

Molecular [Co(III)Co(II)] \times 2 Assemblies of A New *bis*-phenol/pyrazolyl Ligand

Gavin A. Craig,^a José Sánchez Costa,^a David Aguilà,^a Leoní A. Barrios,^a Olivier Roubeau,^b
Simon J. Teat^c and Guillem Aromí^{a,c}

Supporting Information

Physical Measurements. Variable-temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID magnetometer. The field applied for temperature-dependent measurements was in the range of linear dependence of M vs. H . The measured values were corrected for the experimentally determined contribution of the sample holder, while Pascal's constants were utilized to estimate diamagnetic corrections to the molar paramagnetic susceptibility. The amount of paramagnetic impurity was estimated by calculating the molar fraction of an $S = 3/2$ system with $g = 2.2$ and the same molar mass as **1** or **2**, that would give a $\chi_M T$ response equivalent to that observed at the lowest measured temperature according to the Curie Law. Elemental analyses were performed in-house with a Perkin-Elmer Series II CHNS/O Analyzer 2400, at the Servei de Microanàlisi of CSIC, Barcelona, Spain. IR spectra were obtained as KBr pellet samples on a Nicolet 5700 FTIR spectrometer. Voltammetry experiments were performed on an SP-150 (BioLogic) potentiostat modulated by EC-Lab V10.02 software. All measurements were carried out in DMF at ambient temperature, with a conventional three-electrode configuration consisting of two platinum wires as the auxiliary and reference electrodes, and a working glassy carbon (GC) electrode (3 mm diameter). TBA.PF₆ was used as supporting electrolyte and the scanning rate was 100 mVs⁻¹. All potentials are referred to the ferrocene/ferrocenium (fc⁺/fc) couple.

X-Ray crystallography. Data for compound **1** were collected on a red block using a single-axis HUBER diffractometer on station BM16 of the European Synchrotron Radiation Facility, Grenoble, France ($T=100$ K and $\lambda=0.7383$ Å). Cell refinement, data reduction and absorption corrections were done with HKL-2000 suite.¹ The structure was solved by direct methods and refined on F² using SHELXTL suite.² All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically at calculated positions on their carrier atom and refined with a riding model, except for the hydroxide hydrogen on O3 and O3B that were omitted in the structural model as they could not be found in difference Fourier maps nor fixed. Apart from the lattice pyridine molecule, there remained at the end of the refinement one large area of the cell that contained only weak electron density peaks that could not be modeled in any way as solvent molecules. Such diffuse/disordered solvent area is likely related to the observed damage of the crystals (even in grease at room temperature) once taken out of their mother liquor. This was analyzed and taken into account by PLATON/SQUEEZE³ that recovered 507 electrons in one large void of 3042 cubic angstroms. These figures would agree with 12 diffuse/disordered pyridine molecules per cell (6 per asymmetric unit, which has 2 [Co₄] units). The SQUEEZE treatment resulted in a decrease of $R1$ by ca. 7%. Poor completeness (92.5%) is likely due both to poor diffraction of the crystal that showed rapid damage even in oil and to geometrical limitations of the single-axis goniometer on BM16. Two datasets were acquired for two kappa positions manually fixed and differing by ca. 20°, close to the maximum

permitted by the goniometer head. Because there are two similar [Co₄] molecules in the asymmetric unit, we attempted to switch the structure to a higher symmetry, without success. PLATON/ADDSYM indeed does not indicate any probable higher symmetry space. Data for compound **2** were collected on a red block on a Bruker APEX II CCD diffractometer on Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory, from a silicon 111 monochromator ($T=100$ K, $\lambda=0.7749$ Å). The structure was solved by direct methods and refined on F^2 using SHELXTL suite.² All non-hydrogen atoms were refined anisotropically. Lattice pyridine molecules were refined with displacement parameters restraints, and one has half occupancy. Hydrogen atoms of the main moiety were found in difference Fourier maps. All hydrogens were placed geometrically on their carrier atom and refined with a riding model. Due to the special position occupied by C2 and C37, the corresponding methyl hydrogens are also on special positions and are thus disordered by symmetry over two half occupied positions. Two residual electron density peaks remained at the end of the refinement both close to the Co1 atom. Both structures have been deposited at the CCDC, with numbers 798852 and 798853.

1 Z. Otwinowski, W.Minor, *Methods in Enzymology* 1997, 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R. M. Sweet, Eds., Academic press (New York).

2 G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112-122

3 A.L.Spek, *J. Appl. Cryst.* 2003, 36, 7-13

Table S1. Crystal data for compounds **1** and **2**.

Compound	1	2
formula	C ₁₇₅ H ₁₃₉ Co ₈ N ₃₁ O ₁₄	C ₈₈ H ₇₇ Co ₄ N ₁₅ O ₉
Fw, g/mol	3371.62	1724.37
crystal system	triclinic	monoclinic
space group	<i>P</i> -1	<i>P2/c</i>
<i>a</i> , Å	16.133(3)	12.4549(7)
<i>b</i> , Å	23.373(5)	12.6214(7)
<i>c</i> , Å	23.517(5)	26.4841(15)
α , deg	88.14(3)	90
β , deg	76.50(3)	91.5270(10)
γ , deg	80.03(3)	90
<i>V</i> , Å ³	8492(3)	4161.8(4)
<i>Z</i>	2	2
ρ_{calc} , g/cm ³	1.331	1.376
μ , mm ⁻¹	1.060	1.068
<i>T</i> , K	100	100
transmission range	0.85 – 0.95	0.88 – 0.96
unique reflections	26563	12046
parameters/restrains	1717 / 0	542 / 97
w <i>R</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.4118	0.1900
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.1561	0.0643
<i>S</i> [<i>I</i> > 2σ(<i>I</i>)]	1.741	1.061
w <i>R</i> 2 (all data)	0.4437	0.2114
<i>R</i> 1 (all data)	0.1792	0.0921
<i>S</i> (all data)	1.741	1.066

Table S2. Bond distances (Å) for the coordination sphere of Co ions in $2[\text{Co}_4(\text{L})_2(\text{OMe})(\text{AcO})(\text{py})_4]\cdot 7\text{py}$ (**1**)

Co1–O4	1.885(6)	Co1B–O4B	1.882(6)
Co1–O6	1.904(6)	Co1B–O6B	1.893(7)
Co1–N5	1.929(7)	Co1B–N5B	1.928(9)
Co1–N9	1.937(8)	Co1B–N9B	1.937(8)
Co1–N1	1.947(7)	Co1B–N10B	1.944(8)
Co1–N10	1.957(7)	Co1B–N1B	1.954(7)
Co2–N2	1.945(6)	Co2B–O3B	1.915(6)
Co2–O3	1.946(6)	Co2B–N6B	1.936(7)
Co2–N6	1.963(7)	Co2B–N2B	1.943(7)
Co2–O1	1.981(6)	Co2B–O1B	1.976(7)
Co3–O3	1.925(6)	Co3B–O3B	1.943(6)
Co3–N7	1.960(6)	Co3B–N7B	1.954(7)
Co3–O2	1.964(6)	Co3B–N3B	1.958(6)
Co3–N3	1.967(6)	Co3B–O2B	1.960(6)
Co4–O7	1.900(6)	Co4B–O5B	1.887(5)
Co4–N12	1.907(7)	Co4B–N11B	1.913(7)
Co4–O5	1.921(6)	Co4B–O7B	1.918(5)
Co4–N8	1.940(8)	Co4B–N12B	1.938(7)
Co4–N11	1.959(7)	Co4B–N8B	1.944(6)
Co4–N4	1.963(7)	Co4B–N4B	1.949(7)

Table S3. Selected interatomic distances (Å) and angles (°) for $[\text{Co}_4(\text{L})_2(\text{OH})(\text{AcO})(\text{py})_4]\cdot 4\text{py}\cdot 2\text{MeOH}$ (**2**)

Co1–O4	1.891(2)	O3#–Co2–O2	83.36(11)
Co1–N3#	1.949(3)	O3#–Co2–N5	91.94(12)
Co1–N2	1.951(2)	O2–Co2–N5	91.38(11)
Co1–O1	1.997(3)	O3#–Co2–N4#	87.73(11)
Co2–O3#	1.888(3)	O2–Co2–N4#	171.07(12)
Co2–O2	1.897(2)	N5–Co2–N4#	88.38(11)
Co2–N5	1.945(3)	O3#–Co2–N1	171.21(11)
Co2–N4#	1.949(3)	O2–Co2–N1	88.23(11)
Co2–N1	1.952(3)	N5–Co2–N1	90.81(11)
Co2–N6	1.956(3)	N4#–Co2–N1	100.70(11)
O4–Co1–N3#	113.77(10)	O3#–Co2–N6	86.50(14)
O4–Co1–N2	116.72(9)	O2–Co2–N6	87.07(12)
N3#–Co1–N2	105.33(11)	N5–Co2–N6	177.92(12)
O4–Co1–O1	108.81(12)	N4#–Co2–N6	92.94(13)
N3#–Co1–O1	106.04(11)	N1–Co2–N6	90.53(13)
N2–Co1–O1	105.36(11)		

Symmetry operation #: -x, y, -z+1/2

Table S3: Bond Valence Sum analysis for compounds **1** and **2**.

Compound	Co site	Calc. BVS Co(II)*	Calc. BVS Co(III)*	Ascribed valence
1	Co1	2.97	3.38	+3
	Co2	1.84	1.98	+2
	Co3	1.87	1.99	+2
	Co4	2.93	3.34	+3
	Co1B	3.00	3.41	+3
	Co2B	1.93	2.07	+2
	Co3B	1.87	2.00	+2
	Co4B	2.98	3.40	+3
2	Co1	1.91	2.05	+2
	Co2	2.94	3.33	+3

* $BVS = (\sum \exp[(Ro-R)/B])/n$, where R are the n measured Co–N or Co–O distances in Å; for Co(II), $Ro(N) = 1.65$ Å and $Ro(O) = 1.692$ Å; for Co(III), $Ro(N) = 1.75$ Å and $Ro(O) = 1.637$ Å; in all cases $B = 0.37$.⁴

4 a) I. D. Brown, D. Altermatt, *Acta Cryst. B* **1985**, 41, 244-247; b) I. D Brown, “The Chemical Bond in Inorganic Chemistry”, Oxford University press, Oxford, 2002.

Figure S1. Cyclic Voltammetry of $[\text{Co}_4(\text{L})_2(\text{OAc})(\text{MeO})(\text{py})_4]$ (**2**) in DMF at room temperature and with a scan rate of 100 mVs^{-1} , using TBA.PF₆ as supporting electrolyte, where the oxidation processes are shown. The wave of the fc^+/fc couple used as reference is also shown.

