ELECTRONIC SUPPORTING INFORMATION

A Co₈ Metallocycle Stabilized by Double Anion- π interactions

Dimitris I. Alexandropoulos, Brian S. Dolinar, Haomiao Xie, Kuduva R. Vignesh, and Kim R.

Dunbar*

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, United

States.

Synthesis

All manipulations were performed under aerobic conditions using reagent grade materials and solvents as received. The starting material $Co(CF_3SO_3)_2$ was prepared following a literature procedure.¹ Infrared spectra were obtained using a Nicolet Nexus 470 FT-IR Spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

[Co₂(dbm)₂(bpym)(MeOH)₄](NO₃)₂ (1). To a stirred, colorless solution of dbmH (0.22 g, 1.0 mmol) and NEt₃ (0.14 mL, 1.0 mmol) in CH₂Cl₂ (15 mL) was added solid bpym (0.16 g, 1.0 mmol). The resulting colorless solution was stirred for a further 10 min, after which time, it was combined with a Co(NO₃)₂·6H₂O (0.29 g, 1.0 mmol) solution in MeOH (15 mL). The resulting dark orange/red solution was stirred for an additional 30 minutes and then filtered. The filtrate was layered with a mixture of Et₂O/hexanes (30 mL, 1:1 v/v) which produced dark orange plates of **1** after one day which were collected by filtration, washed with hexanes (3 x 5 mL) and dried in air. The yield was 75% (0.36g). Anal. Calc. for C₄₂H₄₄N₆O₁₄Co₂ **(1)**: C, 51.75; H, 4.55; N, 8.62 %. Found: C, 51.89; H, 4.67; N, 8.48 %. Selected ATR data (Nujol mull, cm⁻¹): 1594 (m), 1579 (m), 1549 (m), 1518 (m), 1458 (vs), 1416 (m), 1377 (vs), 1308 (m), 1221 (m), 1178 (w), 1070 (w), 1022 (w), 940 (w), 828 (w), 755 (m), 723 (m), 689 (w), 674 (m), 624 (w), 526 (w).

 $[Co_8(dbm)_8(bpym)_8](CF_3SO_3)_8$ (2). This compound was prepared in the same manner as 1 but by using Co(CF_3SO_3)_2 (0.05 g, 0.1 mmol) in place of Co(NO_3)_2·6H_2O. After 2 days, orange needle-like crystals of 2 had appeared which were collected by filtration and washed with hexanes (3 x 5 mL); the yield was 60% (0.28g). Anal. Calc. for C₁₉₂H₁₃₆N₃₂O₄₀S₈F₂₄Co₈ (2): C, 48.91; H, 2.91; N, 9.51 %. Found: C, 48.78; H, 2.76; N, 9.38 %. Selected ATR data (Nujol mull, cm⁻¹): 1592 (m), 1575 (m), 1548 (m), 1518 (m), 1459 (vs), 1407 (m), 1377 (vs), 1310 (m), 1261 (s), 1225 (w), 1158 (m), 1094 (w), 1027 (s), 940 (w), 820 (w), 760 (m), 720 (s), 688 (m), 657 (m), 639 (m), 574 (w).

Single crystal X-ray crystallography

Crystals of **1** and **2**·1.25 CH₂Cl₂·Et₂O were immersed in Paratone® oil and selected under ambient conditions using a MiTeGen microloop or nylon loop. The crystals were placed in a stream of cold N₂ at 114(1) K (for **1**) and 110 K (for **2**) on a Bruker D8-QUEST diffractometer equipped with a I μ S Mo microsource ($\lambda = 0.71073$ Å). An initial unit cell was determined using SAINT from a set of 3 ω -scans consisting of 30 0.5° frames and a sweep width of 15°. From this unit cell, a data collection strategy to collect all independent reflections to a resolution of at least 0.83 Å was implemented using APEX3.² Full details of the data collections are presented in Table S1.

For each structure, the data were corrected for absorption using SADABS-2014/5.³ The space group was determined from analysis of the systematic absences and E-statistics using XPREP. The structures were solved using the intrinsic phasing routine in SHELXT.⁵ The non-hydrogen atoms were located from the difference Fourier map and refined using a least-squares refinement algorithm in SHELXL-2014.⁶ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions and refined with thermal parameters constrained to their parent atom. Specific details of the structure refinements are presented below. The programs used for molecular graphics were MERCURY⁷ and Diamond.⁸

Complex	1	$2 \cdot 1.25 \text{ CH}_2\text{Cl}_2 \cdot \text{Et}_2\text{O}$	
Empirical formula	$C_{42}H_{44}Co_2N_6O_{14}$	$C_{197.25}H_{148.51}Cl_{2.51}Co_8F_{24}N_{32}O_{41}S_8$	
Formula weight	974.69	4895.70	
Temperature/K	114(1)	110.0	
Crystal system	triclinic	tetragonal	
Space group	<i>P</i> 1	I-4	
a/Å	9.4457(3)	26.9720(7)	
b/Å	10.5805(3)	26.9720(7)	
c/Å	12.3374(3)	14.8470(4)	
α/\circ	97.9340(10)	90	
β/°	104.9220(10)	90	
γ/°	112.4450(10)	90	
Volume/Å ³	1061.91(5)	10801.0(6)	
Ζ	1	2	
$\rho_{calc}g/cm^3$	1.524	1.505	
μ/mm^{-1}	0.857	0.807	
F(000)	504	4973.0	
Crystal size / mm ³	$0.488 \times 0.285 \times 0.156$	$0.278\times0.184\times0.077$	
Dediction	ΜοΚα	$M_{2}K_{2}() = 0.71072)$	
Kadiation	$(\lambda = 0.71073)$	MOK α ($\lambda = 0.71073$)	
2Θ range for data collection/°	4.808 to 50.804	4.776 to 54.22	
	$-9 \le h \le 11$		
Index ranges	$-12 \le k \le 12$	$-31 \le h \le 34, -29 \le k \le 34, -18 \le 1$ < 19	
	$-14 \le l \le 14$	_ 17	
Reflections collected	11476	34484	
	3884	11873	
Independent reflections	$R_{int} = 0.0183$	$R_{int} = 0.0434$	
	$R_{sigma} = 0.0193$	$R_{sigma} = 0.0515$]	
Data/restraints/ parameters	3884 / 0 / 297	11873/700/881	
Goodness-of-fit on F ²	1.089	1.079	
Final $\mathbb{R}^{a,b}$ indexes [I>=2 σ (I)]	$R_1 = 0.0251, wR_2 = 0.0623$	$R_1 = 0.0370, wR_2 = 0.0749$	
Final R ^{<i>a,b</i>} indexes [all data]	$R_1 = 0.0282, wR_2 = 0.0641$	$R_1 = 0.0513, wR_2 = 0.0834$	
Largest diff. peak / hole / e Å-3	0.30 / -0.36	0.30/-0.34	

 Table S1. Crystal data and structural refinement parameters for compounds 1 and 2.

 ${}^{a}\mathbf{R}_{1} = \Sigma(||F_{o}| - |F_{c}||)/\Sigma|F_{o}|. \ {}^{b}\mathbf{w}\mathbf{R}_{2} = [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]]^{1/2}, w = 1/[\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp],$ where $p = [\max(F_{o}^{2}, 0) + 2F_{c}^{2}]/3$

 Table S2. Selected interatomic distances and angles for 1 and 2.

	Com	pound 1		
Bond lengths (Å)				
Co(1)-O(1)	2.0202(11)	Co(1)-O(4)	2.1194(12)	
Co(1)-O(2)	1.9869(11)	Co(1)-N(1)	2.1439(13)	
Co(1)-O(3)	2.1058(13)	Co(1)-N(2)	2.1491(13)	
Bond angles (°)				
O(1)-Co(1)-O(3)	89.34(5)	O(2)-Co(1)-N(2)	91.67(5)	
O(1)-Co(1)-O(4)	88.18(5	O(3)-Co(1)-O(4)	173.05(5)	
O(1)-Co(1)-N(1)	99.75(5)	O(3)-Co(1)-N(1)	88.91(5)	
O(1)-Co(1)-N(2)	177.34(5)	O(3)-Co(1)-N(2)	90.32(5)	
O(2)-Co(1)-O(1)	90.99(4)	O(4)-Co(1)-N(1)	85.12(5)	
O(2)-Co(1)-O(3)	94.09(5)	O(4)-Co(1)-N(2)	91.86(5)	
O(2)-Co(1)-O(4)	92.44(5)	O(2)-Co(1)-N(2)	77.60(5)	
O(2)-Co(1)-N(1)	168.89(5)			
Compound 2				
Bond lengths (Å)				

Co(1)-O(1)	2.012(4)	Co(2)-O(3)	1.999(4)
Co(1)-O(2)	2.008(4)	Co(2)-O(4)	1.997(4)
Co(1)-N(1)	2.159(5)	Co(2)-N(3)	2.153(5)
Co(1)-N(2)	2.179(5)	Co(2)-N(4)	2.120(5)
Co(2)-N(5)	2.136(5)	Co(2)-N(7)	2.152(5)
Co(2)-N(6)	2.146(5)	Co(2)-N(8)	2.179(5)
Bond angles (°)			
O(1)-Co(1)-N(1)	169.25(17)	O(3)-Co(2)-N(3)	167.49(18)
O(1)-Co(1)-N(2)	92.22(18)	O(3)-Co(2)-N(4)	91.29(18)
O(1)-Co(1)-N(5)	97.23(16)	O(3)-Co(2)-N(7)	95.0(2)
O(1)-Co(1)-N(6)	90.98(19)	O(3)-Co(2)-N(8)	91.29(17)
O(2)-Co(1)-O(1)	88.5(2)	O(4)-Co(2)-O(3)	91.5(2)
O(2)-Co(1)-N(1)	90.3(2)	O(4)-Co(2)-N(3)	84.14(19)
O(2)-Co(1)-N(2)	94.47(18)	O(4)-Co(2)-N(4)	96.44(19)
O(2)-Co(1)-N(5)	92.2(2)	O(4)-Co(2)-N(7)	165.47(19)
O(2)-Co(1)-N(6)	169.0(2)	O(4)-Co(2)-N(8)	90.2(2)
N(1)-Co(1)-N(2)	77.22(16)	N(3)-Co(2)-N(8)	100.41(17)
N(5)-Co(1)-N(1)	93.49(17)	N(4)-Co(2)-N(3)	77.61(17)
N(5)-Co(1)-N(2)	168.56(18)	N(4)-Co(2)-N(7)	96.41(18)

N(5)-Co(1)-N(6)	77.0(2)	N(4)-Co(2)-N(8)	172.9(2)
N(6)-Co(1)-N(1)	92.19(19)	N(7)-Co(2)-N(3)	92.0(2)
N(6)-Co(1)-N(2)	96.52(19)	N(7)-Co(2)-N(8)	76.7(2)

S3. Bond valence sum (BVS) calculations for Co atoms in **1** and **2**.

Compound 1			Compound 2		
Atom	Co ^{II}	Co ^{III}	Atom	Co ^{II}	Co ^{III}
Col	2.11	1.96	Col	<u>2.07</u>	1.87
			Co2	<u>2.11</u>	1.91

Magnetism

Variable-temperature direct current (DC) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet and operating in the 2.0-300 K range. The diamagnetic contribution of the polypropylene bag used to hold the sample was subtracted from the raw data. Pascal's constants⁹ were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities (χ_M).

The magnetic susceptibility data of compound **1** were fit with the PHI program using the following spin Hamiltonian (Eq. 1):

$$\widehat{H}_{1} = -2J_{1}(\vec{S}_{1} \cdot \vec{S}_{2}) + D\left(\sum_{i=1}^{2} \left(S_{zi}^{2} - \frac{1}{3}\vec{S}_{i}^{2}\right)\right) + \mu_{B}g\left(\sum_{i=1}^{2} \vec{S}_{i}\right)H$$
(1)

The first term in \hat{H}_1 describes the isotropic Co...Co exchange interaction, where J_1 is the Co...Co exchange parameter. The third term represents the axial zero-field splitting, D, assuming parallel anisotropic tensors for both metal centers. The last term accounts for the Zeeman interactions, where μ_B is the Bohr magneton, g is the electronic Lande factor for Co²⁺, and H is the magnetic field. Similar studies were performed for **2**, using the following spin Hamiltonian (Eq. 2):

$$\widehat{H}_{2} = -2J_{2}\left(\sum_{i=1}^{7} \left(\vec{S}_{i} \cdot \vec{S}_{i+1} + \vec{S}_{8} \cdot \vec{S}_{1}\right)\right) + D\left(\sum_{i=1}^{8} \left(S_{zi}^{2} - \frac{1}{3}\vec{S}_{i}^{2}\right)\right) + \mu_{B}g\left(\sum_{i=1}^{8} \vec{S}_{i}\right)H$$
(2)

References

- 1. *Inorganic Syntheses*, John Wiley & Sons, Inc., 2002, pp. 75-121.
- 2. Bruker-AXS, *Journal*, 2015.
- 3. G. M. Sheldrick, *SADABS*, 1996.
- 4. G. M. Sheldrick, *Journal*, 2012.
- 5. G. M. Sheldrick, Acta Crystallogr. Sect. A, Found. and Adv., 2015, 71, 3-8.
- 6. G. M. Sheldrick, Acta crystallogr. Sect. C, Struc. Chem., 2015, C71, 3-8.
- C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.
- 8. W. Pennington, *Journal of Applied Crystallography*, 1999, **32**, 1028-1029.
- 9. G. A. Bain and J. F. Berry, *Journal of Chemical Education*, 2008, **85**, 532.