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Details of Crystal Structure Refinements, Selected Bond Lengths, and Angles

All three structural determinations were carried out at low temperature (123 or 173 K) to prevent rapid solvent loss from the crystals, which were coated with paraffin oil containing a drop of the recrystallisation solvent before being transferred to the diffractometer. Non-H atoms were refined with anisotropic thermal parameters apart from some exceptions described below. H atoms were included in calculated positions (except for on lattice solvent molecules, where they were omitted from the refinement) with isotropic thermal parameters and refined as riding atoms.

In **$[Co_4(L^2)_6(BF_4)][BF_4]_7 \cdot H_2O \cdot 7MeCN$** (space group *R*–3), the asymmetric unit contains one-third of each of the two independent complex units (which lie on a C_3 axis passing through one Co atom and through the center of the opposite triangular face). The asymmetric unit also contains 5.3333 $[BF_4]^-$ anions, of which three are in general positions, six are on threefold axes and therefore have 1/3 presence in the asymmetric unit, and two are on threefold axes but with only 50% occupancy, i.e., they contribute one-sixth of an anion to the asymmetric unit. Four MeCN molecules were located in general positions and two more lying on threefold axes, which passed through all three atoms and which therefore contribute 1/3 MeCN to the asymmetric unit. Finally, two isolated electron-density peaks on special positions were assigned as oxygen atoms of water molecules, both with 1/3 presence in the asymmetric unit. The atoms of the disordered $[BF_4]^-$ anions and some atoms from disordered solvents were refined with isotropic thermal parameters. All other non-H atoms were refined with anisotropic thermal parameters. Geometric restraints were applied to two of the anions to keep their geometry sensible. Given the weakness of the data (only data with $2\theta < 45°$ were used in the refinement) and the resolution problems associated with a very long *c*-axis, the refinement is excellent ($R1 = 7.2\%$).

Selected bond lengths (Å) and angles (degrees)

Co(1)-N(51)	2.093(6)	Co(3)-N(171)	2.102(6)
Co(1)-N(71)	2.127(5)	Co(3)-N(191)	2.137(6)
Co(1)-N(11)	2.124(6)	Co(3)-N(201)	2.137(5)
Co(1)-N(61)	2.143(6)	Co(3)-N(131)	2.142(6)
Co(1)-N(21)	2.143(5)	Co(3)-N(181)	2.154(6)
Co(1)-N(81)	2.174(6)	Co(3)-N(141)	2.156(6)
Co(2)-N(111A)	2.147(5)	Co(4)-N(231)	2.135(5)
Co(2)-N(111B)	2.147(5)	Co(4)-N(231C)	2.135(5)
Co(2)-N(111)	2.147(5)	Co(4)-N(231D)	2.135(5)
Co(2)-N(121)	2.171(5)	Co(4)-N(241C)	2.151(5)
Co(2)-N(121A)	2.171(5)	Co(4)-N(241)	2.151(5)
Co(2)-N(121B)	2.171(5)	Co(4)-N(241D)	2.151(5)

N(51)-Co(1)-N(71)	97.1(2)	N(171)-Co(3)-N(191)	99.3(2)
N(51)-Co(1)-N(11)	92.9(2)	N(171)-Co(3)-N(201)	176.1(2)
N(71)-Co(1)-N(11)	98.5(2)	N(191)-Co(3)-N(201)	77.3(2)
N(51)-Co(1)-N(61)	77.5(2)	N(171)-Co(3)-N(131)	94.4(3)
N(71)-Co(1)-N(61)	172.6(2)	N(191)-Co(3)-N(131)	92.3(2)
N(11)-Co(1)-N(61)	86.9(2)	N(201)-Co(3)-N(131)	87.5(2)
N(51)-Co(1)-N(21)	170.2(2)	N(171)-Co(3)-N(181)	76.8(2)
N(71)-Co(1)-N(21)	85.5(2)	N(191)-Co(3)-N(181)	87.8(2)
N(11)-Co(1)-N(21)	77.3(2)	N(201)-Co(3)-N(181)	101.2(2)
N(61)-Co(1)-N(21)	100.8(2)	N(131)-Co(3)-N(181)	171.1(2)
N(51)-Co(1)-N(81)	87.3(2)	N(171)-Co(3)-N(141)	86.8(2)
N(71)-Co(1)-N(81)	76.7(2)	N(191)-Co(3)-N(141)	168.0(2)
N(11)-Co(1)-N(81)	175.2(2)	N(201)-Co(3)-N(141)	96.9(2)
N(61)-Co(1)-N(81)	97.9(2)	N(131)-Co(3)-N(141)	76.8(2)
N(21)-Co(1)-N(81)	102.6(2)	N(181)-Co(3)-N(141)	103.8(2)
N(111A)-Co(2)-N(111B)	93.9(2)	N(231)-Co(4)-N(231C)	97.09(19)
N(111A)-Co(2)-N(111)	93.9(2)	N(231)-Co(4)-N(231D)	97.09(19)
N(111B)-Co(2)-N(111)	93.9(2)	N(231C)-Co(4)-N(231D)	97.09(19)
N(111A)-Co(2)-N(121)	170.3(2)	N(231)-Co(4)-N(241C)	86.21(18)
N(111B)-Co(2)-N(121)	76.8(2)	N(231C)-Co(4)-N(241C)	76.83(19)
N(111)-Co(2)-N(121)	89.62(19)	N(231D)-Co(4)-N(241C)	173.44(19)
N(111A)-Co(2)-N(121A)	89.62(19)	N(231)-Co(4)-N(241)	76.83(19)
N(111B)-Co(2)-N(121A)	170.3(2)	N(231C)-Co(4)-N(241)	173.44(19)
N(111)-Co(2)-N(121A)	76.8(2)	N(231D)-Co(4)-N(241)	86.21(18)

N(121)-Co(2)-N(121A)	100.04(18)	N(241C)-Co(4)-N(241)	100.08(17)
N(111A)-Co(2)-N(121B)	76.8(2)	N(231)-Co(4)-N(241D)	173.44(19)
N(111B)-Co(2)-N(121B)	89.62(19)	N(231C)-Co(4)-N(241D)	86.21(18)
N(111)-Co(2)-N(121B)	170.3(2)	N(231D)-Co(4)-N(241D)	76.83(19)
N(121)-Co(2)-N(121B)	100.04(18)	N(241C)-Co(4)-N(241D)	100.08(17)
N(121A)-Co(2)-N(121B)	100.04(18)	N(241)-Co(4)-N(241D)	100.08(17)

Crystals of **$[Co_4(L^2)_6(ClO_4)][ClO_4]_7$•13MeCN** lost solvent and decomposed almost immediately on removal from the mother liquor. The data was accordingly very weak, and the presence of a 40 Å *c*-axis resulted in diffraction spots overlapping. Only data with $2\theta < 40°$ were used in the refinement. Only the Co, Cl, and 26 of the 32 O atoms could be refined anisotropically: attempts to introduce more variables into the refinement made it unstable, and all remaining atoms were therefore refined with isotropic thermal parameters. All anisotropic atoms had isotropic restraints (ISOR) applied to them to prevent their thermal ellipsoids from becoming too eccentric. The asymmetric unit contains 1 complete complex molecule, its 8 associated perchlorate anions, and 13 MeCN molecules. Of these, 11 were located completely: further residual electron-density peaks were assigned as C atoms of fractional site occupancy, adding up to a total of 6 atoms, which we have approximated as two further MeCN molecules. The quality of the final refinement ($R1$ = 21.6%) precludes any detailed discussion of bond distances and angles, but it is clear that the complex structure is essentially the same as that of the fluoroborate analogue (above).

Crystals of **$[Ni_2(L^2)_3][ClO_4]_4$•4MeCN•0.5($^iPr_2O$)** likewise lost solvent rapidly, and the resulting weak diffraction meant that only data with $2\theta < 45°$ could be used in the refinement. Apart from that, the solution and refinement were relatively straightforward, with an entire dinuclear complex and its associated four anions present in the asymmetric unit. One of the perchlorate anions [Cl(2)] was disordered with one of the O atoms disordered over two sites with 50% occupancy in each. There was evidence for further disorder, which could not be resolved. Of the four MeCN molecules, three were relatively well behaved, but the fourth was disordered over two

sites by pivoting about the N atom (such that the N atom had 100% occupancy, but the two C atoms were each disordered over two sites with 50% occupancy in each). An additional cluster of residual electron-density peaks clearly corresponded to disordered solvent of some sort. It was not possible to resolve this disorder sensibly, thus the electron-density peaks were assigned as C atoms with fractional site occupancies that added up to 3.5, corresponding approximately to one-half of a di-isopropyl ether molecule. ISORs were applied to some of these disordered atoms to prevent their thermal ellipsoids from becoming too eccentric; two of them (with low site occupancies) were refined isotropically. Also, geometric restraints (SADI) were applied to the disordered perchlorate anion. The quality of the final refinement ($R1$ = 5.6%) is fine given these problems.

Selected bond lengths (Å) and angles (degrees)

Ni(1)-N(151)	2.087(5)	Ni(2)-N(251)	2.070(5)
Ni(1)-N(121)	2.089(5)	Ni(2)-N(241)	2.082(4)
Ni(1)-N(111)	2.092(5)	Ni(2)-N(201)	2.085(5)
Ni(1)-N(101)	2.099(5)	Ni(2)-N(221)	2.091(5)
Ni(1)-N(131)	2.114(4)	Ni(2)-N(211)	2.091(5)
Ni(1)-N(141)	2.135(5)	Ni(2)-N(231)	2.122(5)

N(151)-Ni(1)-N(121)	104.90(19)	N(251)-Ni(2)-N(241)	78.73(18)
N(151)-Ni(1)-N(111)	88.11(19)	N(251)-Ni(2)-N(201)	167.4(2)
N(121)-Ni(1)-N(111)	162.4(2)	N(241)-Ni(2)-N(201)	93.14(18)
N(151)-Ni(1)-N(101)	90.65(19)	N(251)-Ni(2)-N(221)	92.55(19)
N(121)-Ni(1)-N(101)	89.23(19)	N(241)-Ni(2)-N(221)	100.82(18)
N(111)-Ni(1)-N(101)	78.7(2)	N(201)-Ni(2)-N(221)	98.4(2)
N(151)-Ni(1)-N(131)	176.91(19)	N(251)-Ni(2)-N(211)	92.02(19)
N(121)-Ni(1)-N(131)	77.28(19)	N(241)-Ni(2)-N(211)	91.59(18)
N(111)-Ni(1)-N(131)	90.23(19)	N(201)-Ni(2)-N(211)	78.5(2)
N(101)-Ni(1)-N(131)	91.58(18)	N(221)-Ni(2)-N(211)	167.39(17)
N(151)-Ni(1)-N(141)	77.88(18)	N(251)-Ni(2)-N(231)	97.86(19)
N(121)-Ni(1)-N(141)	94.56(18)	N(241)-Ni(2)-N(231)	176.48(19)
N(111)-Ni(1)-N(141)	99.8(2)	N(201)-Ni(2)-N(231)	90.37(18)
N(101)-Ni(1)-N(141)	168.50(16)	N(221)-Ni(2)-N(231)	78.3(2)
N(131)-Ni(1)-N(141)	99.85(17)	N(211)-Ni(2)-N(231)	89.4(2)