Semi-coordination in Co(II) Schiff-base Single-Ion Magnets

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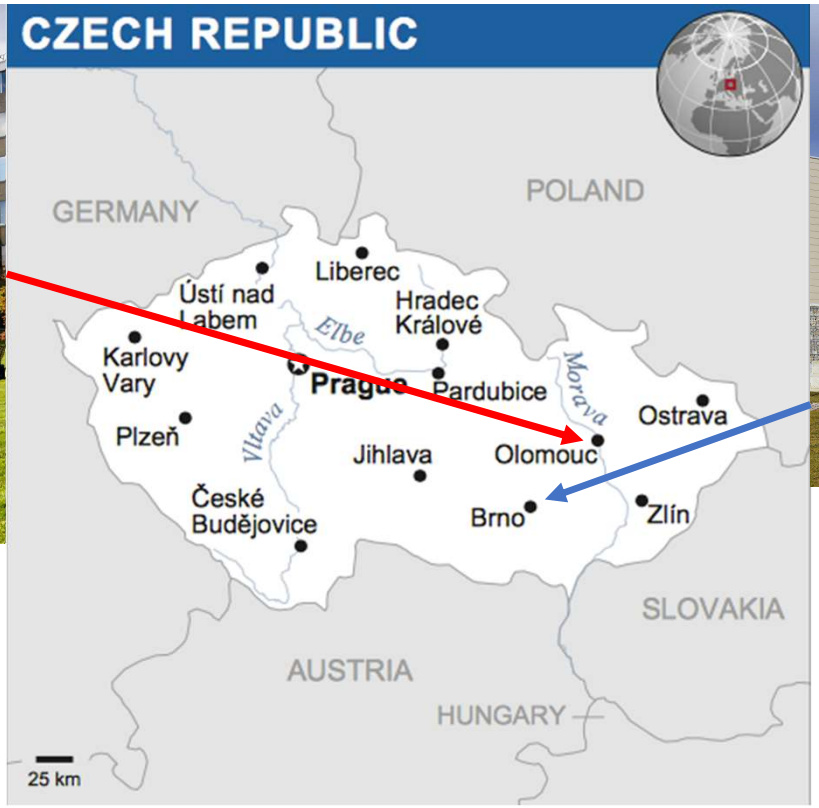
FUNMAT 2023, Krakow



Faculty of Science,
Palacky University
Olomouc

Department of Inorganic Chemistry

Synthesis of coordination compounds
Molecular Magnetism
X-ray diffraction lab

Central European Institute of Technology,
Brno University of Technology
Brno

Magneto-Optical and THz Spectroscopy (RGL: Neugebauer)
HFHF-EPR, FIRMS

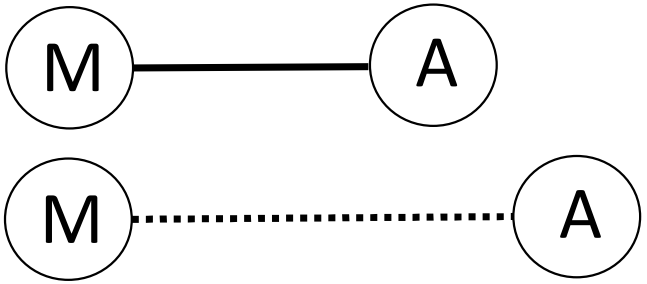
Synthesis of coordination compounds, organic radicals
Thin films of molecular compounds

Semi-coordination

- Noncovalent analog of the coordination bond introduced by Brown et al. in 1967, 'intermediate type of bonding between coordination and nonbonding, very weakly coordinated' [1]
- It usually implies the noncovalent nature of corresponding interactions with the major contribution derived from electrostatics and minor contributions from charge polarization and charge transfer [2]
- Simple initial criterion for the M···A pair: d(M ···A) < $\sum R_{vdW}$, but significantly longer than typical covalent bond (>> $\sum R_{cov}$)
- Criteria resulting from the topological analysis (QT-AIM):

(1) attractive non-covalent interaction (at BCP: $\nabla^2\rho(\mathbf{r}) > 0$ and $\boldsymbol{H}(\boldsymbol{r}) > 0$)

(2) Lagrangian kinetic energy $\boldsymbol{G}(\mathbf{r})$ vs. potential energy density $\boldsymbol{V}(\mathbf{r})$ at the BCPs (3, −1): $|\boldsymbol{V}(\mathbf{r})| / \boldsymbol{G}(\mathbf{r}) < 1.0$ for non-covalent interactions [3]

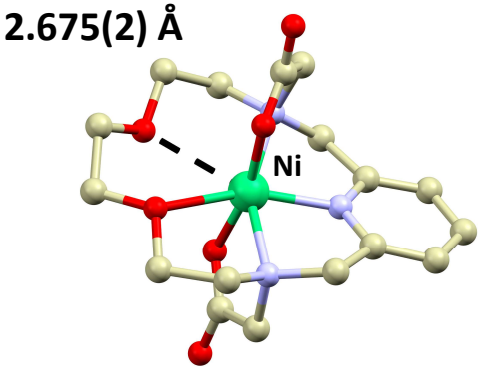


[1] I. V. Ananyev *et al*., *Acta Cryst. B76*, **2020**, 436–449
[2] Z.M. Efimenko *et al*., *Inorg. Chem*., **2020***,* 59, 2316–2327.
[3] E. Espinosa *et al*., *J. Chem. Phys*. **2002**, 117, 5529

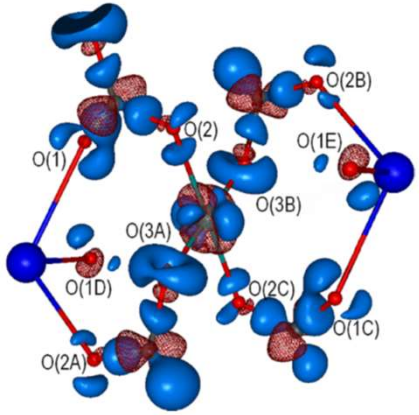
Motivation: SIMs and semi-coordination

- The Single-ion Magnets (SIMs) often contain M–A bonds which fulfil initial criterion, *e.g*. complexes with macrocyclic ligands. How are the ligand field and magnetic anisotropy affected?

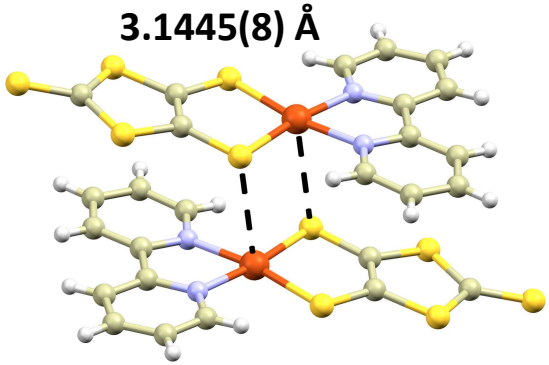
- Semi-coordination can affect magnetic properties. Mediation of ferromagnetic exchange interaction in $NaCu(CO_3)_2$ or antiferromagnetic exchange interaction in the Cu(II) complex.



B. Drahos *et al*. *EJIC*., **2018,** 4286.



Y.V. Nelyubina *et al*. *Inorg. Chem.* **2013**, 52, 14355.



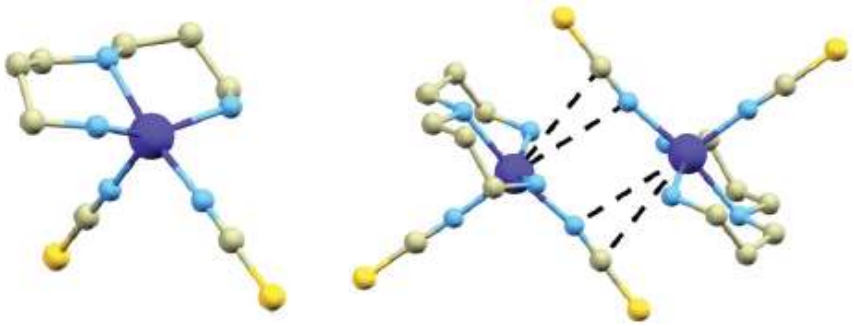
V.A. Starodub *et al*. *J. Phys. Chem. Sol.* **2013**, 73, 2, 350.

Co(II) Single-Ion Magnets – semi-coordination

$$\hat{H} = -J(\vec{S}_1 \cdot \vec{S}_2) + \sum_{i=1}^{z} D_i(\hat{S}_{z,i}^2 - \hat{S}_i^2/3) + E_i(\hat{S}_{x,i}^2 - \hat{S}_y^2) + \mu_B B g_i \hat{S}_{a,i}$$

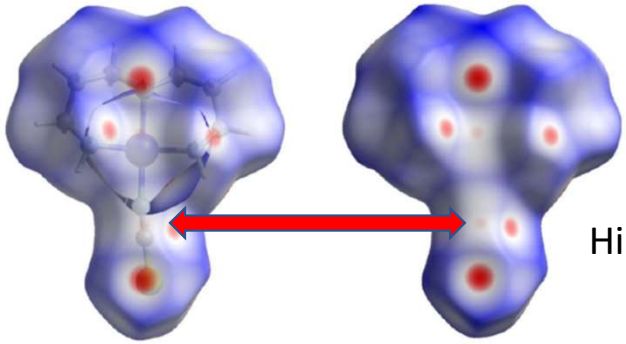
- $[Co(dpt)(NCS)_2]$, dpt = dipropylenetriamine

$Co(NCS)_2$ + dpt = $[Co(dpt)(NCS)_2]$



Pentacoordinate $\tau = 0.46$,

d(Co···N) = 3.541(2) Å
d(Co···C) = 3.652(2) Å
d(Co···Cg) = 3.550 Å

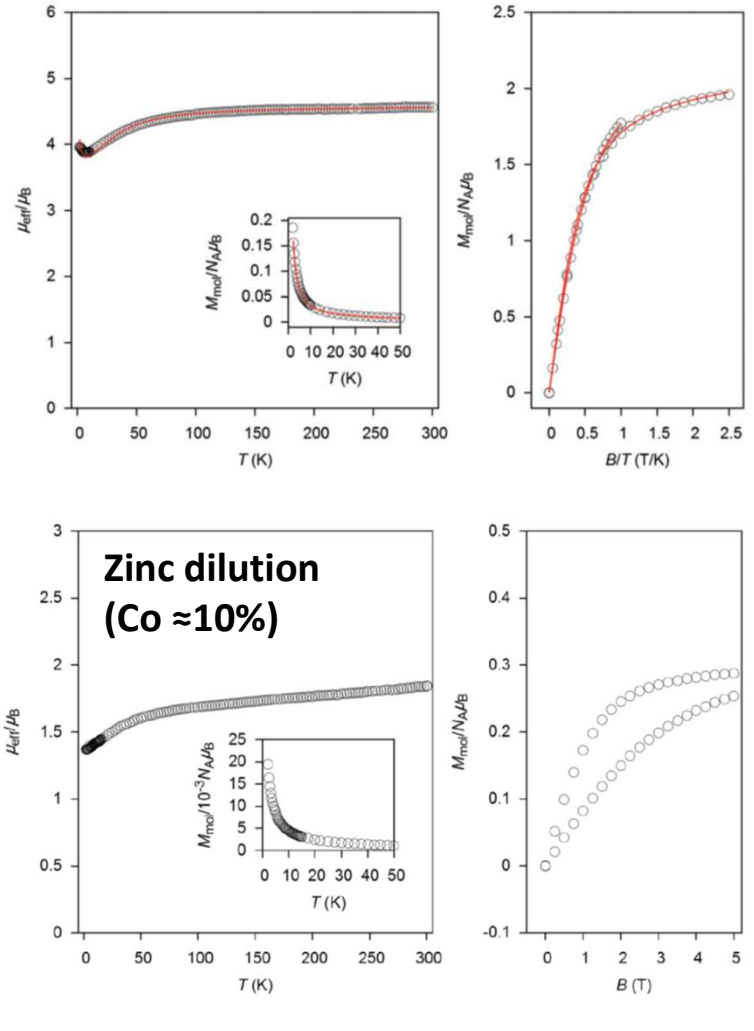


Hirschfeld surface (d_{norm})

D. Jayatilaka and M.A. Spackman, *CrystalExplorer package*

J = +0.25 cm^{-1}, $|D|$ = 36 cm^{-1}, E/D = 0.22 (D<0), 0.33 (D>0)

CASSCF/NEVPT2:
D = +34.0 cm^{-1}, E/D = 0.22



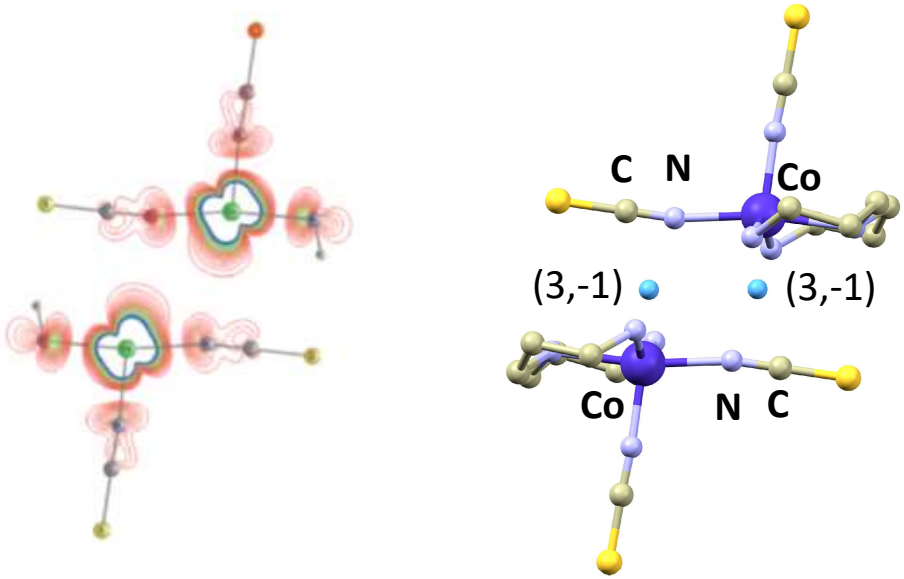
I. Nemec et al. *Dalton Trans.*, **2016**, (31), 12479

Co(II) Single-Ion Magnets – semi-coordination

- [Co(dpt)$(NCS)_2$], dpt = dipropylenetriamine

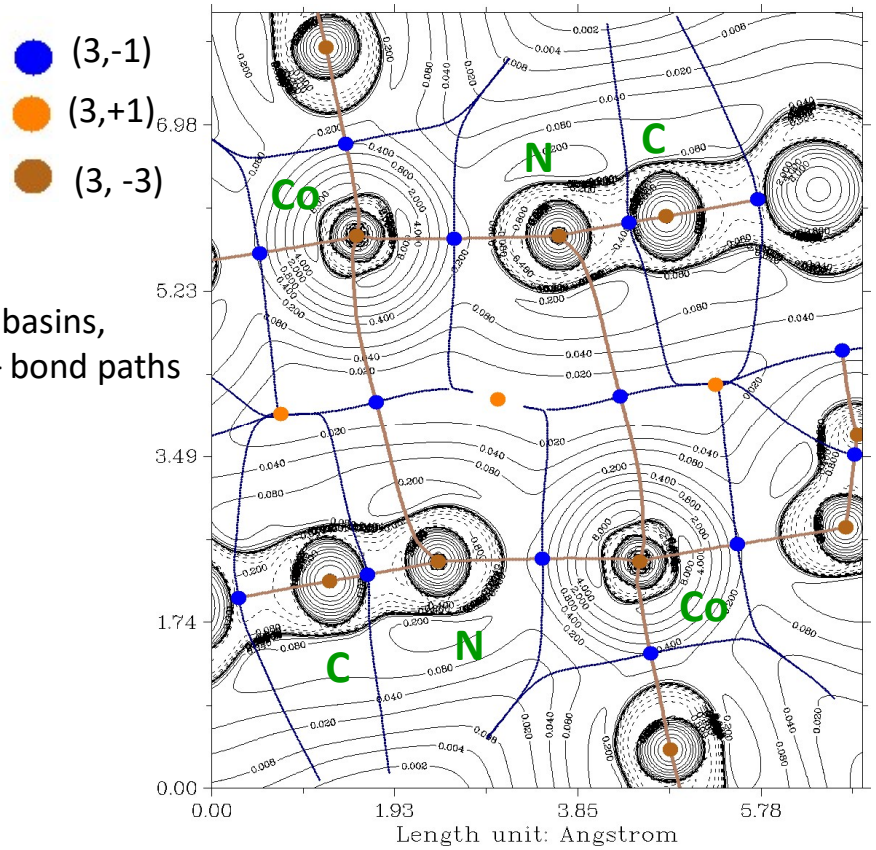
BS-DFT calculations
B3LYP/ZORA/-def2-TZVP(-f)

J = +0.22 cm^{-1}



Non-covalent exchange pathway

L. Havlicek et al. *Polyhedron*., **2022**, (223), 115962



blue lines – basins,
brown lin. – bond paths

BCPs for Co···N:
type (3,-1)

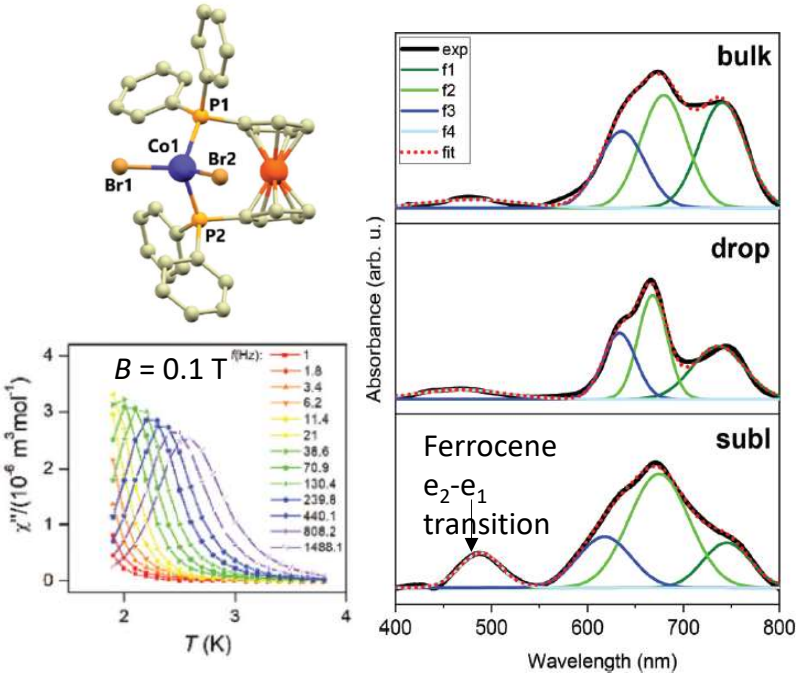
$E_{int} = |V(r)|/2$ = 1.6 kcal/mol

$\nabla^2\rho(r)$ = 0.0126267
$H(r)$/a.u. = 0.000321
$V(r)$/a.u. = -0.002513
$G(r)$ /a.u. = 0.002835

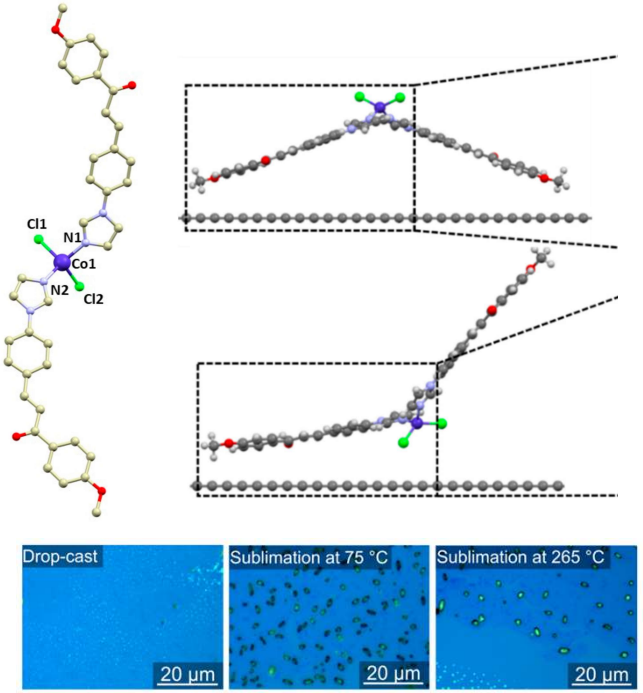
$\nabla^2\rho(r) > 0$
$H(r) > 0$
$|V(r)|/G(r) = 0.886 < 1$
non-covalent character

Motivation: SIMs and semicoordination

- Can semi-coordination stabilize low-coordinate Co(II) species?
- Two kinds of deposition processes: thermal evaporation or wet techniques (drop-cast)



J. Hruby *et. al. Dalton Trans.* **2020**, 49, 11697



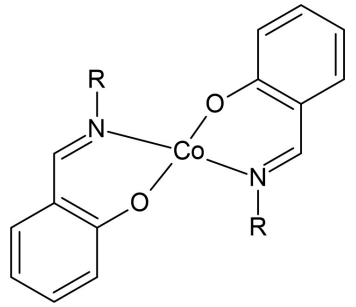
J. Hruby *et. al. Molecules.* **2020**, 25, 5021

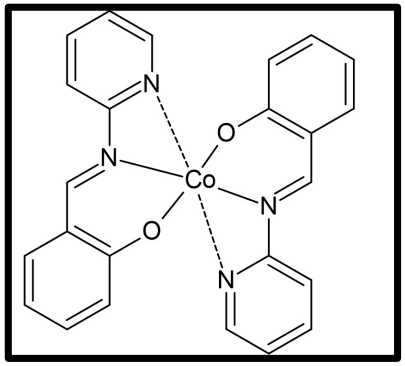
Both deposits were very sensitive to moisture and molecules (partially) decomposed during sublimation.

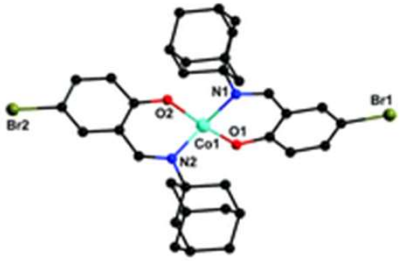
Can we improve stability of the tetracoordinate molecules during an after deposition by using complexes with formally saturated (by semi-coordination) coordination sphere?

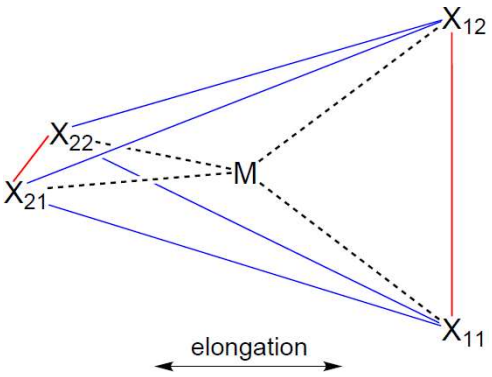
Motivation: Co(II) SIMs with bidentate Schiff base ligands

- Bidentate Schiff base ligands, N,O donor set
- Magnetic anisotropy is governed by deformation of tetracoordinate tetrahedron (parameter of axial distortion ε_T)
- Zero-field SIMs (D = -20 to -50 cm^{-1})

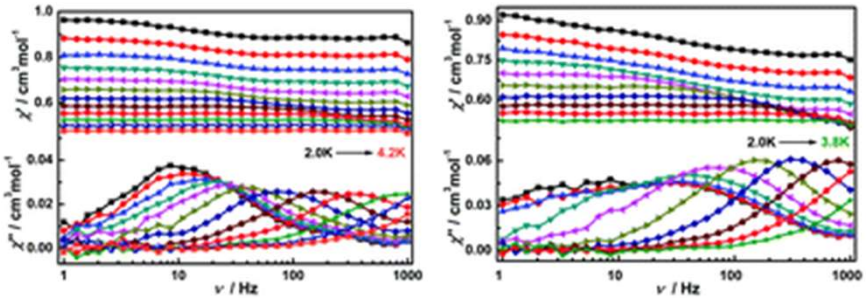








$$\epsilon_T = \frac{\alpha_o}{\alpha_a}$$

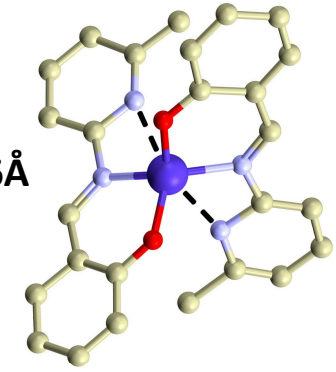


$$\alpha_o = \frac{1}{4}\sum_{i=1}^{2}\sum_{j=1}^{2} \angle X_{1i} M X_{2j}$$

$$\alpha_a = \frac{1}{2}\sum_{i=1}^{2} \angle X_{i1} M X_{i2}$$

bite angles

d(Co···N) > **2.6Å**

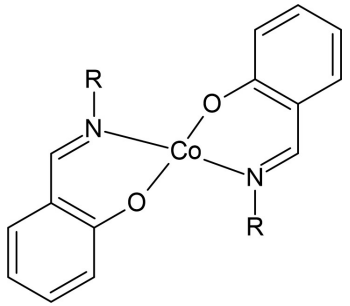


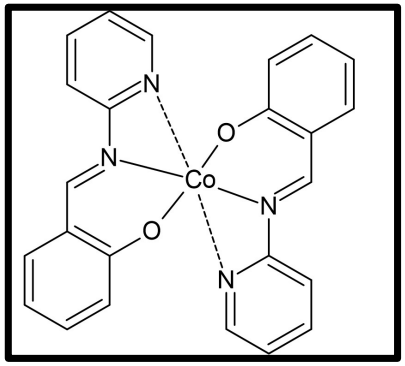
L. Xuet al., *Z. Strukt. Khimii*, **2006**, 47, 1003

Guo Peng et al. *Dalton Trans*., **2020**, 49, 5798

S. Ziegenbalg et al. *Inorg. Chem*., **2016**, 55, 8, 4047

Motivation: Co(II) SIMs with bidentate Schiff base ligands



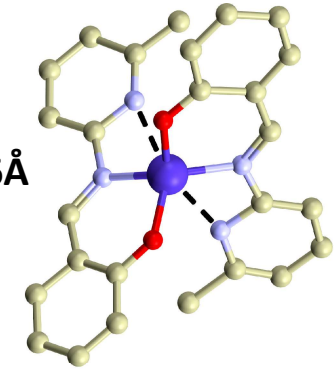


(i) Structural/QT-AIM investigations

(ii) Magnetism

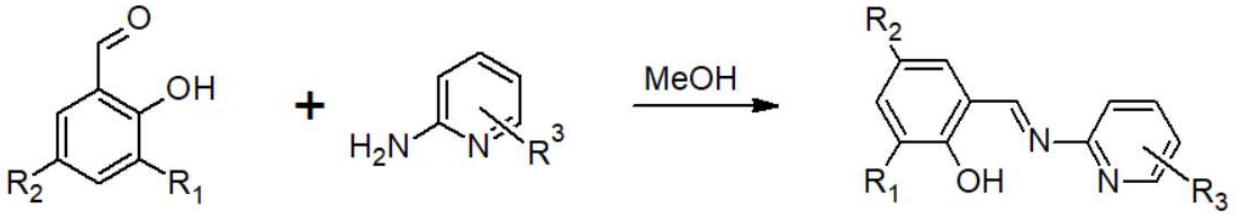
(iii) Depositions by thermal evaporation

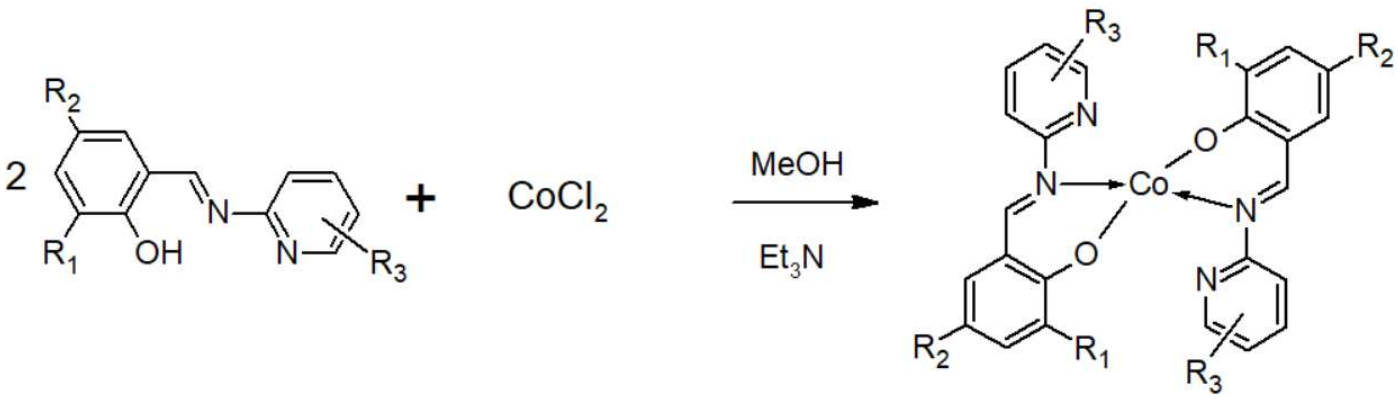
d(Co···N) > **2.6Å**



L.Xuet al., *Z. Strukt. Khimii*, **2006**, 47, 1003

Synthesis

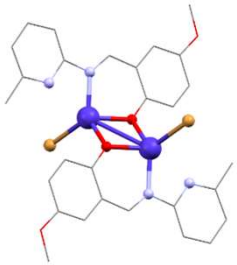


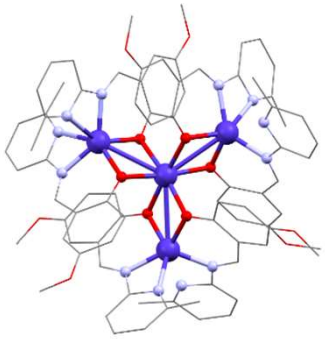


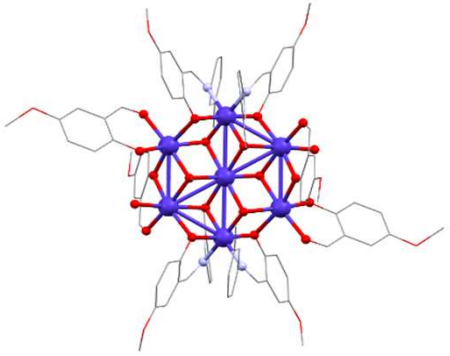
$R_1 = R_2 = -H, -X, -OMe, -NO_2$

$R_3 = -H, -X, -CH_3, -CH_2CH_3, -CF_3$

Different reaction conditions (stoichiometric ratios, pH, reaction times…) → polynuclear complexes





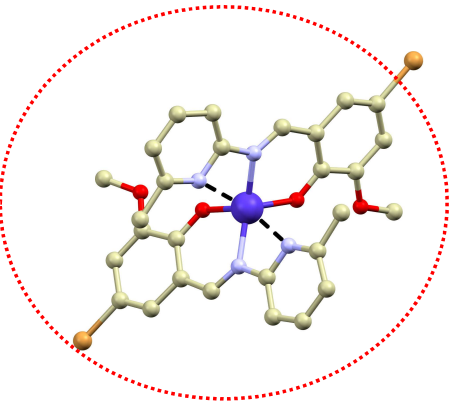


Crystal structure

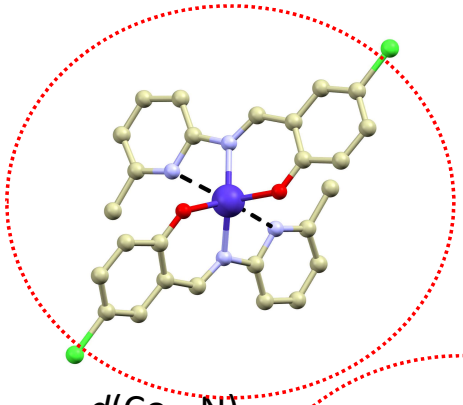
c.n. 4+2

c.n. 4+1

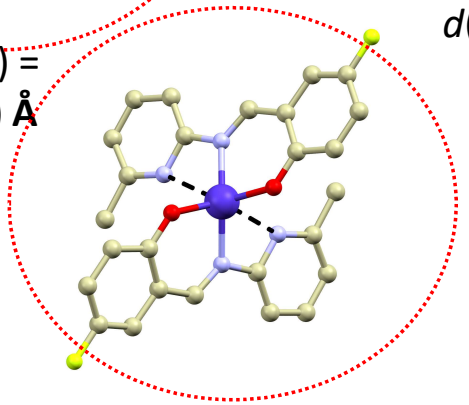
c.n. 4



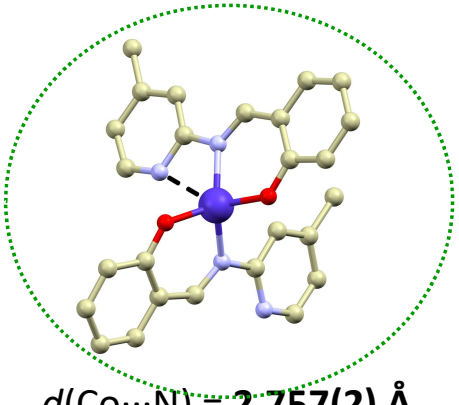
d(Co···N) =
2.499(2), 2.565(2) Å



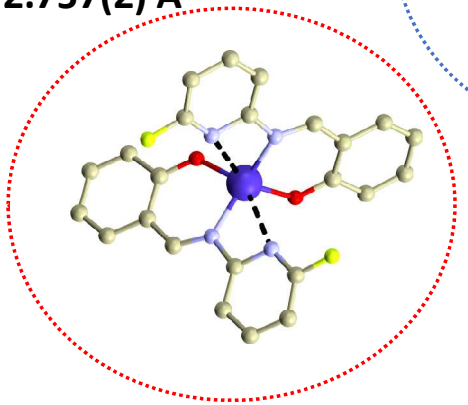
d(Co···N) =
2.614(2) Å



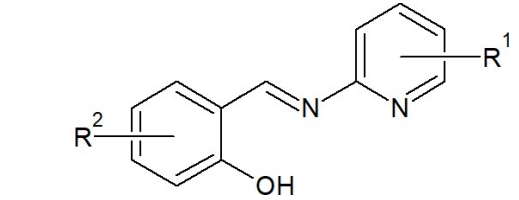
d(Co···N) = **2.659(2) Å**

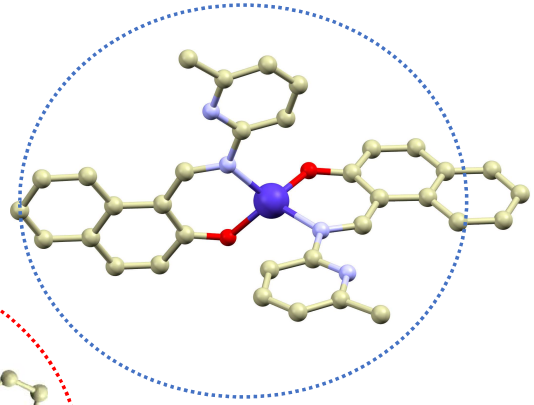


d(Co···N) = **2.757(2) Å**



d(Co···N) = **2.801(4) Å**

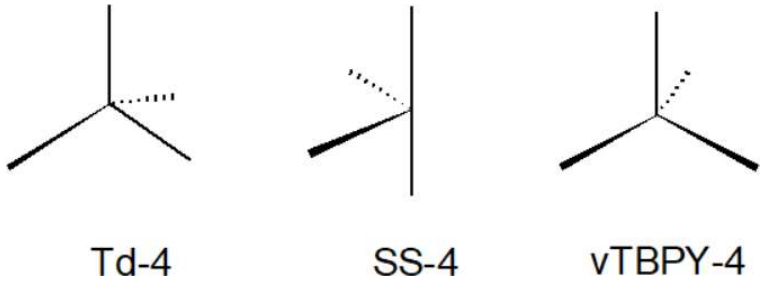




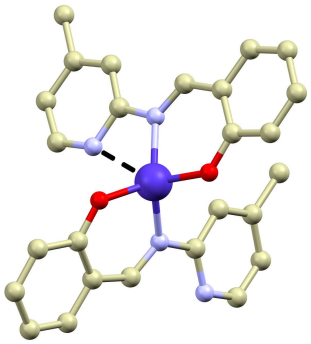
2.500 2.600 2.700 2.800

Shape of coordination polyhedron

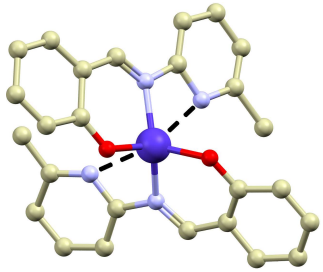
S. Alvarez *Chem. Rev.* **2015**, 115, 24, 13447–13483



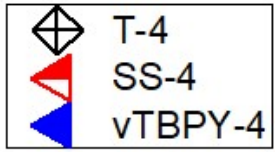
c.n. 4+1

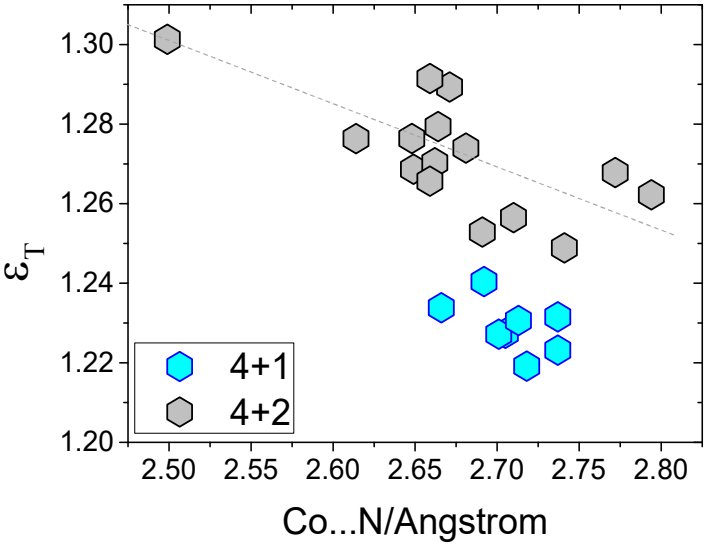


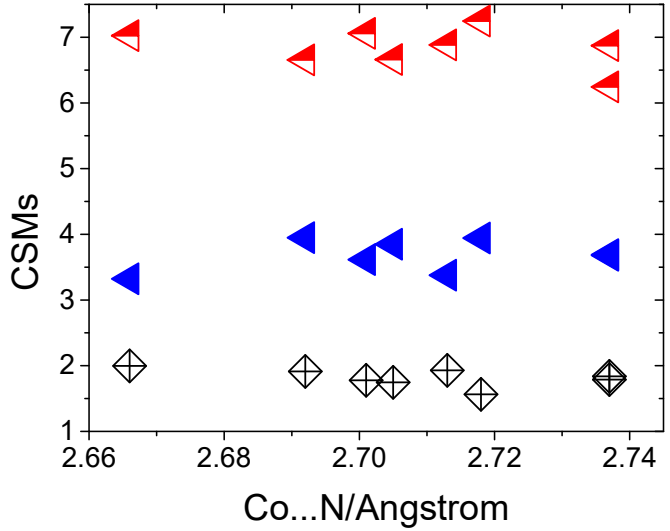
c.n. 4+2

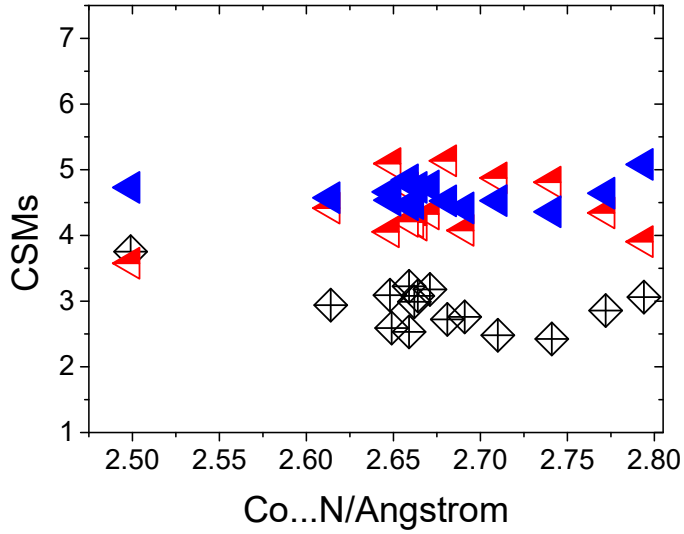


Axial elongation







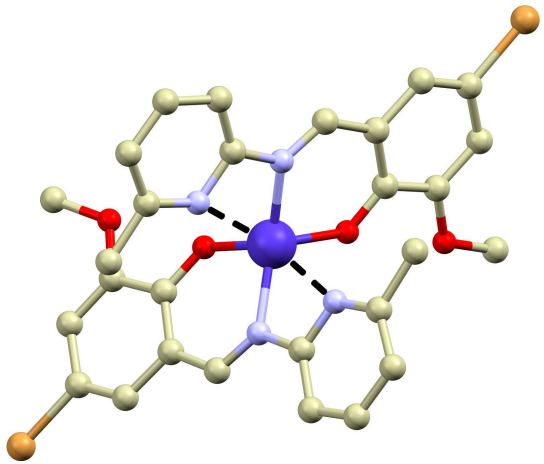


shorter Co···N distance ≈ larger axial distortion

4+2 geometry exhibits larger distortions

QT-AIM

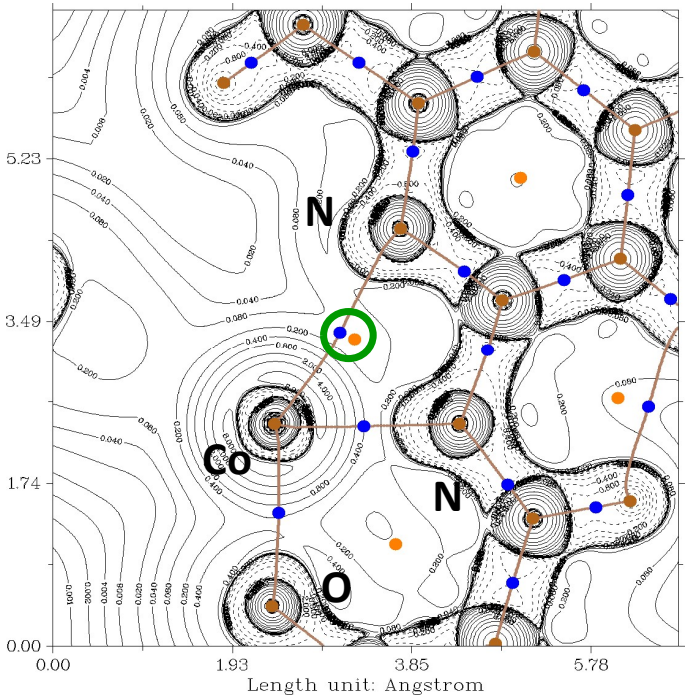
[Co(3MeO-5Br-pymep)$_2$]



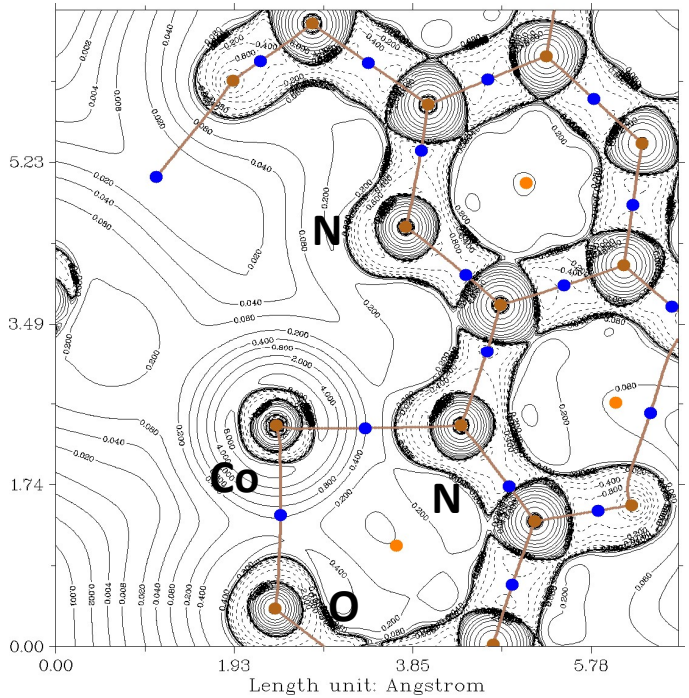
d(Co···N) = 2.499(2), 2.565(2) Å

$\nabla^2\rho(\mathbf{r})$ B3LYP (def2-TZVP)

(3,-1)
(3,+1)
(3, -3)



d(Co···N) = 2.499(2) Å



d(Co···N) = 2.565 (2) Å

BCPs for Co···N:
type (3,-1)

$V(\mathbf{r})$/a.u. = -0.02878
$H(\mathbf{r})$/a.u. = -0.0007
$G(\mathbf{r})$ /a.u. = 0.02807
$\nabla^2\rho(\mathbf{r})$ = 0.1095

$\nabla^2\rho(\mathbf{r}) > 0$, $H(\mathbf{r}) < 0$
weakly covalent character

$|V(\mathbf{r})|/G(\mathbf{r}) = 1.03 > 1$
weak covalent character

$E_{int} = |V(\mathbf{r})|/2 =$ 9.0 kcal/mol

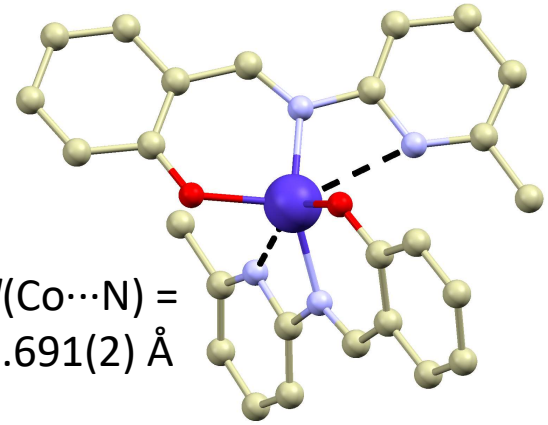
other Co-N/O bonds: 42-55 kcal/mol

QT-AIM

A. D. Becke and K. E. Edgecombe, *J. Chem. Phys*. **1990**, 92, 5397

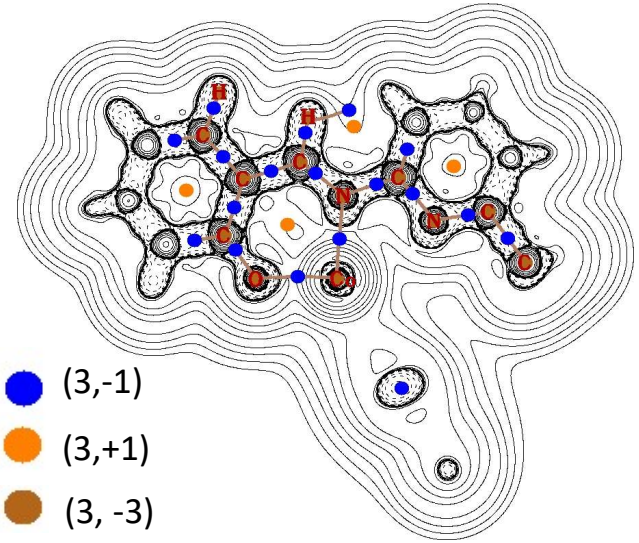
E.R. Johnson et al. *J. Am. Chem. Soc*. **2010**, 132, 18

[Co(pymep)$_2$]

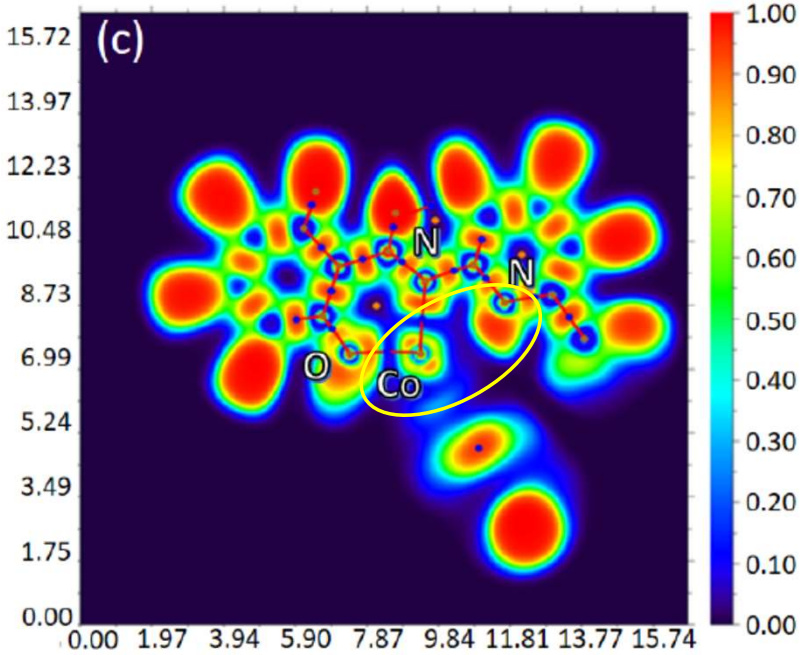


d(Co···N) = 2.691(2) Å

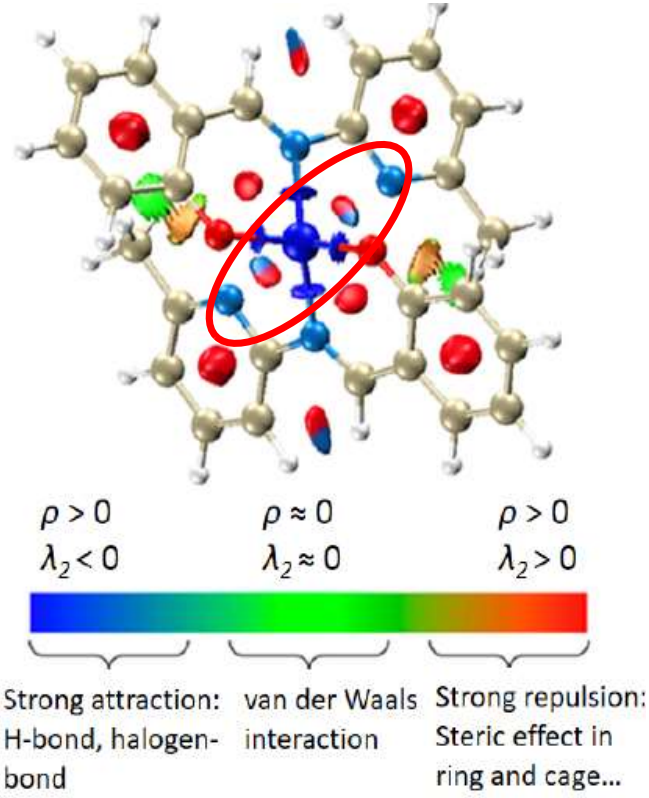
$\nabla^2\rho(\mathbf{r})$



Electron localization function



Non-covalent interaction index



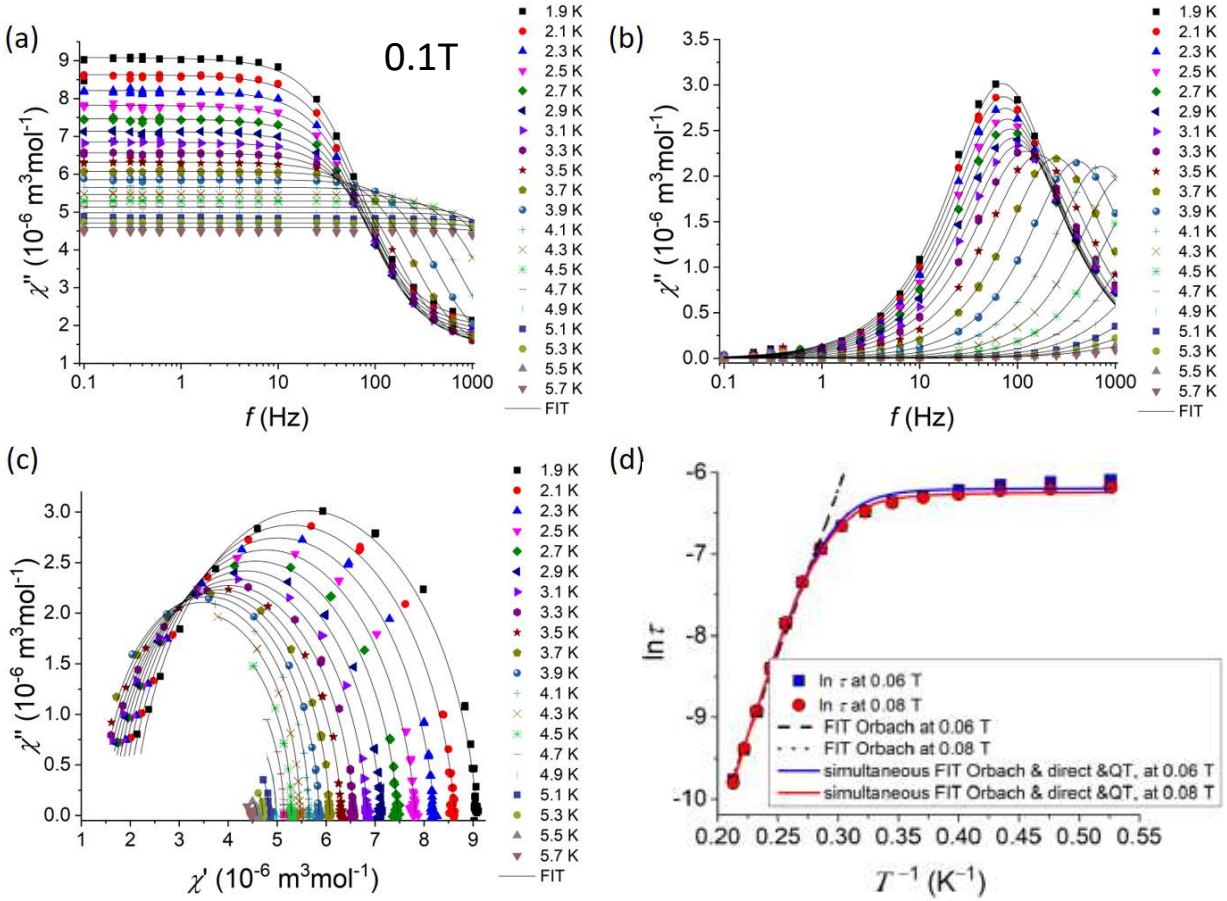
No BCP but interaction is attractive and very likely with dominant electrostatic character

Dynamic magnetic data

U_{eff} = 48.2 K, $\tau_0 = 9\times10^{-9}s^{-1}$

$$\frac{1}{\tau} = \frac{1}{\tau_{Orbach}} + \frac{1}{\tau_{Raman}} + \frac{1}{\tau_{direct}} + \frac{1}{\tau_{QT}}$$

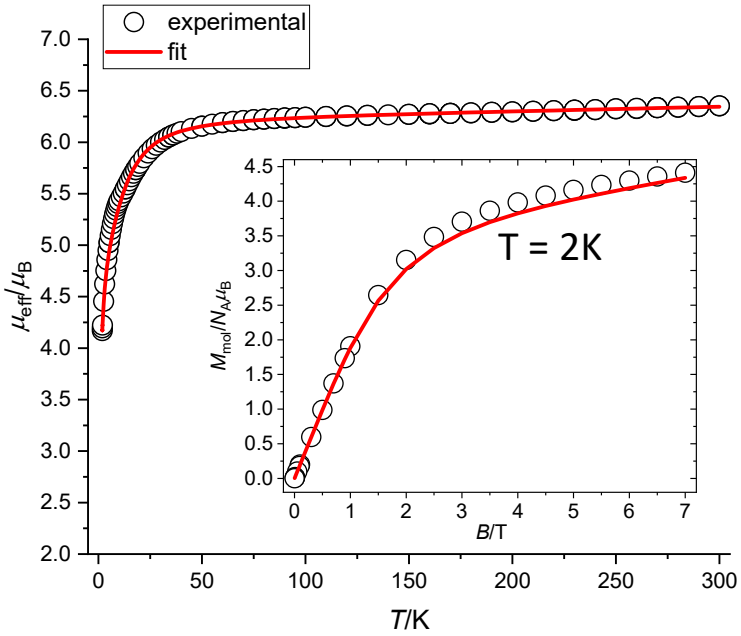
$$= \frac{1}{y_0}\exp\left(-\frac{U}{k_B T}\right) + d\left(\frac{1+eH^2}{1+fH^2}\right)T^n + aH^m T + \frac{b_1}{1+b_2H^2}$$



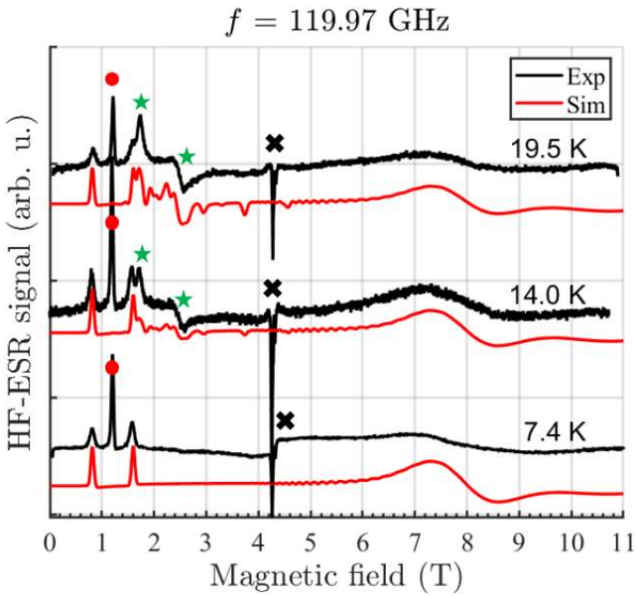
Magnetic properties

Magnetism – DC data

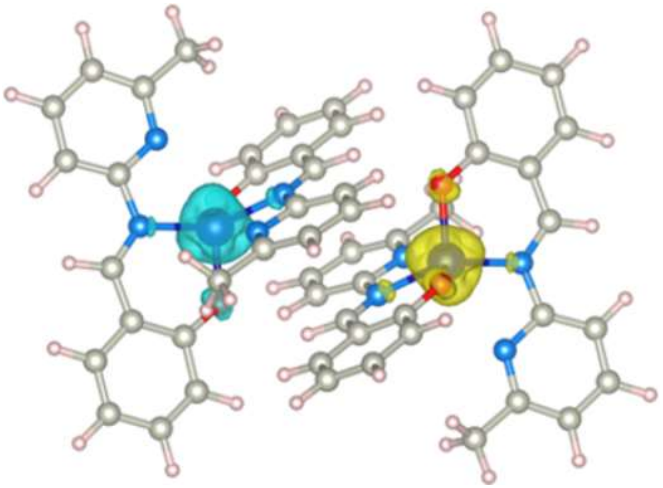
$D < -20\text{cm}^{-1}$, $E/D = 0.122$, $J = -0.3\ \text{cm}^{-1}$



HF-EPR



BS-DFT



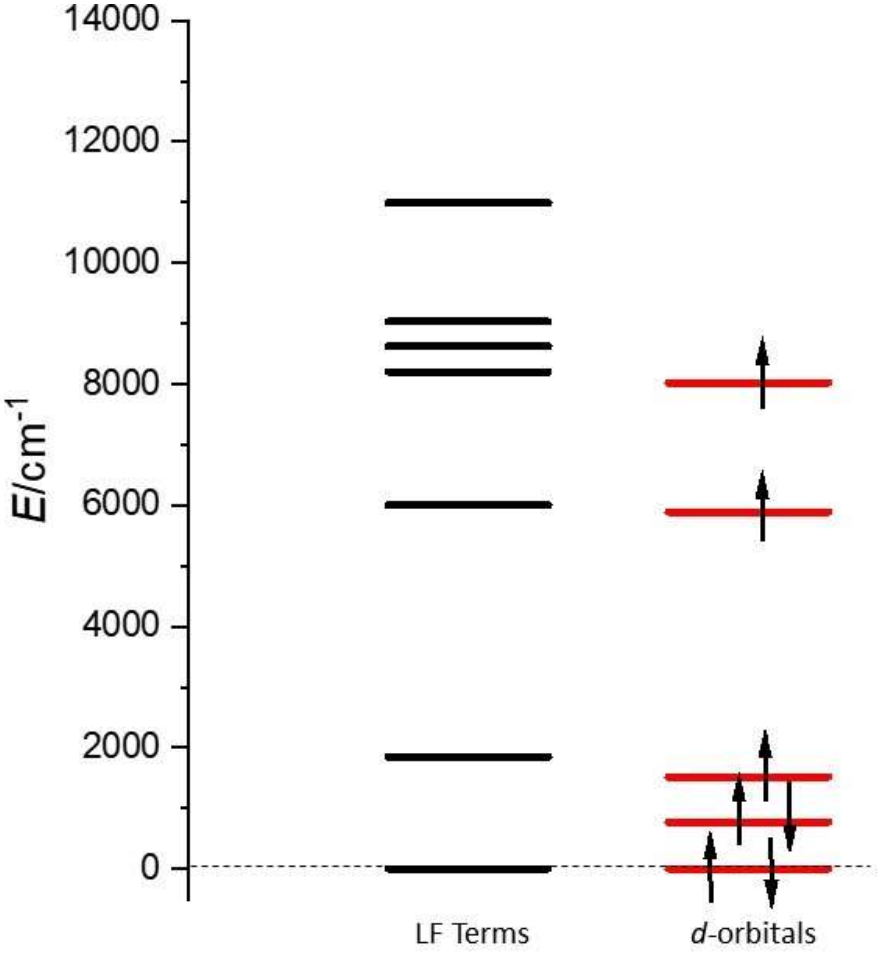
$J = -0.25\ \text{cm}^{-1}$
B3LYP/ZORA/-def2-TZVP(-f)

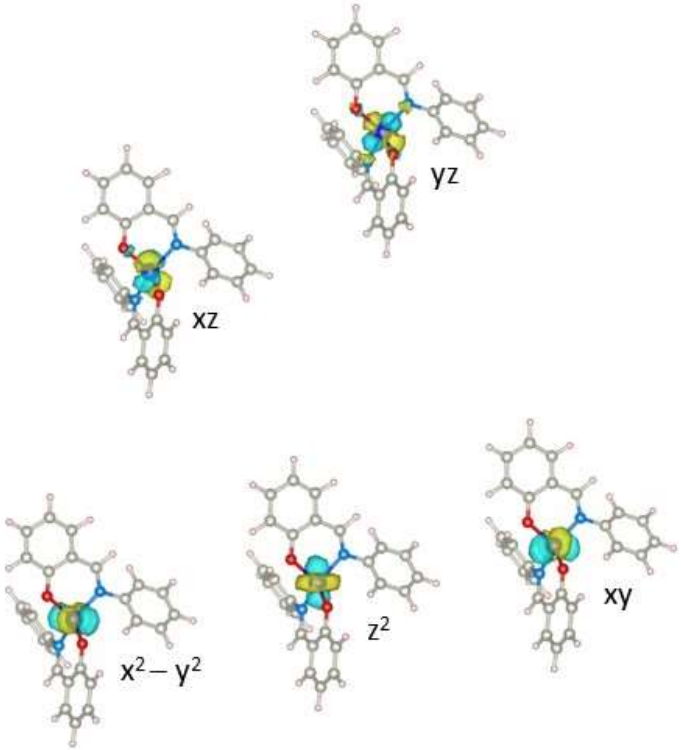
$$\hat{H} = -J\left(\hat{S}_1 \cdot \hat{S}_2\right) + D\left(\hat{S}_z^2 - \frac{S^2}{3}\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + \mu_B B g \hat{S}_a$$

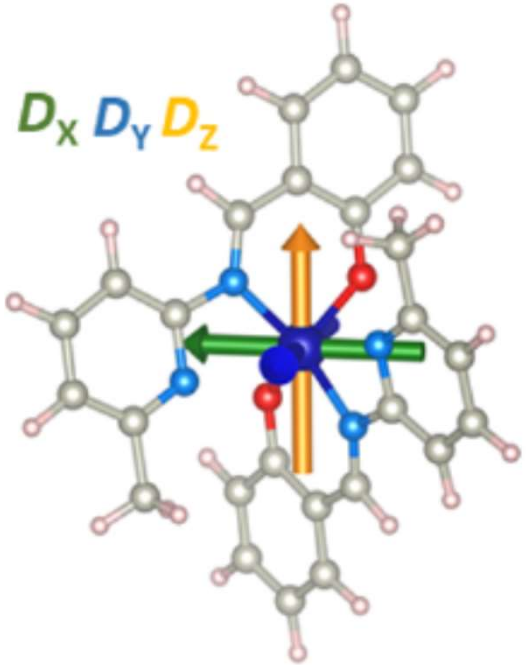
$g_{iso} = 2.272$, $D = -15.3\ \text{cm}^{-1}$, $E/D = 0.012$, $J = -0.27\ \text{cm}^{-1}$

CASSCF/NEVPT2 calculations
AILFT

D **= -24.2 cm^{-1}, *E*/*D* = 0.084**
(magnetometry: *D* = -15.3 cm^{-1}, *E*/*D* = 0.012
HFEPR: *D* < -20cm^{-1}, *E*/*D* = 0.122)

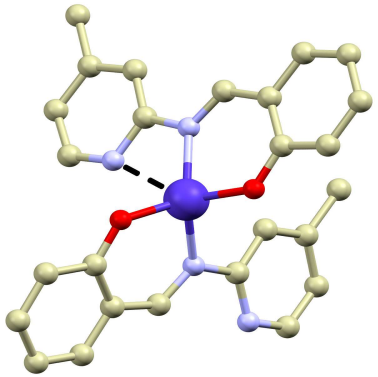




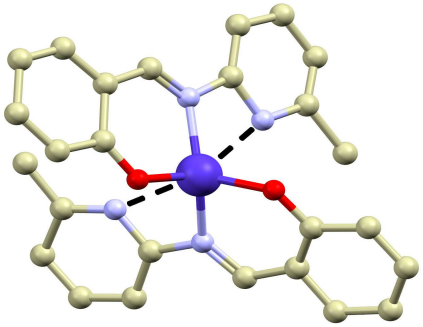


CASSCF/NEVPT2 calculations
AILFT

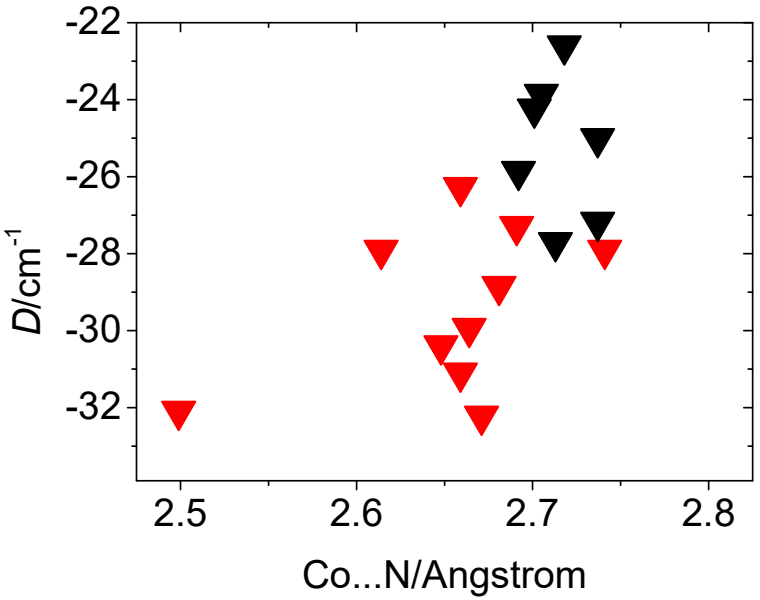
c.n. 4+1 ▼



c.n. 4+2 ▼

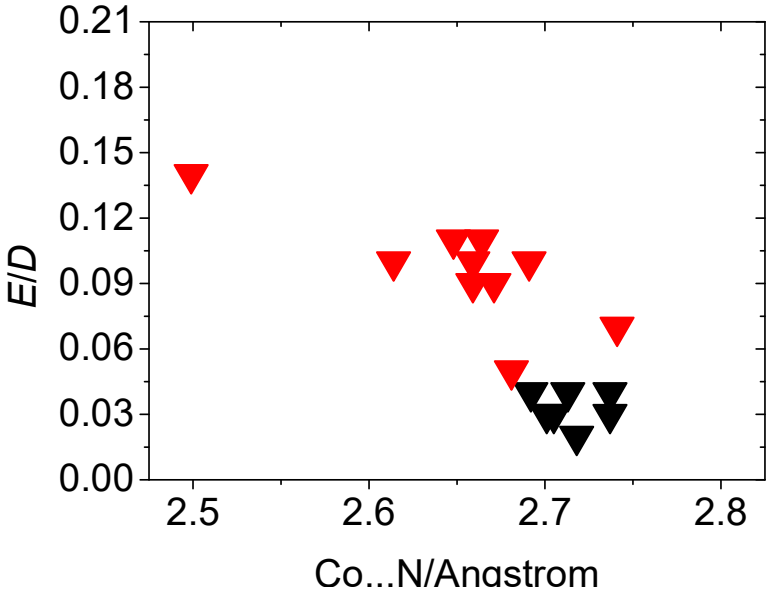


D



shorter Co···N contact ≈ larger |*D*|

E/D

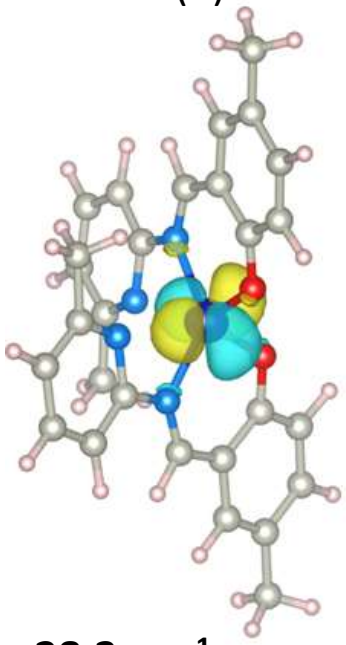


shorter Co···N contact = larger *E*/*D*

CASSCF/NEVPT2 calculations

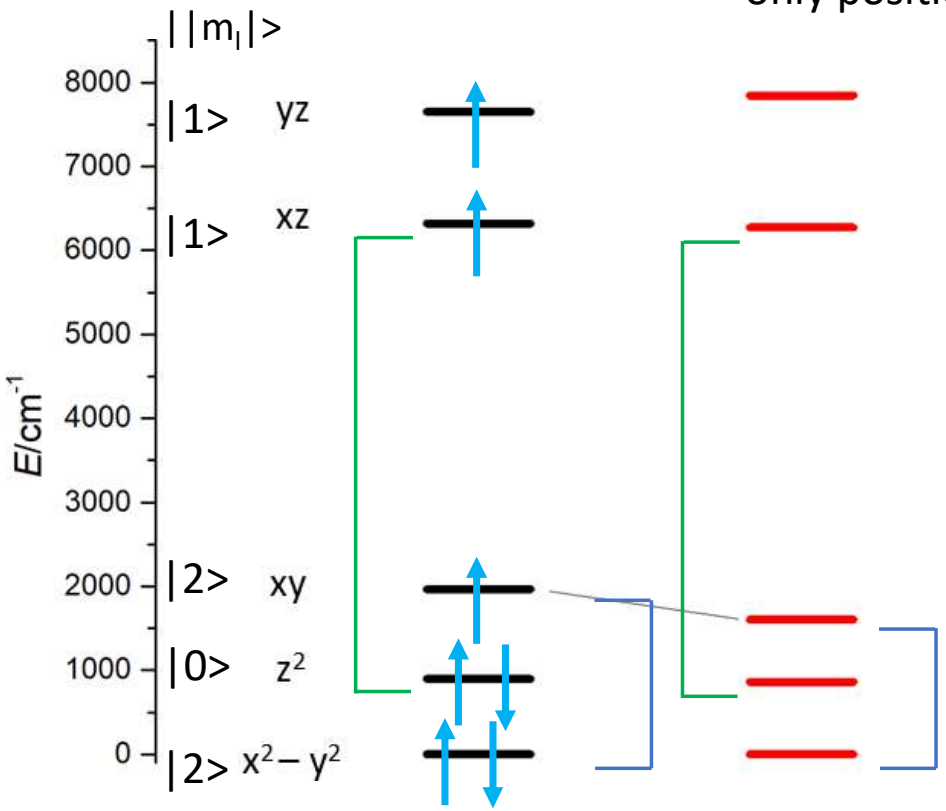
crystal structure coordinates

d(Co···N) = 2.6951(9) Å

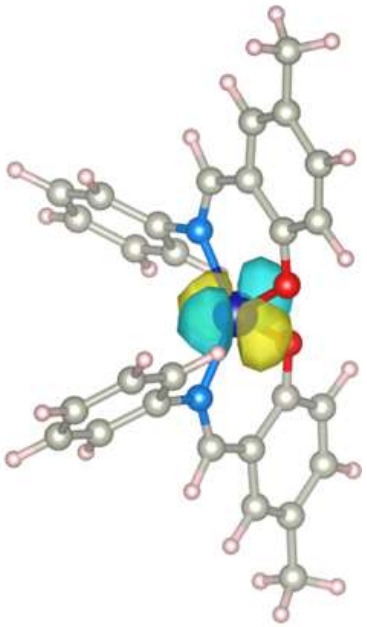


***D* = -28.3 cm^{-1}**

***E*/*D* = 0.11**



pyridine rings substituted by Ph rings
only positions of Ph rings DFT optimized



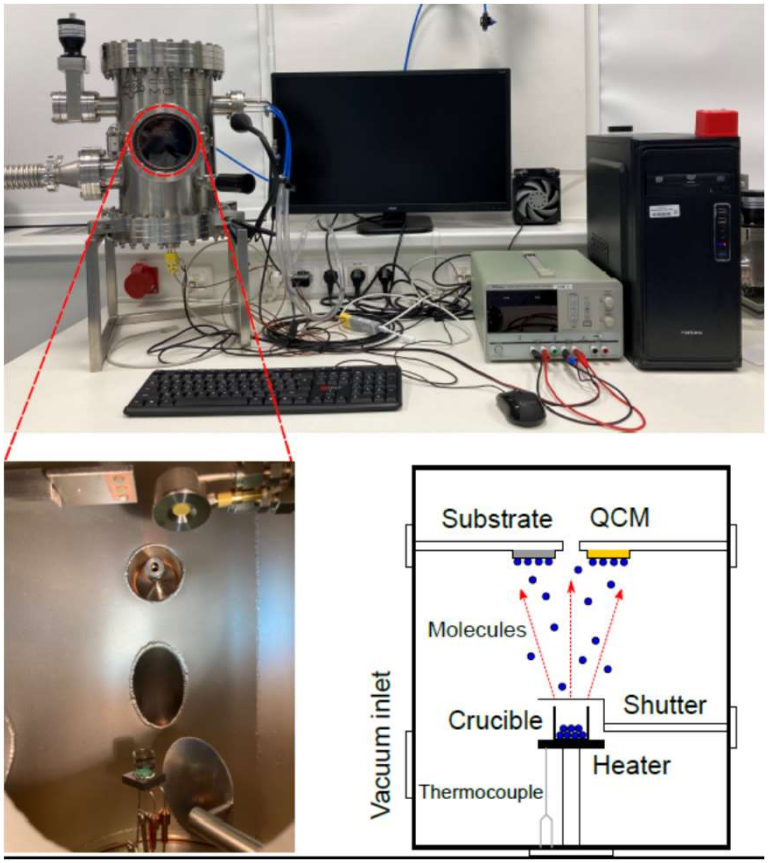
***D* = -40.1 cm^{-1}**

***E*/*D* = 0.04**

- lobes of d_{xy} points towards lone pairs of pyridine nitrogen atoms – destabilization $E(d_{xy})\uparrow$
- absence of pyridyl groups – $E(d_{xy})\downarrow$ decrease of d_{xy} energy
- lowering of d_{xy} energy leads to increase of $|D|$

S. Gomez-Coca *et al. J. Am. Chem. Soc.* **2013**, 135, 18, 7010

Depositions on graphene



Home-built high-vacuum sublimation chamber
Base pressure: 1 x 10^{-6} mbar
•QCM for film thickness monitoring
•Heated crucible for molecules
•Temperature monitoring by thermocouple

Dr. Jakub Hrubý
Phd at CEITEC Brno
currently: NHMFL,
Tallahassee, USA

Šárka Vavrečková
MSc at CEITEC Brno
currently: Friedrich-Schiller Universitat Jena, Germany

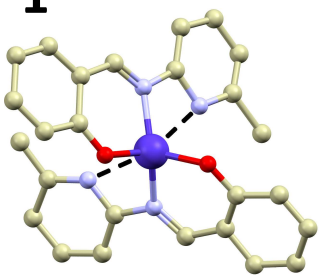
Wet deposition
- From diluted solutions (drop-casting)

Characterization
- XPS
- AFM
- micro-Raman spectrocopy

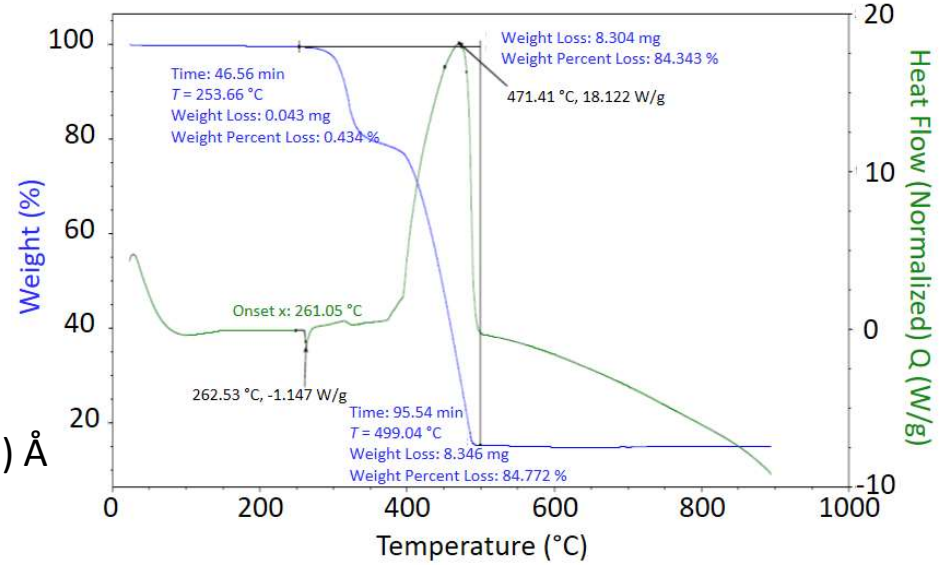
Substrates used
- Graphene on Si/SiO_2

Depositions on graphene

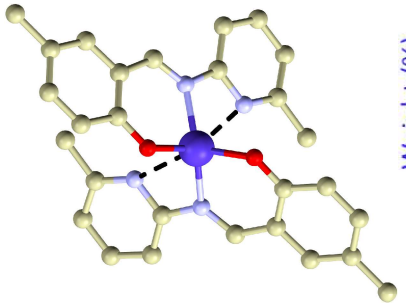
1



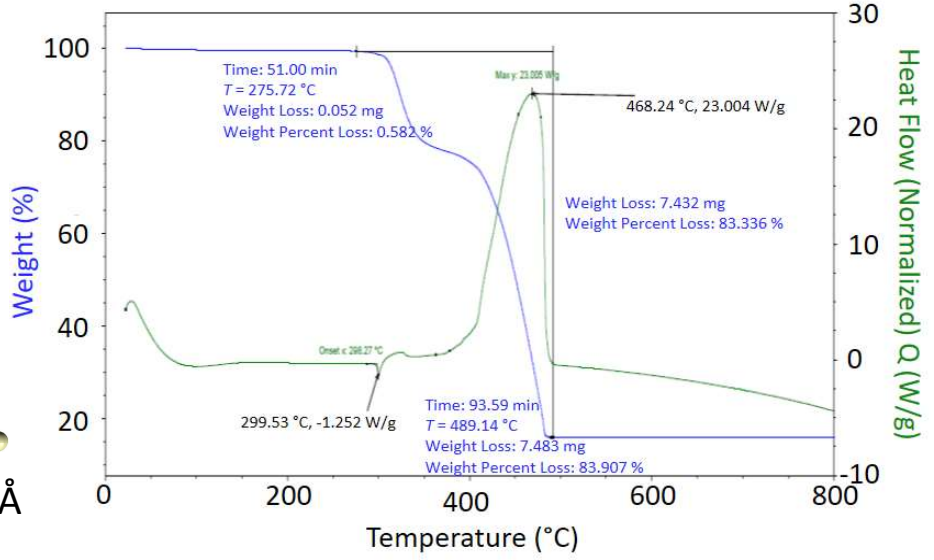
d(Co···N) = 2.6908(19) Å



2



d(Co···N) = 2.6951(9) Å



Thermal evaporation

starts of deposition were detected at 270 °C for **1** and at 283 °C for **2**.

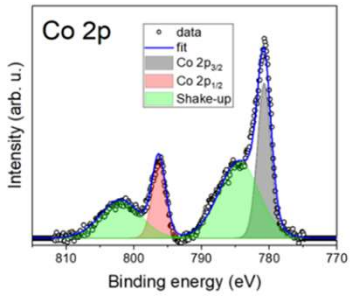
Both compounds were thermally evaporated for 4 days.

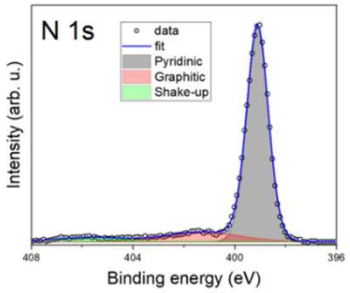
Drop casting

A solution (*c* =1 mM) was drop-casted under ambient conditions, where 4 x 10 µL of the solution was deposited onto a substrate.

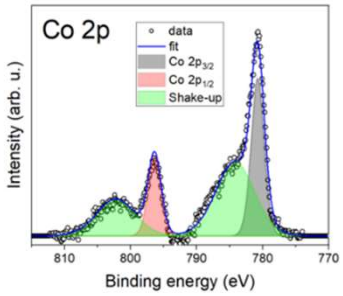
Depositions on graphene: AFM & XPS

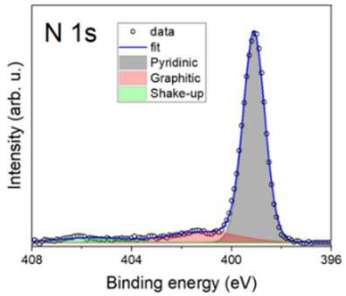
1 Bulk



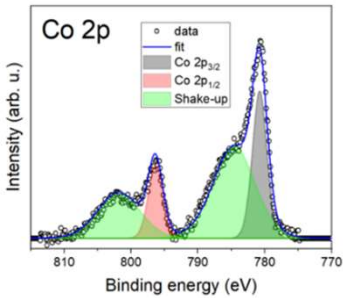


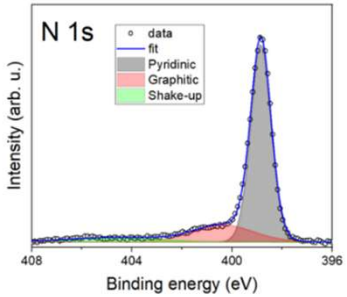
1 Thermal deposition

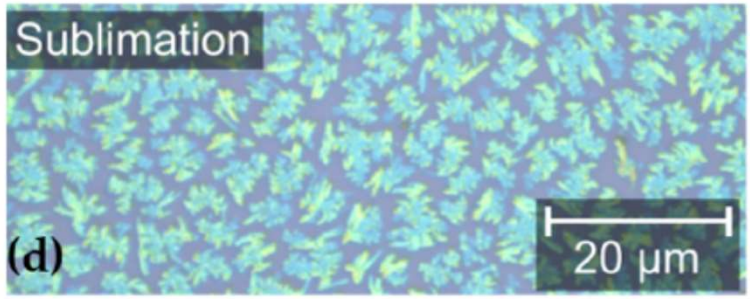


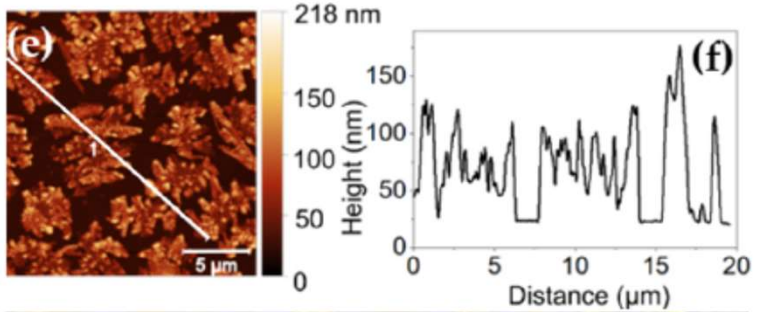


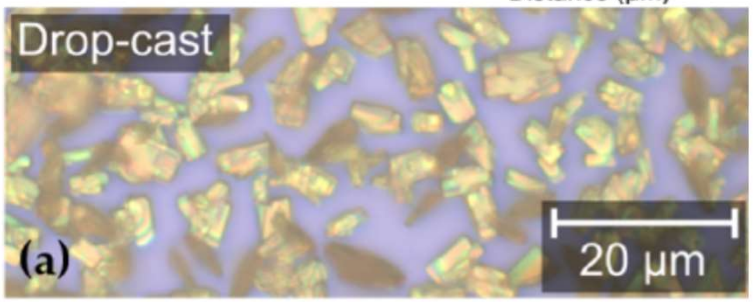
1 Drop-casting

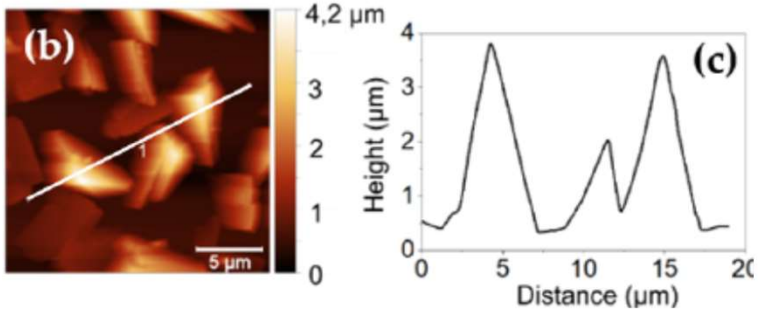






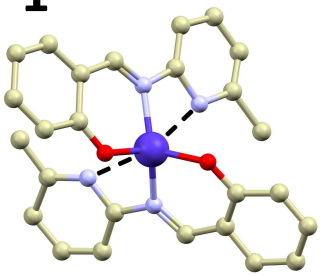




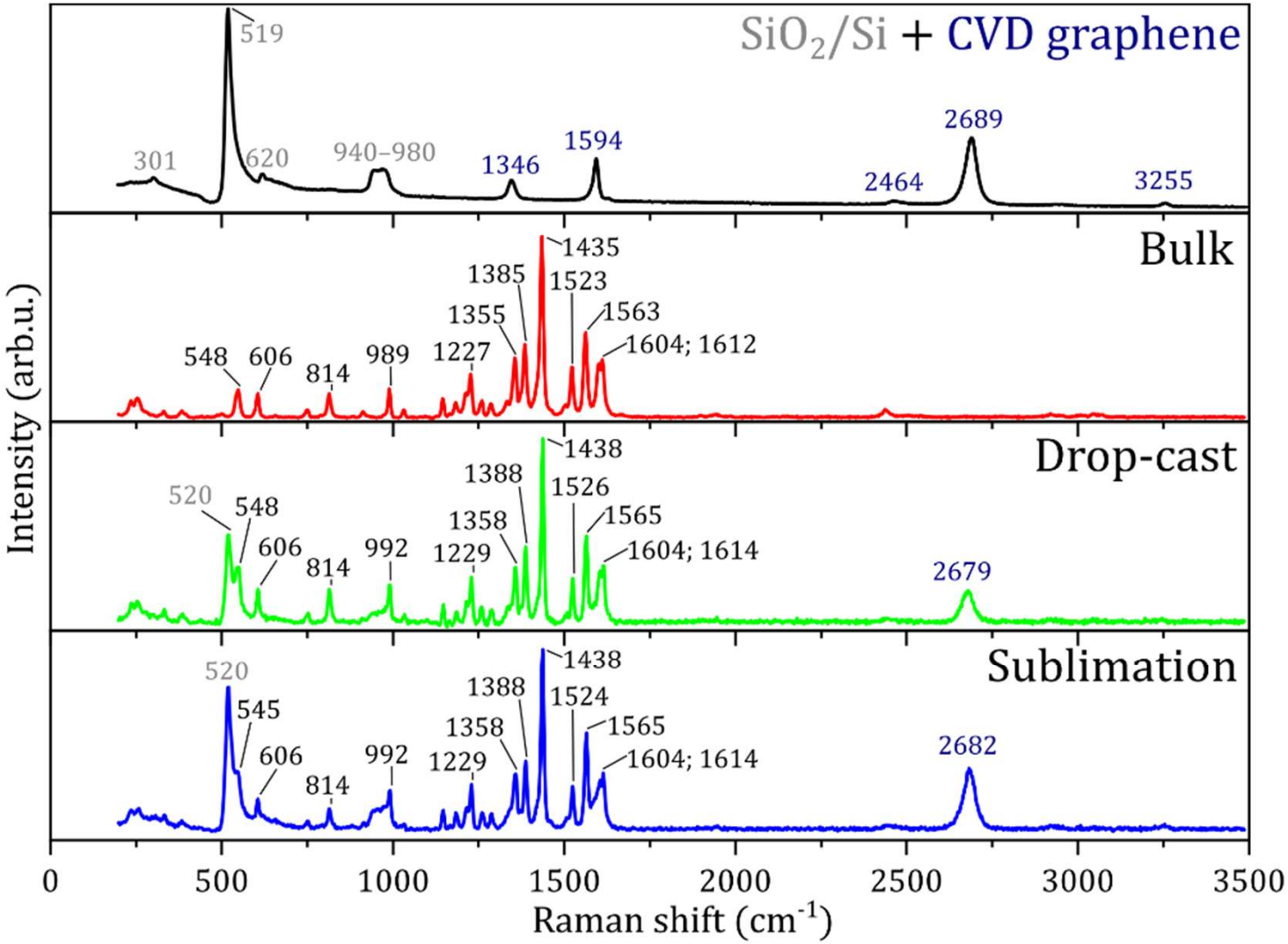


Depositions on graphene: micro-Raman

1



d(Co···N) = 2.6908(19) Å



Submitted to PCCP

Conclusions

- We employed semi-coordination in design and synthesis of Co(II) field-induced SIMs
- We confirmed that the Co···N interactions have attractive and electrostatic nature
- We explained how the Co···N interactions influence the value of *D* parameter
- We successfully used some of the prepared complexes for deposition on the graphene by thermal evaporation

Acknowledgement

Theoretical calculations

Radovan Herchel (UP Olomouc, CZ)

HF-EPR

Jorge G. Navarro (CEITEC Brno, CZ)
Vinicius T. Santana (CEITEC Brno, CZ)
Petr Neugebauer (CEITEC Brno, CZ)

SQUID magnetometry

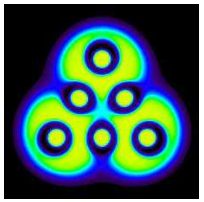
Ivan Šalitroš (STU Bratislava, SK)
Eric McInnes (University of Manchester, UK)

Funding

"Semicoordination: a way to chemically stable molecular nanomagnets" (Grant Agency of Czech Republic, 23-07175S)

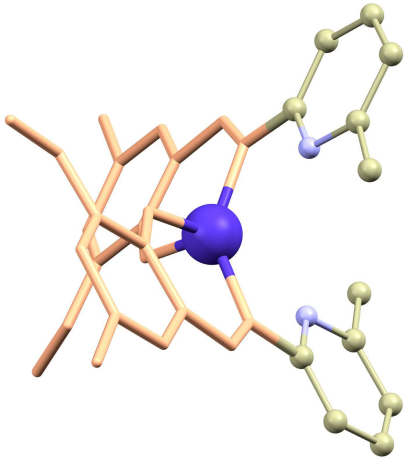
Used computational methods

- All DFT and CASSCF/NEVPT2 calculations were performed using ORCA 4.2 computational package [1]
- Coordinates from X-ray diffraction experiments were used as inputs for single-point DFT at B3LYP (def2-TZVP) level. Hirshfeld atom refinements (HAR) using NoSpherA2 module in Olex2 1.5 [2] at B3LYP (def2-SVP or def2-TZVPD) level were used for obtaining final structural file.
- All geometry optimization was done by DFT at B3LYP (def2-TZVP) level including D3BJ dispersion correction
- Geometry optimization of the selected molecular fragments were done by DFT at B3LYP (def2-TZVP) level
- Calculations of ZFS parameters were done using CASSCF/NEVPT2 calculations. Active space was set to five d-orbitals of Co(II), {CAS (7,5) , *S* = 3/2, 10 quartet and 40 doublet roots)
- QTAIM calculations were performed using MultiWFN software [3]
- Topology of coordination polyhedra was determined calculating continuous shape measures (CSMs) using SHAPE 2.1 software [4]

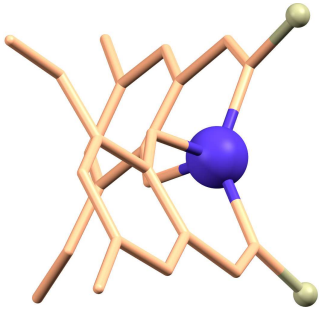


[1] (a) F. Neese, *Rev.: Comput. Mol. Sci*., **2012**, 2, 73–78;
(b) F. Neese, *Rev.: Comput. Mol. Sci*., **2018**, 8, e1327.
[2] (a) O.V Dolomanov *et al*. *J. Appl. Cryst.*, **2009**, 42, 339-341.;
(b) F. Kleemiss *et al*. *Chem. Sci*., **2021**,12, 1675-1692
[3] T. Lu and F. Chen. *J. Comput. Chem*., **2012**, 33, 580
[4] P. Alemany et al. *Rev. Comp. Chem*., **2017**, 30, 289

CASSCF/NEVPT2 calculations

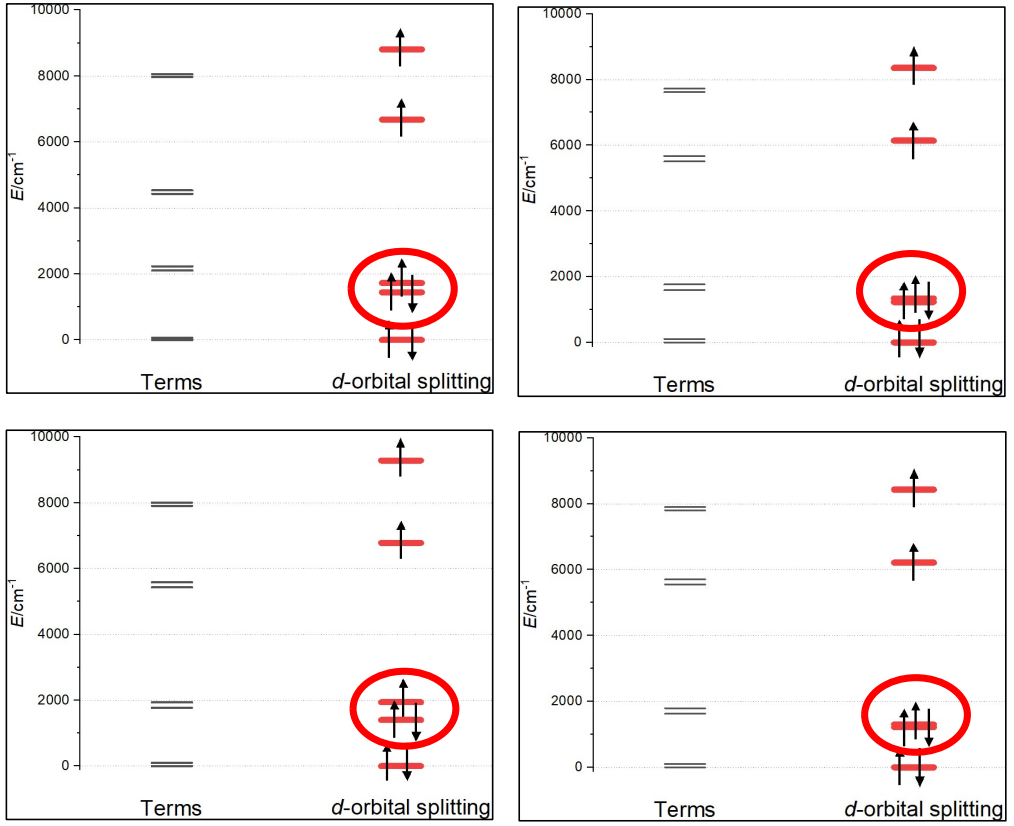


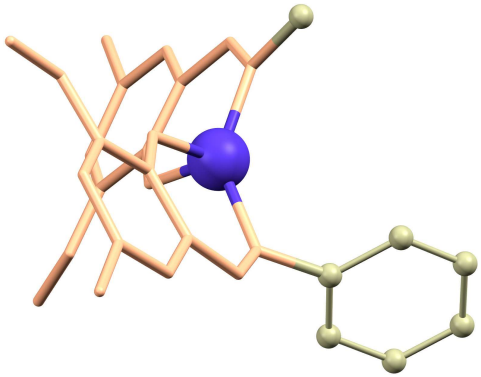
D = -31.7 cm^{-1}
E/D = 0.14



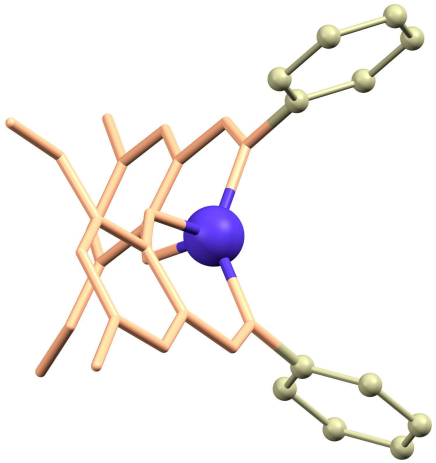
D = -37.0 cm^{-1}
E/D = 0.05

d(Co···N) = 2.499 Å





D = -53.1 cm^{-1}
E/D = 0.04



D = -51.5 cm^{-1}
E/D = 0.04

energy of d_{xy} is changing