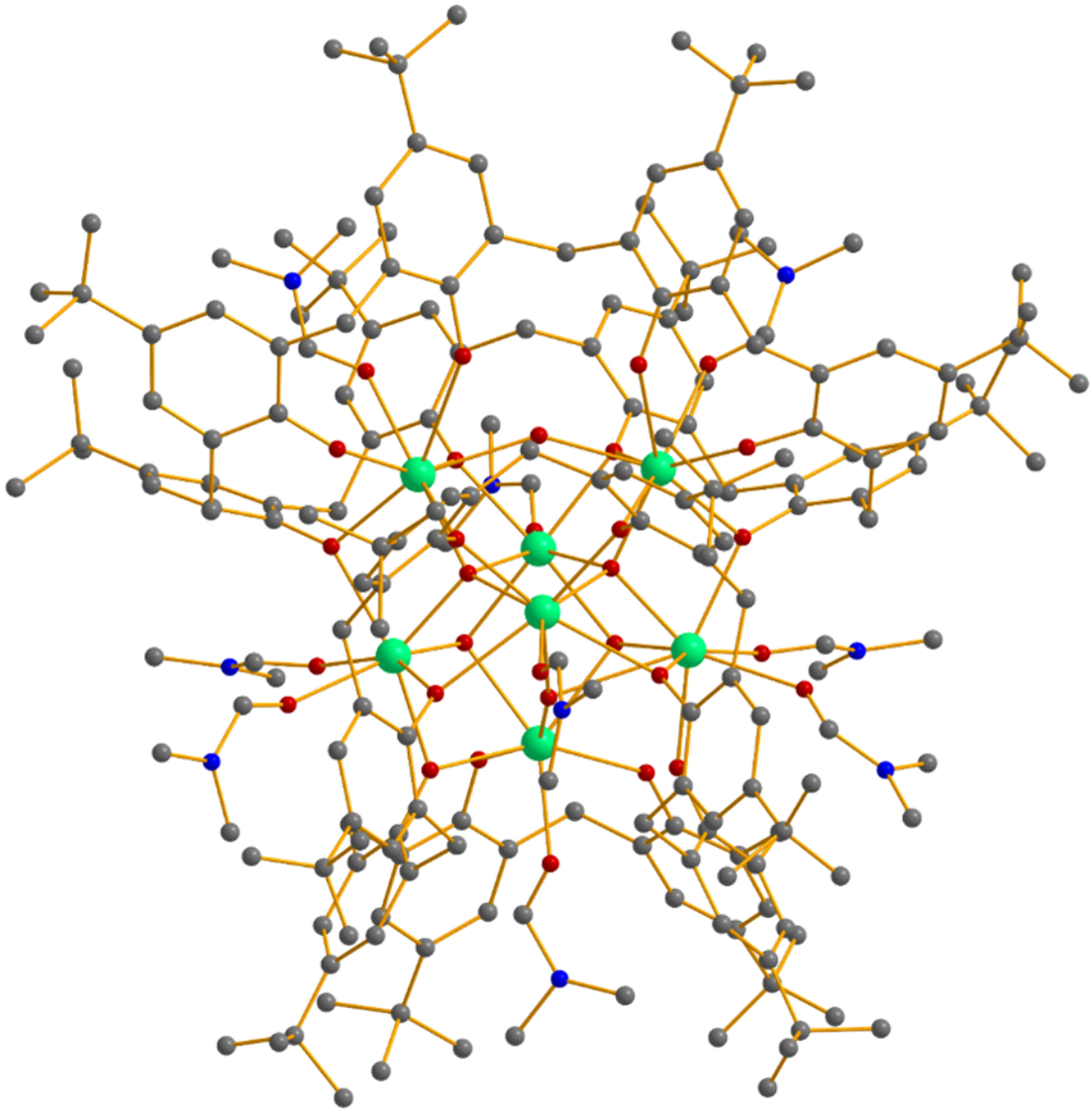


**Figure S17**. Structure of compound **36**. Colour code: Dy = green, O = red, N = blue, C = grey. H atoms omitted for clarity.

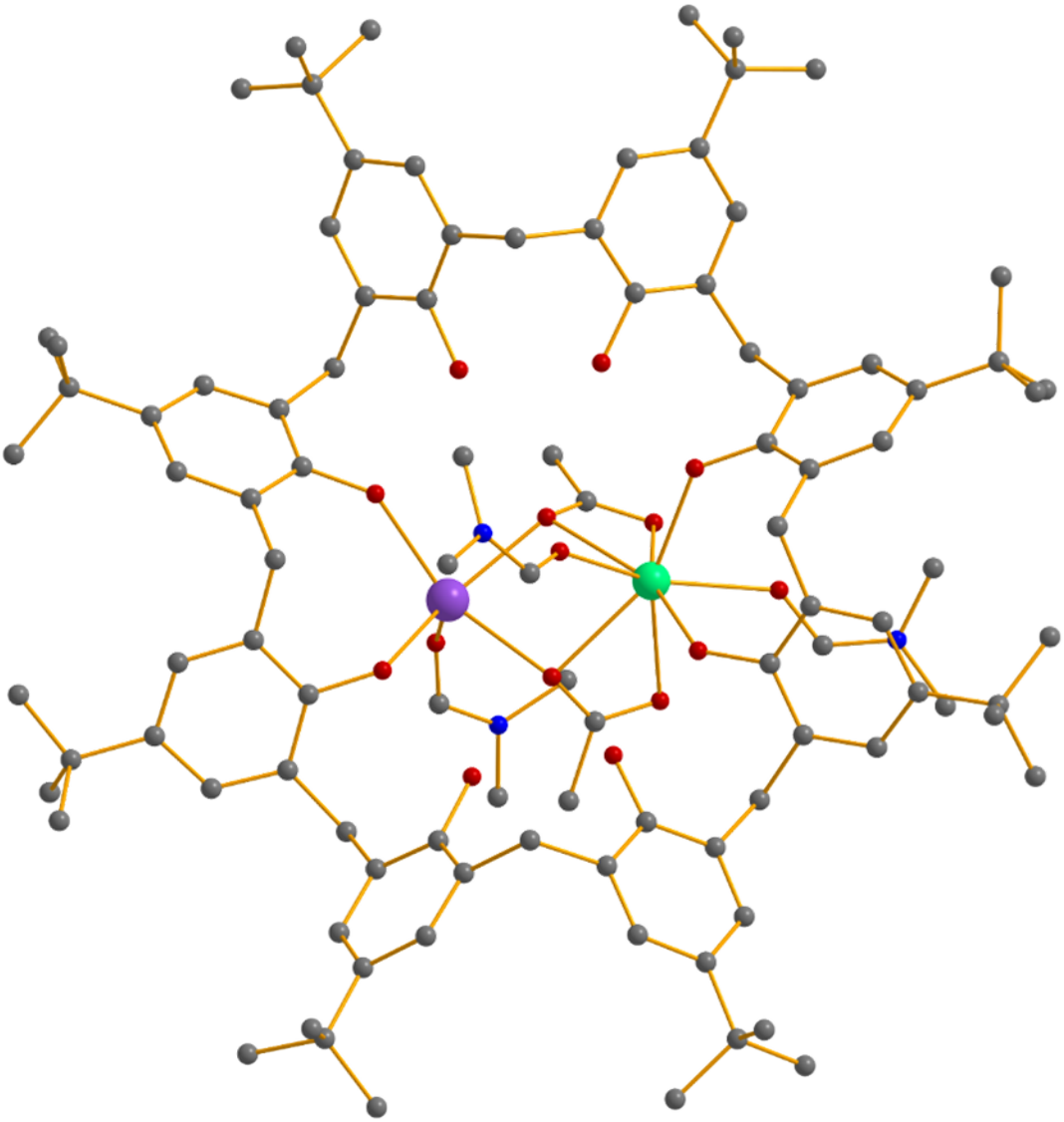


**Figure S18**. Structure of compound **37**. Colour code: Dy = green, Na = purple, O = red, N = blue, C = grey. H atoms omitted for clarity.

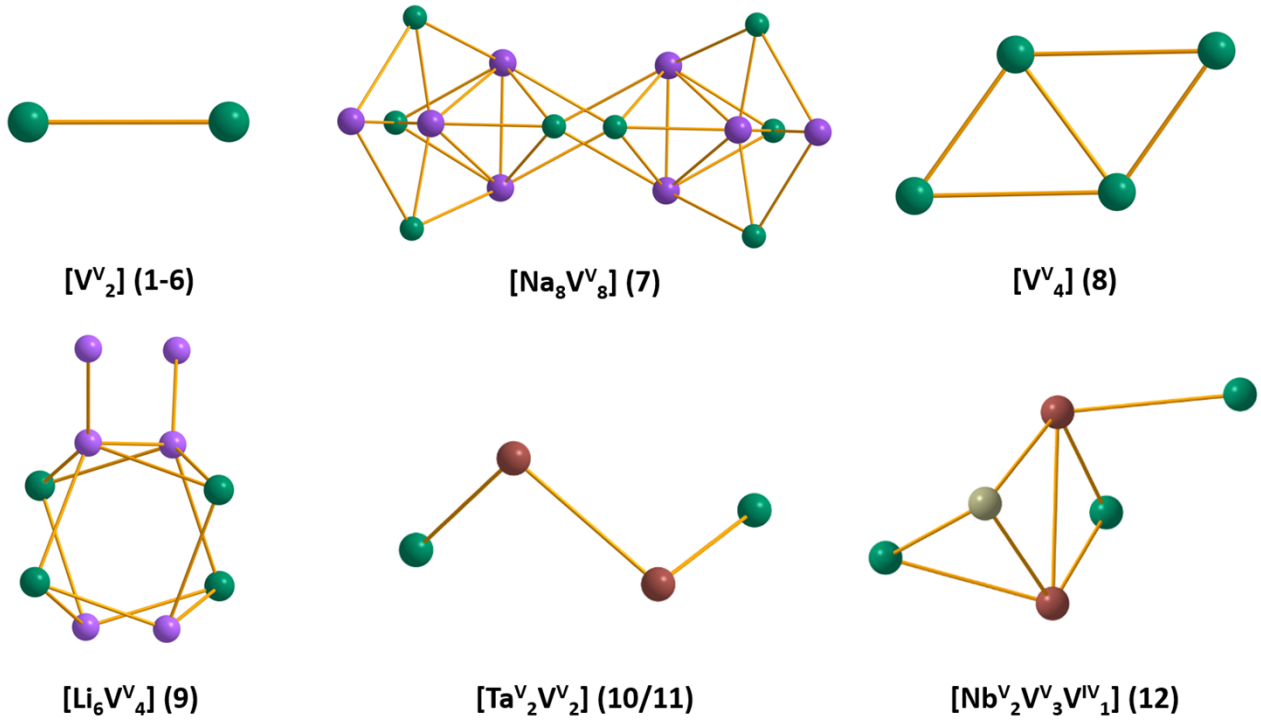



**Figure S19**. Metallic skeletons of the polymetallic V-based clusters in the review.

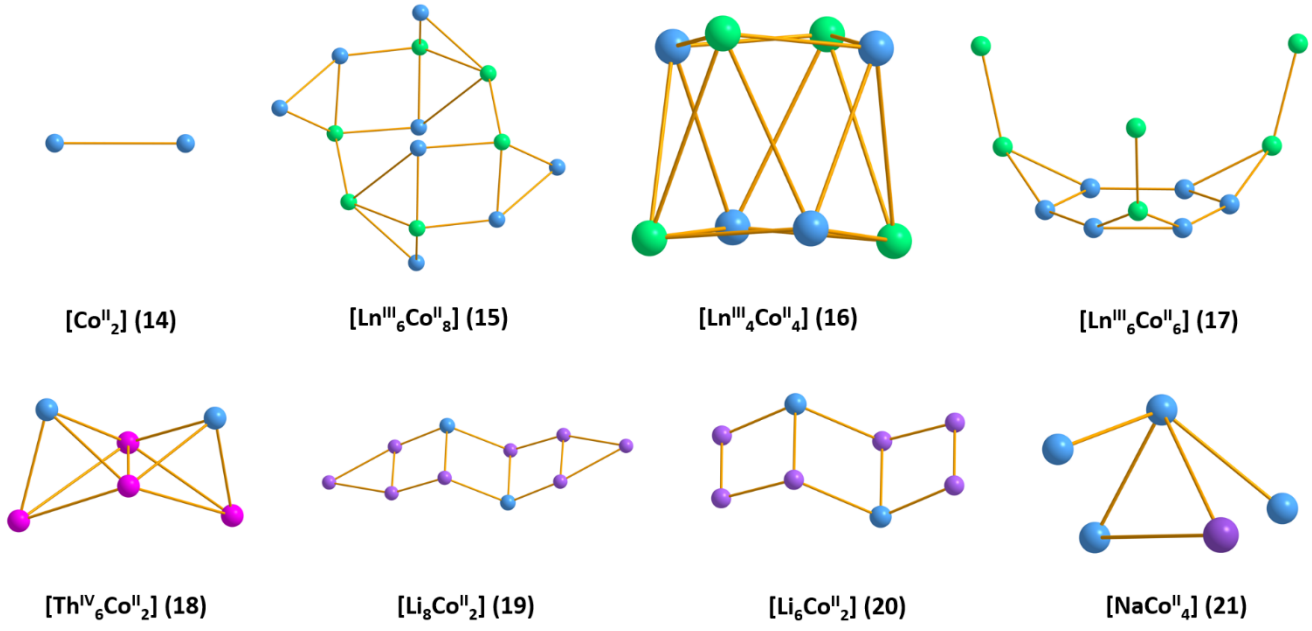
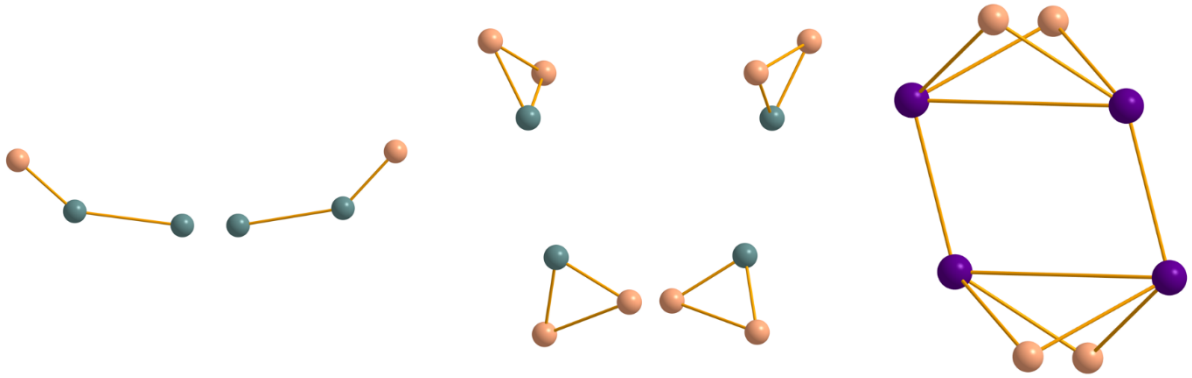
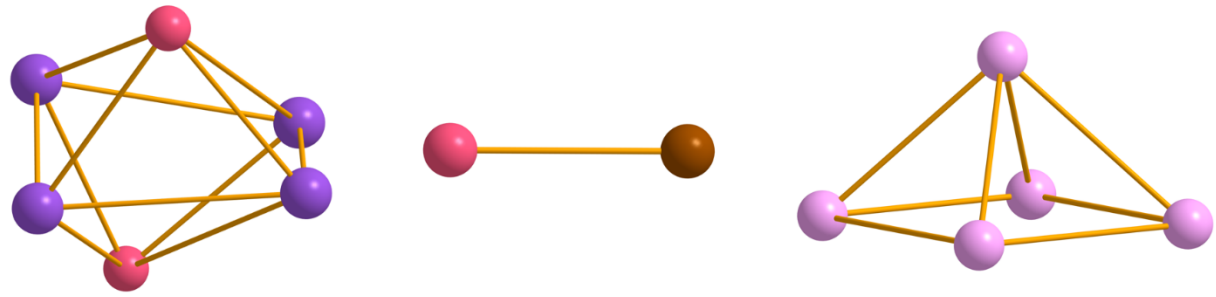



**Figure S20**. Metallic skeletons of the Co-based clusters in the review.



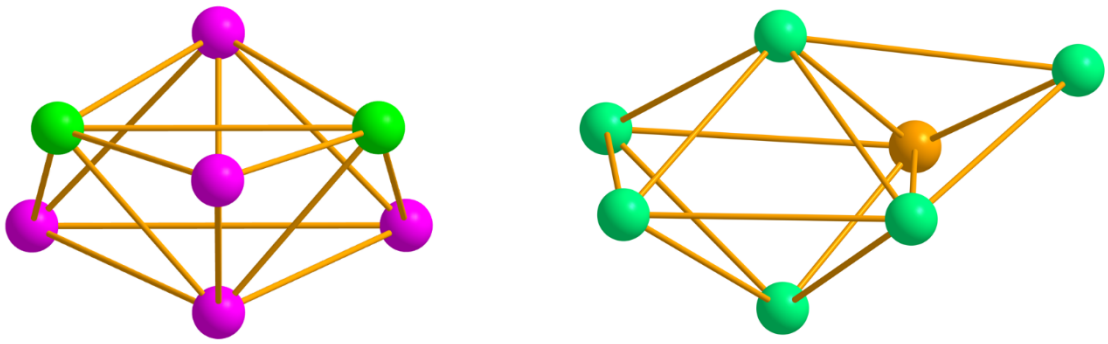
$[Ge^{II}_4Fe^{0}_2]$ (22) $[Ge^{IV}_4Fe^{-I}_8]$ (23) $[K_4Fe^{III}_4]$ (24)

**Figure S21**. Metallic skeletons of the Fe-based clusters in the review.



$[Na_4Mn^{III}_2]$ (25) $[Mn^{III}Mn^{IV}]$ (26) $[Mn^{II}_5]$ (27)

**Figure S22**. Metallic skeletons of the Mn-based clusters in the review.



$[Th^{IV}_5Ni^{II}_2]$ (28) $[Ln^{III}_6Cr^{III}]$ (29)

**Figure S23**. Metallic skeletons of the polymetallic Ni- and Cr-based clusters in the review.

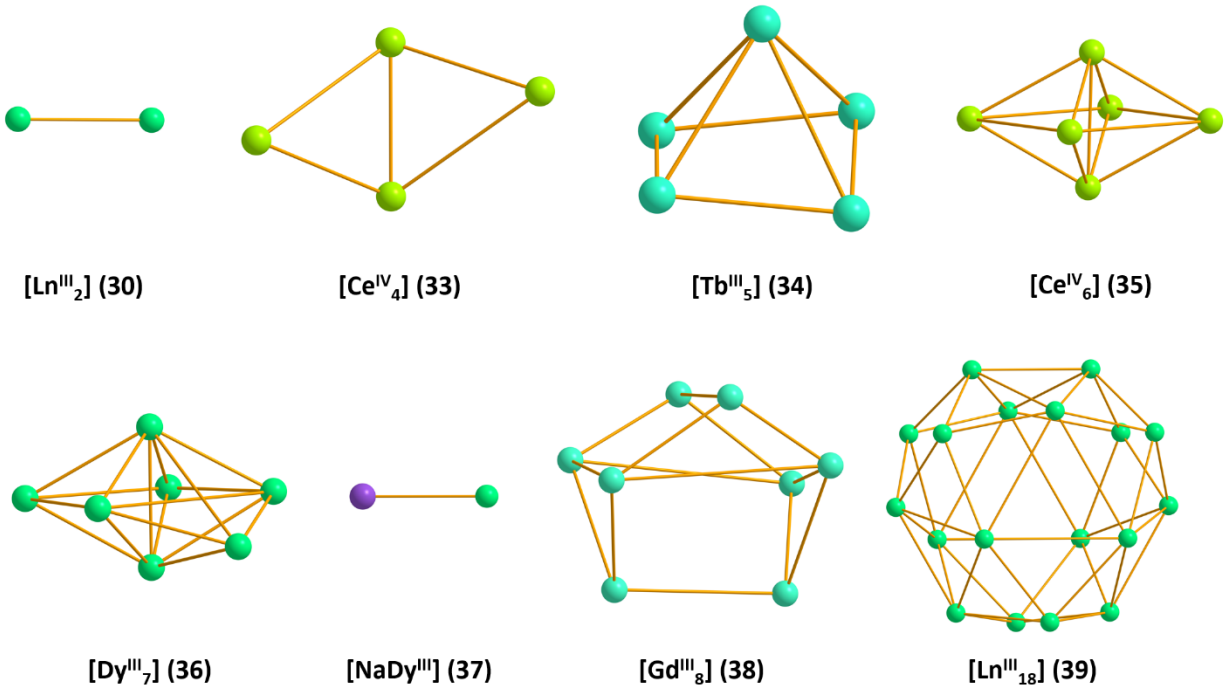



**Figure S24**. Metallic skeletons of the polymetallic Ln-based clusters in the review.