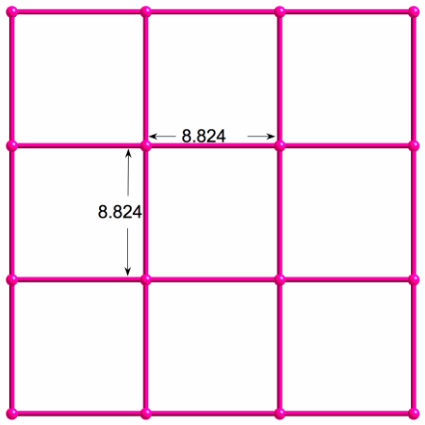
SUPPLEMENTARY INFORMATION

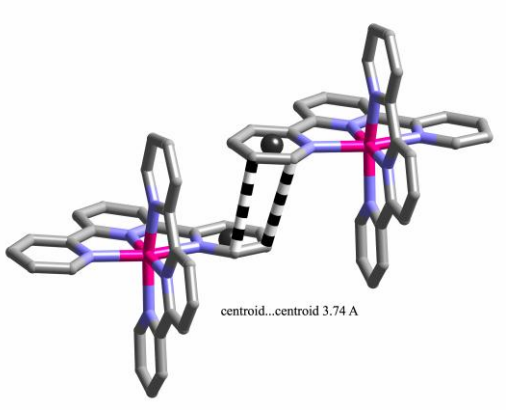
A) Partial views of the lattices of Co(II) complexes of 2,2';6',2''-terpyridine (tpy) and several of its 4' derivatives showing the patterns of metal atom arrays resulting from use of the criterion that Co…Co ≤10 Å may indicate the possibility of intercation magnetic interactions. Each node represents a Co atom and each line a Co…Co vector of ≤10 Å. For each complex, the composition of the crystalline material, the temperature of the structure determination and whether or not susceptibility measurements on the solid covering the range in which spin crossover occurs are available (possession of this last property being indicated by an asterisk) are noted. The references given cover studies of both structure and extended temperature dependence of the magnetism, with some of the structure reports including measurements of room-temperature magnetic moments only. In most cases, the Co arrays are 1- or 2-dimensional and perspective views are given only for the few 3-dimensional cases. Angles within the 2-dimensional arrays are indicated only where they differ from 90 °. As well, in the rare instances where inequivalent Co sites are present in the lattice, this is indicated by different colours (pink and blue). The accompanying figures show the stacking contacts apparent for the close complex cation species in these arrays, with inter-aromatic ring C…C contacts <3.5 Å being indicated by dashed lines and the ring centroids for the stacked rings shown as black spheres. In some cases where C…C contacts <3.5 Å are not evident, CH…C contacts <3.0 Å are also shown as dashed lines.

Where available, data for analogous Fe(II) complexes are also given.

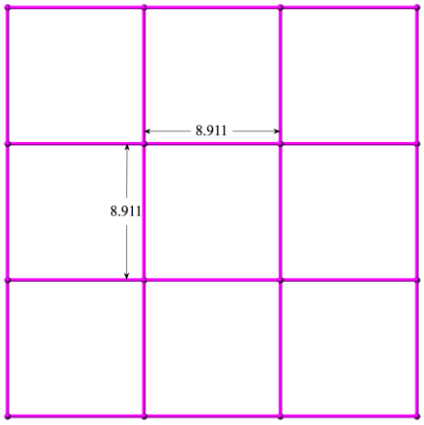
B) Hirshfeld surfaces for polymorphs of $[Co(HOtpy)_2](CF_3SO_3)_2.H_2O$

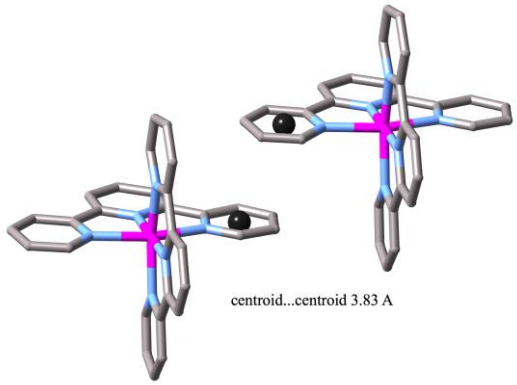
Part A



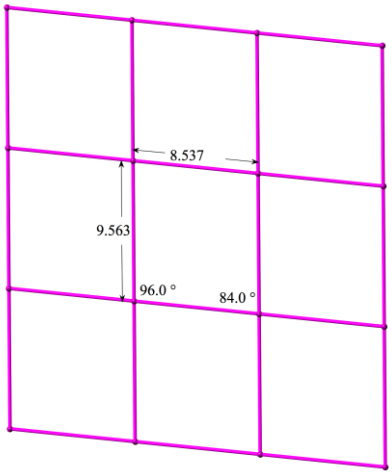


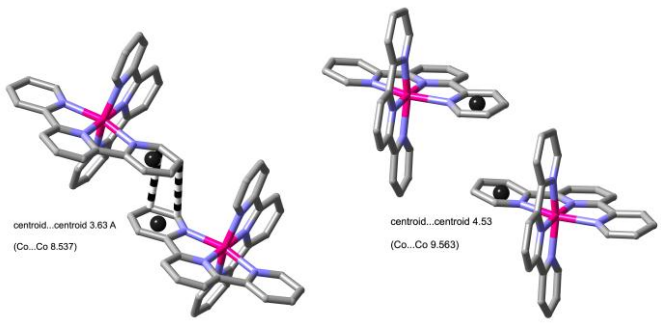
1. $[Co(tpy)_2]I_2.2H_2O$, 120 K, *.[SI1] (Continuous sheets of fused squares.)



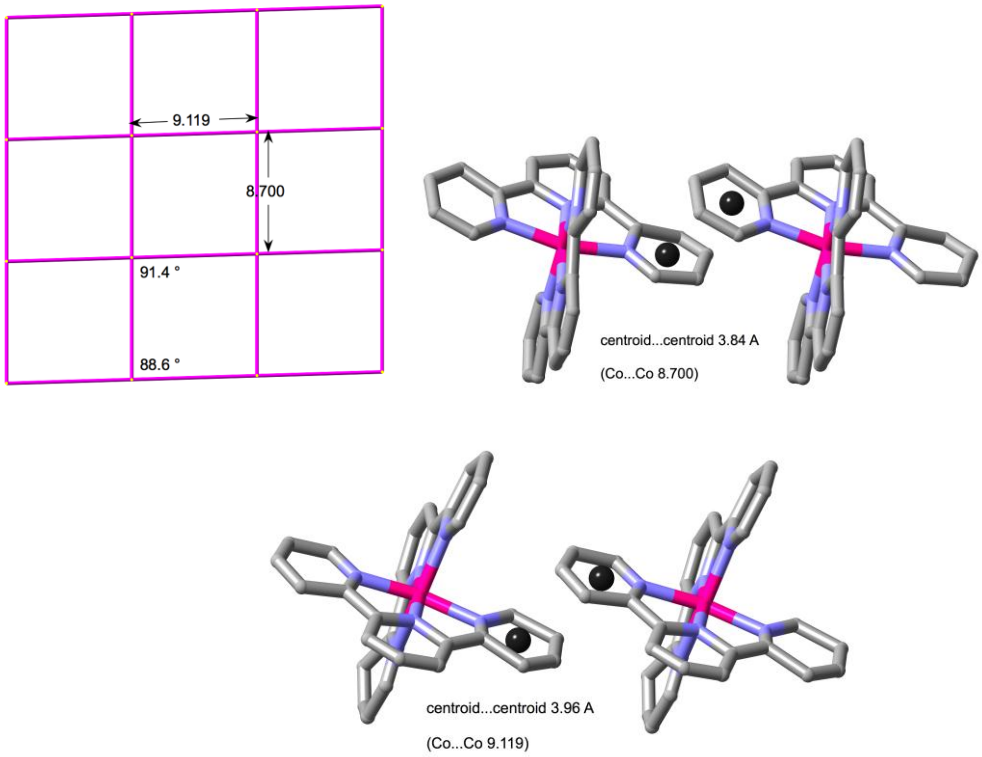


2. $[Co(tpy)_2]I_2.2H_2O$, 295 K, *.[SI1] (Continuous sheets of fused squares.)

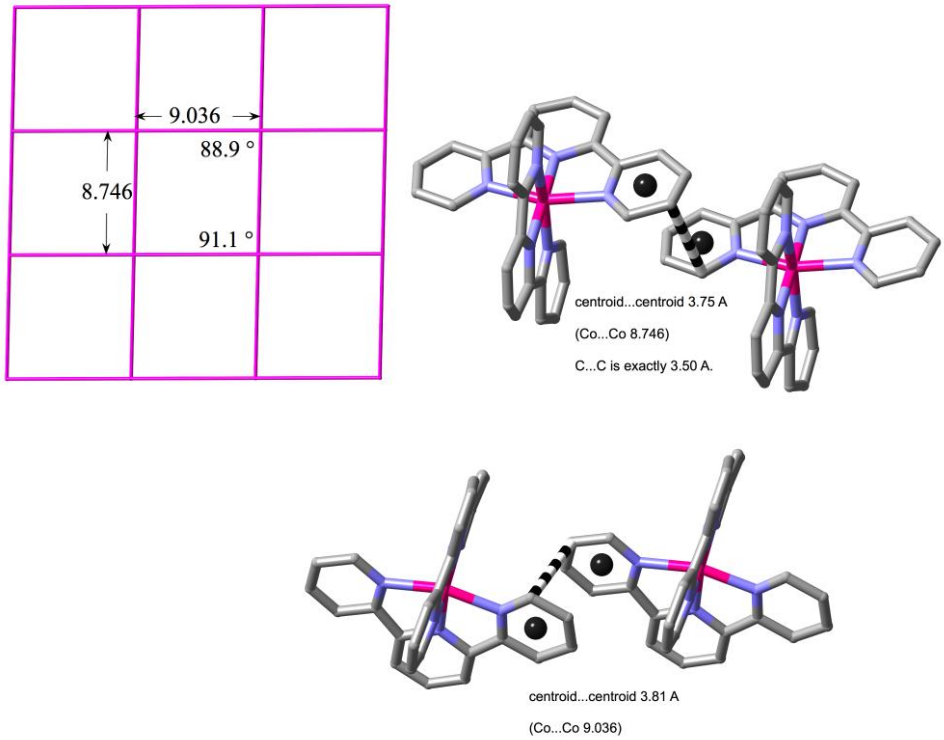




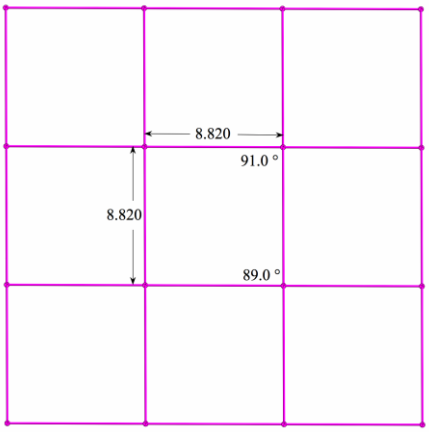
3. $[Co(tpy)_2]Br_2.3H_2O$, 295 K.[SI2] (Continuous sheets of fused rhombs.)

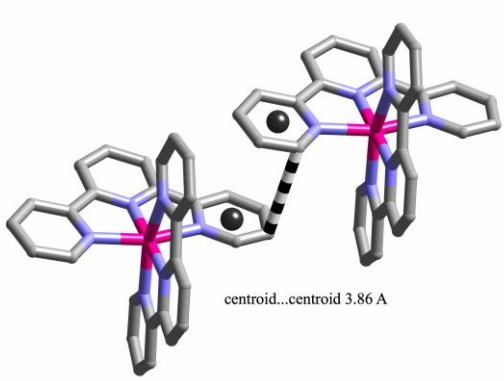


4. $[Co(tpy)_2](NCS)_2.2H_2O$, 295 K (polymorph I).[SI3] (Continuous sheets of fused rhombs.)

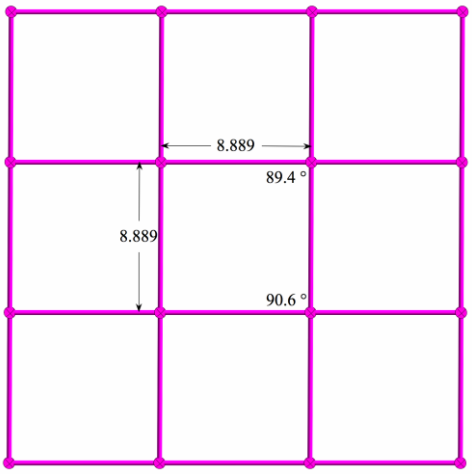


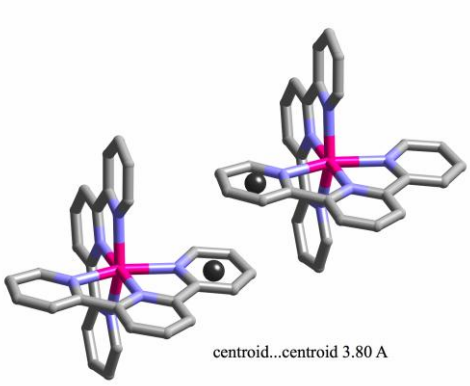
5. $[Co(tpy)_2](NCS)_2.2H_2O$, 295 K (polymorph II).[SI3] (Continuous sheets of fused rhombs.)





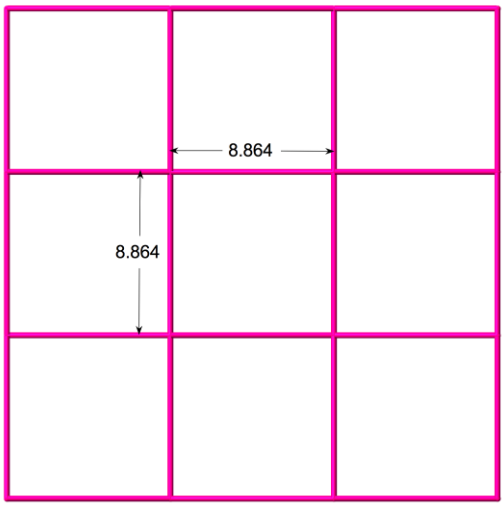
6. $[Co(tpy)_2](BF_4)_2$, 30 K, *.[SI4,SI5] (Continuous sheets of fused rhombs.)

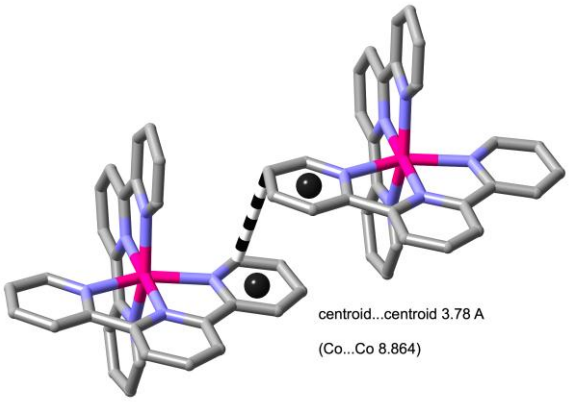




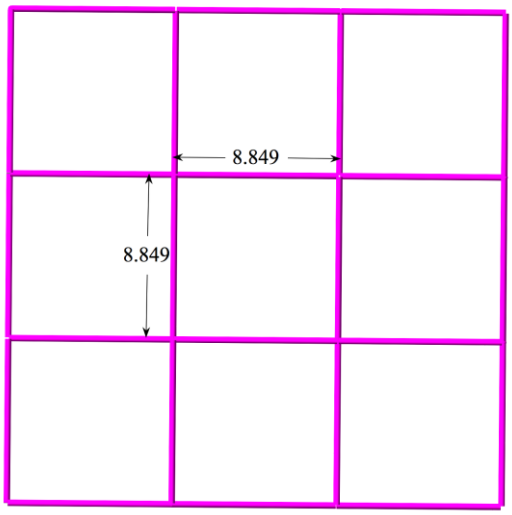
7. $[Co(tpy)_2](BF_4)_2$, 375 K, *.[SI4,SI5] (Continuous sheets of fused rhombs.)

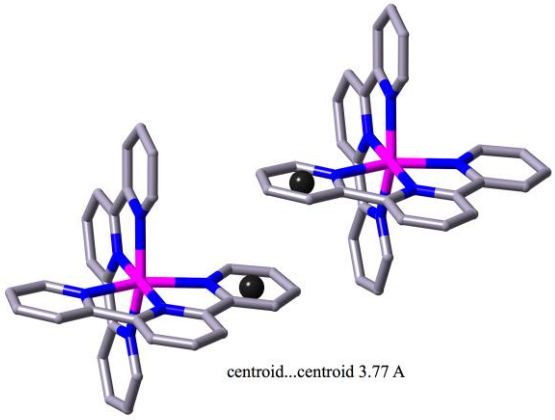
(a) 1.3 hydrate, 295 K, *.[SI6-SI11] (Continuous sheets of fused squares.)



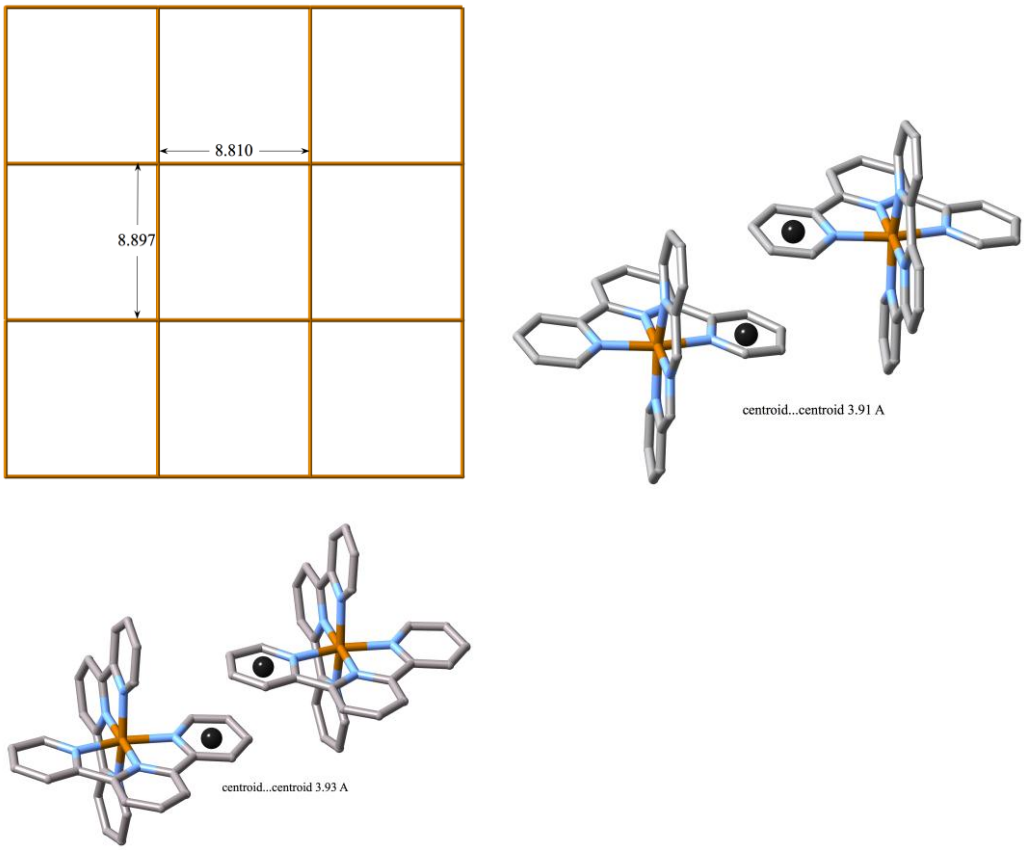


(b) hemihydrate, 293 K, *.[S12] (Continuous sheets of fused squares.)

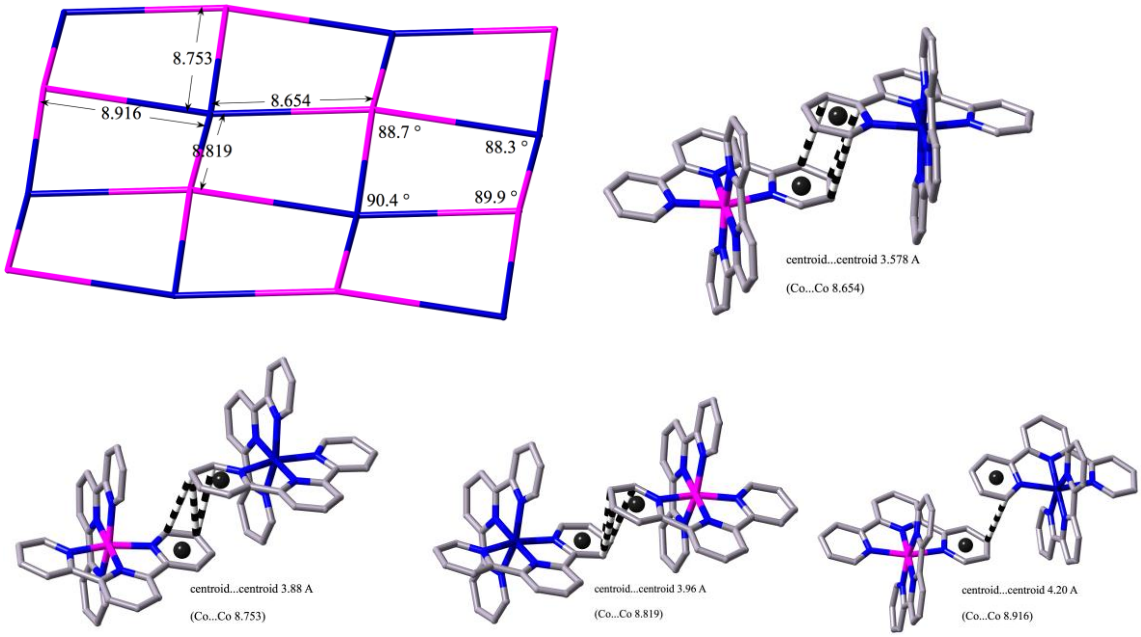




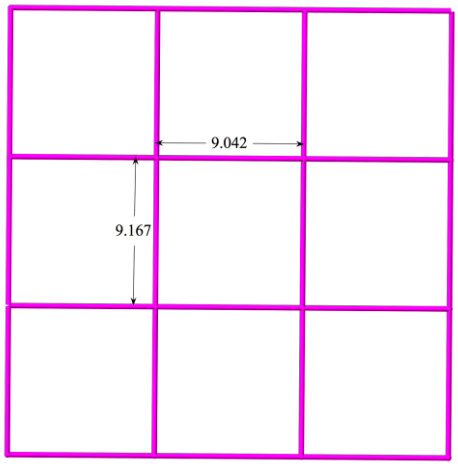
8. $[Co(tpy)_2](ClO_4)_2$, *.[SI6-SI12]

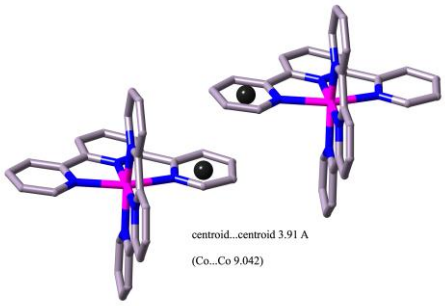


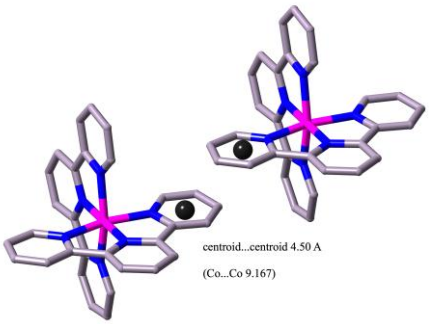
9. $[Fe(tpy)_2](ClO_4)_2$, 293 K.[SI12] (Continuous sheets of fused rectangles.)



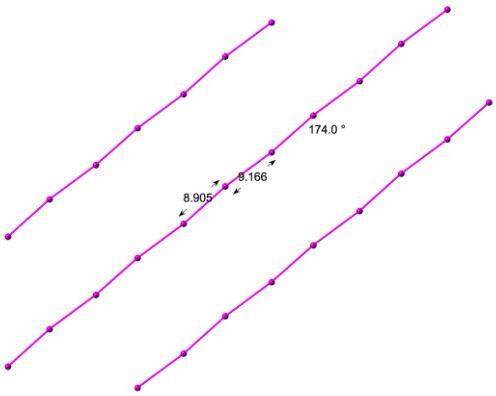
10. $[Co(tpy)_2](PF_6)_2.2CH_3CN$, 123 K, *.[SI10,SI11,SI13] (Puckered sheets of fused rhombs.)

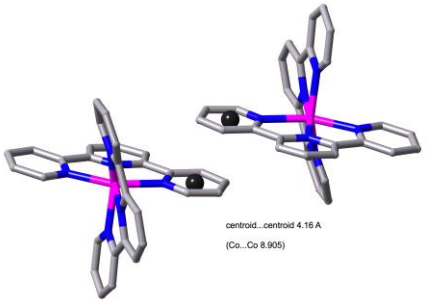


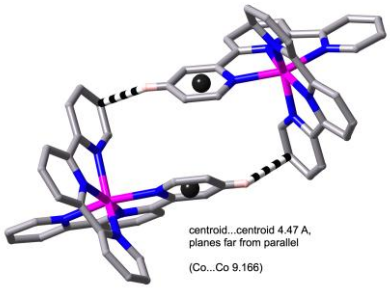




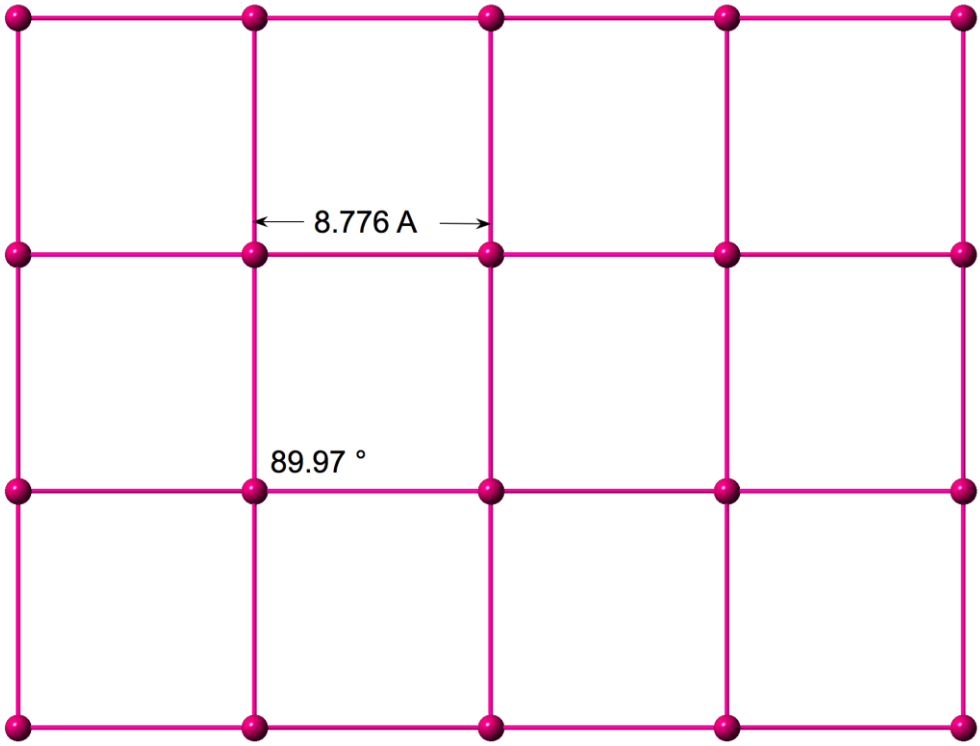
11. $[Co(tpy)_2][C(CN)_3]_2$, 293 K.[SI14] (Continuous sheets of fused rectangles.)

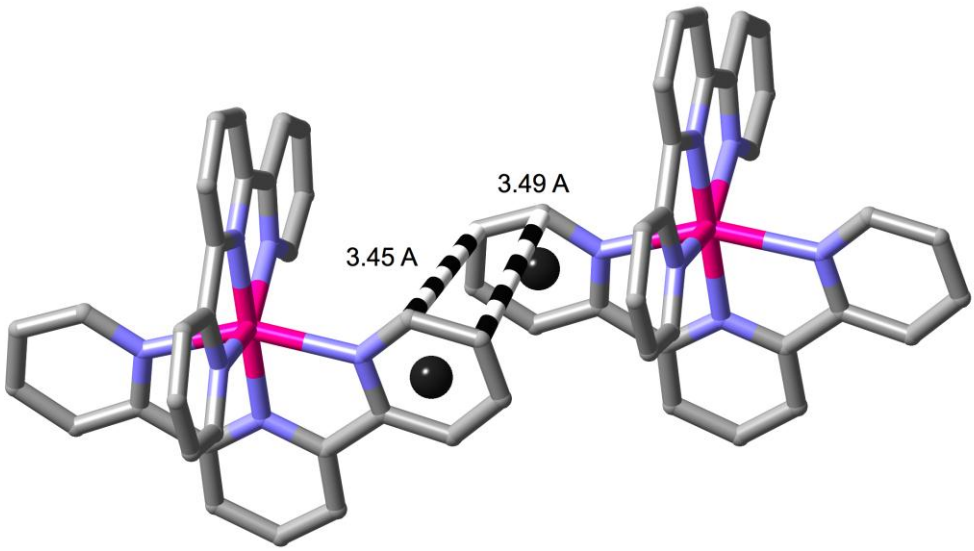




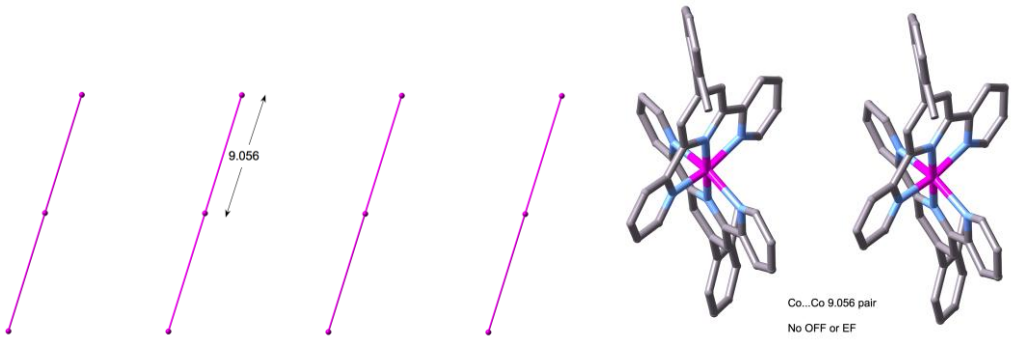


12. $[Co(tpy)_2]_2[Bi_2I_9]I$, 150 K.[SI15] (Sheets of « isolated », gently undulating chains.)

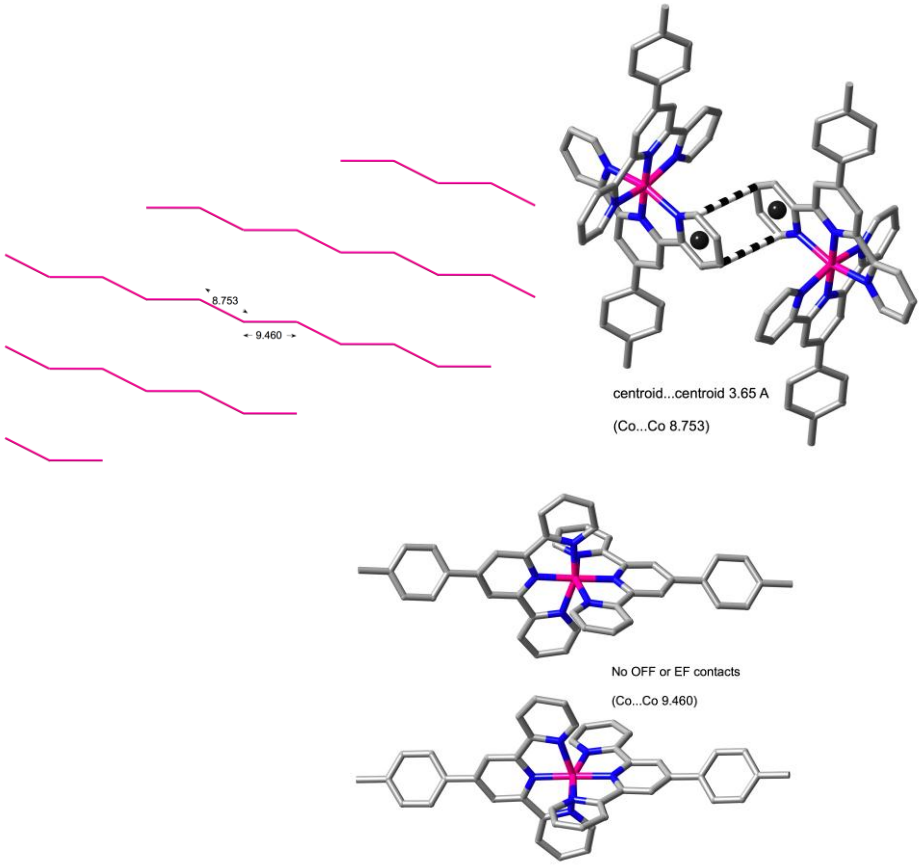




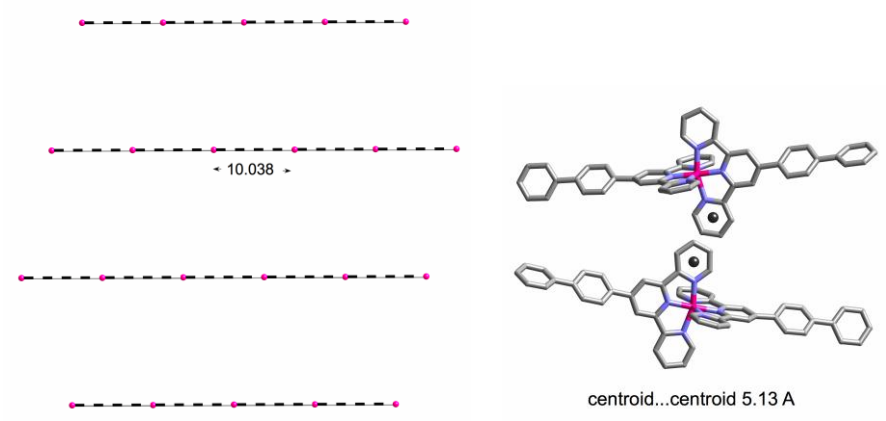
13. $[Co(tpy)_2](NO_3)_2.2H_2O$, 298 K[SI16] (Sheets, parallel to the *ab* plane and very slightly puckered, with a single Co…Co separation.) Magnetism data*.[SI17]



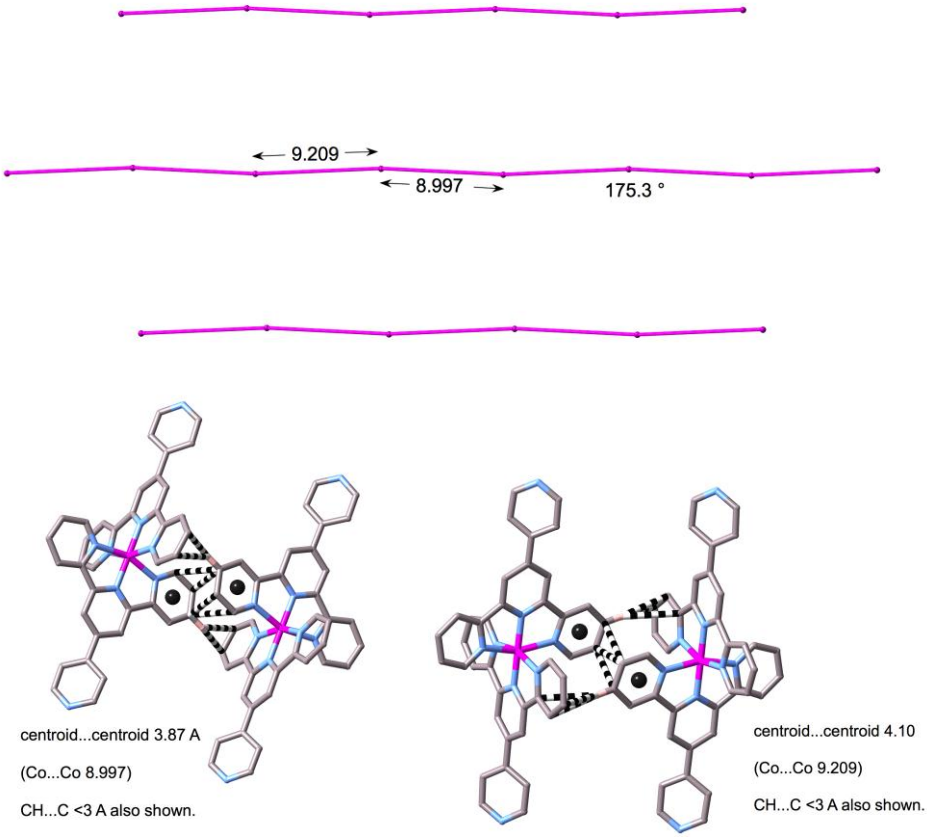
14. $[Co(2\text{-tolyl-tpy})_2]Cl_2.2.25CH_3OH$, 114 K.[SI18] (Sheets of « isolated » linear chains.)



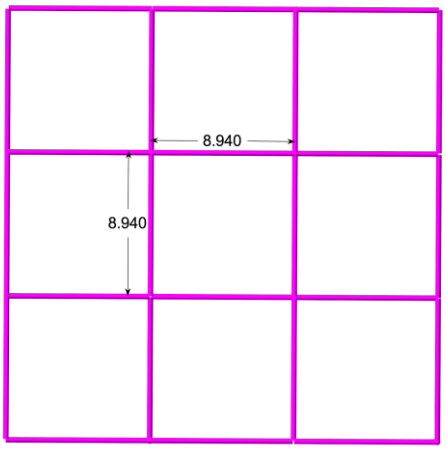
15. $Co(4\text{-tolyl-tpy})_2][Cu_6(CN)_8]$, 293 K.[SI19] (Sheets of « isolated » zig-zag chains.)

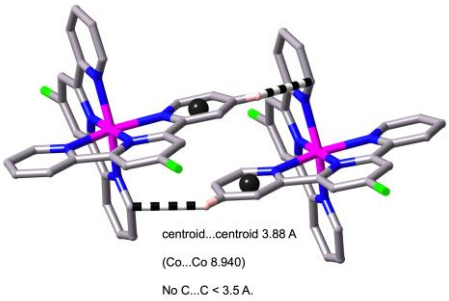


16. $[Co(biphenyl\text{-}tpy)_2](PF_6)_2.THF$, 180 K (no Co…Co contacts ≤10 Å).[SI20] (Sheets of « isolated » Co centres.)

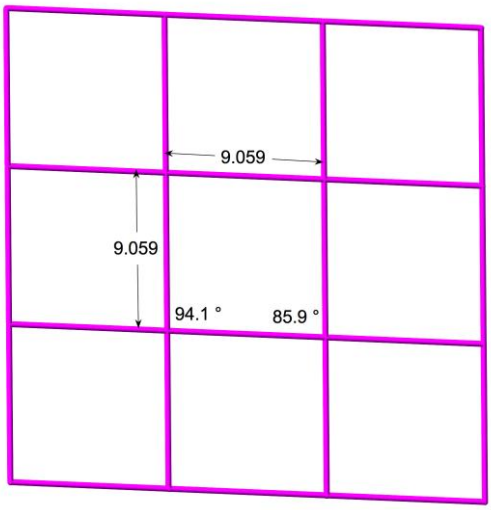


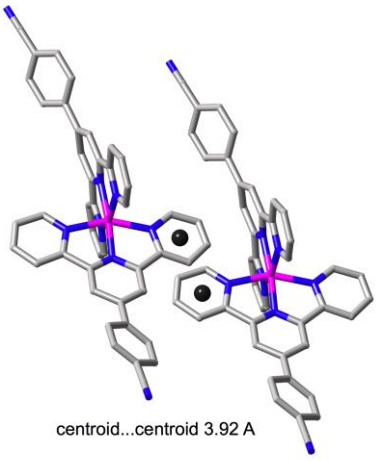
17. $[Co(4\text{-}pyridyl\text{-}tpy)_2](NO_3)_2.CH_3CN.4H_2O$, 100 K.[SI21] (Sheets of « isolated », gently undulating chains.)



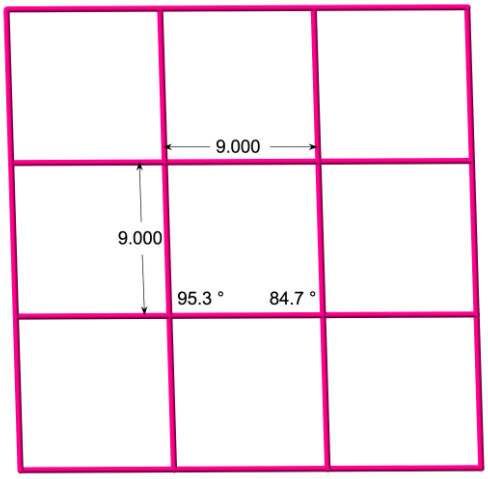


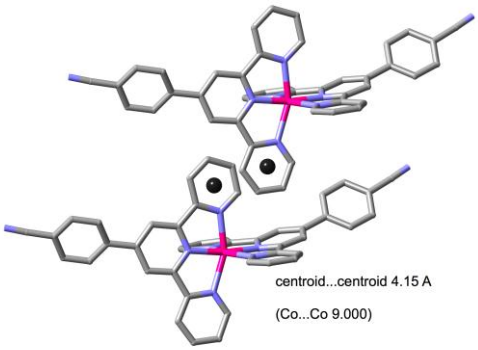
18. $[Co(Cltpy)_2](PF_6)_2$, 173 K.[SI13] (Sheets of fused squares.)



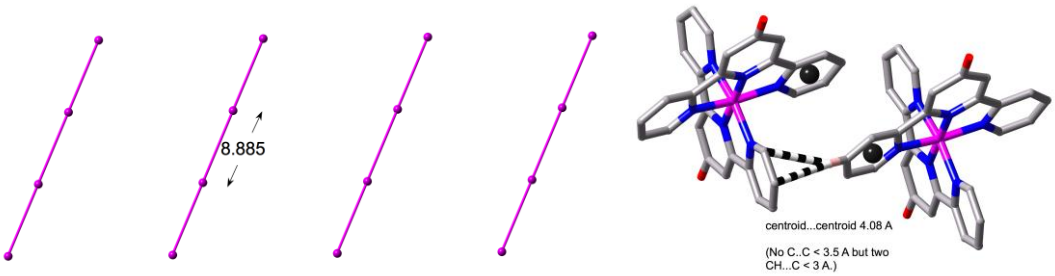


19. $[Co(NCphenyltpy)_2]Cl_2$, 291 K.[SI22] (Sheets of fused rhombs.)

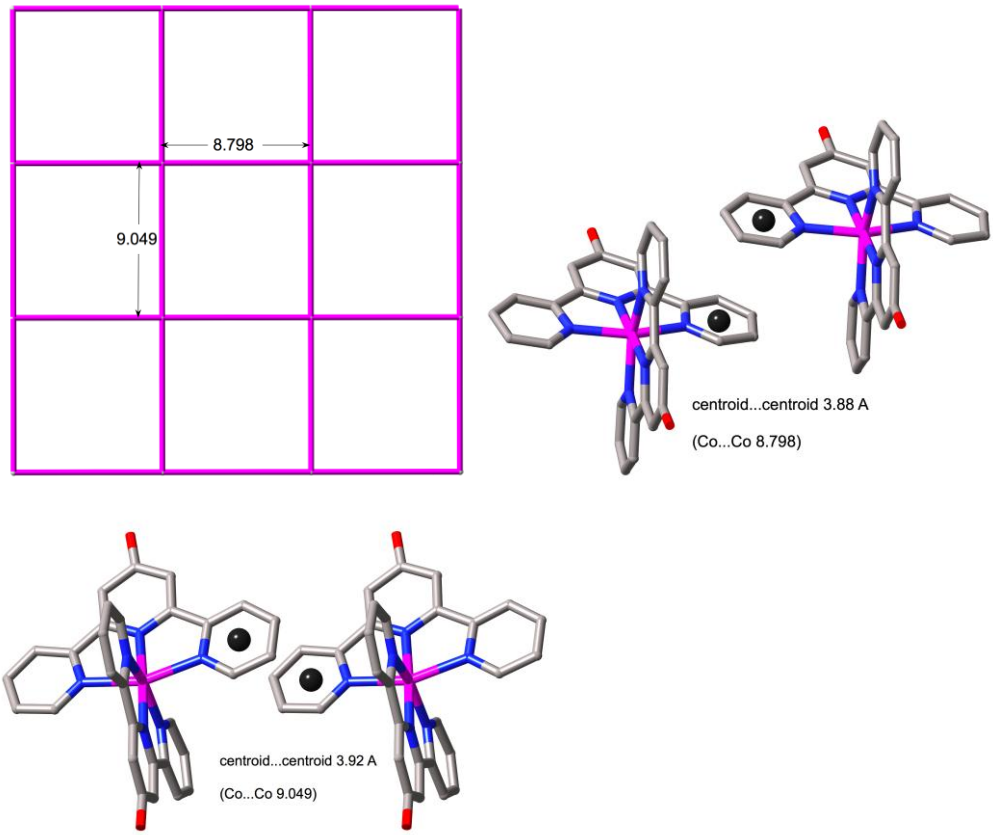




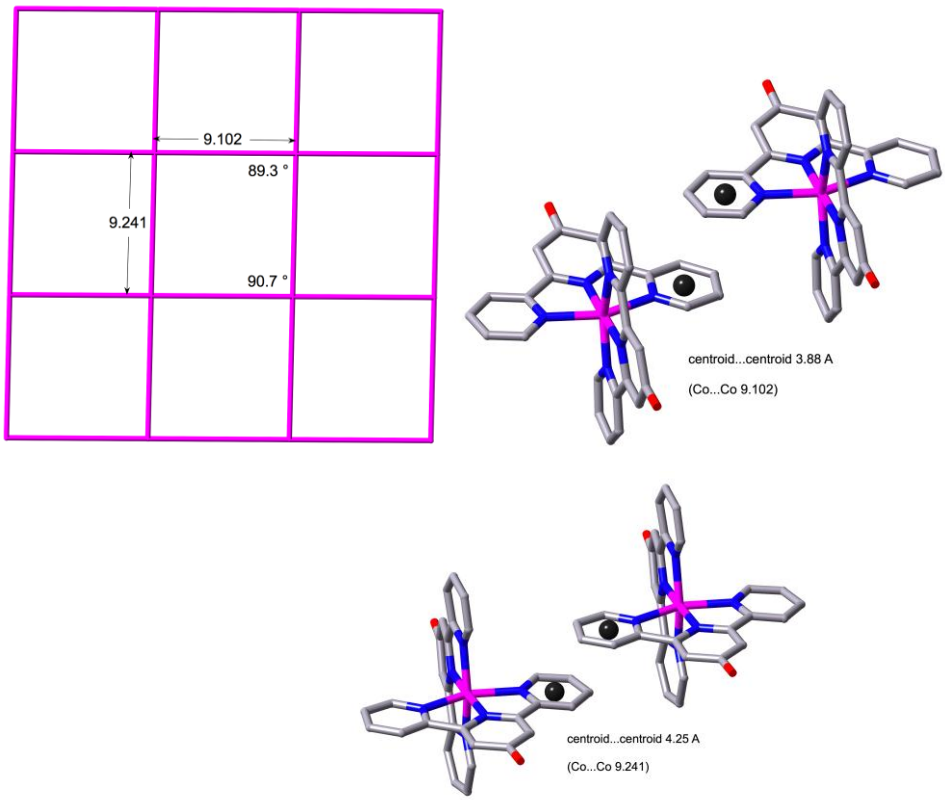
20. $[Co(NCphenyltpy)_2](BF_4)_2.CH_3NO_2$, 120 K.[SI23] (Sheets of fused rhombs.)



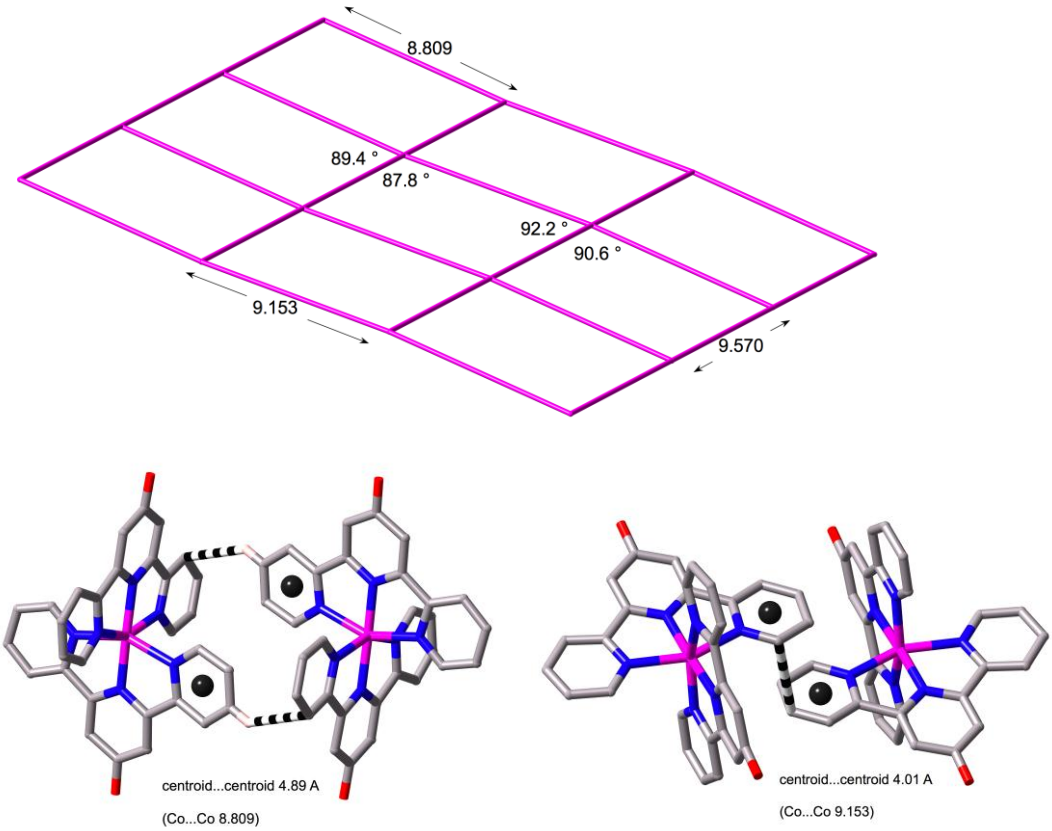
21. $[Co(HOtpy)_2]I_2.5H_2O$, 293 K, *.[SI24] (Sheets of « isolated » linear chains.)

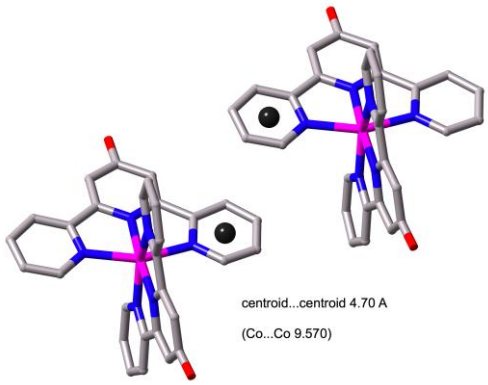


22. $[Co(HOtpy)_2](ClO_4)_2.H_2O$, 293 K, *.[SI25] (Sheets of fused rectangles.)

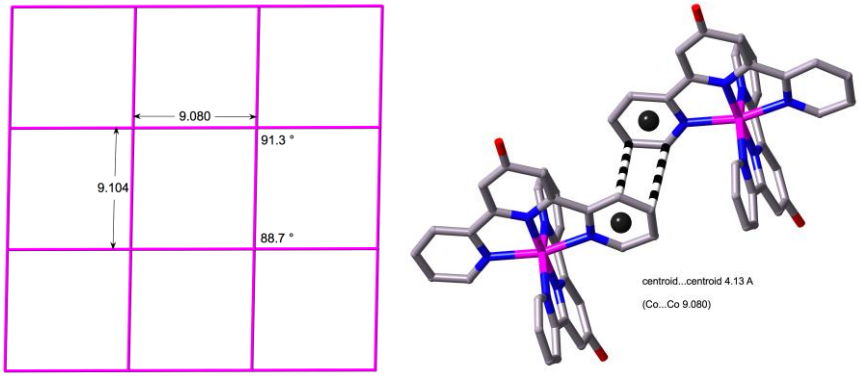


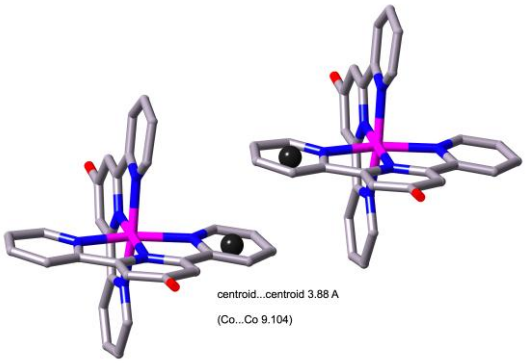
23. $[Co(HOtpy)_2](CF_3SO_3)_2.H_2O$, 293 K, *.[SI26] Polymorph I. (Sheets of fused rhombs.)



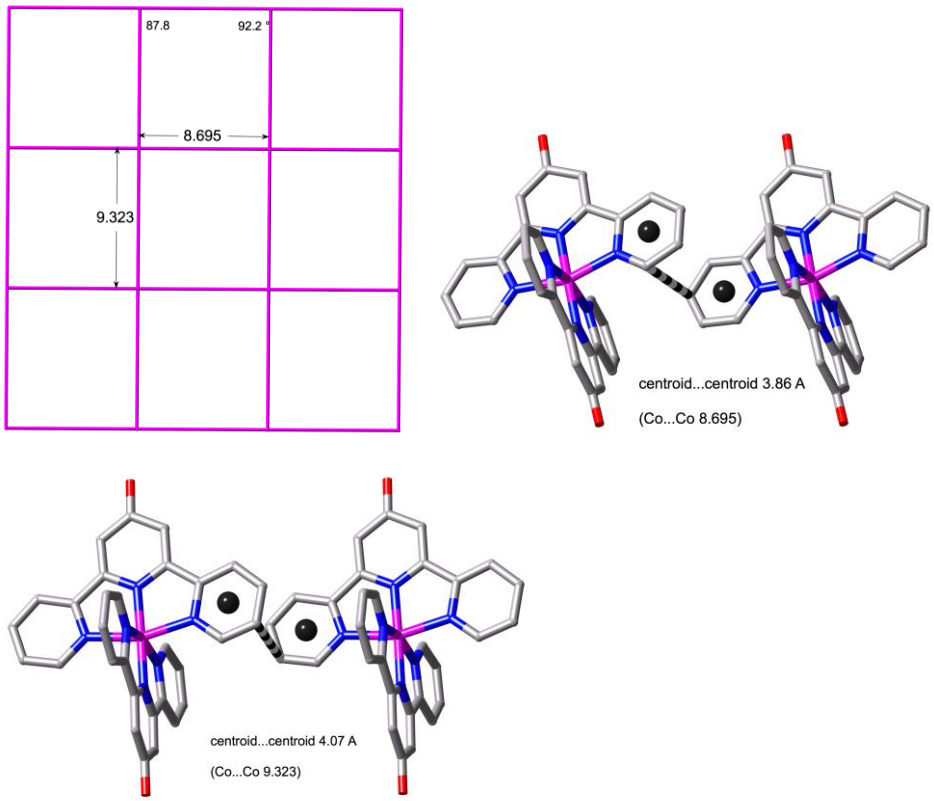


24. $[Co(HOtpy)_2](CF_3SO_3)_2.H_2O$, 293 K, *.[SI26] Polymorph II. (Slightly puckered sheets of fused rhombs of two sizes.)

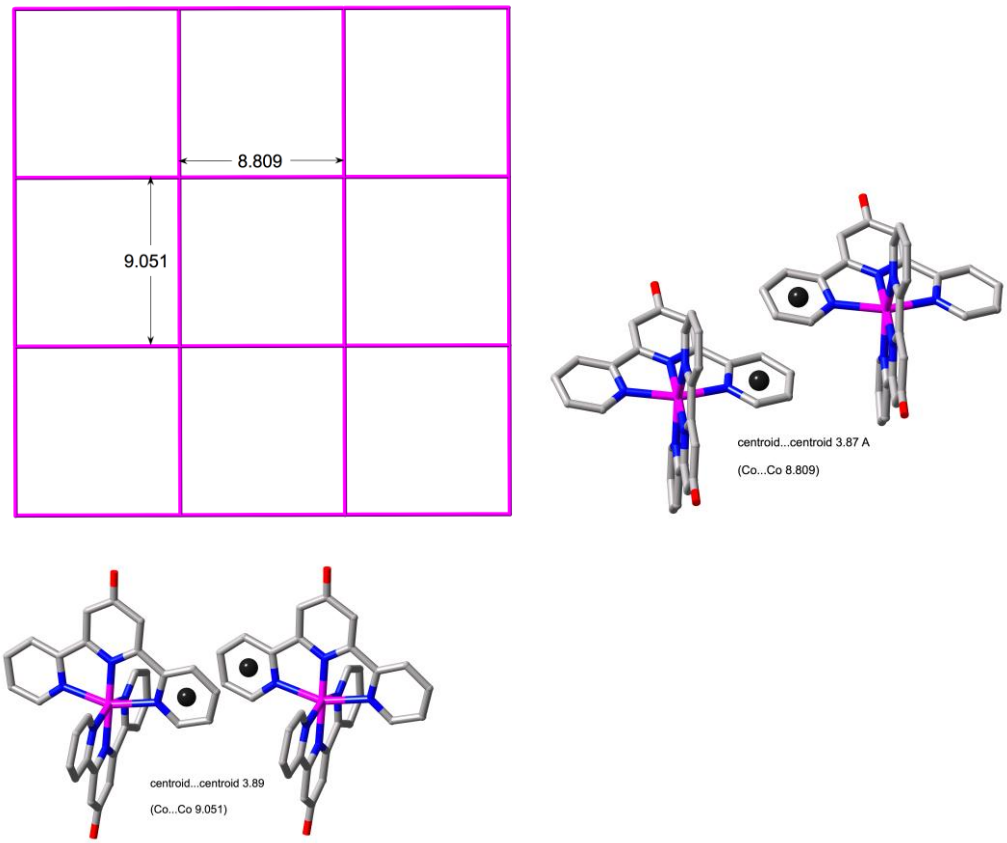




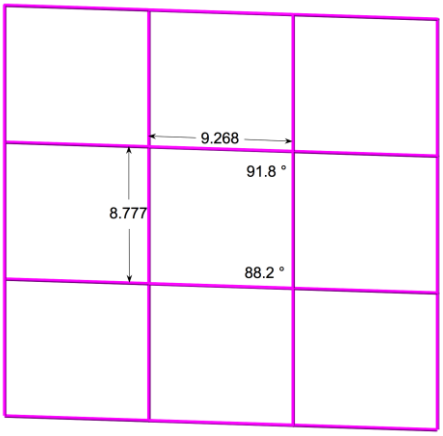
25. $[Co(HOtpy)_2](CF_3SO_3)_2.H_2O$, 120 K, * ; low precision structure.[SI26] (Sheets of fused rhombs.)

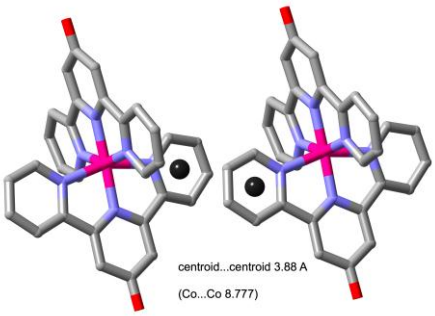


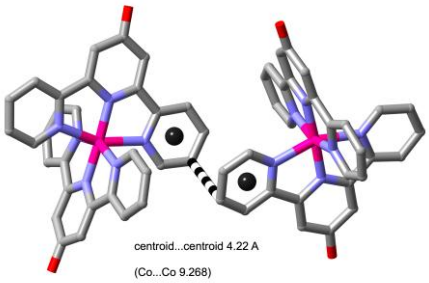
26. $[Co(HOtpy)_2](BF_4)_2.H_2O$, 293 K, * ; polymorph I.[SI24] (Sheets of fused rhombs.)



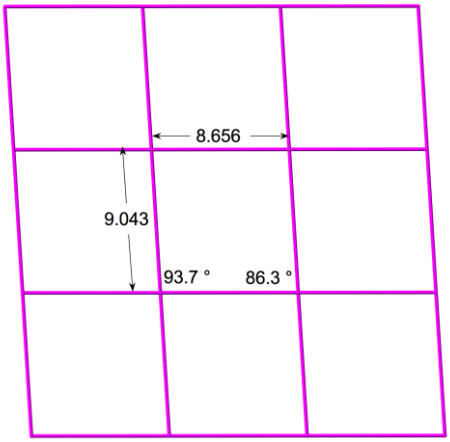
27. $[Co(HOtpy)_2](BF_4)_2.H_2O$, 293 K, * ; polymorph II.[SI24] (Sheets of fused rectangles.)

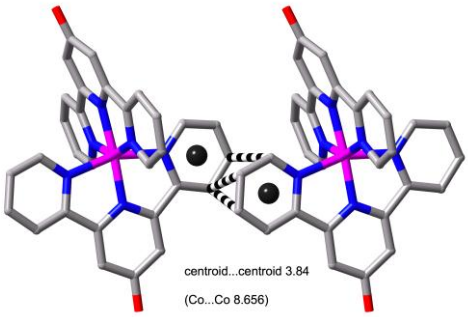


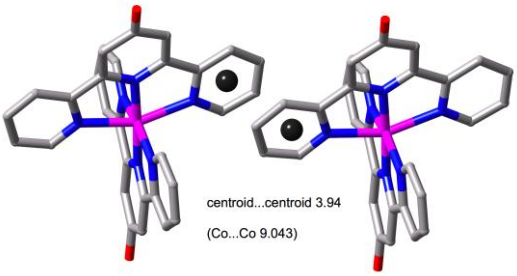




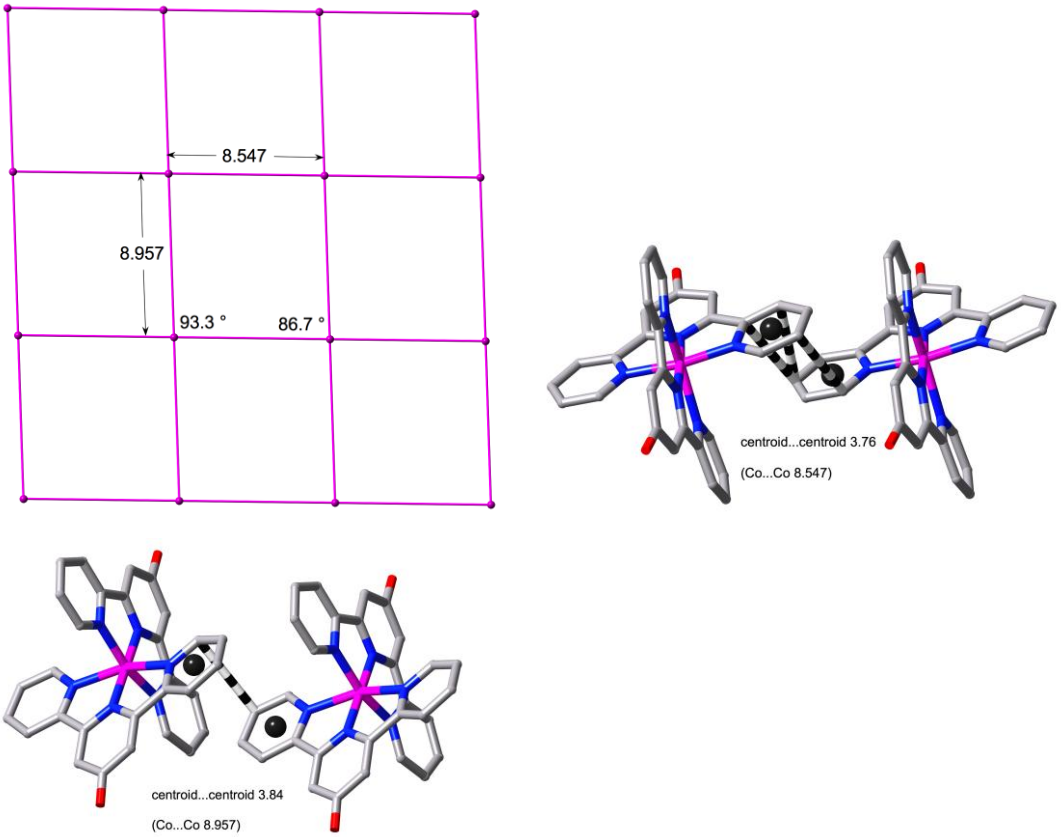
28. $[Co(HOtpy)_2][SiF_6].3CH_3OH.H_2O$, 293 K, *.[SI24] (Sheets of fused rhombs.)



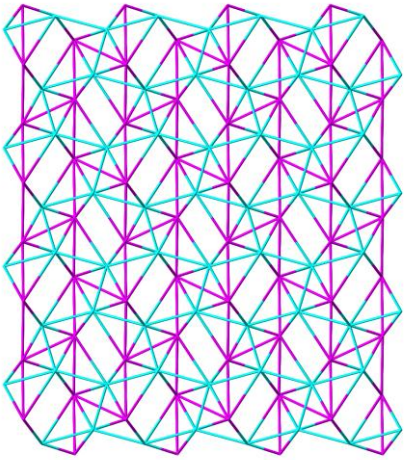




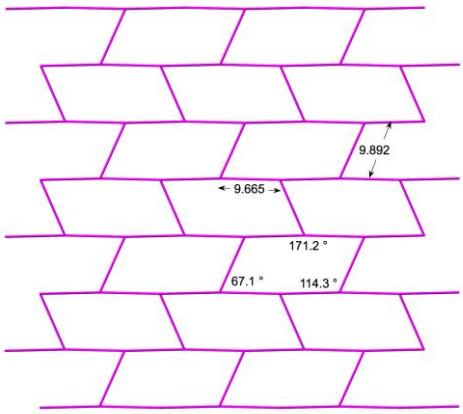
29. $[Co(HOtpy)_2]_2(BF_4)_2[SiF_6].2CH_3OH$, 293 K, *.[SI24] (Sheets of fused rhombs.)



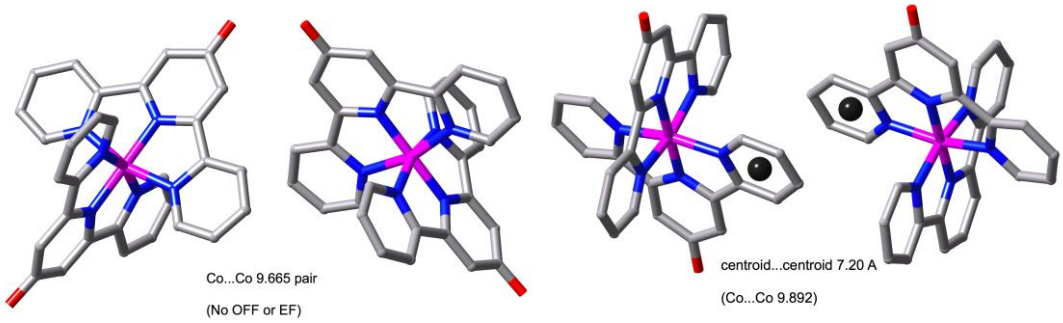
30. $[Co(HOtpy)_2]_2(BF_4)_2[SiF_6].2CH_3OH$, 105 K, *.[SI24] (Sheets of fused rhombs.)

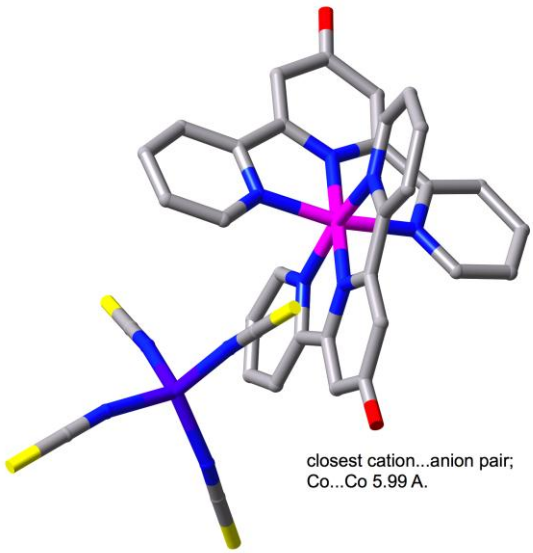


3D array (blue = Co in $[Co(NCS)_4]$)

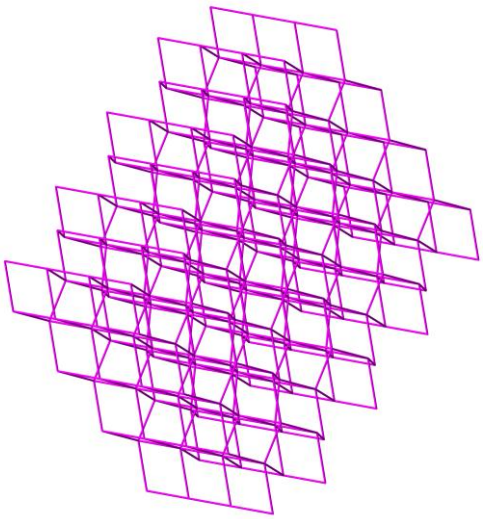


Sheet of Co in $[Co(HOtpy)_2]$ units

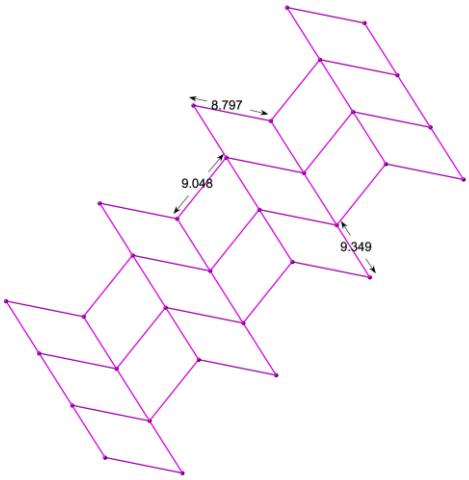




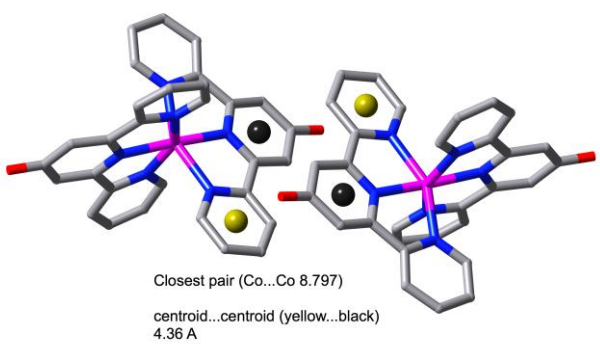
31. $[Co(HOtpy)_2][Co(NCS)_4].0.5CH_3OH$, 293 K, *.[SI24] (Three-dimensional array but the Co ions bound to HOtpy can be considered to lie in sheets formed by fused hexagonal units.)

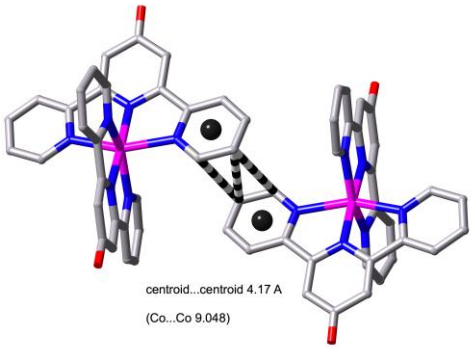


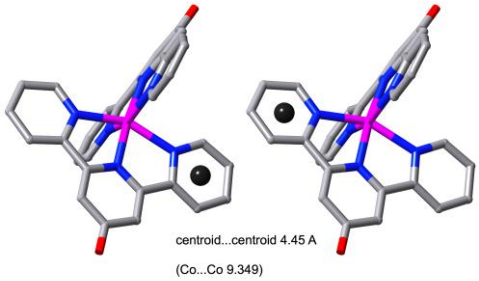
3D array

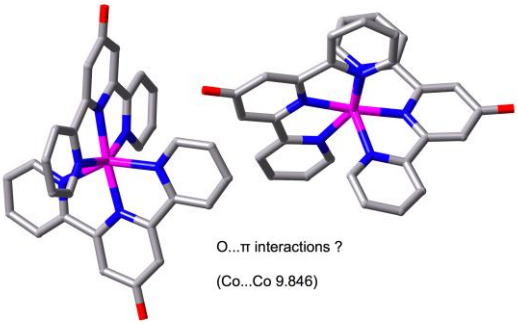


Corrugated sheet for Co…Co <9.5 Å.

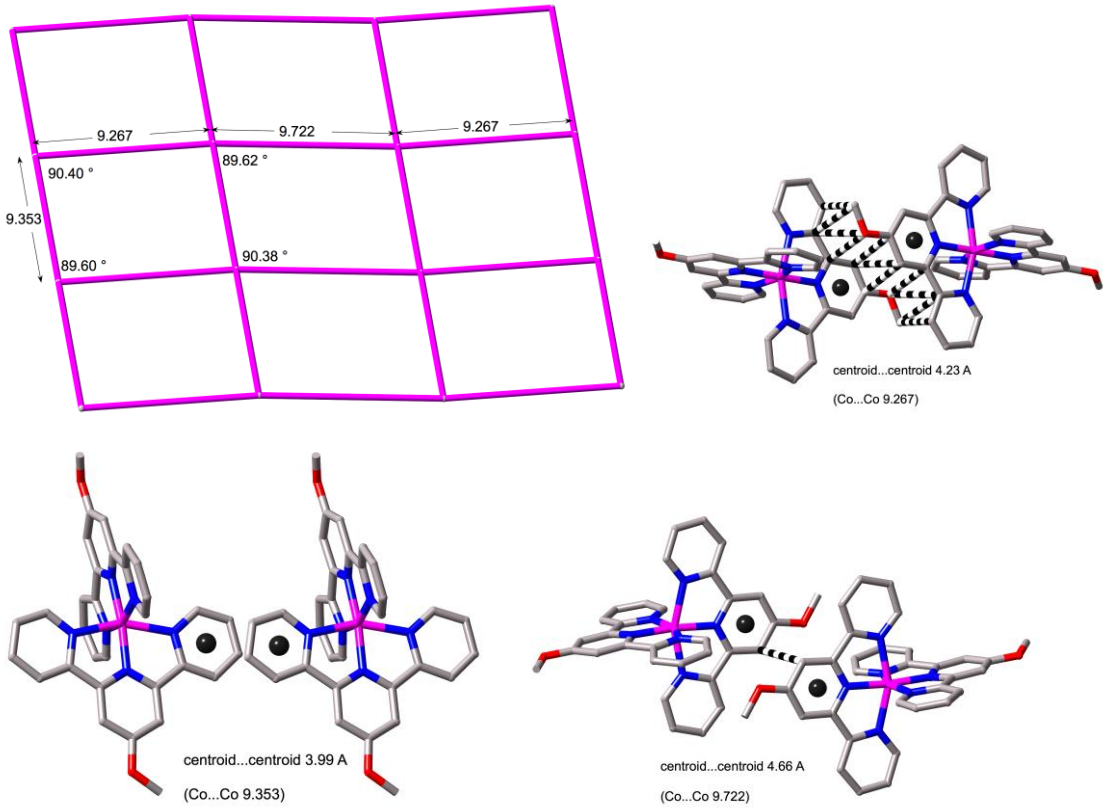




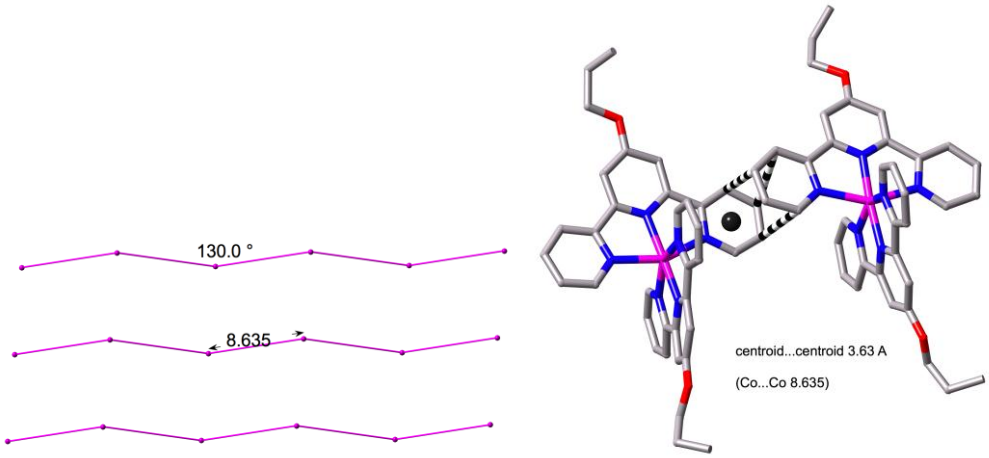




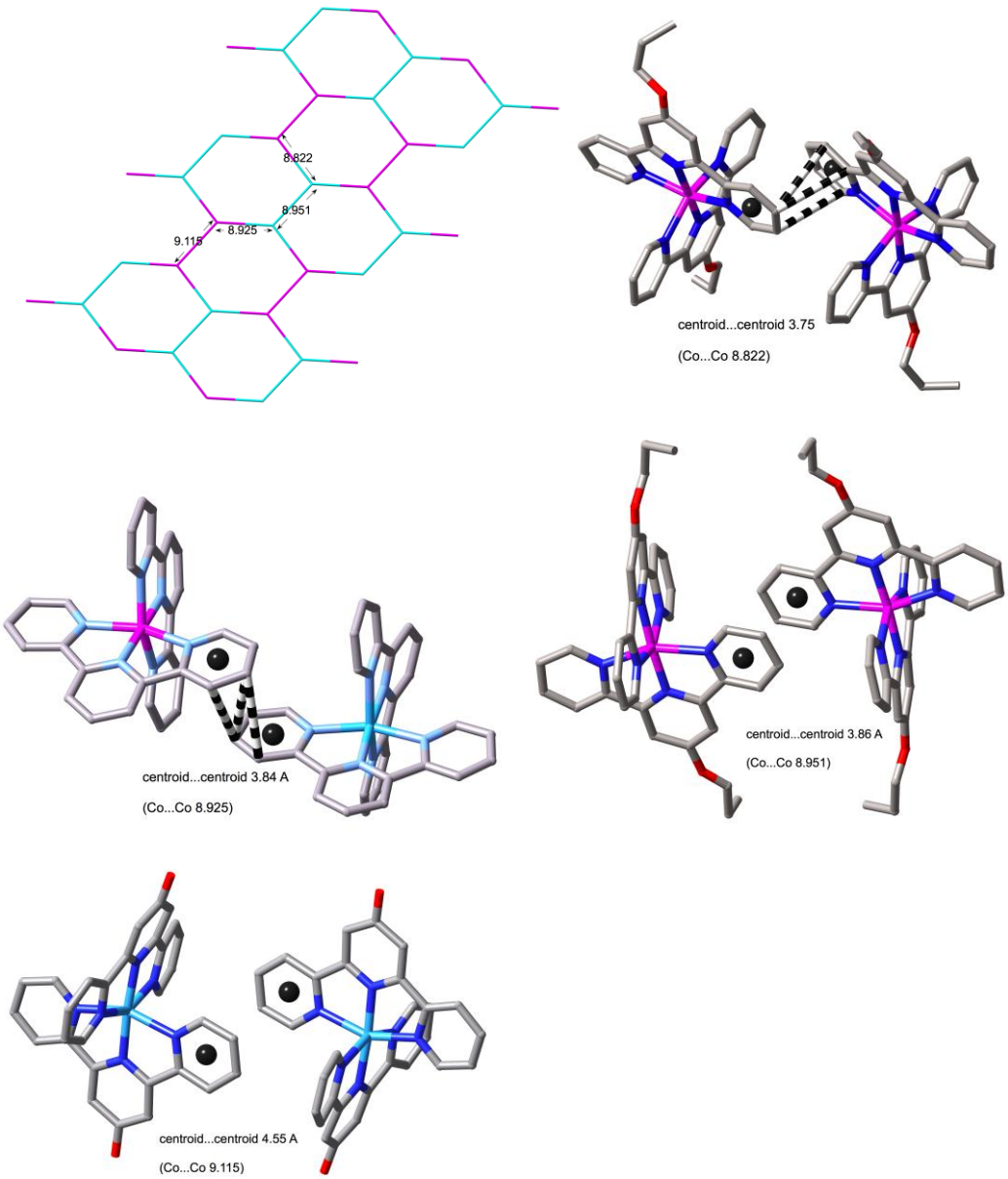
32. [Co(HOtpy)(Otpy)]PF_6, 293 K, *.[SI24] (Three-dimensional array involving four different Co…Co distances < 10 Å.)



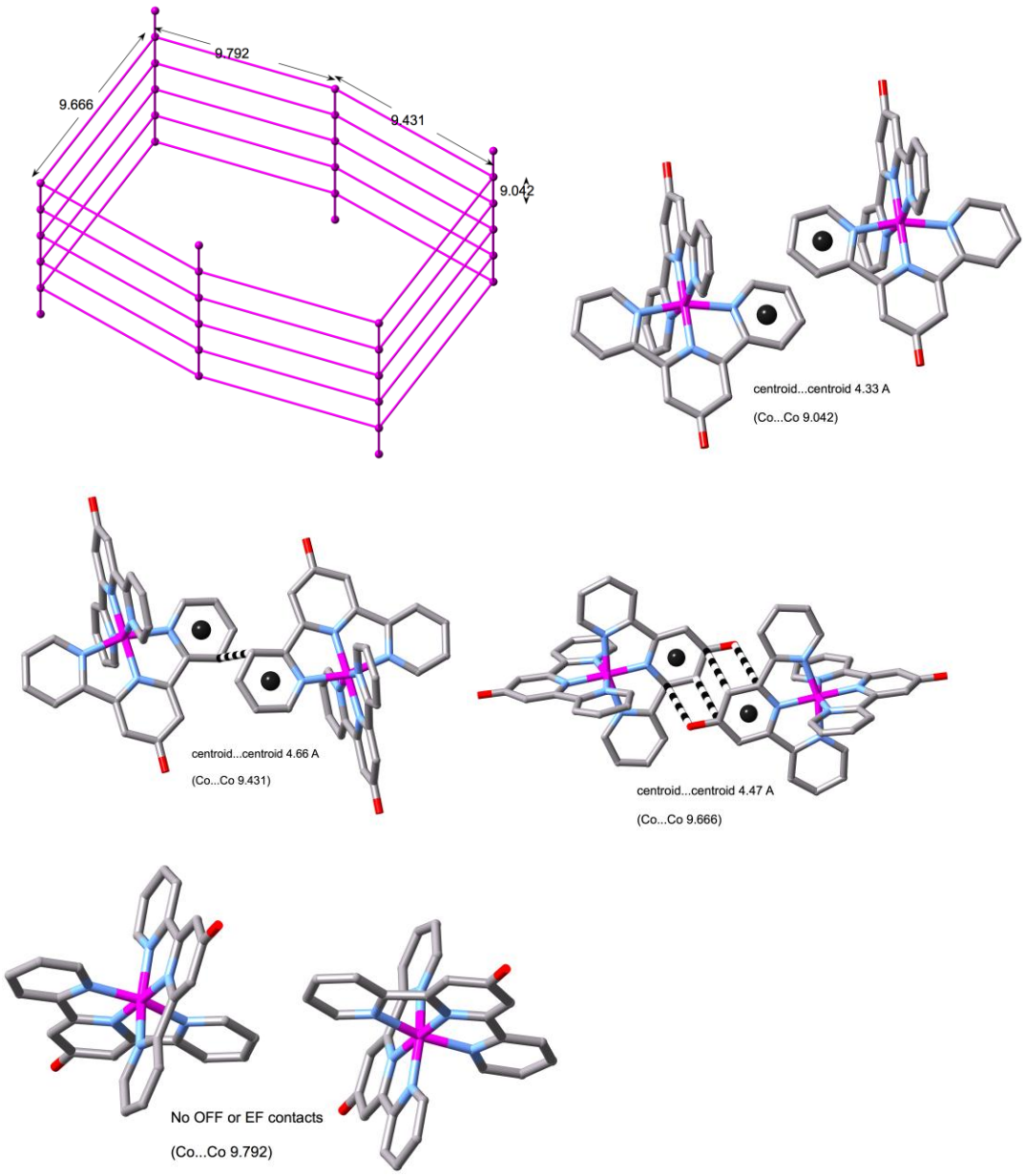
33. $[Co(CH_3Otpy)_2](PF_6)_2$, 173 K.[SI13] (Slightly puckered sheets of fused rhombs of two sizes.)



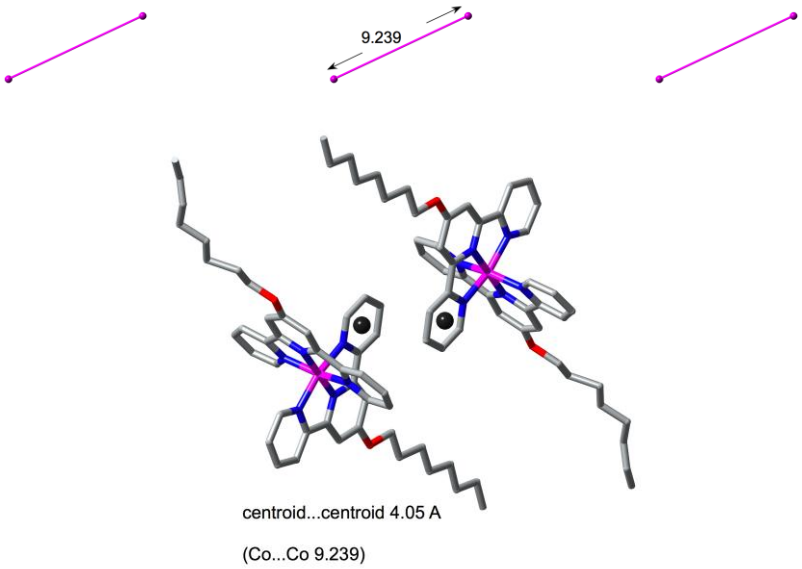
34. $[Co(n\text{-}C_3H_7Otpy)_2](PF_6)_2.CH_3CN.(C_2H_5)_2O$, 173 K.[SI13] (Sheets of « isolated » zig-zag chains.)



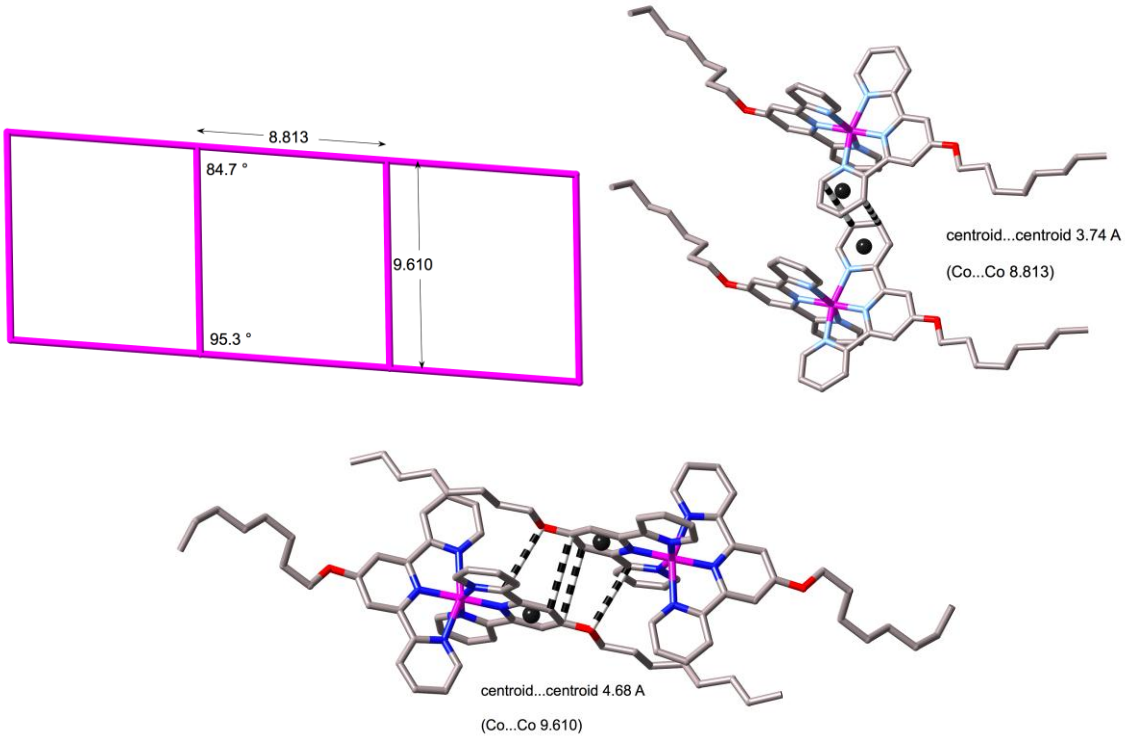
35. $[Co(n\text{-}C_3H_7Otpy)_2](PF_6)_2.CH_3CN$, 173 K.[SI13] (Sheets of fused hexagons of two slightly different sizes.)



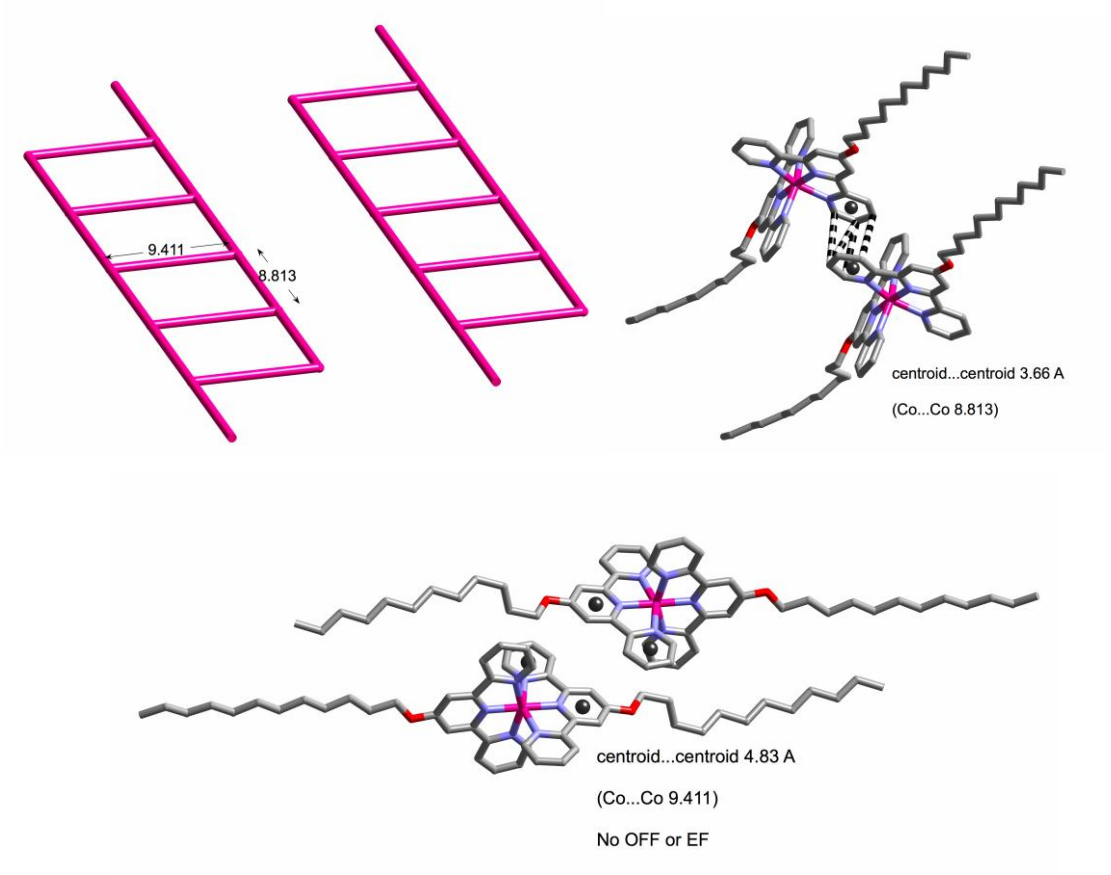
36. $[Co(n\text{-}C_4H_9Otpy)_2](PF_6)_2.3H_2O$, 123 K, *.[SI27] (Three-dimensional structure based on short links between sheets of fused hexagonal units.)



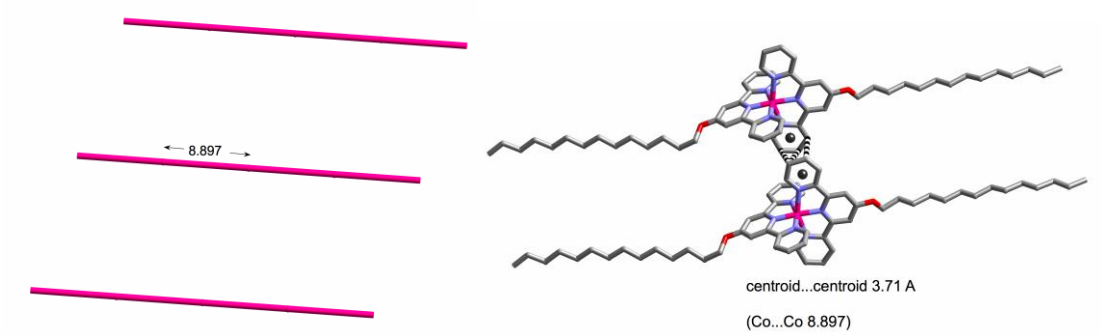
37. $[Co(n\text{-}C_8H_{17}Otpy)_2](BF_4)_2.H_2O$, 123 K, *.[SI27]



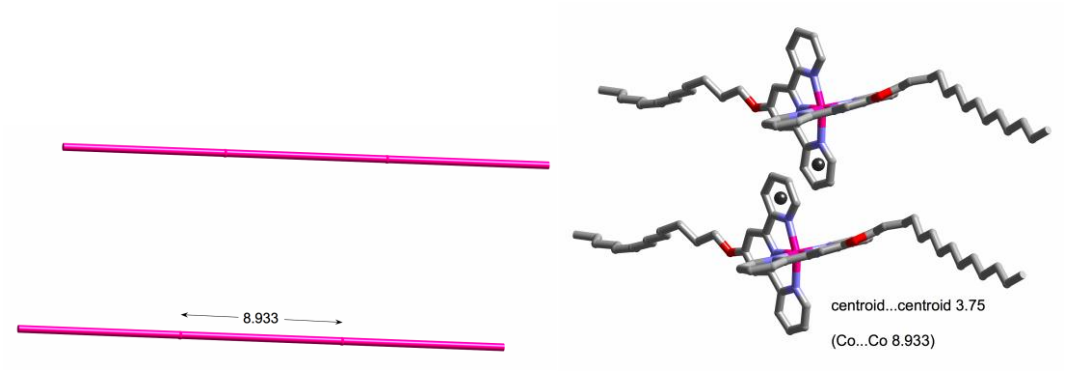
38. $[Co(n\text{-}C_8H_{17}Otpy)_2](ClO_4)_2$, 123 K, *.[SI27] (Sheets of « isolated » ladder-like arrays.)



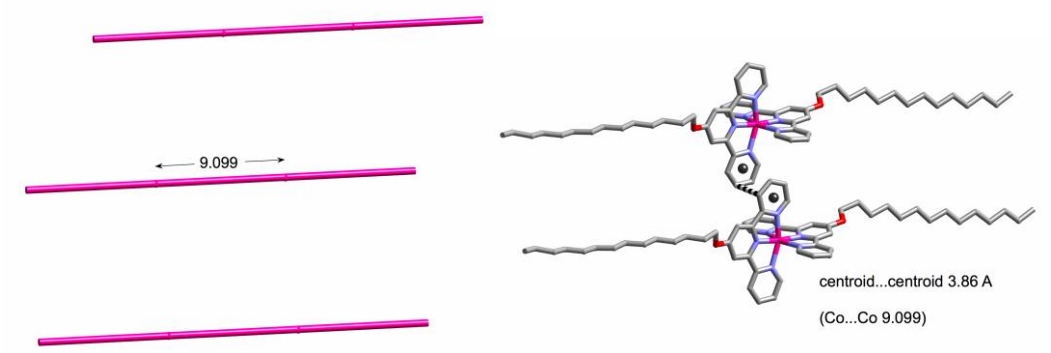
39. $[Co(n\text{-}C_{12}H_{25}Otpy)_2](BF_4)_2.C_2H_5OH.0.5H_2O$, 180 K, *.[SI28] (Sheets of « isolated » ladder-like arrays.)



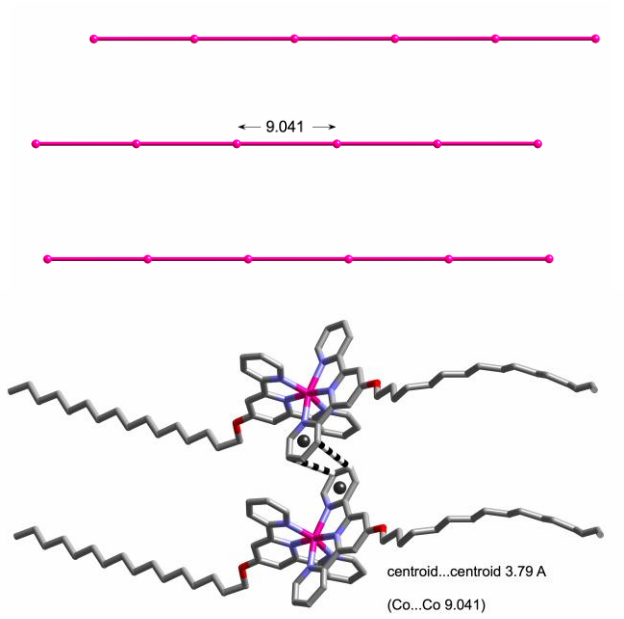
40. $[Co(n\text{-}C_{14}H_{29}Otpy)_2](BF_4)_2.CH_3OH$, 10 K (low spin form), *.[SI29] (Slightly undulating sheets of « isolated » linear chains.)



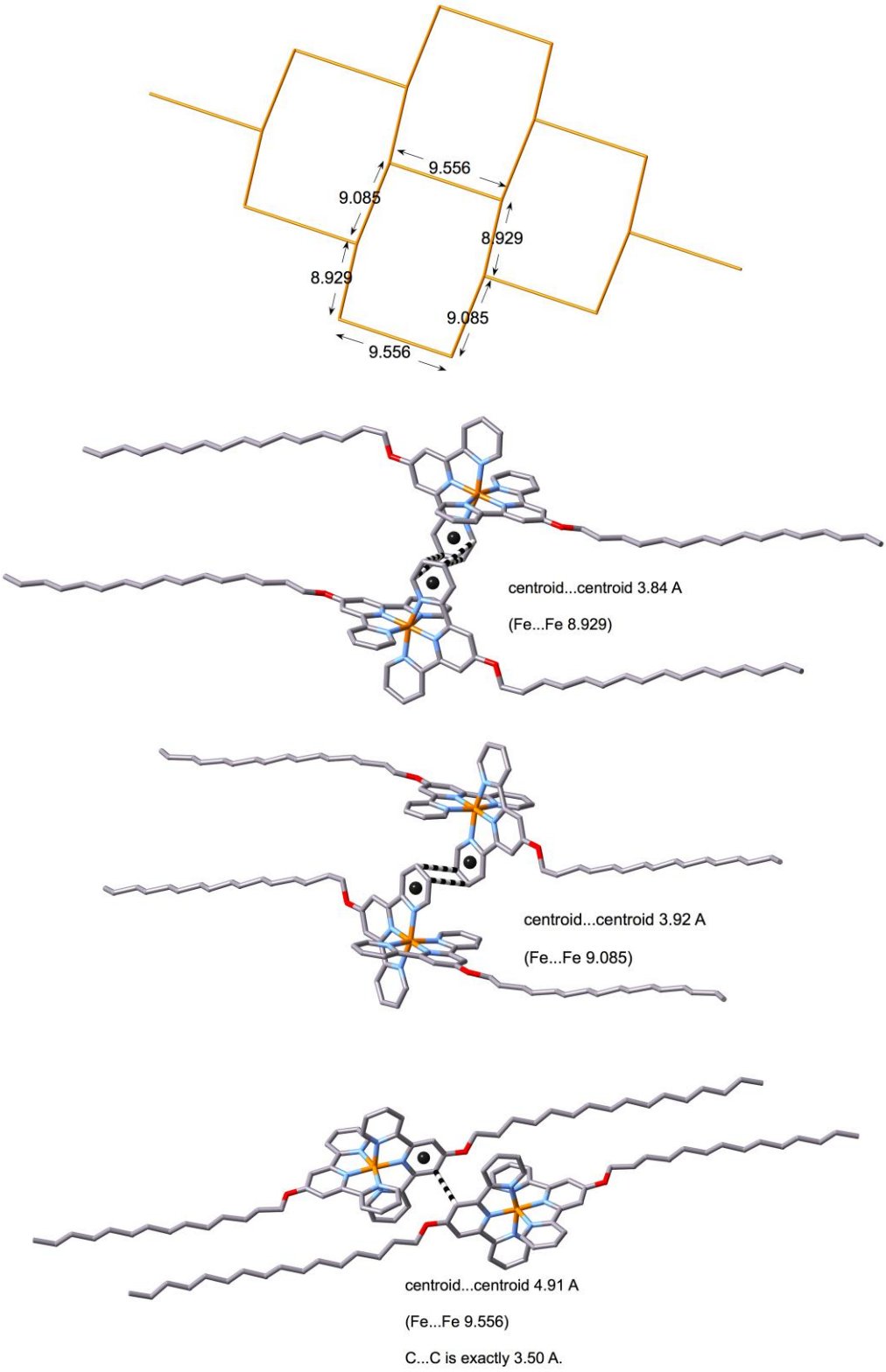
41. $[Co(n\text{-}C_{14}H_{29}Otpy)_2](BF_4)_2.CH_3OH$, 190 K (intermediate spin form), *.[SI29] (Sheets of « isolated » linear chains.)



42. $[Co(n\text{-}C_{14}H_{29}Otpy)_2](BF_4)_2.CH_3OH$, 190 K (high spin form), *.[SI29]



43. $[Co(n\text{-}C_{16}H_{33}Otpy)_2](BF_4)_2.CH_3OH$, 133 K, *.[SI30]



44. $[Fe(n\text{-}C_{16}H_{33}Otpy)_2](ClO_4)_2.(CH_3)_2CO$, 120 K.[SI31]

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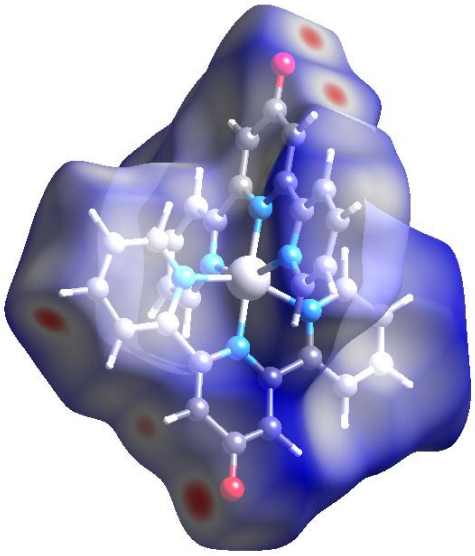
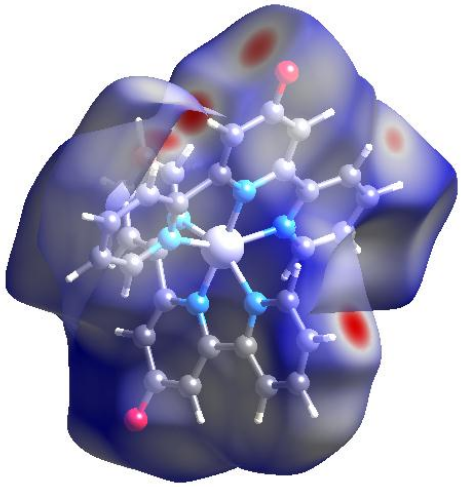
Part B



Hirshfeld surface for polymorph 1 of $[Co(HOtpy)_2](CF_3SO_3)_2.H_2O$



Hirshfeld surface for polymorph 2 of $[Co(HOtpy)_2](CF_3SO_3)_2.H_2O$