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Fluorinated phenolates in monomeric and dimeric Co(II) compounds

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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ABSTRACT

Five structures of two monometallic cobalt aryloxide compounds and two bimetallic cobalt-thallium compounds with bridging fluorinated aryloxide ligands $(OC_6F_5 = OAr^F, OC_6H_3(CF_3)_2 = OAr')$ are presented with magnetic susceptibility and spectroscopic characterization data. The monometallic compounds, $[Co(OAr^F)_2(DME)]_2$, **1**, and $[Co(OAr')_2(DME)]_2$, **2**, are prepared by metathesis reactions between two equivalents of TlOAr and one of Col₂. The heterobimetallic compounds $[Tl_2Co(OAr^F)_4]$ -2 toluene, **3a**, and $[Tl_2Co(OAr')_4]_2$ -2 toluene, **4**, were prepared with a 4:1 ratio of the thallium aryloxide to Col₂. An unsolvated form of $[Tl_2Co(OAr^F)_4]$, **3b**, was also structurally characterized. Magnetic susceptibility studies revealed that **3b** is a simple, isolated high-spin Co^{II} with Curie–Weiss behavior. Dimeric compounds **1** and **2** are also high-spin Co^{II} but exhibit antiferromagnetic coupling, via superexchange through two μ_2 -OAr^F ligands, as supported by DFT calculations. Compound **4** exhibits ferromagnetic behavior which is ascribed to the presence of μ_3 -OAr ligands, instead of μ_2 -OAr groups.

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1. Introduction

Our laboratory has been investigating homoleptic and heteroleptic transition metal complexes of highly perfluorinated aryloxide [1-4] and alkoxide [2,5] ligands including pentafluorophenoxide $(OC_6F_5 = OAr^F)$ and bis-3,5-trifluoromethylphenoxide $(OC_6H_3(CF_3)_2 = OAr')$. We are interested in effects of extensive fluorination on the reactivity of the phenoxide oxygen atom, how the types of compounds formed with these fluorinated ligands differ from their protio analogs, and how these ligand differences affect reactivity of the transition metal complexes. Spectroscopic studies [2] have shown that these fluorinated oxygen donor ligands act as medium field ligands similar to F⁻ or OH⁻ and are therefore compatible with high oxidation state transition metals. We have previously reported the synthesis of homoleptic anions of the form [M(OAr)₄]²⁻ for Fe(II) [4], Co(II) [1], Ni(II) [2], and Cu(II) [1,3]. In each case we have prepared the heterobimetallic thallium derivatives [Tl₂M(OAr)₄] because of the subsequent ease of metathesis of the thallium cation for less-coordinating cations. We now report the structural, electronic, and magnetic characterization of the [Tl₂Co(OAr)₄] compounds, whose preliminary characterization has been reported [1]. As is often the case with cobalt, the connectivity and electronic structure were observed to be different than other late metals and more varied. For the first time, we have

observed differences in coordination number at the transition metal as a function of the aryloxide ligand.

Structural studies [2] for the Ni(II) compound $[Tl_2Ni(OAr^F)_4]$ indicated a monomeric pseudo-tetrahedral S = 1 species with TI atoms bridging two edges of the tetrahedron, as shown in Scheme 1. In contrast, the $[Tl_2Cu(OAr)_4]$ complexes [3] with both OAr^F and OAr' exhibited extended structures in which approximately square planar Cu(II) centers were bridged to one another through two thallium centers forming $\{Tl_2O_4\}$ octahedra as also shown in Scheme 1. Solution susceptibility studies suggested that these extended structures did not persist in solution.

Herein we report the solid state structures of the $[Tl_2Co(OAr)_4]$ compounds for both the OAr^F and OAr' ligands, including unsolvated and toluene solvate forms of the former. We have also prepared two neutral $\{(DME)Co(OAr)_2\}$ synthons for potential use in preparing other heterobimetallic complexes.

2. Experimental

2.1. General conditions

All studies were carried out at room temperature on a Schlenk line or in a nitrogen-filled glovebox. Bulk solvents (hexanes, CH₂Cl₂, THF, and toluene) were dried in a nitrogen-filled MBraun SPS (solvent purification system) using Al₂O₃, and CD₂Cl₂ was distilled from CaH₂. Celite was dried overnight *in vacuo* while



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Scheme 1. Previously observed [Tl₂M(OAr^F)₄] structural motifs.

heated to 125 °C with an oil bath. All other reagents were obtained commercially and were not purified further. NMR spectra were measured on a Varian 300 MHz spectrometer. ¹H chemical shifts were referenced to (CH₃)₄Si via the resonance of residual protiosolvent and ¹⁹F shifts were referenced to internal CFCl₃. UV–Vis data were collected utilizing a Shimadzu 3600 UV-Vis-NIR spectrophotometer. Solution phase magnetic susceptibilities were determined by Evans' method [6,7] in d₆-acetone, CD₃CN, or CD₂Cl₂ with 10% (Me₃Si)₂O and the same solution as internal reference and are reported after correction using appropriate diamagnetic terms [8,9]. SQUID data were collected with a Quantum Design MPMS SQUID susceptometer by loading powdered samples into gel capsules placed in plastic straws, and the resulting susceptibilities were corrected for diamagnetic contributions [10]. Microanalyses were performed by Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, BRD.

2.2. Electronic structure calculations

A C_2 -symmetrized version of compound **1** was calculated using the Amsterdam Density Functional package [11], with TZ2P basis sets for all atoms, using all electrons, and a spin-unrestricted system with six unpaired electrons. A comparison of the calculated distances and angles with the single-crystal X-ray diffraction data are presented in Table S1.

Table 1Summary of X-ray crystallographic data.

2.3. X-ray diffraction data

Crystallographic data are collected in Table 1. Data were collected on APEX-CCD-detector equipped Bruker diffractometers, and were corrected for absorption using semi-empirical, multiscan methods. All structures were solved by heavy-atom methods and the remaining non-hydrogen atoms were located from subsequent difference maps. All structures were refined with anisotropic thermal parameters for all non-hydrogen atoms; hydrogen atoms were treated as idealized contributions. All software is contained in various libraries (SHELXTL, SMART and SAINT) maintained by Bruker AXS, Madison, WI.

2.4. Synthetic procedures

2.4.1. $\{Co(OAr^F)_2(DME)\}_2$, 1

A portion of TIOAr^F (4.476 g, 11.55 mmol) dissolved in 4 mL THF was added to one half equiv Col₂ (1.806 g, 5.777 mmol) in 50 mL THF forming a dark purple solution with yellow (presumed TII precipitate. After stirring overnight, the reaction mixture was filtered through Celite, removing the yellow precipitate, and the product was concentrated to dryness. The product was recrystallized from a 2:1 ratio of DME:THF and hexanes affording X-ray quality blockhabit purple crystals in 17.6% yield (after three recrystallizations). UV–Vis (THF) (λ_{max} , nm (ε_{M} , M⁻¹ cm⁻¹)):513 (120) 551 (142) 580 (141) 594 (138). μ_{eff} (Evans' method) = 6.39 µB. Anal. Calc. for C₃₂H₂₀O₈F₂₀Co₂: C, 37.30; H, 1.96; F, 36.88. Found: C, 37.16; H, 1.91; F, 37.05%.

2.4.2. {Co(OAr')2(DME)}2, 2

A portion of TlOAr' (0.218 g, 0.504 mmol) dissolved in 4 mL DME was added to one half equiv CoI₂ (0.0787 g, 0.252 mmol) in 6 mL THF forming a dark blue-green solution with yellow (presumed TII precipitate). After stirring overnight, the reaction mixture was filtered through Celite, removing the yellow precipitate, and the product was concentrated to dryness. The product was recrystallized from DME and hexanes affording X-ray quality block-habit purple crystals in 50% yield after three recrystallizations. UV–Vis (CH₂CL₂) (λ_{max} , nm (ε_{M} , M⁻¹ cm⁻¹)) 493 (236) 587 (255) 660 (186). μ_{eff} (Evans' method) = 5.26 μ_{B} . Anal. Calc. for

	1	3a	3b	4
Formula	C32H20C02F20O8	C ₇₆ H ₃₂ Co ₂ F ₄₀ O ₈ Tl ₄	C ₂₄ CoF ₂₀ O ₄ Tl ₂	C39H20C0F24O4Tl2
Formula weight	1030.34	2768.36	1199.91	1476.22
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	C2/c	ΡĪ	C2/c	ΡĪ
a (Å)	11.7321(5)	11.7969(15)	6.5075(5)	11.835(4)
b (Å)	17.9147(8)	13.9222(17)	26.410(2)	13.059(4)
<i>c</i> (Å)	17.9686(9)	25.231(3)	15.7928(12)	15.915(5)
α (°)	_	96.740(2)	_	100.657(6)
β (°)	105.746(2)	102.643(2)	90.6020(10)	96.325(6)
γ (°)	-	96.954(3)	-	113.222(5)
$V(Å^3)$	3634.9(3)	3969.1(9)	2714.1(4)	2175.3(12)
Ζ	4	2	4	2
$ ho$ (calc), (g cm $^{-3}$)	1.883	2.316	2.937	2.254
μ (Mo Ka), (mm $^{-1}$)	1.066	8.648	12.622	7.910
T (K)	100(2)	218(2)	100(2)	150(2)
$R(F)(\%)^{a}$	0.0345	0.0549	0.0416	0.0657
$R(wF^2)(\%)^{b}$	0.0706	0.0930	0.1048	0.1354
Collected	24829	26265	8276	10728
Unique	3744	15513	3082	7513
R _{int}	0.0321	0.0335	0.0408	0.0427
Observed	3250	11930	2852	5960

^a $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

^b $R(\omega F^2) = \{ \sum [\omega (F_o^2 - F_c^2)^2] / \sum [\omega (F_o^2)^2] \}^{1/2}; \ \omega = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP], \ P = [2F_c^2 + max(F_o, 0)] / 3.$

 $C_{40}H_{32}O_8F_{24}Co_2;$ C, 39.56; H, 2.66; F, 37.54. Found: C, 39.71; H, 2.62; F, 37.33%.

2.4.3. [Tl₂Co(OC₆F₅)₄], 3b

In the dry box four equivalents of Tl $(OC_6F_5)_4$ (1.29 g, 3.33 mmol) were dissolved in THF and one equivalent of Col₂ (0.261 g, 0.833 mmol) was added while the solution was stirring. A dark deep blue colored solution with yellow precipitate was formed. After the solution was stirred overnight, it was filtered through Celite and the solvent was removed in vacuo. A dark purple solid remained, which was triturated three times with 2 mL of hexane. The product was dissolved in a minimum amount of toluene, filtered and layered with hexane for recrystallization. The recrystallization was left in the refrigerator and after one day the solvents were pumped off. The product was filtered leaving a purple colored solid with a 73% yield. ¹H NMR $(\delta, \text{ppm}, C_6H_5Br)$: 2.64 (s, 3H, $C_6H_5-CH_3$), 7.79 (b, 5H, $C_6H_5-CH_3$) ¹³C NMR (δ , ppm, C₆H₅Br): 22.15(s, C₆H₅-CH₃), 139.76 (ipso, C₆H₅-CH₃), 129.87 (ortho, C₆H₅-CH₃), 130.70 (meta, C₆H₅-CH₃), 126. 94 (para, C_6H_5 -CH₃) ¹⁹F NMR (δ , ppm, C_6H_5Br): -162.64 (s, OC_6F_5). UV–Vis (toluene) [λ_{max} , nm (ε_{M} , M^{-1} cm⁻¹)]: 584.9 (530), 511 (320), 530 (350) UV–Vis (THF) $[\lambda_{max}, nm (\varepsilon_{M}, M^{-1} cm^{-1})]$: 533 (230), 586 (340).

2.4.4. [Tl₂Co(OC₈F₆H₃)₄·toluene]₂, **4**

In the drv box four equivalents of $Tl(OC_8F_6H_3)_4$ (3.76 g. 8.68 mmol) were dissolved in THF and one equivalent of Col2 (0.679 g, 2.17 mmol) was added while the solution was stirring. A dark blue colored solution with yellow precipitate was formed. After the solution was stirred overnight, it was filtered through Celite and the solvent was removed in vacuo. The dark blue solid was triturated three times with 2 mL of hexane. The product was dissolved in a minimum amount of toluene, filtered and layered with hexane for recrystallization. The recrystallization was left in the refrigerator and after one day the solvents were pumped off. The product was filtered leaving a purple colored crystalline solid with a 52% yield. Crystals were suitable for X-ray crystallography. ¹H NMR (δ, ppm, CD₂Cl₂): 2.64 (s, 3H, C₆H₅-CH₃), 7.79 (br, 5H, C₆H₅-CH₃) ¹³C NMR (δ, ppm, CD₂Cl₂): 22.15(s, C₆H₅-CH₃), 139.76 (ipso, C₆H₅-CH₃), 129.87 (ortho, C₆H₅-CH₃), 130.70 (meta, C₆H₅-CH₃), 126. 94 (para, C₆H₅-CH₃) ¹⁹F NMR (δ, ppm, CD₂Cl₂): -73.74 (S, CF₃). UV–Vis (toluene) $[\lambda_{max}, nm (\epsilon_{M}, M^{-1} cm^{-1})]$: 547 (300), 598 (430) UV–Vis (THF) [λ_{max} , nm (ϵ_{M} , M⁻¹ cm⁻¹)]: 479 (110), 482 (110), 522 (200), 544 (230), 599 (300). Anal. Calc. for C35.5H16 O₄F₂₄CoTl₂: C, 29.81; H, 1.13; F, 31.88. Found: C, 30.28; H, 1.61; F, 29.34%. The lack of agreement in the F analysis is likely due to poor combustion, not uncommon in highly fluorinated species.

3. Results and discussion

3.1. Synthesis and electronic spectra

Preparation of $[Co_2(OAr^F)_4(DME)_2]$, **1**, and $[Co_2(OAr')_4(DME)_2]$, **2**, proceeds readily via metathesis of Col_2 with two equivalents of the appropriate TlOAr in THF/DME solution. The synthesis and some spectroscopic characterization of the $[Tl_2Co(OAr)_4]$ compounds **3b** and **4** have been reported previously [1], as was the same information for {K(18-crown-6)}_2[Co_2(OPh)_6] [1]. Compounds **1**, **3**, and **4** are presented in Scheme 2 with composition and connectivity. Compound **2** is proposed to be very similar to **1**, based on similarity of all other characterization data. All compounds appear purple in the solid state and in solution. The electronic spectra in the visible region have several absorbances between ~480–600 nm with extinction coefficients less than 1000, consistent with weak LMCT (O 2*p* to Co 3*d*) or *d*-*d* transitions for low-symmetry, high spin Co^{II} centers.

3.2. Structural

Crystallographic data collection parameters are presented in Table 1. The dimeric $[(DME)(Ar^FO)Co(\mu_2-OAr^F)_2Co(OAr^F)(DME)]$, **1**, consists of two highly distorted trigonal bipyramidal centers as shown in Fig. 1, with important distances and angles collected in Table 2. The two cobalt atoms are 3.1392(3) Å apart (Co–Co in cobalt metal = 2.50 Å [13]) and related by a twofold axis running along the O(2)–O(3) vector, through the two μ_2 -bridging aryloxides. The axis of the trigonal bipyramid is the O(3)–Co(1)–O(4) vector (corresponding angle is 167.55(5)°) and the equatorial plane corresponds to that containing the O(1), O(2), and O(5) atoms in which the O–Co–O angles are 110.40(4)°, 111.82(5)°, and 136.86(4)°. The two largest O–Co–O angles around cobalt give a τ_5 value of 0.53, calculated as shown in Equation 1, where α and β are the largest and second largest O–M–O angles respectively. An ideal square pyramid has a τ value

$$\tau_5 = \frac{|\alpha - \beta|}{60^{\circ}}$$

of zero [14] and a trigonal bipyramid has a τ_5 value of 1.0. The angles (°) at the bridging oxygen atoms are 99.39(7) (Co(1)–O(2)–Co(1_2)) and 104.46(7) (Co(1)–O(3)–Co(1_2)). The terminal Co–O bond length of 1.9267(12) Å is slightly shorter than those previously reported (1.937(2) and 1.962(2) Å) for the OAr^F ligand with Co [1]. No Co- μ_2 -OAr^F linkages have been structurally characterized previously but the longer Co–O(3) and Co–O(2) distances of 2.0582(10) and 1.9857(10) Å, respectively, are reasonable compared to the terminal linkage. Only five other Co(DME) adducts,



Scheme 2. Co(II) fluorinated aryloxide compounds.



Fig. 1. ORTEP diagram of $[Co(OAr^F)_2(DME)]_2$, **1.** Hydrogen atoms and DME methyl groups have been omitted for clarity. Ellipsoids are shown at the 50% probability level.

all octahedral with chelating DME, have been crystallographically characterized with Co–O distances (Å) of 2.120(6) and 2.140(7) [15] in [Co(DME)(hfac)_2] (RADJIQ; hfac = hexafluoroacetylacetonate), distances 2.141(8) and 2.179(8) [16], in [Co(DME) {(^tBuCO)_2As}_2] (ECUGIS), distances 2.10(1) and 2.08(1) [17], in [Co₃(µ₃-Cl)(µ₃-SO₄)(O₂CCF₃)₃] (EFASCO) distances 2.127(7) and 2.210(6) [18], in [Co(DME)₂(κ^2 -CoCl₄)] (ENOQII), and an average of 2.105(8) [17] in [Co(DME)₂(κ^2 -CoCl₄)] (ENOQO) respectively. The Co–O(5) distance (Å) in **1** is slightly longer at 2.0346(12) and the Co–O(4) noticeably longer at 2.2073(12). This very long contact to DME suggests that **1** may be considered a four-coordinate complex with very weak interaction with the second DME oxygen atom.

The heterobimetallic $[Tl_2Co(OAr^F)_4]$ was crystallized in a solvated form with two equivalents of toluene per cobalt center, 3a, and in an unsolvated form, 3b. The solvated form 3a is very similar to the previously characterized [Tl₂Ni(OAr^F)₄]·2 toluene. This solvate, $[Tl_2Co(OAr^F)_4]$ 2 toluene, **3a**, also exhibits close contacts in the solid state between thallium and oxygen atoms and is depicted in Fig. 2. In this case, two complementary contacts effectively dimerize the compound in the solid state, and the toluene molecules surround the dimer via M-to- π -arene interactions to Tl(1) and Tl(4), with Tl \cdots C distances averaging 3.48(6) Å, as shown in Fig. S1. Only two of the four thallium atoms participate in the dimerization, namely Tl(2) and Tl(3). Whereas the intramolecular Tl-O bonds have similar lengths to those in ${\bf 3b}$ and average 2.64(5) Å, the dotted contacts in **3a** are noticeably longer at 3.005(5) and 3.223(5) Å. The other two thallium atoms, Tl(1) and Tl(4) each bond to two toluene molecules as shown in the Supplementary material, Fig. S1.

The unsolvated form **3b** exhibits distinctly different packing such that the Tl centers do not bind to any of the arene rings directly. On the left side of Fig. 3 only the intramolecular contacts are shown in which the pseudo-tetrahedral cobalt center is clearly seen. The τ_4 values of 0.69 and 0.67 are observed in the two crystallographically independent Co centers, based on the

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Selected interatomic distances, bond lengths and angles.^a

Compound	Distances	(Å)	Angles	(°)
1	Co(1)-O(1)	1.9267(12)	O(1)-Co(1)-O(2)	135.86(4)
	$C_0(1) = O(2)$	1.9857(10)	O(1) = Co(1) = O(3) O(1) = Co(1) = O(4)	101.58(5)
	Co(1) - O(4)	2.2073(12)	O(3)-Co(1)-O(4)	167.55(5)
	Co(1)-O(5)	2.0346(12)	O(1)-Co(1)-O(5)	111.82(5)
	O(1) - C(1)	1.315(2)	O(2)-Co(1)-O(5)	110.40(4)
	O(2) - C(7)	1.339(3)	O(3)-Co(1)-O(2)	78.08(5)
	O(3) - C(11)	1.337(3)	O(3)-Co(1)-O(5)	106.42(4)
			O(4) = CO(1) = O(2) O(4) = Co(1) = O(5)	89.04(5) 75.82(5)
			$C_0(1) = O(2) = C_0(1/2)$	104.46(7)
			Co(1_2)-O(3)-Co(1)	99.39(7)
			C(1)-O(1)-Co(1)	127.27(12)
			C(7)-O(2)-Co(1)	127.77(4)
30	$T_{1}(1) = O(1)$	2 6754)	C(11) = O(3) = CO(1) O(1) = TI(1) = O(4)	130.31(3) 63 35(11)
Ja	TI(1) = O(1) TI(1) = O(4)	2.614(4)	O(2) - T(2) - O(3)	65.16(12)
	Tl(2)-O(2)	2.548(4)	O(5)-Tl(4)-O(8)	63.33(12)
	Tl(2)-O(3)	2.656(4)	O(7)-Tl(3)-O(6)	63.89(12)
	Tl(3)–O(6)	2.717(4)	O(1)-Co(1)-O(2)	111.94(16)
	TI(3) = O(7)	2.611(4)	O(1) - Co(1) - O(3) O(1) - Co(1) - O(4)	131.16(19)
	TI(4) = O(3)	2.031(4) 2.650(4)	O(2) = CO(1) = O(3)	91 46(16)
	Co(1) - O(1)	1.949(4)	O(2)-Co(1)-O(4)	131.78(19)
	Co(1)-O(2)	1.936(4)	O(3)-Co(1)-O(4)	104.37(15)
	Co(1)-O(3)	1.980(4)	O(5)-Co(2)-O(7)	136.7(2)
	Co(1)-O(4)	1.953(4)	O(5)-Co(2)-O(8)	90.96(17)
	$C_0(2) = O(5)$	1.949(4) 1 971(4)	O(7) = CO(2) = O(8) O(5) = Co(2) = O(6)	108.18(17) 105.62(16)
	$C_0(2) = O(0)$	1.950(4)	O(6)-Co(2)-O(7)	92.00(17)
	Co(2)-O(8)	1.940(4)	O(6)-Co(2)-O(8)	129.2(2)
			Co(1)-O(1)-Tl(1)	101.65(15)
			Co(1)-O(1)-C(1)	126.8(4)
			C(1) = O(1) = TI(1) C(7) = O(2) = Co(1)	127.6(4) 127.2(4)
			C(7) = O(2) = CO(1) C(7) = O(2) = TI(2)	127.3(4) 129.3(3)
			Co(1)-O(2)-Tl(2)	103.24(16)
			C(13)-O(3)-Co(1)	118.3(3)
3b	Tl(1)-	2.628(4)	O(1_2)-Tl(1)-	65.47(11)
	$O(1_2)$	2(72(4))	$O(2_2)$	117 0(2)
	$O(2 \ 2)$	2.072(4)	$O(1) = O(1) = O(1_2)$	117.0(2)
	Co(1)-O(1)	1.941(4)	O(1)-Co(1)-O(2_2)	123.90(16)
	Co(1)-O(2)	1.977(4)	O(1)-Co(1)-O(2)	94.05(15)
	O(1) - C(1)	1.321(7)	$O(2_2)-Co(1)-O(2)$	105.1(2)
	0(2)-C7	1.329(7)	C(1) - O(1) - CO(1) C(1) - O(1) - TI(1, 2)	126.5(3) 120.0(2)
			$C(1) = O(1) = \Pi(1_2)$ $C_0(1) = O(1) = \Pi(1_2)$	129.9(3) 101 14(15)
			C(7)-O(2)-Co(1)	120.4(3)
			$C(7)-O(2)-Tl(1_2)$	128.1(3)
		0 = (0(0)	$Co(1)-O(2)-Tl(1_2)$	98.70(15)
4	TI(1) = O(1)	2.548(6)	O(1) - TI(1) - O(2) O(1) - TI(1) - O(4)	65.97(17)
	TI(1)=O(2) TI(1)=O(4)	2.645(5)	$O(1) - \Pi(1) - O(4)$ $O(2) - \Pi(1) - O(4)$	63 24(16)
	Tl(2) - O(3)	2.502(6)	O(1)-Co(1)-O(2)	89.8(2)
	Co(1)-O(1)	1.988(6)	O(1)-Co(1)-O(2B)	84.7(2)
	Co(1)-O(2)	2.017(5)	O(1)-Co(1)-O(3)	98.1(2)
	Co(1)-O(3)	2.017(6)	O(2)-Co(1)-O(2B)	80.7(2)
	$C_0(1) = O(2B)$	2.244(5) 1.977(6)	U(2) = U(1) = U(3) U(3) = Co(1) = U(2B)	101.7(2) 176.3(2)
	CO(1)-O(4D)	1.377(0)	O(4B) - Co(1) - O(2B)	148.0(3)
			O(4B)-Co(1)-O(2)	115.8(2)
			O(4B)-Co(1)-O(3)	95.2(2)

^a Numbers in parentheses are estimated deviations of the last significant figure.

$$\tau_4 = \frac{360^\circ - |\alpha + \beta|}{141^\circ}$$

quantification described [19] for four-coordinate complexes. The average unbridged O–Co–O angle is $116(10)^{\circ}$ and the unique angle bridged by thallium is much narrower at $94.05(15)^{\circ}$. The thallium atom bridges on two edges of the tetrahedron have an average Tl–O distance of 2.65(3) Å. The aryloxide ligands each in turn bridge



Fig. 2. ORTEP diagram of [Tl₂Co(OAr^F)₄]-2 toluene, **3a**. Thallium oxygen contacts (Å) shown with dotted lines are Tl(2)···O(6) 3.005(5) and Tl(3)···O(3) 3.223(5). Toluene molecules are removed for clarity. Ellipsoids are shown at the 50% probability level.



Fig. 3. ORTEP diagrams of $[Tl_2Co(OAr^F)_4]$, **3b.** One neutral unit is shown on the right. Intermolecular close contacts are shown on the left in which thallium-heteroatom distances (Å) shown with dotted lines are $Tl(1) \cdots O(2C)$ 3.179(3), $Tl(1) \cdots F(1A)$ 3.352(3), $Tl(1) \cdots F(4AA)$ 3.071(3), $Tl(1) \cdots F(6C)$ 3.388(3), and $Tl(1) \cdots F(7B)$ 3.461(4). Ellipsoids are shown at the 50% probability level.

thallium and cobalt centers but the average Co–O distance of 1.96(2) Å is shorter than the terminal Co–O distance in five-coordinate **1**. There are also intermolecular contacts in **3b** between the thallium atoms and adjacent oxygen and fluorine atoms, depicted on the right side of Fig. 3. These contacts are the only ones present at less than 4 Å but are still clearly long and do not survive in solution, as indicated by solution magnetic susceptibility data [1].

In contrast, the bis-3,5-trifluoromethylphenoxide derivative **4**, {{Tl₂Co(OAr')₄}₂}·2 toluene crystallizes as a bridged dimer with two μ_2 -OAr' ligands, as shown in Fig. 4. The two cobalt atoms are 3.251(2) Å apart and related by an inversion center. The τ_5 value for this cobalt center is 0.47 which is marginally closer to a square

pyramidal geometry than trigonal bipyramidal, but again highly distorted as in **1**. The largest angle at Co(1) is that spanning O(3)–Co(1)–O(2B) and is 176.3(2)°. Three distinct Tl-arene interactions are present. The Tl(1) center binds to three carbons of the aryl group from O(3) with an average distance (Å) of 3.67(8), while the other sp^2 hybridized carbons are all at least 3.91 Å away. The Tl(2) atom bonds η^6 to both a toluene molecule (average 3.25(9) Å) and η^6 to the aryl group connected to O(4) (average 3.36(5) Å). Unlike in **1**, which has one terminal and one bridging aryloxide per Co atom, all aryloxides in **4** are bridging between Tl and Co. The two aryloxides that bridge the two Co are μ_3 due to their interaction with Tl(1) as shown in Fig. 4. The two clearly distinct structures



Fig. 4. ORTEP diagram of [Tl₂Co(OAr')₄]-2 toluene, **4.** Thallium-arene contacts (Å) are shown with dotted lines. Fluorine atoms are removed for clarity. Ellipsoids are shown at the 50% probability level.

in **3** and **4** mark the first time that we have seen any substantial structural difference in metal fluorinated phenolate compounds that differ only in the aryloxide unit, OC_6F_5 versus $OC_6H_3(CF_3)_2$.

3.3. Magnetism

Variable temperature susceptibility studies carried out with a SQUID susceptometer demonstrate that compound **3b** behaves as a simple Curie–Weiss magnet, as shown in Fig. S2, in the Supplementary information. The data were fit to Eq. (2) giving a Curie constant, C, of 2.52 K-cm³/mol and a Weiss constant, Θ , of -2.12 K, indicating slight intermolecular antiferromagnetic coupling.

$$\chi = \frac{C}{T - \Theta} \tag{2}$$

The room temperature moments for both the solid state (μ_{eff} = 4.49 μ_B) and the solution (μ_{eff} = 4.46 μ_B ; Evans' method [1]) are in good agreement with one another. The individual Co centers are effectively isolated from each other, and the susceptibility is normal for a high-spin, tetrahedral center [12].

Fig. 5. Variable temperature magnetic susceptibility data for [Co(DME)(OAr^F)₂]₂, 1.

Fig. 6. Molecular orbital representation of 121B- α from C2-symmetrized [Co(DME)(OAr^F)2]2, C2-1.

Analogous studies shown in Fig. 5 on the dimeric compound **1** also revealed Curie–Weiss behavior with good agreement between room temperature solid (6.31 μ_B) and solution (6.39 μ_B) μ_{eff} values. In this compound, however, the two cobalt centers are clearly bridged and the magnitude of susceptibility indicates intramolecular antiferromagnetic coupling of the two cobalt centers via the bridging aryloxide ligands in the {Co₂(μ_2 -OAr^F)₂} core. Numerous dimeric Co^{II}₂(μ_2 -X)₂ compounds have been reported in the literature, and many of these with some degree of magnetic characterization [20,21]. Among those antiferromagnetic behavior is often seen, though systems with complete variable-temperature studies and detailed fitting of the data are quite rare, perhaps due to the challenges associated with an accurate description of Co^{II} magnetism.

All-electron DFT calculations were carried out an a C_2 -symmetric version of **1** (C_2 -**1**), with six-unpaired electrons Fig. 6 shows an occupied orbital in which Co *d*-orbitals from both Co atoms have in-phase overlap with a *p*-orbital from the bridging aryloxide. Other occupied orbitals also exhibiting both Co and bridging aryloxide oxygen contributions are shown in Fig. 7. Attempts to calculate electronic structures for different, lower spin states of C_2 -**1** were unsuccessful, and did not lead to aufbau solutions. Rotation of the μ_2 -OAr^F ligands about their O- C_{ipso} axes was noticed in geometry optimization attempts, however, suggesting that the angle of the phenoxide plane with respect to the { Co_2O_2 } core plays a role in the magnitude of antiferromagnetic coupling.

The ferromagnetic or antiferromagnetic coupling character between two Cu centers is well-known to depend on the Cu–O–Cu angle [22]. More acute angles are associated with ferromagnetic coupling, whereas more obtuse angles correlate with antiferromagnetic coupling, as detailed in a variety of {Cu₂(μ_2 -OH})-containing compounds [22]. A more recent study with Cu(II) alkoxide complexes reiterated the role of the Cu–O–Cu angle (θ) while also noting the importance of the angle of the alkoxide carbon atom to the Cu–O–Cu plane (τ) [23]. In aryloxide compounds,

Fig. 7. Molecular orbital representations of (left to right) 102B- α , 120B- β , and 122B- α from C₂-symmetrized [Co(DME)(OAr^F)₂]₂, C₂-1.

Fig. 8. Variable temperature magnetic susceptibility data for $[Tl_2Co(OAr')_4]\mbox{-}2$ toluene, 4.

the angle of the *ipso* carbon to the M–O–M plane can vary as well as the angle of rotation about the O–C_{*ipso*} bond. The 121B- β representation in the center of Fig. 7 clear shows the overlap of the Co 3*d*, O 2*p*, and the aryl π^* orbitals. The relationship between this angle of rotation to the type and degree of coupling will be of interest as more magnetically characterized examples of non-chelating aryloxide ligands in {M₂(μ_2 -OAr)₂} moieties are reported.

In contrast, the variable temperature magnetic behavior of compound **4**, $[Tl_2Co(OAr')_4]_2$, clearly shows a different room temperature solid-state susceptibility, 8.53 μ_B , versus the solution value of 6.06 μ_B , and increased ferromagnetic behavior with decreasing temperature, as shown in Fig. 8. The geometry of the bridging aryloxides is different from those in **1** in two ways that may account for the lack of antiferromagnetic coupling. First, the μ_3 -Tl atoms bond to the remaining oxygen lone-pair from the μ_3 -OAr' ligands, as shown in Fig. 4, and the angle between the aryloxide ring and the best {Co₂O₂} plane is decreased from 72.9° in **1** to 65.2° in **4**. The former effect would seem more likely responsible for the lack of antiferromagnetism, but why the difference in aryloxide has such a profound effect on the structure is unknown.

4. Summary

The structures of five cobalt compounds with fluorinated aryloxide ligands are reported. Two dimeric structures of the form [(DME)(ArO)Co(μ_2 -OAr)_2Co(DME)] display antiferromagnetic coupling via superexchange through the bridging aryloxide ligands. Two compounds with the [Tl₂Co(OAr)₄] stoichiometry exhibit one monomeric structure and one dimeric, apparently determined by the difference in OAr group. The monomer with the OC₆F₅ ligand is a simple isolated Co(II) center, but the compound with the $OC_6H_3(CF_3)_2$ ligand has a dimeric structure in the solid state with substantial ferromagnetic coupling.

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Appendix A. Supplementary material

CCDC 891130, 901763, 901764, and 901765 contain the supplementary crystallographic data for **1**, **3a**, **3b**, and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.09.032.

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