Unusual magnetic properties of a two-coordinate heteroleptic linear cobalt(II) complex†

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The synthesis and characterization of two-coordinate cobalt(II) complexes CoAr$'_2$ (1) and Ar$'$CoN(SiMe$_3$)$_2$ (2) (Ar$'$ = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$) are reported. The magnetic data for 2 show that it has an unexpectedly high μ_{eff} of 5.65 μ_B whereas the bent complex 1 has a significantly lower moment.

It has been shown that Fe(II) ions with rare linear, or almost linear, two coordination in Fe{C(SiMe$_3$)$_3$}$_2$,[1] Fe(N^{t}Bu$_2$)$_2$[2] or Fe(NHAr*)$_2$[3] (Ar* = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$) display essentially free ion magnetic properties with unquenched orbital angular momentum (OAM). This behavior was explained on the basis of the orbital splitting pattern for the d^6, Fe^{2+} ion in a linear field, which is shown in Fig. 1. The OAM is associated with the degenerate $d_{x^2-y^2}$ and d_{xy} orbitals, which can be interconverted by a 45° rotation. An electron can move from one of these orbitals into its degenerate partner without change of spin.[4] Bending the geometry lifts the degeneracy (Δ_g in $D_{\infty h}$ $\rightarrow$ A_1 + A_2 in C_{2v}) and results in partial quenching of the OAM because the two orbitals are no longer interconvertible by a symmetry operation in the C_{2v} point group. Application of these considerations to other (high-spin) electron configurations predicts unquenched OAM only for d^1, d^3, and d^8 ions in linear fields. Of these, stable two-coordinate complexes are known for the d^8 configuration alone and just two nickel(II) complexes, Ni(SAr*)$_2$[5] and Ni(NHAr$'$)$_2$[6] (Ar$'$ = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$), have linear coordination. Their effective magnetic moment (μ_{eff}) values of 2.58 and 2.79 μ_B suggest little OAM, however. These unexpected results have led us to investigate other open-shell two-coordinate complexes that have essentially linear geometries in the solid state. These complexes are rare, and apart from the iron(II) d^6 and nickel(II) d^8 species mentioned above, and some d^5 complexes which can have no OAM, only Cr(SAr*)$_2$ (d^4)[5] and Co(SAr*)$_2$ (d^7)[5] have linear metal coordination in the crystalline phase.[5] For Cr(SAr*)$_2$, μ_{eff} = 4.93 μ_B, which is very close to the spin-only value and consistent with the predicted quenching of OAM. However, the 5.75 μ_B measured for the linear Co(SAr*)$_2$ is well in excess of the 3.87 μ_B spin-only or the spin and orbital angular momentum value of 5.2 μ_B of the ^4F ground state. In addition, the *quasi* two-coordinate species Ar$'$CoN(H)Ar$^\#$ (Ar$^\#$ = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Me$_3$)$_2$) had a μ_{eff} of 4.65 μ_B, indicating considerable OAM, although its coordination was bent (133.90(6)° in the high-spin S = 3/2 state).[7] These data prompted us to synthesize further examples of two-coordinate Co(II) complexes with linear, or near linear, coordination for magnetic study. We now describe the synthesis and characterization of the two-coordinate complexes CoAr$'_2$ (**1**) and Ar$'$CoN(SiMe$_3$)$_2$ (**2**). In particular, complex **2** is the first linearly coordinated heteroleptic Co(II) species and has an unexpectedly large effective magnetic moment.

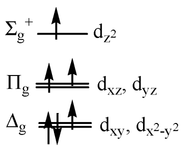
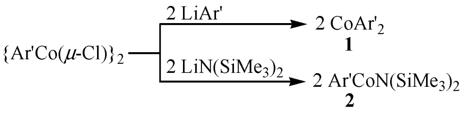


Fig. 1 Expected electron configuration for a d^6, Fe^{2+} ion in linear coordination.

Compounds **1** and **2** were prepared by simple metathesis of the cobalt(II) monoaryl chloride complex {Ar$'$Co(μ-Cl)}$_2$[8] with the corresponding lithium salt in hexanes at room temperature (Scheme 1) and isolated as air and moisture sensitive dark green (**1**) or orange (**2**) crystals in high yields (see ESI†). **1** and **2** are thermally stable and can be stored at room temperature under an inert atmosphere for several months. The UV-vis spectra of **1** and **2** are similar. They feature broad, strong absorptions in the ultraviolet region (**1** at 360 nm; **2** at 380 nm) and very broad, relatively weak absorptions in the visible region (**1** at 481 nm; **2** at 485 nm).

The structures of **1** and **2** were determined by X-ray crystallography. Complex **1** is the second example of a two-coordinate Co(II) diaryl. The only previously known species was CoAr$^\#_2$, which has the less crowded Ar$^\#$ ligands.[9] The structure (Fig. 2) has a crystallographically imposed mirror plane passing through the Co^{2+} ion with a C–Co–C angle of 159.34(8)°, which is slightly smaller than those in the two crystallographically independent molecules of CoAr$^\#_2$ (162.8(1) and 172.2(2)°),[6] but similar to those in the Mn(II) or Fe(II) diaryls: MMes*$_2$ (Mes* = C$_6$H$_2$-2,4,6-^{t}Bu$_3$; M = Mn, 159.7(1)°; M = Fe, 157.9(2)°)[10,11] and MAr$'_2$ (M = Mn, 160.19(9)°; M = Fe, 159.34(6)°).[12,13]‡ It was proposed that the bent geometry in



Scheme 1 Preparation of **1** and **2**.

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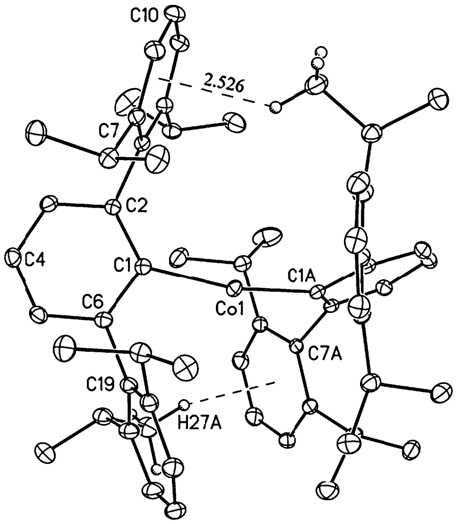

Fig. 2 Thermal ellipsoid (30%) plot of **1**. H atoms (except H atoms on C27 and C27A) are not shown. Selected bond lengths (Å) and angles (°): Co1–C1 2.014(2), Co1–C6 2.878(8), Co1–C19 3.055(6), H27A···cnt 2.526, C1–Co1–C1A 159.34(8), C2–C7–C10 169.19(6).

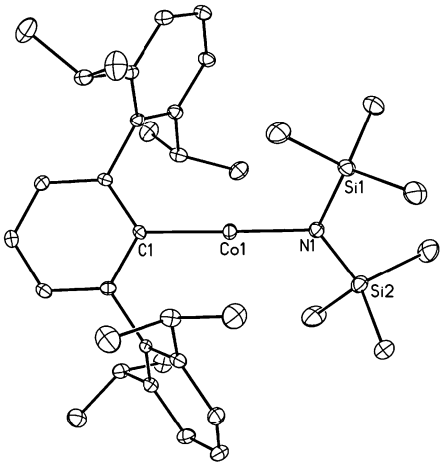

Fig. 3 Thermal ellipsoid (30%) plot of **2** without H atoms. Selected bond lengths (Å) and angles (°): Co1–C1 1.9732(16), Co1–N1 1.8747(14), N1–Si1 1.717(2), N1–Co1–C1 179.02(11).

CoAr$^{\#}_2$ was due to weak interactions between the Co^{2+} and the *ipso* carbons of the flanking C_6H_2-2,4,6-Me_3 rings (2.679(2) and 2.740(2) Å).[9] In **1**, however, the closest contact is 2.878 Å (Co···C(6)), so that the Co···C interactions, if they exist, are very weak. Instead, the bending may be due to packing forces and steric effects, which may also contribute to the strain apparent in the deviation of the C(1) atom from the plane of the central aryl ring (0.075(2) Å) and in the angle of *ca.* 17.4° between the Co–C(1) vector and the plane of the C(1) ring. The Co(1)–C(1) bond length (2.014(2) Å) is marginally longer than those in CoAr$^{\#}_2$ (ave. 2.001 Å)[9] and Ar′CoN(SiMe$_3$)$_2$ (**2**) (1.9732(16) Å, see below), probably as a result of the steric effects of the two large Ar′ ligands. Significantly, the C(7) aryl ring, instead of being drawn to the Co(II) ion *via* a metal–ligand secondary interaction, is bent away from the cobalt as indicated by the C(2)–C(7)–C(10) angle (*ca.* 169.2°). This may be a result of the intra-molecular interaction involving CH–π electron interactions between the methyl group of the isopropyl substituent and the C(7) aryl ring (H(27A)···centroid 2.53 Å). Such CH–π interactions may also contribute to the bent geometry at the cobalt(II). The existence of CH–π interactions is well-known and shows influence on the conformations of the structures.[14,15]

Complex **2** is the first two-coordinate heteroleptic linear cobalt(II) complex. The structure (Fig. 3) shows that the Co(II) ion is coordinated to an Ar′ ligand and an amido group and has an essentially linear geometry (C–Co–N = 179.02(11)°). As mentioned above, the only other linearly coordinated Co(II) species in the solid state is Co(SAr$^{\#}$)$_2$,[5] although Co{N(SiMe$_3$)$_2$}$_2$ has also been shown to be linear in the gas phase.[16] All other two-coordinate cobalt(II) complexes (see Table S1 in the ESI†), such as CoAr$^{\#}_2$,[9] Co{N(SiMePh$_2$)$_2$}$_2$,[17,18] Co{N(R)BMes$_2$}$_2$ (R = Ph or Mes, Mes = C_6H_2-2,4,6-Me_3),[19] and Ar′CoN(H)Ar$^{\#}$[7] display considerable bending in the solid state with apparent secondary cobalt–ligand approaches, which increase the effective coordination numbers.[20] In contrast, no such cobalt–ligand secondary interactions were observed in **2**. The Co(1)–C(1) distance (1.9732(16) Å) in **2** is somewhat shorter than that in CoAr$^{\#}_2$ (ave. 2.001(3) Å)[9] and is comparable to those in {Co(Mes)(μ-Mes)}$_2$ (Co–C(terminal) = 1.988(3) Å)[21] and Ar′CoN(H)Ar$^{\#}$ (1.992(2) Å).[7] The Co(1)–N(1) bond length (1.8747(14) Å) is slightly shorter than those in two-coordinate Co{N(SiMePh$_2$)$_2$}$_2$ (1.898(3) and 1.904(3) Å)[9] and Co{N(Ph)BMes$_2$}$_2$ (1.910(3) Å),[19] probably due to the presence of cobalt–ligand secondary interactions, which afforded higher effective coordination numbers in these complexes. The Si(1)–N(1)–Si(2) plane has a torsion angle of *ca.* 44.6° to the central aryl ring of the Ar′ ligand. In addition, the two flanking C_6H_3-2,6-$^iPr_2$ rings show torsion angles of *ca.* 69.4 and 71.1°, respectively, to the central aryl ring and adopt *quasi* parallel orientation to the Si(1)–N(1)–Si(2) plane.

Magnetic studies were also performed on **1** and **2**. For **1**, the effective magnetic moment of 4.38 μ_B obtained by the Evans' method[22,23] at 293.5 K is somewhat higher than the μ_{eff} of 3.81 μ_B observed in CoAr$^{\#}_2$.[9] In **2**, however, a μ_{eff} of 5.82 μ_B was obtained by the Evans' method at 293.5 K. More detailed variable temperature magnetic susceptibility measurements were carried out in order to confirm the unexpectedly large moment. Complex **2** exhibits Curie–Weiss behavior between 2 and 170 K (see the inset to Fig. 4) with a small Weiss temperature, Θ, of −1.9 K and a Curie constant, C, of 3.99 emu K mol^{-1}; the corresponding μ_{eff} is 5.65 μ_B, a value that is close to that obtained from the Evans' measurement. In the linear two-coordinate environment of the cobalt(II) ion in **2**, the expected orbital electronic configuration is $(d_{x^2-y^2},d_{xy})^4(d_{xz},d_{yz})^2(d_{z^2})^1$ (*cf.* Fig. 1), affording $S = 3/2$, in which there should be little if any first-order orbital contribution to the magnetic moment. Hence the observed $\chi_M T$ of **2** has been fit with the expressions,[24–28] given in the ESI†, for the zero-field splitting arising from higher order spin–orbit terms mixed into the electronic ground state. The fit obtained between 2 and 170 K[27] (see Fig. 4) yields g = 2.77(2), $|D|$ = 2.17(5) cm^{-1}, and $N\alpha$ = 0.00260(5) emu mol^{-1}, parameters that are reasonable for a linear cobalt(II) complex in the presence of a second-order orbital contribution to the moment that results from spin–orbit mixing of the electronic states; the rather larger than expected

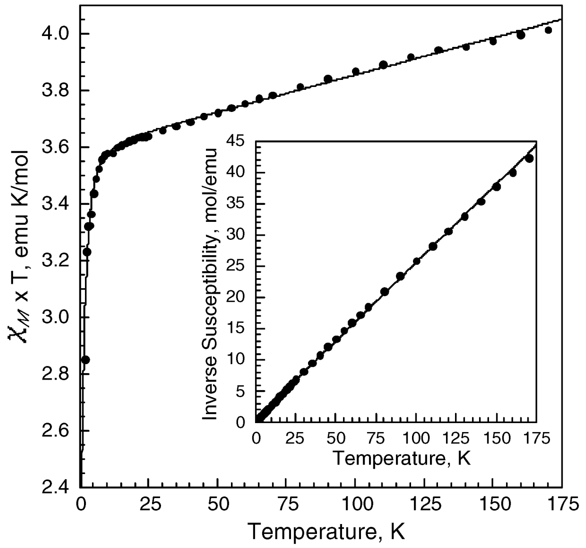

Fig. 4 The temperature dependence of $\chi_M T$ observed for **2** between 2 and 170 K. The solid line corresponds to a fit with $S = 3/2$, $g = 2.77(2)$, $|D| = 2.17(5)$ cm^{-1}, and $N\alpha = 0.00260(5)$ emu mol^{-1}, where $|D|$ is the magnitude of the zero-field splitting and $N\alpha$ is the second-order Zeeman contribution to the magnetic susceptibility. Inset: the temperature dependence of $1/\chi_M$ of **2** and its Curie–Weiss law linear fit.

g and μ_{eff} values indicate the importance of this mixing in a linear cobalt(II) complex.

The CW EPR spectrum of **2** (Fig. S1, ESI†) 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 by using EasySpin 3.1,[28] and assuming an $S = 3/2$ and a g-matrix = [3.2, 2.6, 2.0], $A(^{59}\text{Co})$ = [100 850 200] MHz, zero-field splitting parameters $D = 2.45$ cm^{-1} and $E = 0.27$ cm^{-1}, and a line width of 12 mT. Both the axial zero-field splittings and the average g-value were fixed to those values determined from the $\chi_M T$ measurements discussed above. The magnitude of the rhombic component, E, of the zero-field splitting and the ^{59}Co hyperfine tensor were then optimized to achieve the best fit.

In summary, neither of the two-coordinate d^7, Co^{2+} complexes **1** or **2** display metal–ligand secondary interactions in their structures because of the steric crowding of the bulky ligands.[5,7,9,17,19] This may be related to the fact that **1** and especially the almost linearly coordinated **2** display larger than expected effective magnetic moments. The origin of these moments is not well understood at present and suggests that a systematic study of the magnetic behavior of a wider range of linearly coordinated complexes is warranted.

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Notes and references

‡ Crystal data for **1** and **2** at $T = 90(2)$ K with MoKα ($\lambda = 0.71073$ Å) radiation. **1**: $C_{60}H_{74}Co$, $F_w = 854.12$, monoclinic, space group $C2/c$, dark green plate, $a = 15.6649(6)$ Å, $b = 15.9068(6)$ Å, $c = 19.7416(8)$ Å, $\beta = 93.6750(10)°$, $V = 4909.1(3)$ Å^3, $Z = 4$, 18 454 total reflections, 5641 unique, $R_{\text{int}} = 0.0160$, $R_1 = 0.0408$ ($I > 2\sigma(I)$ data), wR_2 = 0.1099 for all data, CCDC 762898. **2**: $C_{36}H_{55}CoNSi_2$, $F_w = 616.92$, orthorhombic, space group $Pca2_1$, orange block, $a = 18.2549(10)$ Å, $b = 10.8473(6)$ Å, $c = 18.5964(10)$ Å, $V = 3682.4(3)$ Å^3, $Z = 4$, 30 329 total reflections, 8440 unique, $R_{\text{int}} = 0.0298$, $R_1 = 0.0308$ ($I > 2\sigma(I)$ data), wR_2 = 0.0830 for all data, CCDC 762897. The possibility of *Pbcn* space group was checked and abandoned.†

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