

SUPPORTING INFORMATION

Unusual Magnetic Properties of a Two-coordinate Heteroleptic Linear Cobalt(II) Complex

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The supporting information contains:

1. Experimental Details
2. Crystallographic Studies
3. Comparison of all two-coordinate Co(II) species
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1. Experimental Details

General Procedures. All manipulations were carried out using modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All of the solvents were dried over an alumina column, stored over 3Å molecular sieves overnight, and degassed three times (freeze-thaw) prior to use. $\{\text{Ar}'\text{Co}(\mu\text{-Cl})\}_2^{\text{S1}}$ and LiAr'^{S2} were prepared according to literature procedures. Melting points were recorded in glass capillaries sealed under N_2 and are uncorrected. UV-vis data were recorded on a Hitachi-1200 spectrometer. Magnetic susceptibility measurements by the Evan's method^{S3,S4} and the ^1H NMR spectra were recorded on a Bruker 300 MHz spectrometer.

CoAr'₂ (1): To a mixture of $\{\text{Ar}'\text{Co}(\mu\text{-Cl})\}_2$ (0.246 g, 0.25 mmol) and LiAr' (0.203 g, 0.50 mmol) was added a mixture of hexanes (30 mL) and Et_2O (0.5 mL) at

room temperature. The resulting dark green solution was stirred for one day, filtered and concentrated to *ca.* 10 mL to afford dark green crystals of **1** suitable for single crystal X-ray crystallography after storage for several days at -18 °C. Yield 0.352 g (82.4%). Mp 161-163 °C. Anal. Calcd. For C₆₀H₇₄Co: C, 84.37; H, 8.73. Found: C, 84.71; H, 9.02. UV-vis (hexane, nm [ϵ , cm⁻¹M⁻¹]): 360 (br., 3600), 409 (shoulder), 481 (vbr., 1600). ¹H NMR (300 MHz, C₆D₆, 20 °C): δ = -3.35 (vbr., 18H, C₆H₃), 1.14 (s, 48H, CH(CH₃)₂), 2.93 (br., s, 8H, CH(CH₃)₂). $\mu_{\text{eff}} = 4.38 \mu_{\text{B}}$ at 293.5 K.

Ar'CoN(SiMe₃)₂ (2): A procedure similar to that of **1**, in which {Ar'Co(μ -Cl)}₂ (0.246 g, 0.25 mmol) and LiN(SiMe₃)₂ (0.085 g, 0.51 mmol) were employed, afforded complex **2** as X-ray quality orange crystals from hexanes. Yield 0.269 g (87.1%). Mp 175-177 °C (decomposed). Anal. Calcd. For C₃₆H₅₅CoNSi₂: C, 70.09; H, 8.99; N, 2.27. Found: C, 70.37; H, 9.31; N, 1.98. UV-vis (hexane, nm [ϵ , cm⁻¹M⁻¹]): 380 (2000), 485 (700). $\mu_{\text{eff}} = 5.82 \mu_{\text{B}}$ at 293.5 K.

2. Crystallographic Studies.

Suitable crystals of **1** and **2** were selected and covered with a layer of hydrocarbon oil under a rapid flow of argon. They were mounted on a glass fiber attached to a copper pin and placed in the cold N₂ stream on the diffractometer. The X-ray data were collected on a Bruker SMART 1000 diffractometer at 90(2) K using Mo K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS.^{S5} The structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.^{S6} All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms in both structures were placed at calculated positions and are included in the refinement using a riding model.

Crystal data for **1** and **2** at T = 90(2) K with Mo K α (λ = 0.71073 Å) radiation. **1**: C₆₀H₇₄Co, *F*_w = 854.12, monoclinic, space group *C2/c*, dark green plate, *a* = 15.6649(6) Å, *b* = 15.9068(6) Å, *c* = 19.7416(8) Å, β = 93.6750(10)°, *V* = 4909.1(3) Å³, *Z* = 4, 18454 total reflections, 5641 unique, *R*_{int} = 0.0160, *R*1 = 0.0408 (*I* > 2 σ (*I*) data), *wR*2 = 0.1099 for all data. **2**: C₃₆H₅₅CoNSi₂, *F*_w = 616.92, orthorhombic, space group *Pca2₁*, orange block, *a* = 18.2549(10) Å, *b* = 10.8473(6) Å, *c* = 18.5964(10) Å, *V* = 3682.4(3) Å³, *Z* = 4, 30329 total reflections, 8440 unique, *R*_{int} = 0.0298, *R*1 = 0.0308 (*I* > 2 σ (*I*) data), *wR*2 = 0.0830 for all data. The possibility of *Pbcn* space group was checked and abandoned. More details are in the CIF file.

3. Comparison of all two-coordinate Co(II) species

Table S1. Comparison of structurally characterized two-coordinate Co(II) complexes:

Complex	Co-C(S), Å	Co-N, Å	L-Co-L, °	μ_{eff}	Ref.
CoAr ₂ (1)	2.014(2)		159.34(8)	4.08	This work
Ar'CoN(SiMe ₃) ₂ (2)	1.9732(16)	1.8747(14)	179.02(11)	5.65	This work
Ar'CoN(H)Ar ^{#a}	1.977(1)	1.875(3)	101.71(11)	1.76	S7
Ar'CoN(H)Ar ^{#b}	1.992(2)	1.880(2)	133.90(6)	4.65	S7
CoAr [#] ₂	2.001		162.8(1), 172.2(2) ^c	3.81	S8
Co(SAr*) ₂	2.1912(6)		179.52(2)	5.75(2)	S9
Co{N(SiMePh ₂) ₂ } ₂		1.902(3)	147.0(1)		S10
Co{N(Ph)BMes ₂ } ₂		1.909(5)	127.1(2)		S11
Co{N(Mes)BMes ₂ } ₂		1.910(3)	168.4(1)		S11

^a is the structure at 90(2) K; ^b is the structure at 240(2) K; ^c corresponds to two crystallographically independent molecules.

4. Magnetic Susceptibility Measurements of **2**.

A crystalline sample of **2** was sealed under vacuum in a 3 mm diameter quartz tube. The sample magnetizations were measured using a Quantum Design MPMSXL7 superconducting quantum interference magnetometer; the sample was zero-field cooled to 2 K and the long moment was measured upon warming from 2 to 320 K in an applied

field of 0.01 T. Above 170 K, the unanchored sample exhibited particle reorientation in the applied field and only the results obtained from 2 to 170 K are reported herein. In order to ensure thermal equilibrium between the sample in the quartz tube and the temperature sensor, the long moment was measured at each temperature until it reached a constant value. A diamagnetic correction of -0.000397 emu/mol, obtained from tables of Pascal's constants, was applied to the measured molar magnetic susceptibility of **2**.

As expected for a magnetically dilute $3d^7$ complex of cobalt(II), **2** exhibits Curie-Weiss behavior between 2 and 170 K (Figure 3 in the paper), with a small Weiss temperature, Θ , of -1.9 K and a Curie constant, C , of 3.99 emuK/mol; the corresponding effective magnetic moments, μ_{eff} , is $5.65 \mu_B$, a value that is substantially higher than the expected spin-only moment of $3.87 \mu_B$.

Because of the linear two-coordinate environment observed for the cobalt(II) ion in **2** the expected orbital electronic configuration, $(d_{x^2-y^2}, d_{xy})^4 (d_{xz}, d_{yz})^2 (d_z^2)^1$, corresponds to three unpaired electrons and $S = 3/2$. Thus the observed $\chi_M T$ of **2** has been fit for zero-field splitting arising from higher order spin-orbit terms in the electronic ground state of a cobalt(II) complex with the following expressions^{S12-S14}

$$\chi_{||} = \frac{Ng^2\mu_B^2}{k_B T} \frac{1 + 9e^{-2D/k_B T}}{4(1 + e^{-2D/k_B T})}, \quad (1)$$

$$\chi_{\perp} = \frac{Ng^2\mu_B^2}{k_B T} \frac{4 + (3k_B T/D)(1 - e^{-2D/k_B T})}{4(1 + e^{-2D/k_B T})}, \quad (2)$$

$$\chi' T = \left(\frac{\chi_{||} + 2\chi_{\perp}}{3}\right)T + N\alpha T, \quad (3)$$

where N is the Avogadro number, μ_B is the Bohr magneton, k_B is the Boltzmann constant, g is the Lande factor, D is the magnitude of the zero field splitting, and $N\alpha$ is the second

order Zeeman contribution to the molar magnetic susceptibility, i.e., the temperature independent paramagnetism.

5. EPR Studies of **2**.

CW EPR spectra were acquired using a Bruker ECS106 X-band spectrometer equipped with an ER4102ST resonator. Cryogenic temperatures were achieved and controlled using an Oxford Instruments ESR900 liquid helium cryostat in conjunction with an Oxford Instruments ITC503 temperature and gas flow controller.

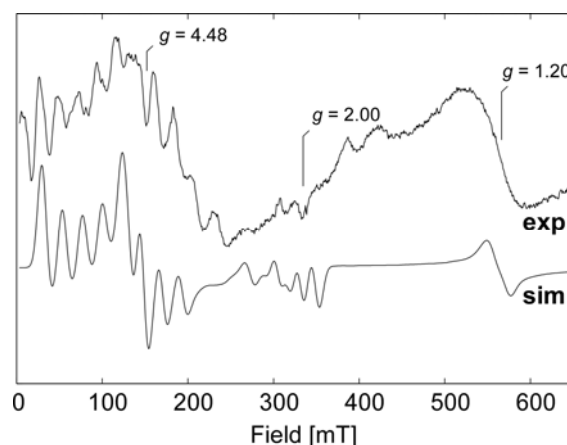


Figure S1. The CW EPR spectrum of **2**. Instrument settings: temperature = 8.0 K; microwave frequency = 9.4777 GHz; microwave power = 0.20 mW; modulation frequency = 100 kHz; modulation amplitude = 1.0 mT; sweep rate = 4 mT/sec. Simulation parameters: $g = [3.2 \ 2.6 \ 2.0]$; g (average) = 2.7, line width = 12 mT, $D = 2.45 \text{ cm}^{-1}$, $E = 0.27 \text{ cm}^{-1}$, ^{59}Co Hyperfine = [100 850 200] MHz.

The CW EPR spectrum of **2** (Fig. S1) has two main features centered at $g = 4.48$ and $g = 1.20$. Only the low-field resonance possesses obvious ^{59}Co ($I = 7/2$) hyperfine structure with an apparent coupling constant greater than 800 MHz. The positions of the major spectral features are well-simulated using EasySpin 3.1^{S15} assuming an $S = 3/2$ spin system with a g -matrix = [3.2, 2.6, 2.0], $A(^{59}\text{Co}) = [100 \ 850 \ 200]$ MHz, zero-field splitting (ZFS) parameters $D = 2.45 \text{ cm}^{-1}$ and $E = 0.27 \text{ cm}^{-1}$, and a line width of 12 mT.

Both the axial ZFS parameter and the average g -value were fixed to those values determined from the susceptibility measurements above. The magnitudes of the rhombic ZFS term E and the ^{59}Co hyperfine tensor were then optimized to achieve the best fit.

References:

- S1. D. Sutton, T. Ngyuen, J. C. Fettinger, M. M. Olmstead, G. J. Long and P. P. Power, *Inorg. Chem.*, 2007, **46**, 4809.
- S2. B. Schiemenz and P. P. Power, *Angew. Chem. Int. Ed.* **1996**, 35, 2150.
- S3. F. Evans, *J. Chem. Soc.* 1959, 2003.
- S4. M. Schubert, *J. Chem. Educ.* 1992, **69**, 62.
- S5. SADABS, version 5.0 package; an empirical absorption correction program from the SAINTPlus NT; Bruker AXS: Madison, WI 1998.
- S6. SHELXL, version 5.1; Bruker AXS: Madison WI 1998.
- S7. C. B. Ni, J. C. Fettinger, G. J. Long and P. P. Power, *Inorg. Chem.*, 2009, **48**, 2443.
- S8. D. L. Kays and A. R. Cowley, *Chem. Commun.*, 2007, 1053.
- S9. T. Nguyen, A. Panda, M. M. Olmstead, A. F. Richards, M. Stender, M. Brynda and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 8545.
- S10. R. A. Bartlett and P. P. Power, *J. Am. Chem. Soc.*, 1987, **109**, 7563.
- S11. H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power and S. C. Shoner, *J. Am. Chem. Soc.*, 1990, **112**, 1048.
- S12. C. J. Oconnor, *Prog. Inorg. Chem.*, 1982, **29**, 203.
- S13. H. Miyasaka, R. Clerac, C. S. Campos-Fernandez and K. R. Dunbar, *Inorg. Chem.*, 2001, **40**, 1663.
- S14. S. R. Marshall, A. L. Rheingold, L. N. Dawe, W. W. Shum, C. Kitamura and J. S. Miller, *Inorg. Chem.*, 2002, **41**, 3599.
- S15. S. Stoll and A. Schweiger, *J. Magn. Reson.* 2006, **178**, 42.