

1 **Synthesis and characterization of Co^{III} inverse**
2 **metallacrowns via use of 6-methyl-2-pyridylaldoxime**

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21 **Abstract**

22 The use of 6-methyl-2-pyridylaldoxime (6-mepaoH) in cobalt carboxylate chemistry
23 has yielded metallacrowns with general formula $[\text{Co}_3^{\text{III}} (\mu_3\text{-O}) (\text{O}_2\text{CMe})_3 (6\text{-mepao})_3]_2 [\text{Co}^{\text{II}}$
24 $(\text{L})_4]$ (**1**·2MeOH·1.5H₂O, L=AcO⁻ and **2**·2.5H₂O, L=NCS⁻). Compounds **1** and **2** display
25 an unusual structural motif in cobalt-oximate chemistry, consisting of Co^{III} triangles
26 centered by one μ₃-oxo ligand. Crystal structure and EPR characterization of Co^{II} anions
27 are reported.

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33 The coordination chemistry of oximes is a growing research field due to the ability
34 of these ligands to act as bridging ligands in which the deprotonated oxygen atom can bind
35 more than one metallic center and thus, the formation of metallic clusters is favored. Oximate
36 ligands are versatile ligands in several research fields as bioinorganic modelization,
37 catalysis, study of corrosion phenomena and synthesis of homometallic and heterometallic
38 clusters with interesting magnetic properties [1].

39 Our interest in the coordination chemistry of 2-pyridyloximes (with general formula
40 $\text{pyC}\{R\}\text{NOH}$, Scheme 1), comes from their ability to act as polydentate ligands, therefore
41 forming clusters with unusual metal ion topologies as metallacrowns (MCs) [2], which are
42 the inorganic structural and functional analogs to crown ethers. In the oximate based MCs
43 the classical motif is a repeat unit $[\text{M}-\text{N}-\text{O}]_n$ which forms a cyclic structure orienting oxygen
44 donors towards the center of a cavity that is capable of binding cations. In the less common
45 inverse motif, the ring metallic ions, rather than anionic oxygen atoms, are oriented towards
46 the center of the cavity that is capable of encapsulating anions. Oximes are one of the
47 classical kind of ligands able to generate [9-MCMN(oxime)-3], [12-MCMN(oxime)-4], [15-
48 MCMN (oxime)-5], [18-MCMN(oxime)-6] and [24-MCM(ox)N(ligand)-8]metallacrown
49 structural types [2].

50 $\text{PyC}(R)\text{NOH}$ ligands, with a variety of R groups, have been widely employed in
51 manganese, nickel or copper cluster chemistry [1], mainly in the search of large clusters with
52 SMM response. In contrast, cobaltpyridyloximate systems are still poorly explored and the
53 most of the reported compounds are neutral mononuclear $[\text{Co}^{\text{III}}(\text{pyC}\{R\}\text{NO})_3]$ complexes
54 or related derivatives in which one $\text{fac}-[\text{Co}(\text{pyC}\{R\}\text{NO})_3]^{\text{n}+}$ complex as ligand generates
55 dinuclear CoCr [3], CoFe [4] or linear trinuclear Co₃ compounds [5] (Scheme 1).
56 Polynuclear cobalt-pyridyloximate systems exhibiting other topologies are reduced to few
57 Co₃ triangular [5d] and some mixed-valent $\text{Co}_4^{\text{II/III}}$ metallacrowns [5b,6].

58 Recently we started the study of the reactivity of R-pyridyloximes including R groups
59 on the pyridinic ring, focusing our attention on the 6-mepaoH ligand (Scheme 1) for which
60 we have recently reported some Ni₅ and Ni₆ clusters and its first manganese derivative [7].
61 Following our work in this field, we present in this paper our initial results concerning the
62 use of 6-mepaoH in cobalt carboxylato chemistry. The reaction at room temperature of

63 $\text{Co}^{\text{II}}(\text{O}_2\text{CMe})_2 \cdot x\text{H}_2\text{O}$ with one equivalent of 6-mepaoH in dichloromethane led to a dark
64 red-brown solution, from which subsequently, was obtained crystals of $[\text{Co}_3^{\text{III}}(\mu_3\text{-O})(\text{O}_2\text{CMe})_3(6\text{-mepao})_3]_2[\text{Co}^{\text{II}}(\text{O}_2\text{CMe})_4] \cdot 2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ ($1 \cdot 2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$) in 70%
65 yield, anal. data: Calc. C, 39.80; H, 3.93; N, 8.98%. Found: C, 38.92; H, 3.73; N, 8.69%.

67 In order to investigate if additional bridging ligands as pseudohalides could link the
68 above Co_3 units generating larger systems, we studied the reaction of $\text{Co}(\text{O}_2\text{CMe})_2 \cdot x\text{H}_2\text{O}$
69 with one equivalent of 6-mepaoH in dichloromethane in basic medium and one equivalent
70 of sodium azido, thiocyanate or dicyanamide. The reaction with thiocyanate co-ligand gave
71 crystals of $[\text{Co}_3^{\text{III}}(\mu_3\text{-O})(\text{O}_2\text{CMe})_3(6\text{-mepao})_3]_2[\text{Co}^{\text{II}}(\text{NCS})_4] \cdot 2.5\text{H}_2\text{O}$ ($2 \cdot 2.5\text{H}_2\text{O}$) in 65%
72 yield, anal. data: Calc. C, 36.45; H, 3.43; N, 11.73; S, 6.71%. Found: C, 36.42; H, 3.29; N,
73 11.86; S, 6.89%.

74 Thiocyanate ligand was able to replace the carboxylato donors in the anionic complex
75 but not in the triangular units, whereas crystalline compounds were not obtained for the
76 remainder pseudohalides. Compounds **1–2** join to the scarce number of isolated $\{\text{M}_3(\mu_3\text{-O})(\text{pyC}\{\text{R}\}\text{NO})_3\}^{\text{n}+}$
77 triangles reported for Mn^{III} [8], Co^{III} [5d] or Cu^{II} [9].

78 Compound **1** [10] consists of $[\text{Co}_3^{\text{III}}(\mu_3\text{-O})(\text{O}_2\text{CMe})_3(6\text{-mepao})_3]^+$ cations,
79 $[\text{Co}^{\text{II}}(\text{O}_2\text{CMe})_4]^{-2}$ anions and MeOH and H_2O solvate molecules. The cationic molecular
80 structure of **1** consists of Co_3^{III} triangles linked by a central $\mu_3\text{-O}^{-2}$ ion (Fig. 1). Each edge
81 of the triangle is defined by one $\eta^1:\eta^1:\eta^1:\mu$ oximate group of a 6-mepao^- ligand (2.111 mode
82 using Harris notation [11]) and one syn-syn carboxylate group. The octahedral environment
83 of each Co^{III} ion is completed by one N-atom from the pyridinic ring of one 6-mepao^-
84 ligand. Shorter bond distances correspond to the linkage with the central oxygen atom
85 whereas the larger ones, around 2.070 Å, are those related with the $\text{Co}-\text{N}_{\text{ring}}$ bonds. The
86 $\mu_3\text{-O}$ atom is placed 0.493(2) Å above the mean Co_3^{III} plane. The $\text{Co}-\text{N}-\text{O}-\text{Co}$ torsion
87 angles are 8.8(3)°, 12.3(3)° and 19.2(3)°. Both enantiomers of the Co_3 unit, related
88 crystallographically, are present in the unit cell.

89 Complex **2** [10] was found to have a molecular structure closely related to **1**, also
90 consisting in both enantiomers, crystallographically non-equivalents, of the $[\text{Co}_3^{\text{III}}(\mu_3\text{-O})(\text{O}_2\text{CMe})_3(6\text{-mepao})_3]^+$
91 triangles (2A and 2B in Fig. 2) and $[\text{Co}^{\text{II}}(\text{NCS})_4]^{-2}$
92 counteranions. In this case both Co_3 triangles are equilaterals with $\text{Co}-(\mu_3\text{-O})$ distances of
93 1.830(1)/1.826(1) Å, $\text{Co}\cdots\text{Co}$ distance of 3.063(1)/3.055(1) Å, $\text{Co}-(\mu_3\text{-O})-\text{Co}$ bond
94 angles of 113.61(9)°/113.5(1)° and $\text{Co}-\text{N}-\text{O}-\text{Co}$ torsion angles of 16.5(3)°/15.4(3)° for
95 2A/2B respectively. Central oxygen atom is placed 0.471(4)/0.474(4) Å out of the mean
96 plane defined by the cobalt atoms of 2A/2B rings. Compounds **1** and **2** could alternatively
97 be described as inverse cationic metallocrowns with formula $\{\text{O}[\text{inv}9\text{-MCCo(III)N(6-mepao)-}$
98 $3](\text{O}_2\text{CMe})_3\}^+$.

99 For **1** one $[\text{Co}^{\text{II}}(\text{O}_2\text{CMe})_4]^{-2}$ complex acts as counteranion. The Co (4) atom is
100 coordinated by four monodentate O_2CMe^- ligands in a distorted tetrahedral environment
101 (Fig. 3) in which the symmetry elements are reduced to one C_2 axis. For **2** the counteranion
102 is one $[\text{Co}^{\text{II}}(\text{NCS})_4]^{-2}$ complex with the cobalt atom Co(3) in a distorted tetrahedral
103 environment, in which one C_3 axis is present (Fig. 3).

104 Due to the diamagnetic nature of the Co_3 clusters, magnetic susceptibility
105 Measurements were not performed. In contrast, the dilute distribution of the
106 pseudotetrahedral counteranions is adequate to obtain good quality EPR spectra (Fig. 4). The
107 ground state under Td symmetry for a Co^{II} ion is a $^4\text{A}_2$ orbital singlet term. At low
108 temperature the degeneracy is removed and it splits in two Kramer doublets ($\pm 1/2$ and $\pm 3/2$).
109 The 2D gap between them places the excited orbital levels T_1 and T_2 relatively close in
110 energy to the ground $\pm 1/2$ doublet and thus, the effective low temperature g' observed values
111 are strongly sensitive to the axial and rhombic zero field splitting parameters.

112 In good agreement with reported distorted tetrahedral Co^{II} systems [12], the spectra
113 for the two compounds show intense perpendicular signals at $g' = 6.52 - 4.65/5.93 - 4.60$
114 and weaker parallel absorptions at $g' = 2.36/2.32$ for 1/2 respectively.

115 In conclusion, in the present work we report the initial results concerning the use of
116 6-mepaoH in cobalt carboxylate chemistry. Compounds **1**·2MeOH·1.5H₂O and **2**·2.5H₂O
117 containing the triangular oxo-centered [Co^{III}(μ₃-O)(O₂CMe)₃(6-mepao)₃]⁺ units are
118 stabilized by mononuclear [Co^{II}(O₂CMe)₄]⁻² anions in **1** or [Co^{II}(NCS)₄]⁻² anions for **2**.
119 The trinuclear [Co^{III}]₃⁺ cationic units of complexes **1** and **2** are members of Co metallocrowns
120 family with inverse motif. The reported compounds point out the stability of the triangular
121 trivalent cobalt clusters in the presence of the adequate counteranions.

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132 **Appendix A. Supplementary data**

133 Crystallographic data have been deposited with the Cambridge Crystallographic Data
134 Center. Copies of this information may be obtained free of charge from The Director, CCDC,
135 12 Union Road, Cambridge, B2 1EZ, UK, on quoting the deposition numbers CCDC 846919
136 (1·2MeOH·1.5H₂O) and 846920 (2·2.5H₂O) (fax: +44-1233-336033; e-mail :
137 deposit@ccdc.cam.ac.uk of <http://www.ccdc.cam.ac.uk>). Supplementary data to this article
138 can be found online at doi:10.1016/j.inoche.2011.11.037.

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- 180 [10] Crystallographic data. **1·2MeOH.1.5H₂O** : C₁₂₈H₁₆₂Co₁₄N₂₄O₆₃, M=3869.84,
181 monoclinic, C2/c, a=27.415(16), b=12.730(7), c=25.073(8) Å, β=98.23(3)°,
182 λ=0.71073 Å, V=8660(7) Å³, Z=2, D_c=1.484 g cm⁻³, μ (MoKα)=1.391 mm⁻¹,
183 T=293(2) K, 23094 reflections collected, 9587 unique (R_{int}=0.0882), R on F (wR² on
184 F²)=0.0378 (0.0884). **2.2.5H₂O**: C₁₁₆H₁₃₀N₃₂Co₁₄O₄₈S₈, M=3822.02, Trigonal, P-
185 3, a=15.601(5), b=15.601(5), c=19.689(1) Å, γ=120(0)°, λ=0.71073 Å, V=4150(2) Å³,
186 Z=1, D_c=1.529 g cm⁻³, μ(MoKα)=1.542mm⁻¹, T=173(2) K, 27292 reflections
187 collected, 7038 unique (R_{int}=0.0653), R on F (wR² on F²)= 0.0488 (0.1067).
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207 **Figures Captions**

208 **Scheme 1.** Structural formulae of the 2-pyridyloxime ligands discussed in the text and
209 scheme of the most usual fac-[Co(pyC{R}NO)₃]ⁿ⁺ octahedral coordination of cobalt with
210 pyridyloximes in mononuclear or complex as ligand compounds.

211 **Figure 1.** Partially labeled plot of the triangular [Co^{III}(μ₃-O)(O₂CMe)₃(6-mepao)₃]⁺ cation
212 of complex **1** and a view of the core of the complex showing the arrangement of the oximate
213 metallacrown ring and carboxylate ligands. Selected interatomic distances (Å) and angles
214 (°): Co(1)⋯Co(2) 3.121(1), Co(1)⋯Co(3) 3.126(1), Co(2)⋯Co(3) 3.108(2), Co(1)—O(1)
215 1.863(3), Co(2)—O(1) 1.866(2), Co(3)—O(1) 1.871(2), Co(1)—O(1)—Co(2) 113.6(1)°,
216 Co(1)—O(1)—Co(3) 113.7(1)°, Co(2)—O(1)—Co(3) 112.5(1)°.

217 **Figure 2.** Enantiomers of the {Co₃(μ₃-O)(6-mepao)₃}⁴⁺ core of complexes **1** and **2**. For **1**,
218 the enantiomers are crystallographically related whereas for **2** are crystallographically
219 independents (left, 2A triangle/right, 2B triangle).

220 **Figure 3.** Partially labeled plot of the [Co^{II}(O₂CMe)₄]⁻² and [Co^{II}(NCS)₄]⁻² counteranions
221 of complexes **1** and **2** respectively. Selected interatomic distances (Å) and angles (°):
222 Co(4)—O(11) 2.018(3), Co(4)—O(12) 1.994(3), O(11)—Co(4)—O(11a) 94.3(1), O
223 (12)—Co(4)—O(12a) 114.2(1), O(11)—Co(4)—O(12), 125.1(1)°, O(11)—Co(4)—O(12a)
224 99.5(1)° for **1** and Co(3)—N(31) 1.935(4), Co(3)—N(32) 1.828(10), N(31)—Co
225 (3)—N(31a) 110.6(2)°, N(31)—Co(3)—N(32) 108.3(1)° for **2**.

226 **Figure 4.** X-band EPR spectrum of a powdered sample of **1** (top) and **2** (bottom) at 4.2 K.

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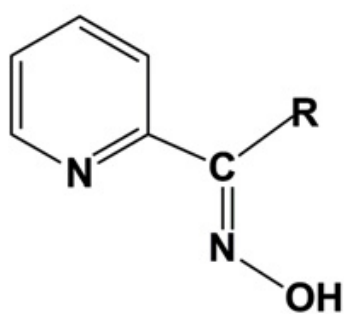
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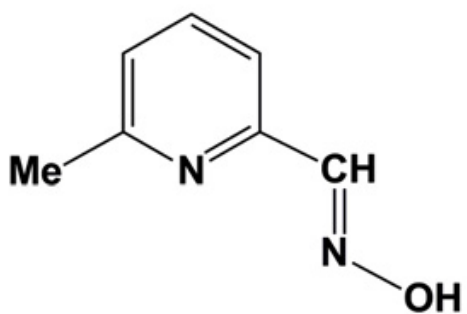
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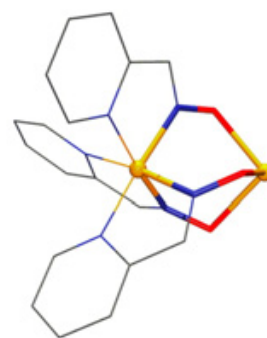
232 **Scheme 1.**



R = H, Me, Ph, py, CN, NH₂



6-mepaoH



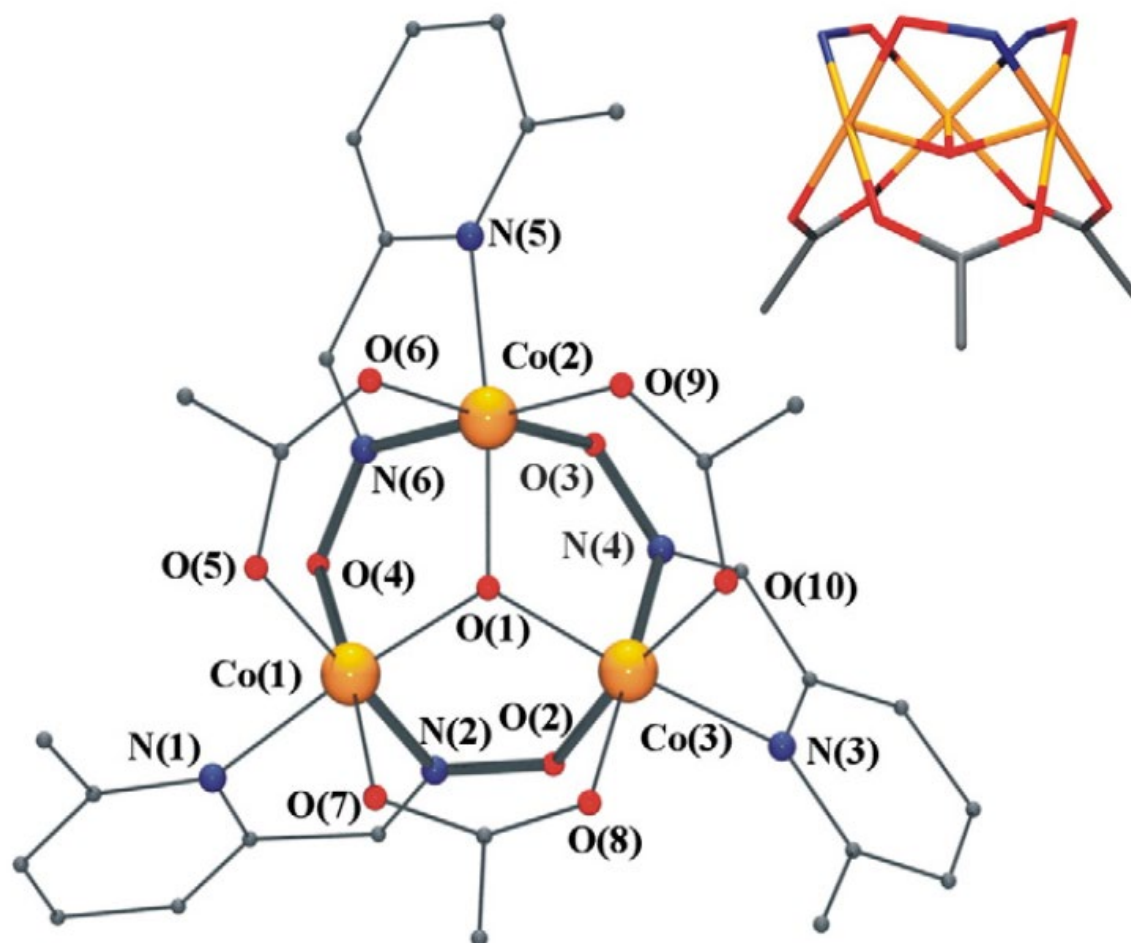
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236 **Figure 1**

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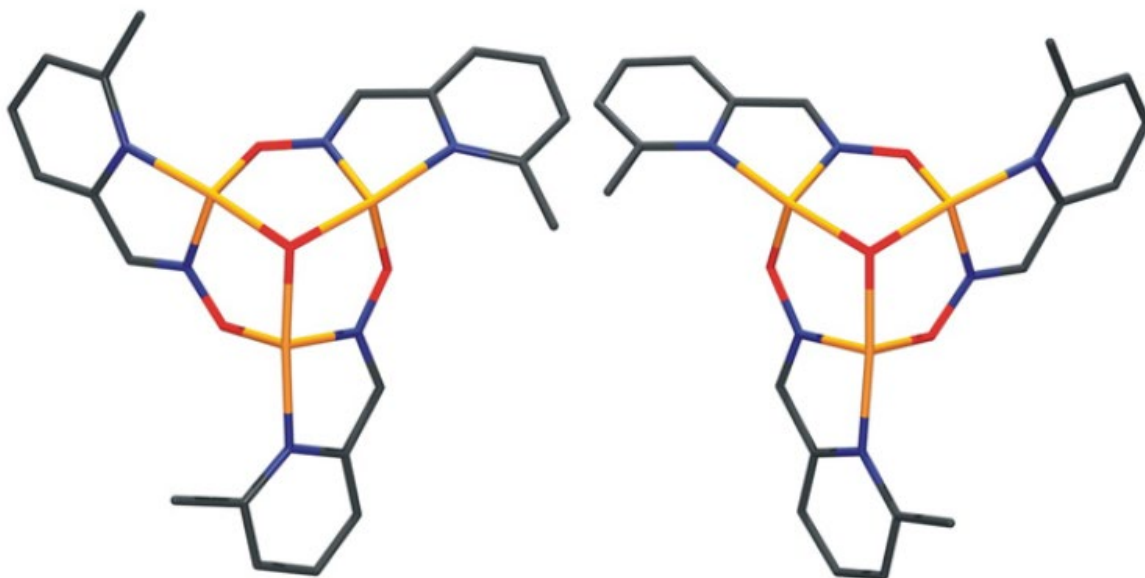
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242 **Figure 2**

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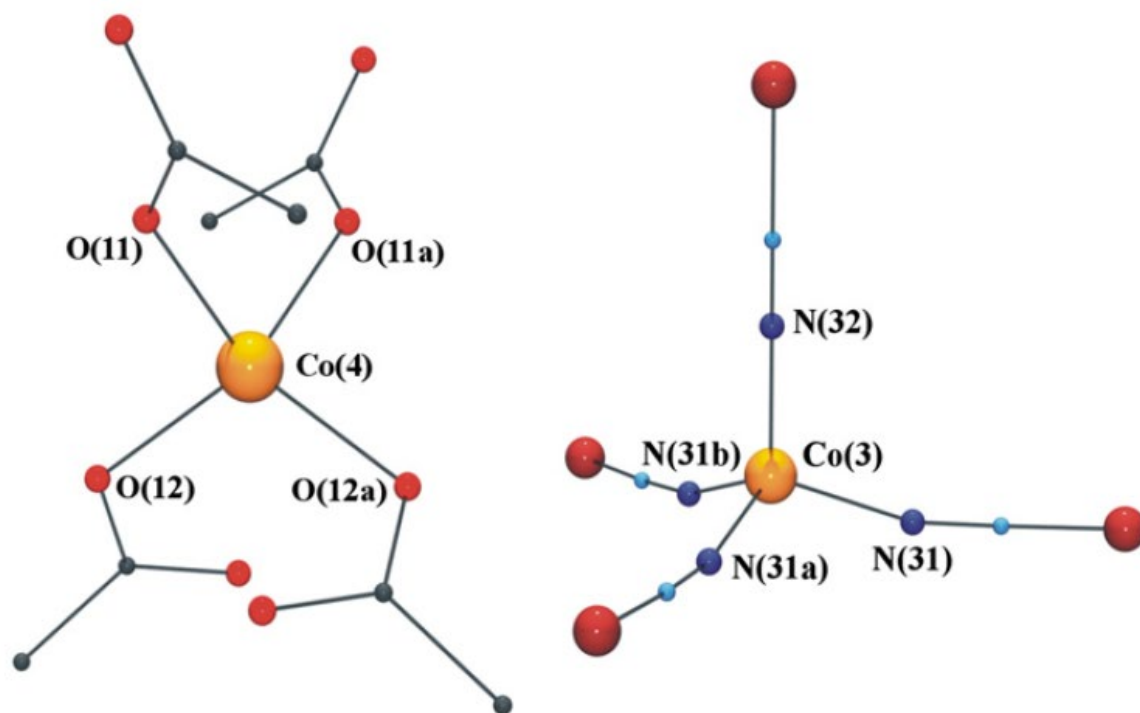
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247 **Figure 3**

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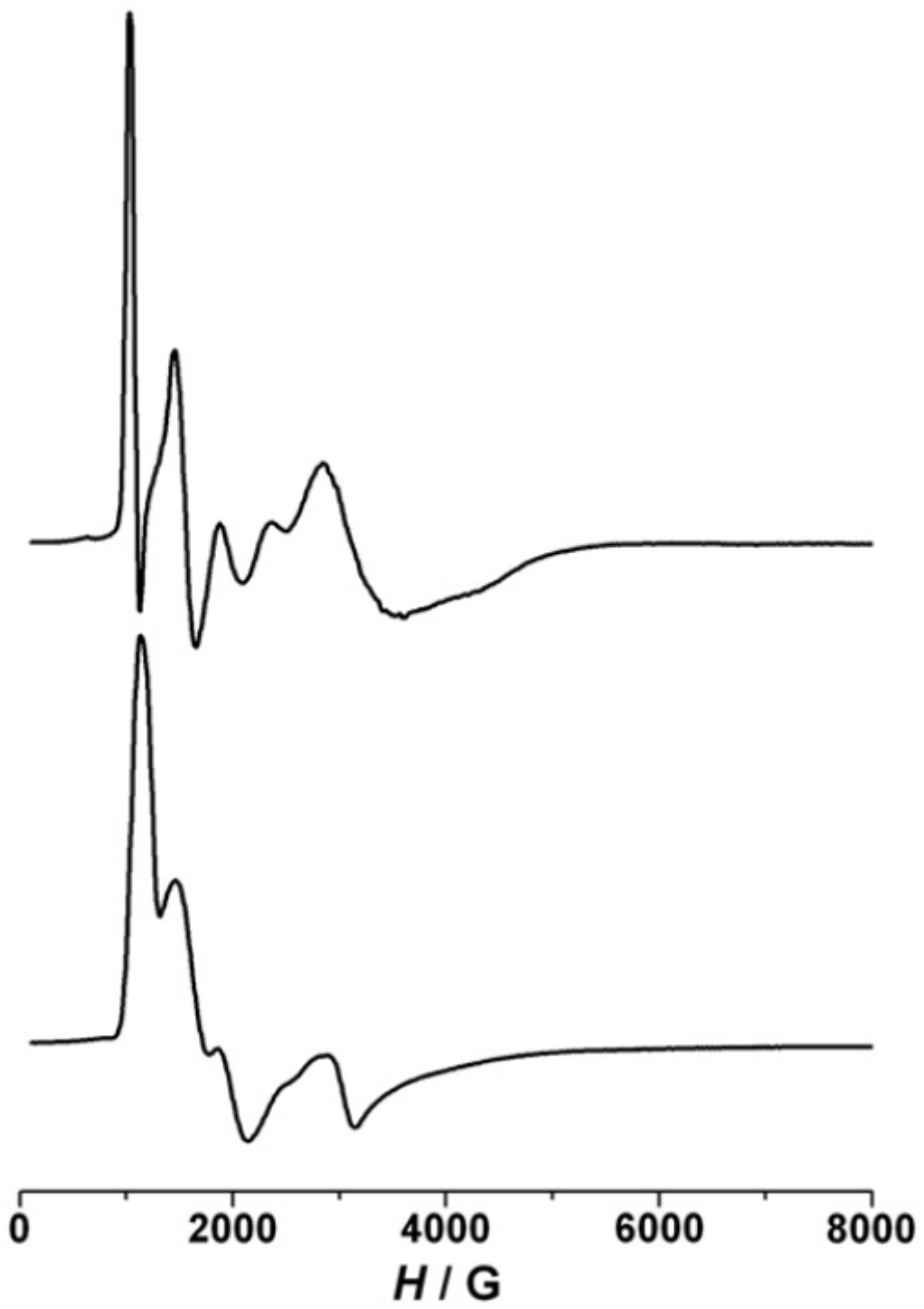
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253 **Figure 4**



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