National School on Neutron and X-ray Scattering
Lecture Date: October 1, 2008

Single Crystal Crystallography

Example 2 –

Finding Chiral Crystals in Racemic Mixtures

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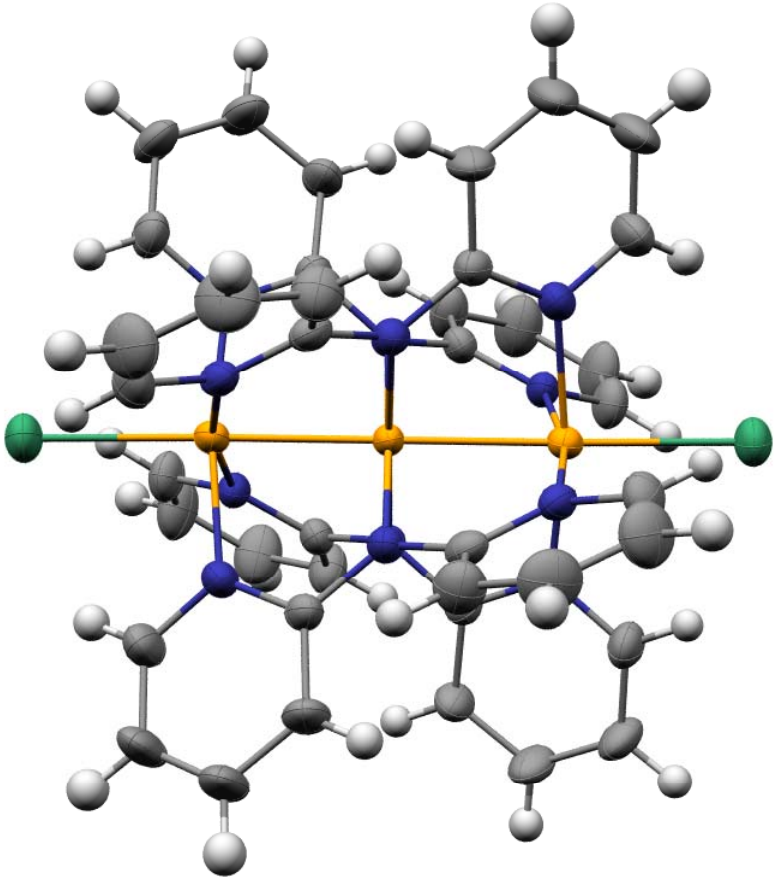
Oak Ridge National Laboratory

Presented at the ACA Annual Meeting, Salt Lake City, July 22, 2007

Extended Metal Atom Chains (EMACs)

$M_3(dpa)_4Cl_2$

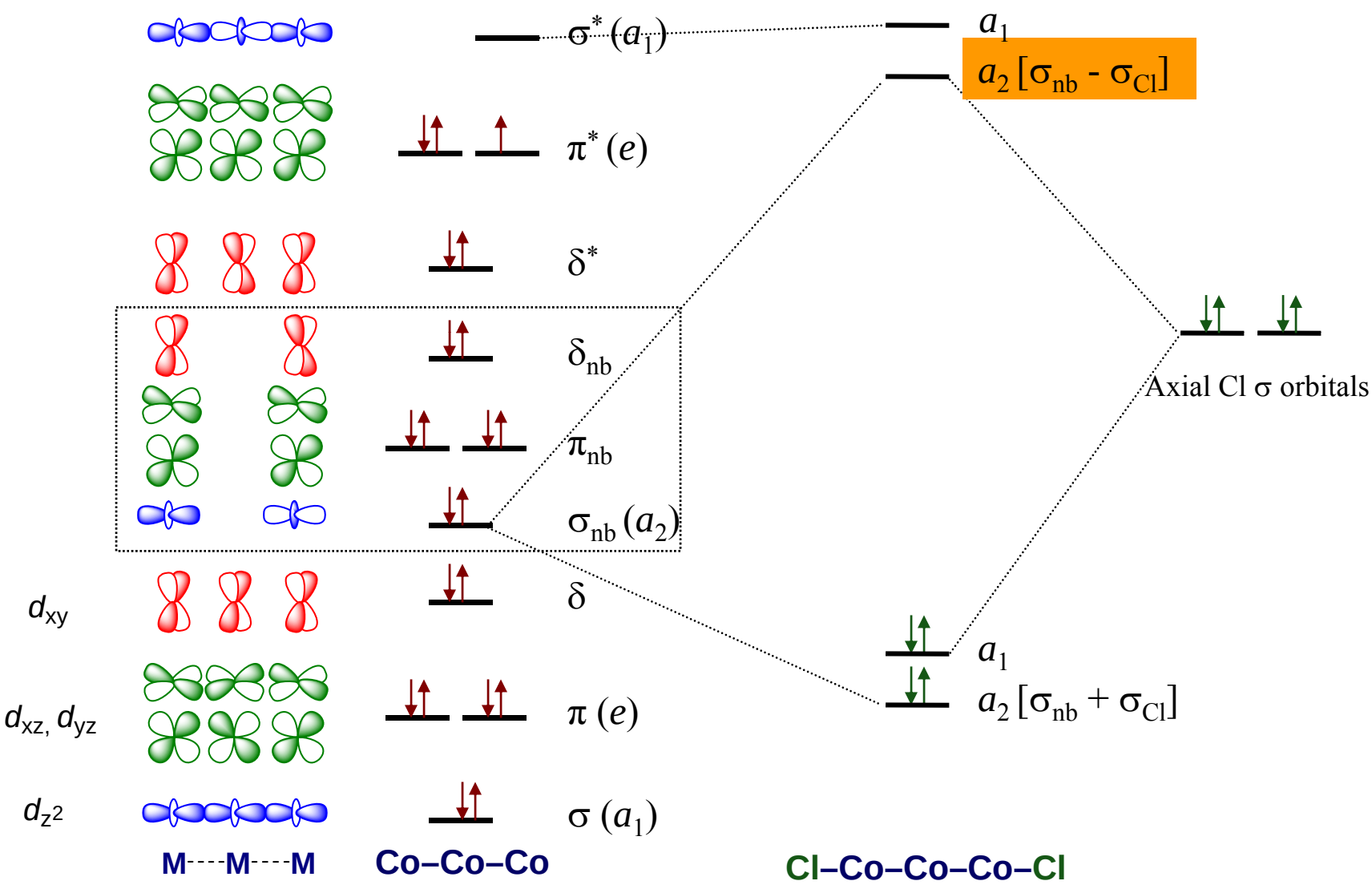


D_4

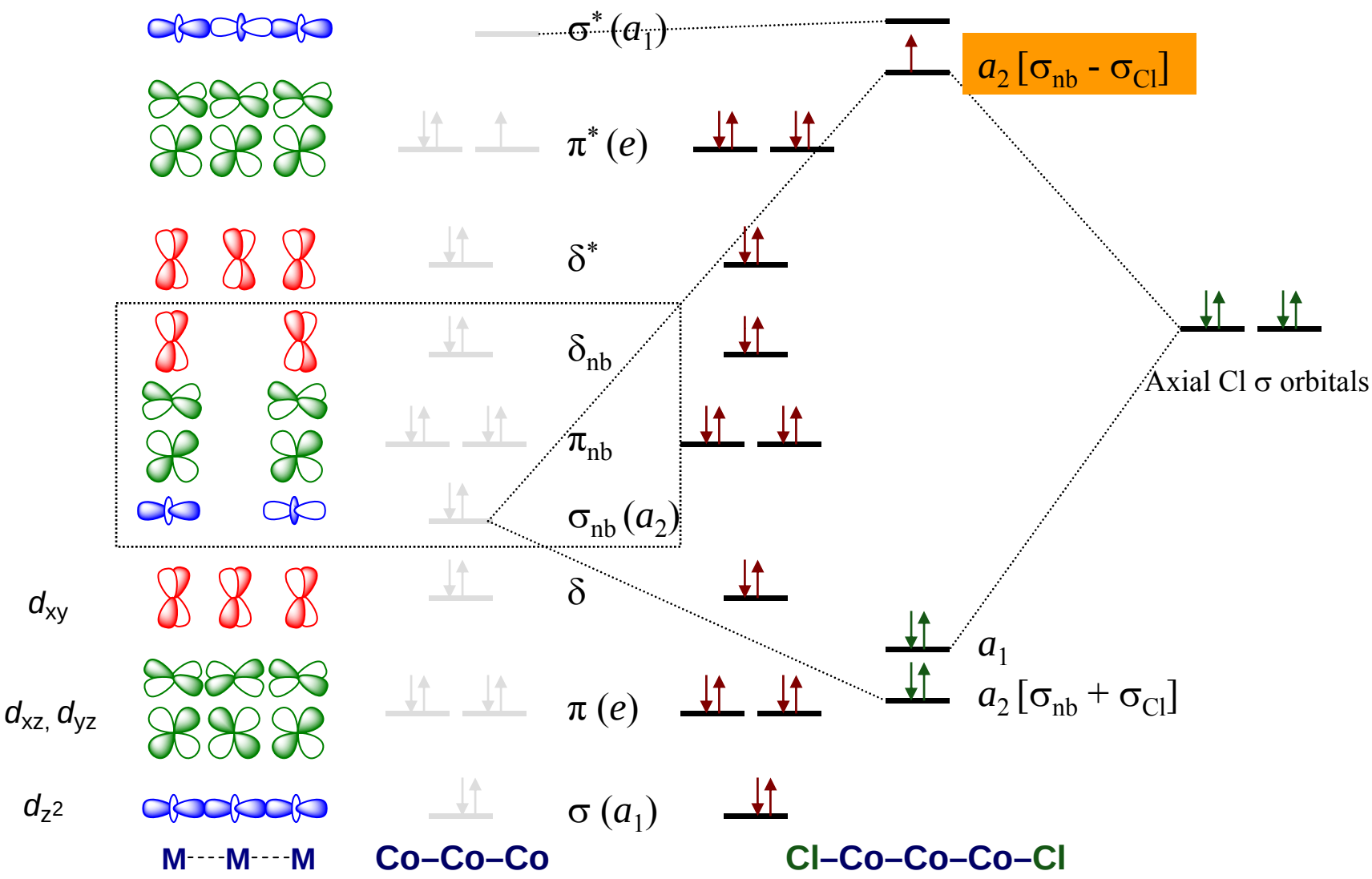
M = Ni^{2+}, Cu^{2+}, Rh^{2+}, Ru^{2+}
dpa = anion of 2,2'-dipyridylamine

F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple Bonds between Metal Atoms*, 3rd Ed. Springer: 2005.

M-M Bonding in Extended Metal Atom Chains (EMACs)

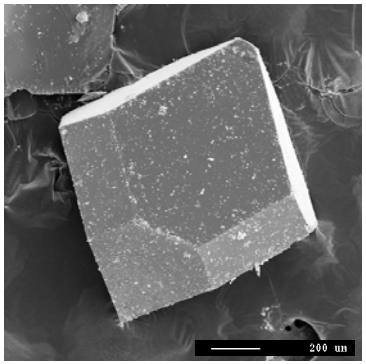


M-M Bonding in Extended Metal Atom Chains (EMACs)

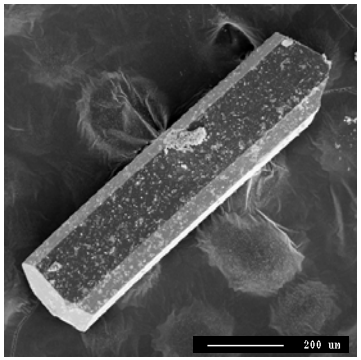


M. Benard, J. F. Berry, F. A. Cotton, C. Gaudin, X. Lopez, C. A. Murillo, and M.-M. Rohmer, *Inorg. Chem.* **2006**, 45, 3932.
J. F. Berry, F. A. Cotton, L. M. Daniels, C. A. Murillo, X.P. Wang, *Inorg. Chem.* **2003**, *42*, 2418.

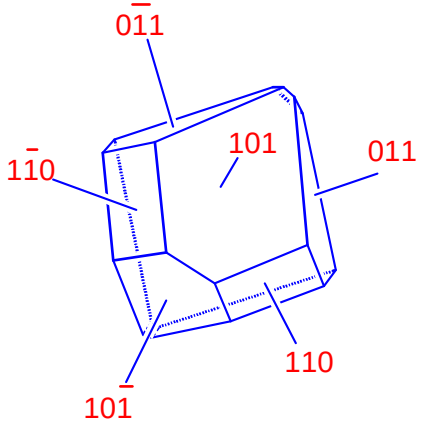
Polymorphism in $Co_3(dpa)_4Cl_2$

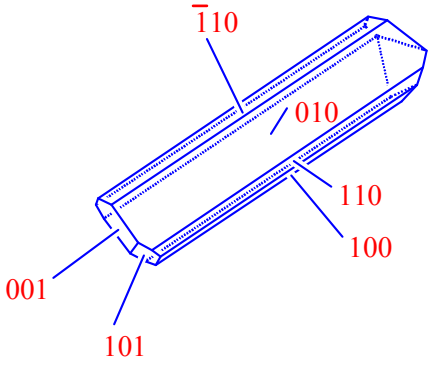


Orthorhombic crystal



Tetragonal crystal





(s-$Co_3(dpa)_4Cl_2 \cdot CH_2Cl_2$) ($u$-$Co_3(dpa)_4Cl_2 \cdot 2CH_2Cl_2$)

Pseudopolymorphs?

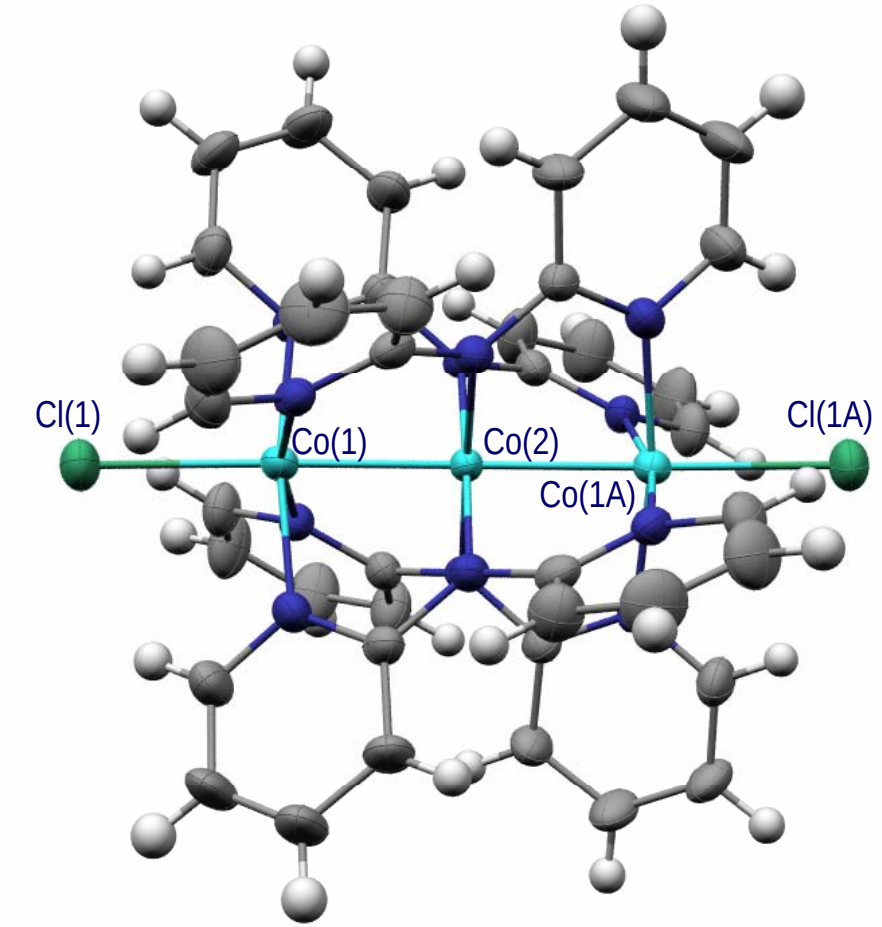
F. A. Cotton, C. A. Murillo, X. P. Wang, *J. Chem. Soc., Dalton Trans.*, **1999**, 3327.

Crystal Structure of s-$Co_3(dpa)_4Cl_2$

Crystal data for
$[Co_3(dpa)_4Cl_2]\cdot CH_2Cl_2$

Orthorhombic, *Pnn*2
a = 12.8145(9) Å
b = 13.955(1) Å
c = 11.1660(9) Å
U = 1996.8(3) Å^3
D_c = 1.685 g/cm^3
Z = 2

T =296(2) K
$R1$ = 0.036
$wR2$ = 0.090



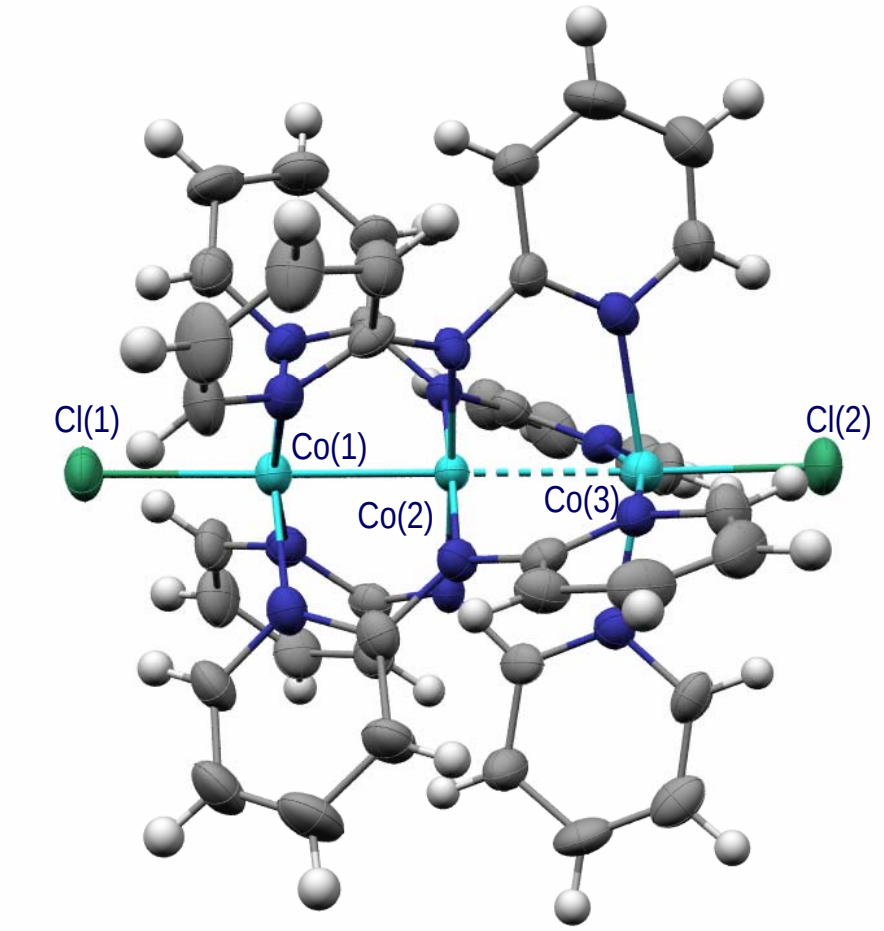
Cl(1) — Co(1) — Co(2) — Co(1A) — Cl(1A)
2.4881(8) **2.3369(4)** **2.3369(4)** 2.4881(8) Å

Crystal Structure of *u*-$Co_3(dpa)_4Cl_2$

Crystal data for
$[Co_3(dpa)_4Cl_2]\cdot 2CH_2Cl_2$

Tetragonal, *I*4
a = 27.378(2) Å
c = 12.318(1) Å
V = 9 233(1) Å^3
D_c =1.58 g/cm^3
Z = 8

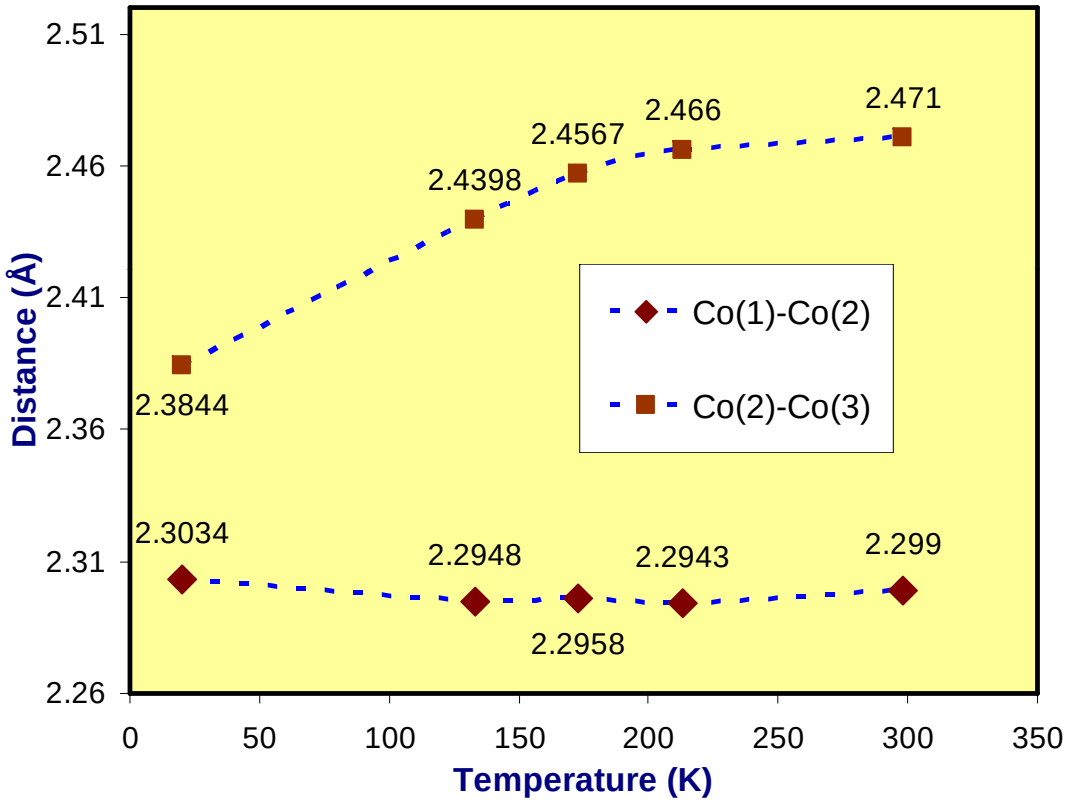
T = 298(2) K
$R1$ = 0.041
wR2 = 0.101

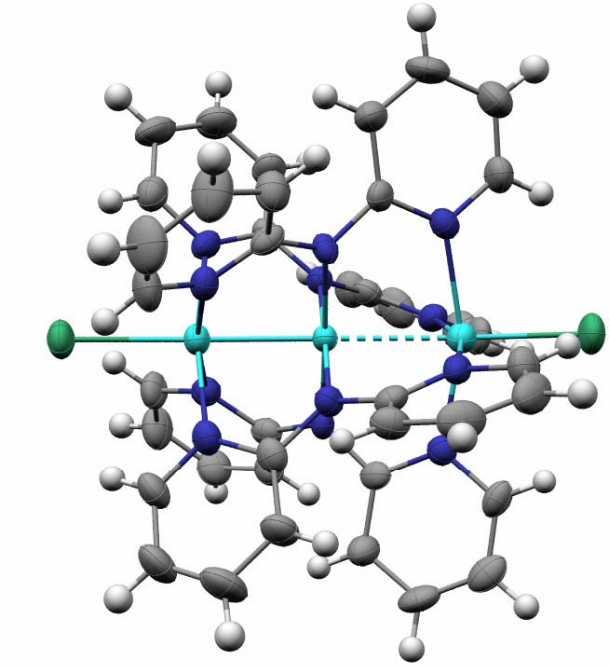


Cl(1) — Co(1) — Co(2) ···· Co(3) — Cl(2)
2.434(2) **2.299(1)** **2.471(1)** 2.363(2) Å

F. A. Cotton, C. A. Murillo, X. P. Wang, *J. Chem. Soc., Dalton Trans.*, **1999**, 3327.

Temperature Dependence of Co—Co Distances in *u*-$Co_3(dpa)_4Cl_2$

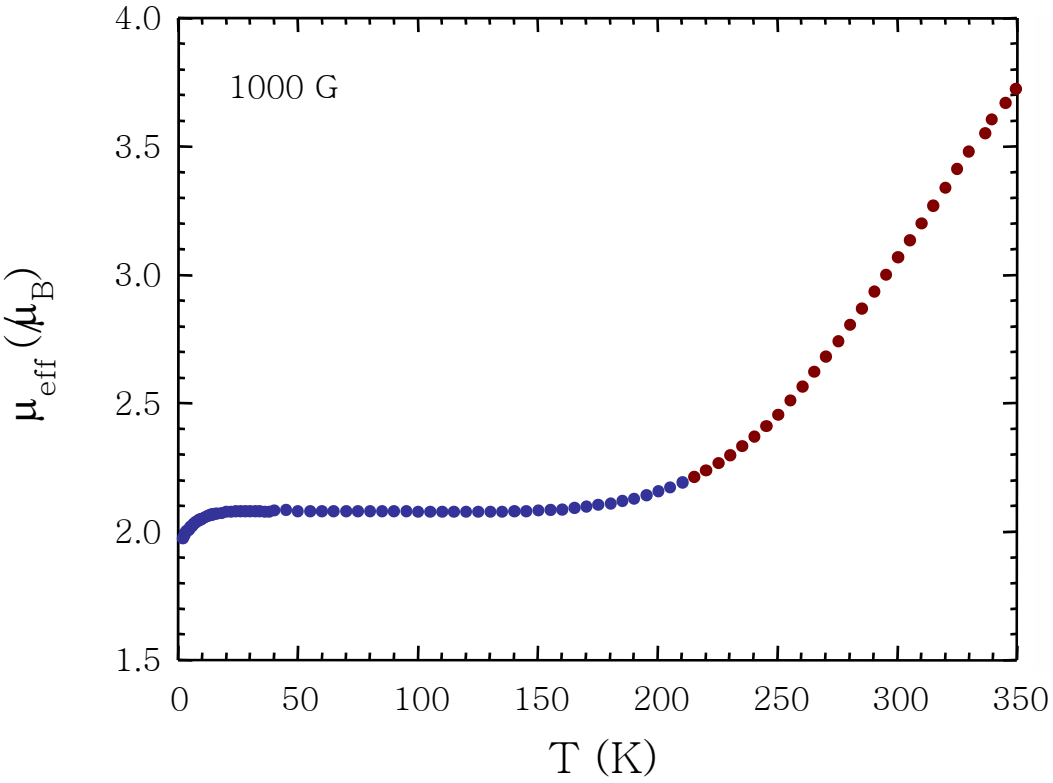


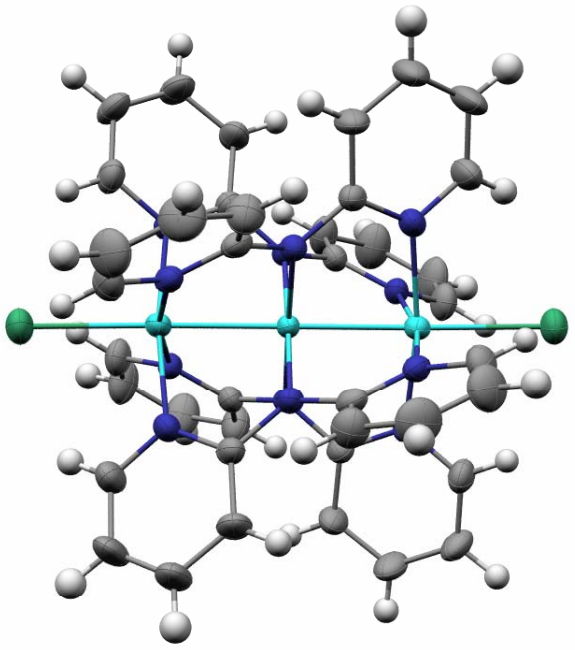


u-$Co_3(dpa)_4Cl_2$

Clerac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Kirschbaum, K; Murillo, C. A.; Pinkerton, A. A; Schultz, A. J; Wang, X. P, *J. Am. Chem. Soc*. **2000**, *122*, 6226

Magnetic Property of s-$Co_3(dpa)_4Cl_2 \cdot CH_2Cl_2$

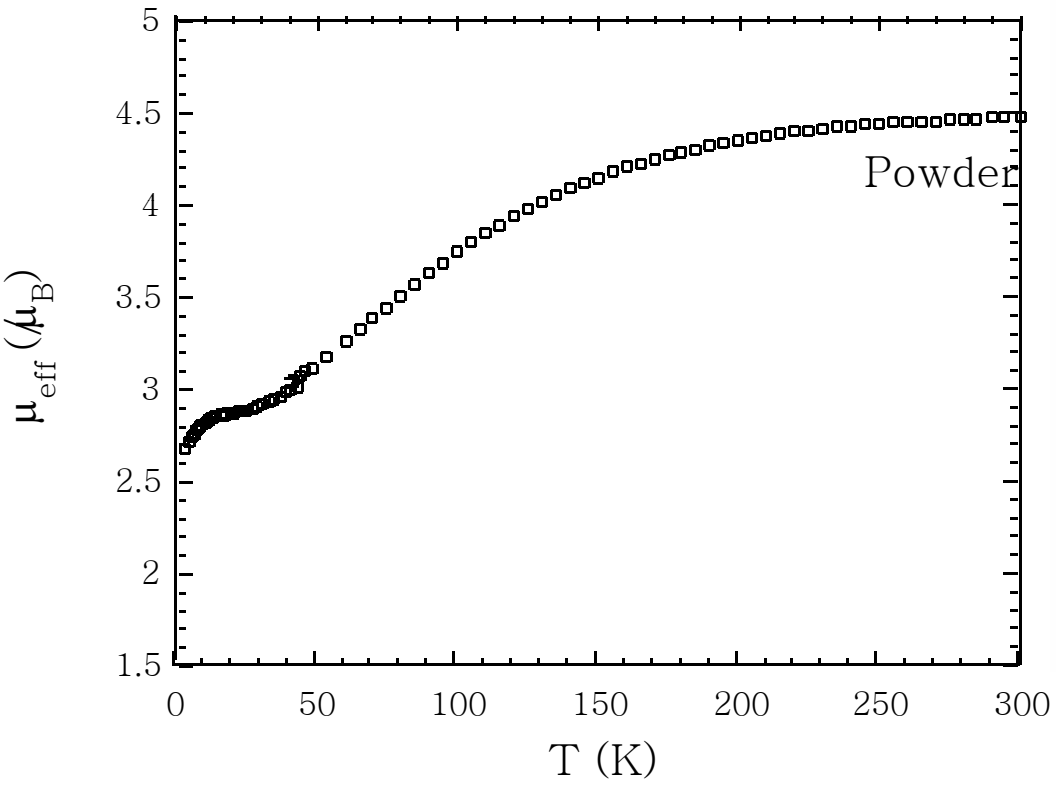


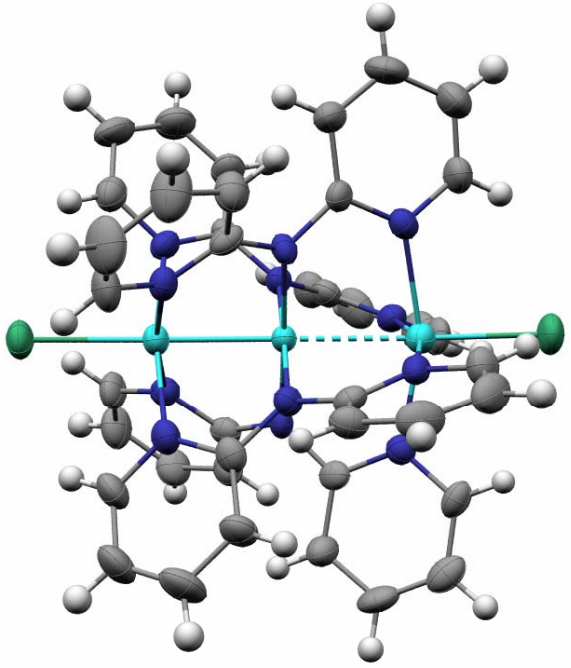


Spin Crossover S = 1/2 To S = 5/2

Magnetic Property of *u*-$Co_3(dpa)_4Cl_2 \cdot 2CH_2Cl_2$

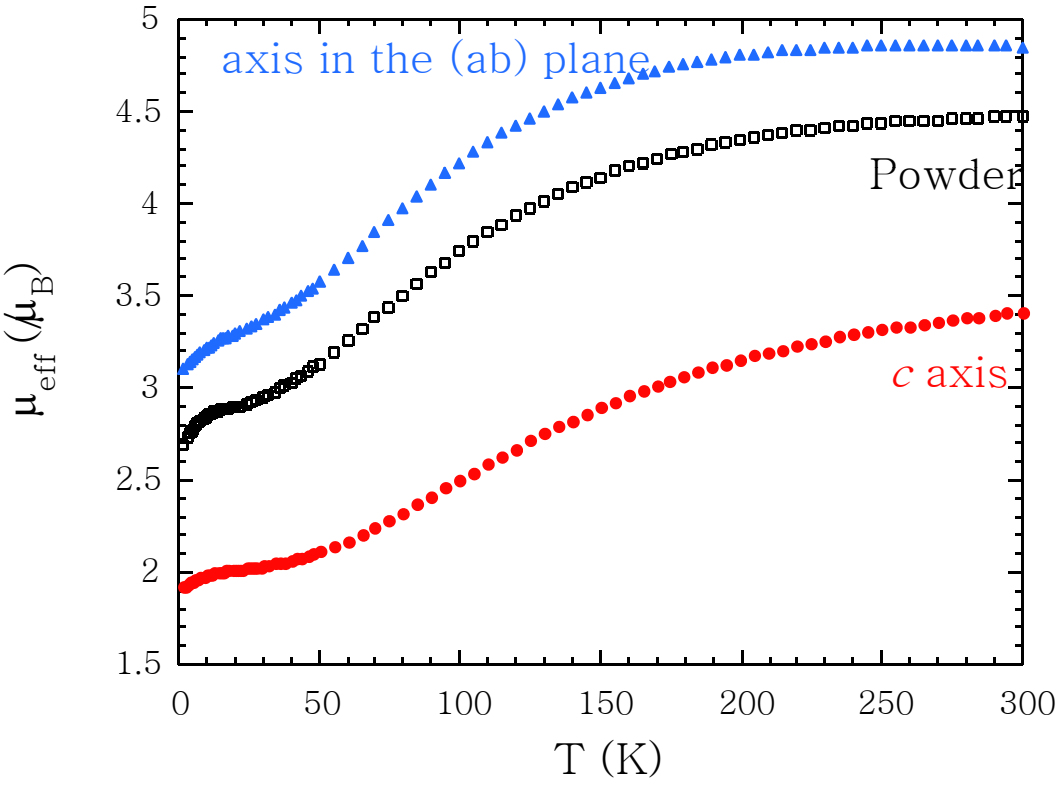
The magnetic data from powder sample could not be explained.

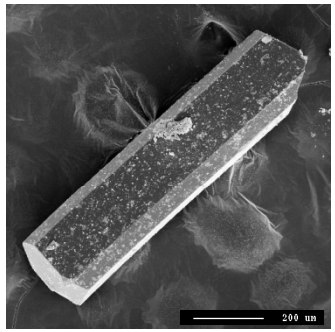




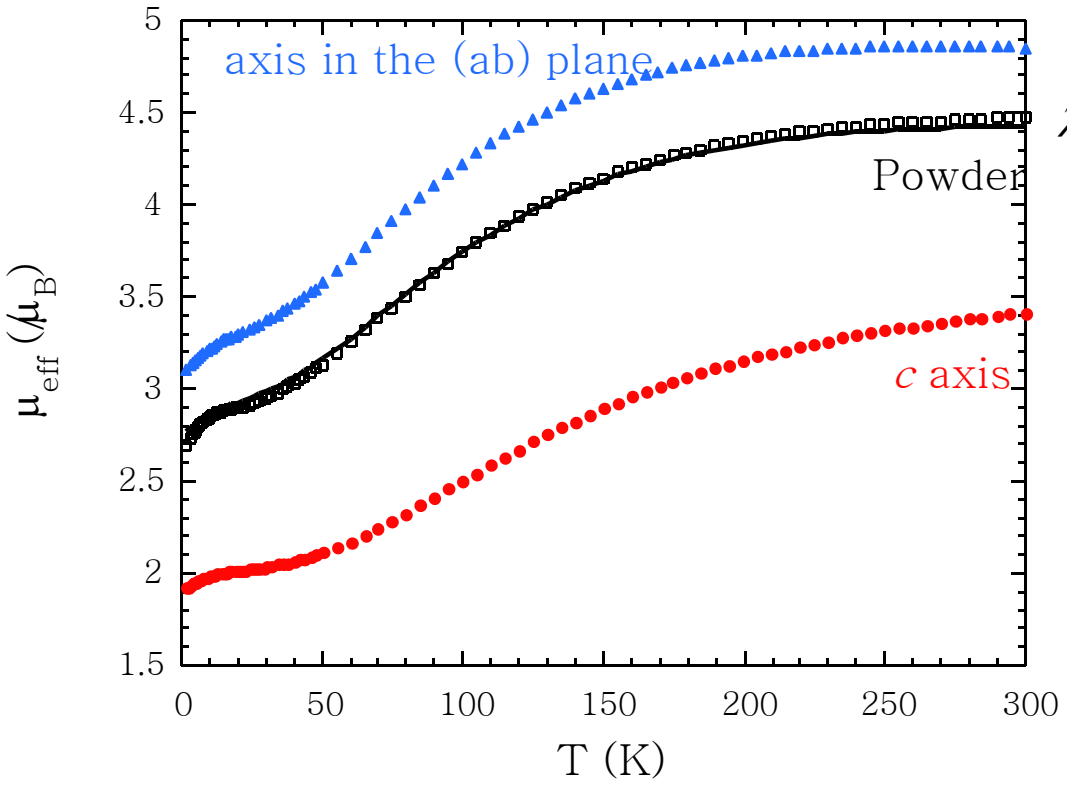
Spin Crossover S = 1/2? To S = ?

Magnetic Property of *u*-$Co_3(dpa)_4Cl_2 \cdot 2CH_2Cl_2$

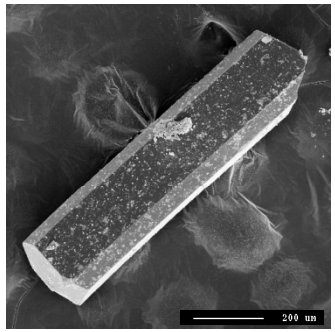




Magnetic Property of *u*-$Co_3(dpa)_4Cl_2 \cdot 2CH_2Cl_2$



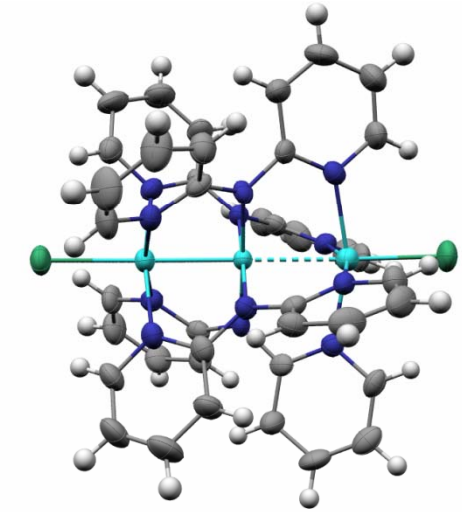
$$\chi = \frac{1}{3}(2\chi_{\perp} + \chi_{\parallel})$$

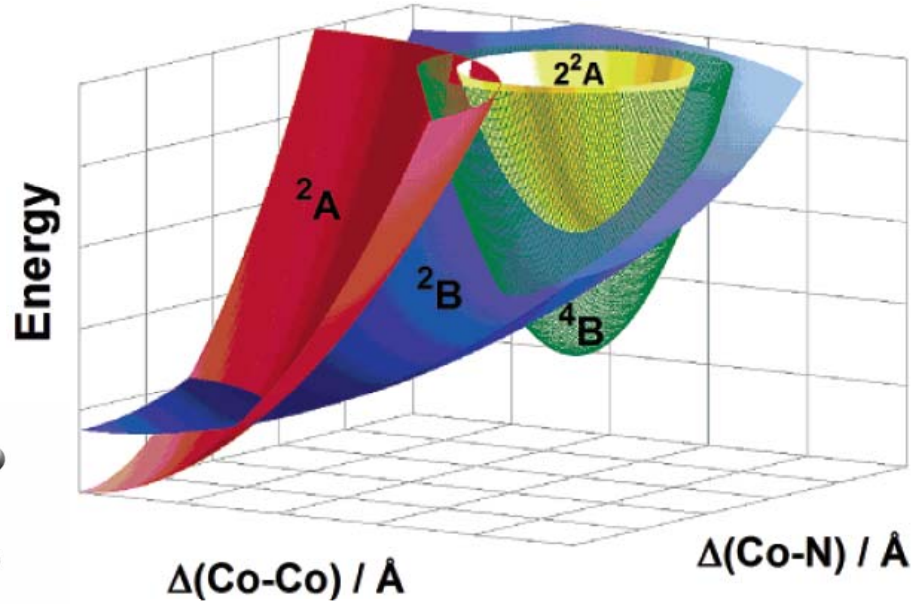


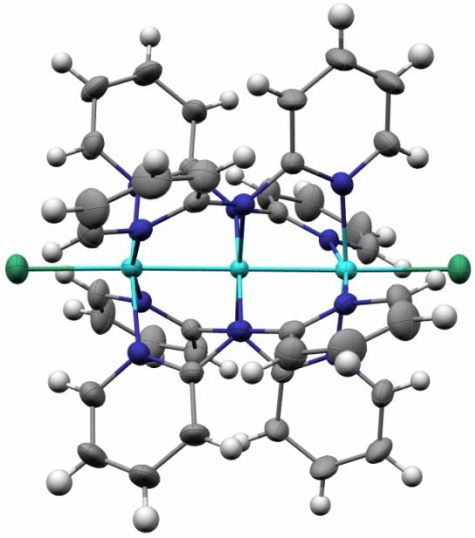
Spin Crossover S = 1/2 To S = 3/2

A Three-State Model for the Polymorphism in $Co_3(dpa)_4Cl_2$

D. A. Pantazis, and J. E. McGrady, *J. Am. Chem. Soc.* **2006**, *128*, 4128







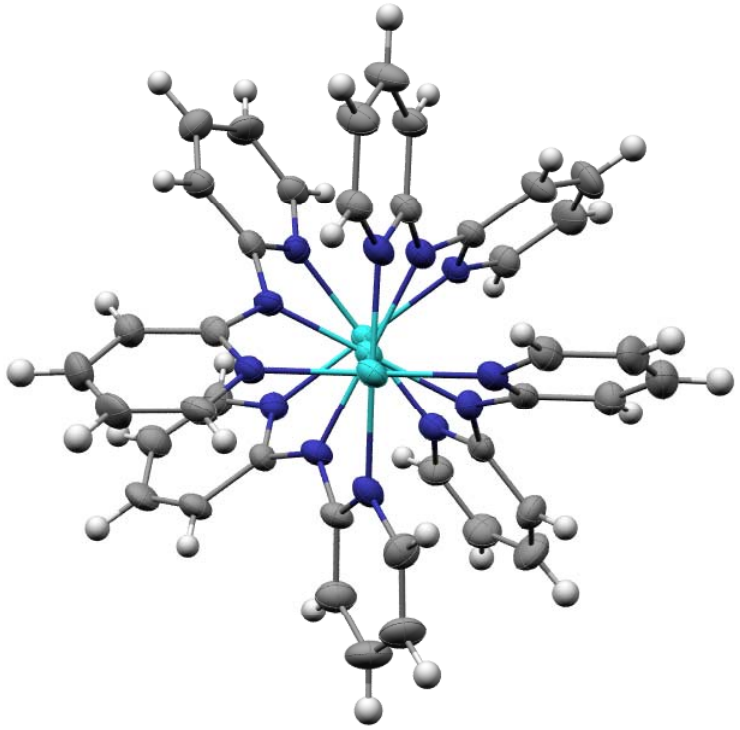
Spin State Isomer: $^2A \rightarrow {}^4B$

Bond Stretch Isomer: $^2A \rightarrow 2^2A$

$^2A \rightarrow {}^2B$

New Linear Tricobalt Complex

$$Co_3(dpa)_4Cl_2 + 2\,AgPF_6 \rightarrow [Co_3(dpa)_4(NCMe)_2][PF_6]_2$$



Clerac, R.; Cotton, F. A.; Dunbar, K. R.; Lu, T. B.; Murillo, C. A.; Wang, X. P. *Inorg. Chem.* **2000**, *39*, 3065-3070.

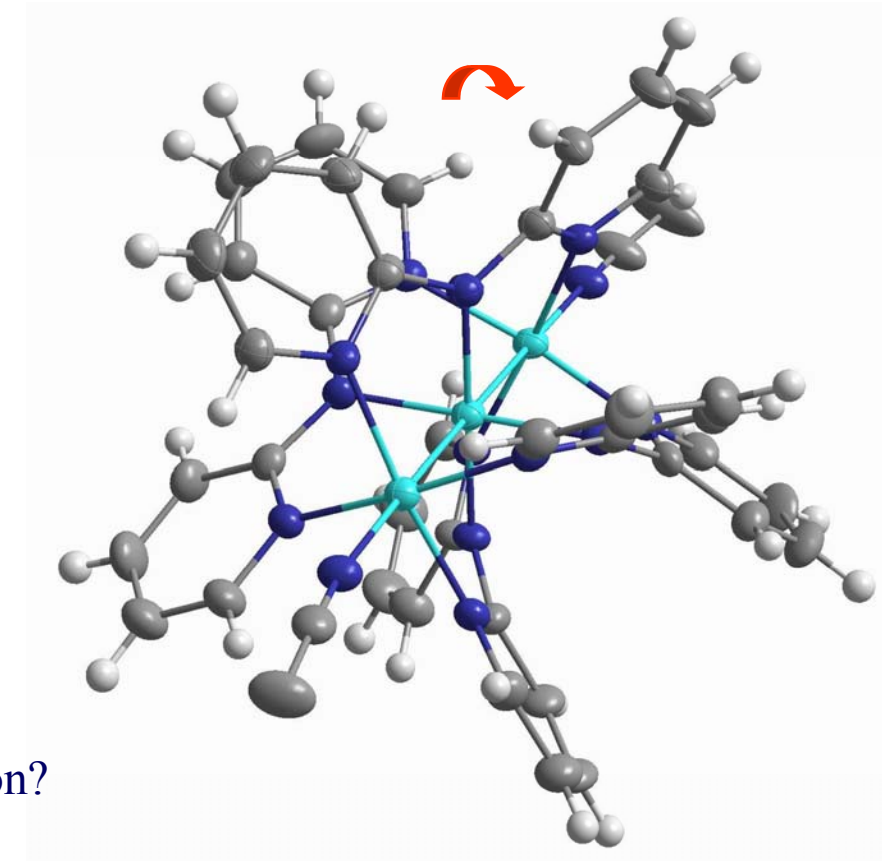
Crystal Structure of $[Co_3(dpa)_4(NCMe)_2][PF_6]_2$

cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a, Å	11.721(2)
b, Å	21.801(3)
c, Å	12.027(5)
α, deg	90
β, deg	111.93(2)
γ, deg	90
V, Å^3	2851(1)
R1, wR2	0.043, 0.110

Flack x 0.05(2)

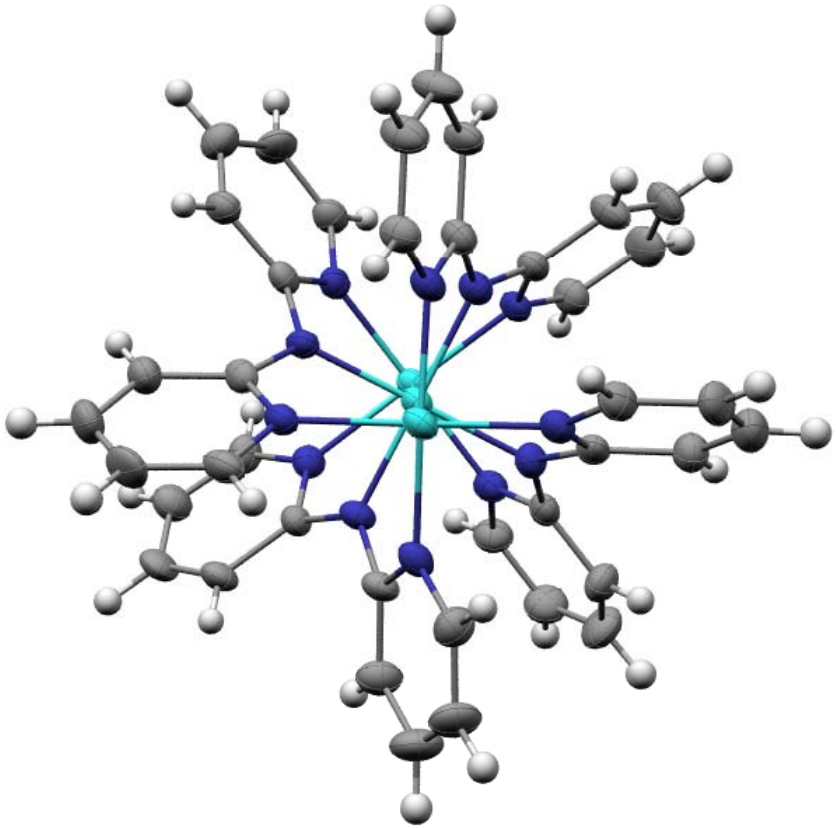
A chiral crystal !

Spontaneous resolution *via* crystallization?

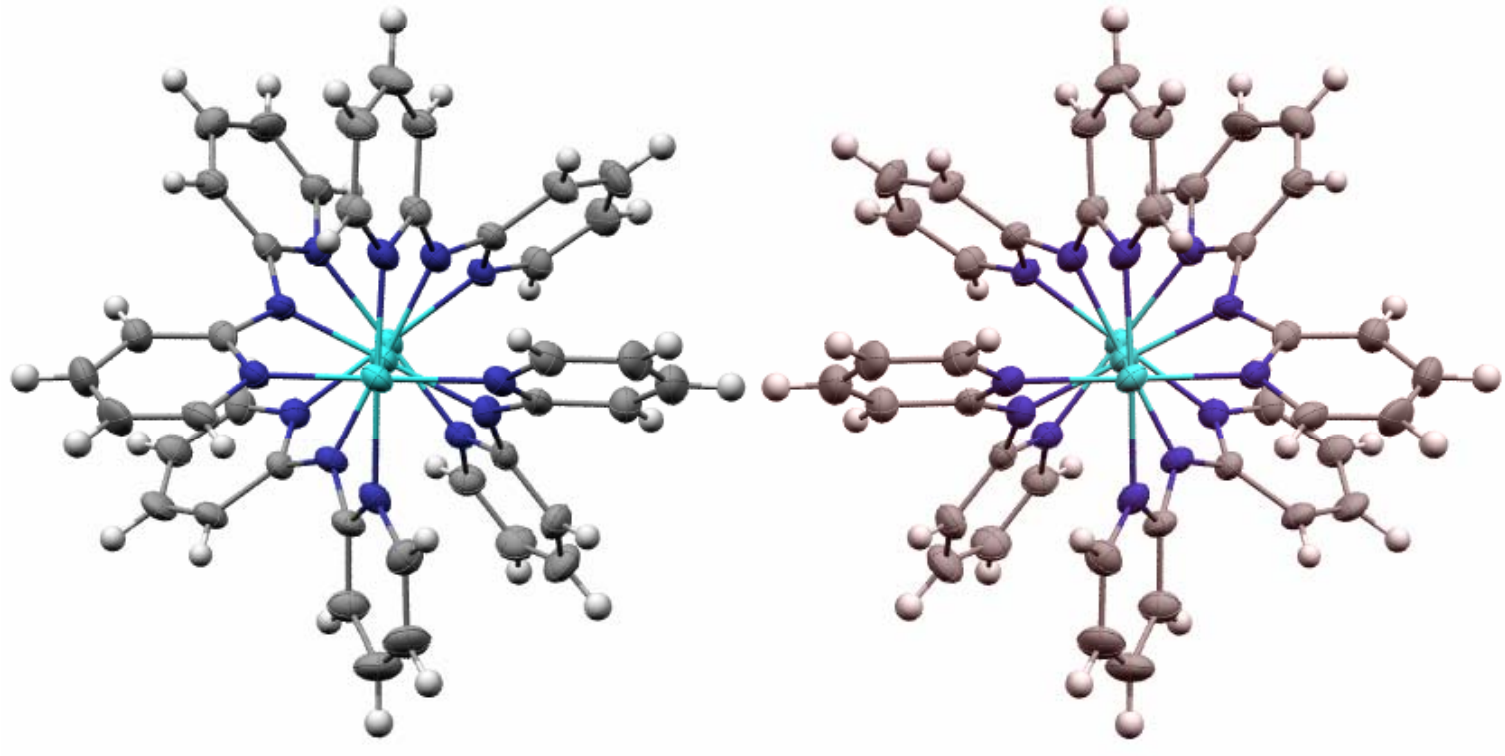


Δ-$[Co_3(dpa)_4(NCMe)_2][PF_6]_2$

Origin of Chirality in $[Co_3(dpa)_4(NCMe)_2][PF_6]_2$



Δ and Λ Enantiomers of $[Co_3(dpa)_4]^{2+}$

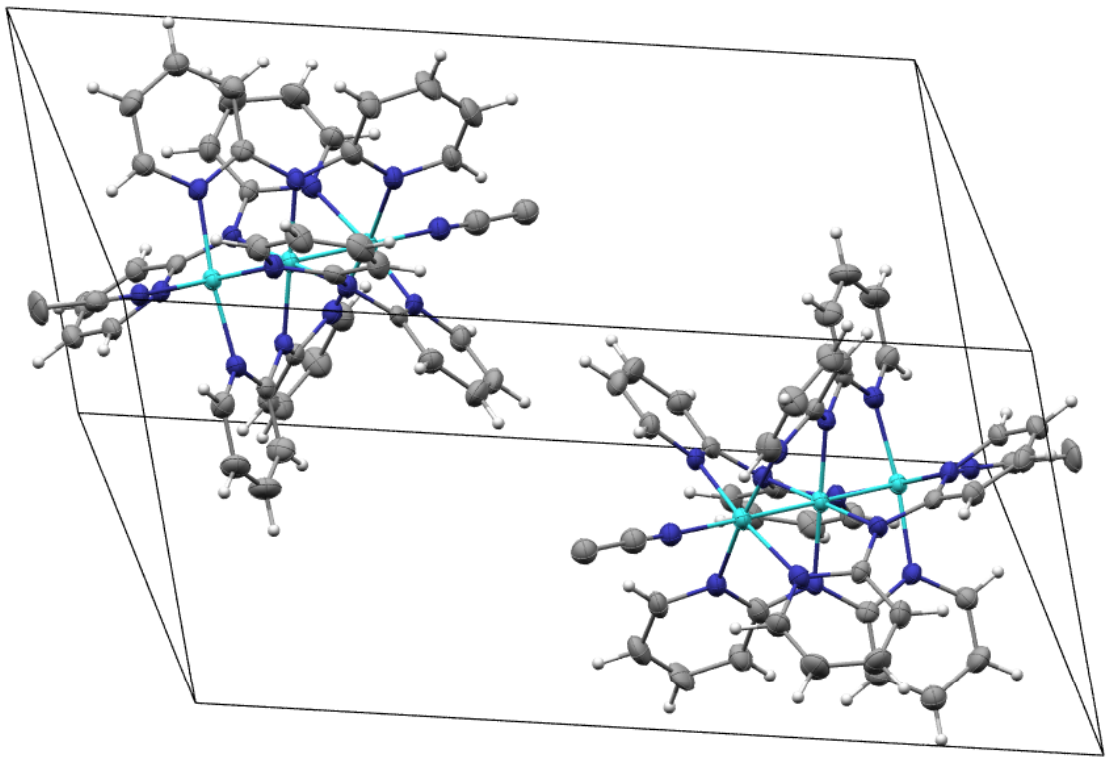


Δ

Λ

Racemic Form of $[Co_3(dpa)_4(NCMe)_2](PF_6)_2$

cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	12.498(2)
b, Å	12.5101(5)
c, Å	19.913(1)
α, deg	99.072(4)
β, deg	104.152(7)
γ, deg	101.106(7)
V, Å^3	2893.0(5)
R1, wR2	0.061, 0.152

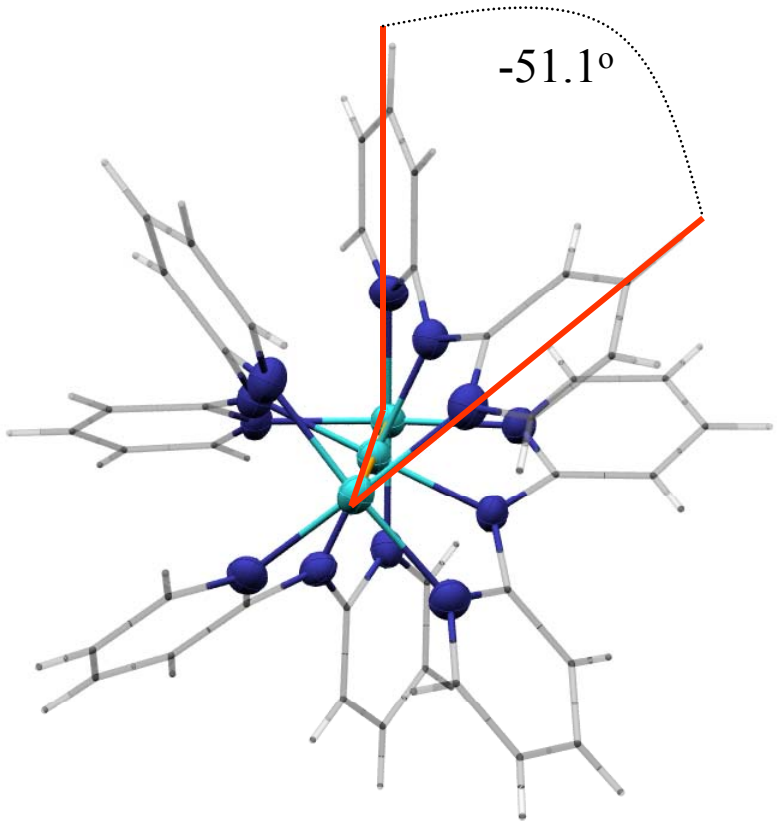


rac-$[Co_3(dpa)_4(NCMe)_2](PF_6)_2 \cdot 3CH_3CN$

Crystal Structure of Λ-$[Co_3(dpa)_4(NCMe)_2](PF_6)_2$

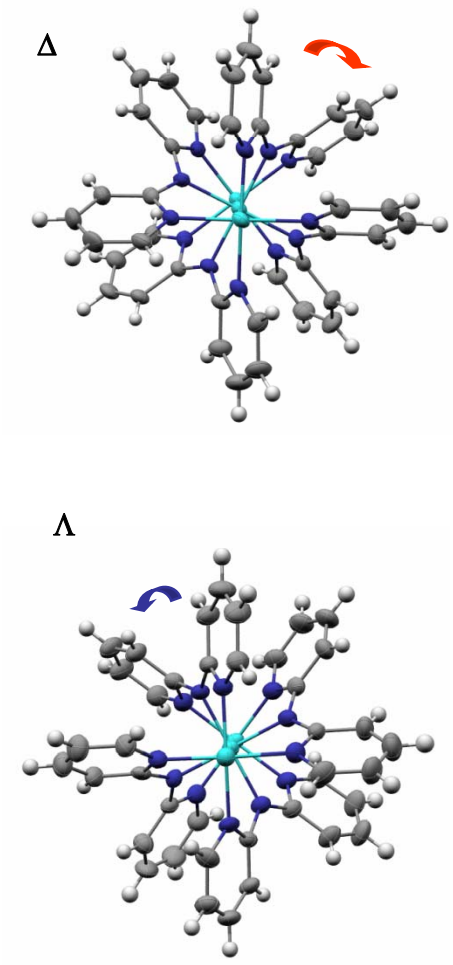
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a, Å	11.7576(7)
b, Å	21.9059(6)
c, Å	12.0621(5)
α, deg	90
β, deg	111.883(3)
γ, deg	90
V, Å^3	2882.9(2)
R1, wR2	0.043, 0.114

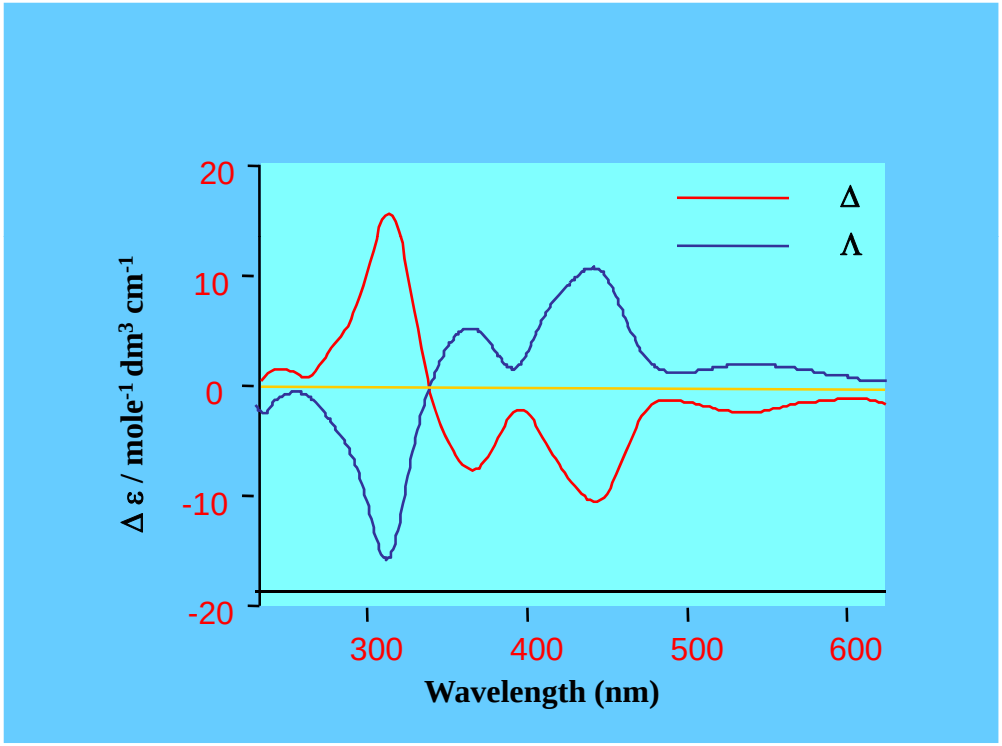
Flack *x* -0.01(2)



Λ-$[Co_3(dpa)_4(NCMe)_2][PF_6]_2$

Circular Dichroism (CD) Spectra of $[Co_3(dpa)_4(NCMe)_2][PF_6]_2$





Each CD spectrum was recorded with a solution prepared from a single crystal of known chirality.