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Single-Source AACVD of Composite Cobalt-Silicon Oxide Thin Films

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Abstract

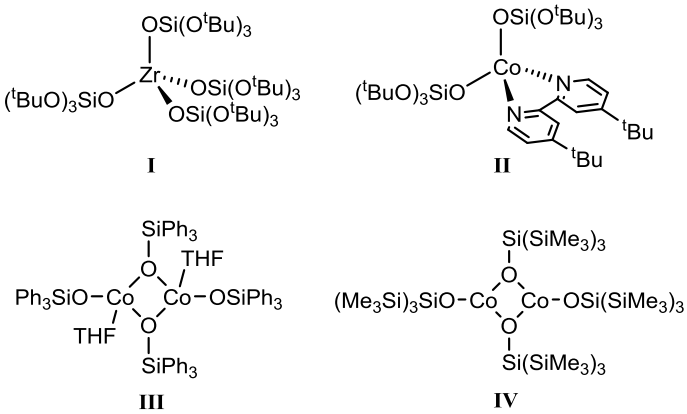
A series of cobalt(II) complexes comprising either triorganosiloxide or tris(tert-butoxy)siloxide ligands have been synthesized and characterized. A mononuclear constitution is enforced through the incorporation of bi- and tridentate N-donor ligands. The resultant 4- or 6-coordinate complexes have been identified by single-crystal X-ray diffraction analysis and have been assessed for their potential as molecular precursors to hybrid cobalt/silicon oxide thin film materials by thermogravimetric analysis. A TMEDA adduct of the bis-ligated Co(II) tris(tert-butoxy)siloxide species has been utilized as a single-source precursor for the AACVD of aesthetically attractive blue composite films. Analysis by PXRD, SEM, EDS and XPS indicated the production of amorphous, continuous films with the bulk compositions reflecting the cobalt, silicon and oxygen stoichiometry of the molecular precursor complex.

Keywords: Cobalt; Siloxide; Single-Source; Aerosol-assisted Chemical Vapour Deposition; AACVD

Introduction

It is estimated that the Earth's crust comprises approximately 90% silicate-based minerals, containing near limitless combinations of dopants and metals.[1] Many examples of metal silicate families occur naturally, ranging from the prolific tectosilicates, including zeolites,[2] to highly crystalline amethysts; transparent, colored quartz crystals, doped with tiny percentages (typically ≤1 %) of transition metal cations to give colored systems.[3] Whereas true metal silicates comprise single solid-state phases of evenly distributed metal cations balanced by anionic orthosilicate units, other composite silica-metal oxide materials contain randomly

distributed and amorphous silicon dioxide and metal oxide phases. As a case in point, it has been known since antiquity that common soda glass, an amorphous metal-silicate material, may be doped with quantities of p-block elements or transition metals to produce aesthetically attractive colored glass,[4] e.g. cobalt-doped glass typically appears blue, absorbing red–orange light through the introduction of the transition metal-based color centers. Despite their architectural appeal, the practicalities of continuous modern float glass production designate the industrial-scale manufacture of batches of such bulk-tinted glasses as economically unattractive. The exploitation of chemical vapor deposition (CVD) for the large area surface modification of flat glass, such as through the application of solar control fluorine-doped tin oxide or 'self-cleaning' TiO_2 layers, is, however, well-precedented in the glass manufacturing industry.[5] A more appealing, yet unprecedented, method of color generation, therefore, is through the deposition of a thin film providing the desired color onto the surface of an untinted glass.

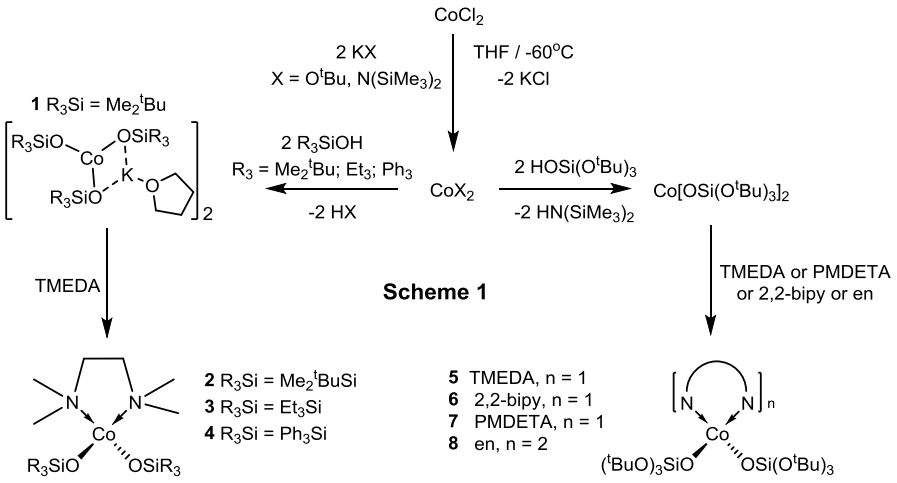


While the use of vapor phase delivery methods for the generation of colored silica-based thin film materials is unknown, a variety of multi- and single-source CVD routes to colorless high-κ dielectric materials have been developed.[6] The potential of molecular metal siloxide complexes to act as thermolytic single-source precursors for the bulk synthesis of carbon-free silica-hybrid heterogeneous catalytic materials has also been demonstrated by Tilley and co-workers.[7] The homoleptic zirconium complex (**I**),[7a] for example, and, of most relevance to the current work, the Co(II) derivative (**II**),[7n] containing the tris(*tert*-butoxy)siloxide ligand have been shown to decompose through a well-defined sequence of β-hydride elimination and condensation events to provide oxide materials with compositions which reflect the Si:metal stoichiometries of the molecular starting materials.

Notwithstanding the potential applications of these species in materials synthesis, a multiplicity of metal siloxide types have also been investigated from a structural or catalytic standpoint.[8] For the specific case of cobalt(II), whereas a variety of mono-siloxide and cluster species have been described,[9] examples of bis-siloxide species are much less precedented. Although their synthesis should be straightforward, the sole examples of this latter compound class are Power's triphenylsiloxide derivative (**III**)[10a] and the similarly dimeric tris(trimethylsilyl)siloxide (**IV**).[10b] In this contribution we describe the synthesis and structural characterization of the first well-defined series of mononuclear Co(II) siloxides and demonstrate that derivatives comprising Tilley's tris(*tert*-butoxy)siloxide ligand may be employed as single-source precursors for the aerosol-assisted chemical vapor deposition (AACVD) of colored cobalt/silicon oxide thin films.[11]

Results and Discussion

Synthesis and Structural Chemistry: A range of Co(II) bis(siloxide) complexes were conveniently prepared using a 1-pot synthesis involving the *in-situ* generation of $[Co\{N(SiMe_3)_2\}_2]$ or $[Co(O^tBu)_2]$ from the reaction of anhydrous $CoCl_2$ with two equivalents of either $KN(SiMe_3)_2$ or KO^tBu. Subsequent silanolysis with two equivalents of the appropriate silanol provided complexes **1 - 8** (Scheme 1). Reactions performed in the absence of additional chelating donors proved difficult to purify and were complicated by the inclusion of potassium chloride from incomplete halide metathesis (*vide infra*). To limit the tendency toward 'ate' complex formation and solid-state oligomerization, therefore, a range of chelating *N*-donor ligands were employed in equimolar quantities to coordinate to the cobalt centers in the syntheses of compounds **2 - 8**.



Scheme 1

The trialkylsiloxides (**2** and **3**) were isolated as sticky, dark blue and purple solids, respectively. Although crystalline materials were afforded by slow evaporation of small samples dissolved in hexane at -40 ^{o}C, at room temperature solid samples were found to quickly lose any structural integrity. The triphenylsiloxide complex **4** was insoluble in non-polar, aliphatic and aromatic solvents. Consequently the reaction solution was filtered warm, allowing separation from the KCl by-product, and, once isolated, the complex displayed notable stability to air and moisture in the solid state. The tris(*tert*-butoxy)siloxide compounds (**5** – **8**) were isolated in high yields by crystallization from saturated solutions in toluene, with the exception of compound **6**, which was precipitated through the addition of cold hexane. The complexes were found to be thermally stable in solution to the reflux point of toluene (110.6 ^{o}C). Isolated yields of the triorganosiloxide complexes **2** - **4** were in the range of 42 – 82% while the alkoxysiloxides (**5** – **8**) could be crystallized reliably in higher yields (78 – 93%). The bulk constitution of each complex was confirmed by CHN elemental analysis.

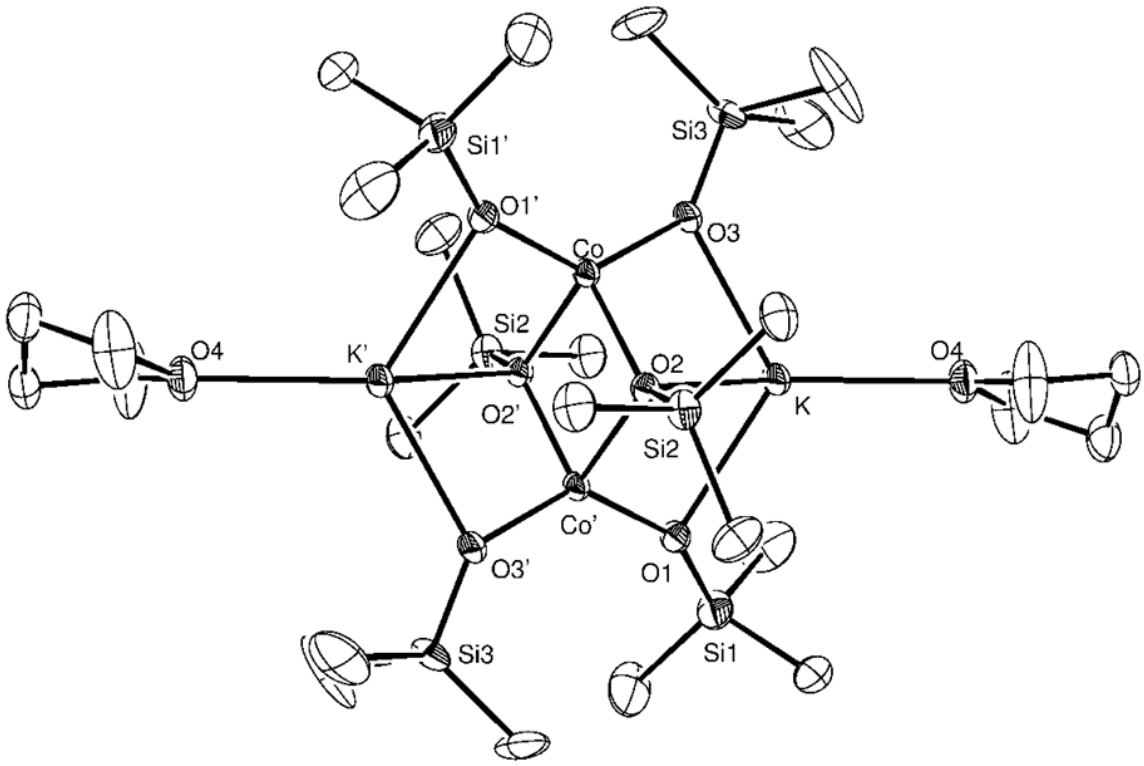


Figure 1: ORTEP representation of compound **1**. Thermal ellipsoids presented at 20% probability. Hydrogen atoms and *tert*-butyl methyl carbons are removed for clarity. Symmetry transformations used to generate equivalent atoms: ' -*x*,-*y*,-*z*+1

The solid-state structures of compounds **1**, **4**, **5**, **6**, **7** and **8** were confirmed through single-crystal X-ray diffraction analysis of crystals grown by cooling toluene or toluene/hexane solutions. The molecular structures are presented in Figures 1 - 6, while details of the X-ray analyses and selected bond length and angle data are presented in Tables 1 – 3, respectively. Each compound was found to be effectively monomeric in the solid state with the exception of compound **1**, which was isolated from a reaction of an *in situ*-formed solution of $[Co\{N(SiMe_3)_2\}_2]$ and $Me_2{}^tBuSiOH$ without the addition of any co-ligand and revealed to be a dimeric potassium cobaltate siloxide cluster (Figure 1). Each cobalt center in **1** occupies a tetrahedral position, accounting for the intense blue color of the compound and the structure may, thus, be considered as two $[Co(OSiMe_2{}^tBu)_3K.THF]$ fragments connected by μ-Co-O-Co bridging interactions. The potassium atom occupies a coordination environment best described as trigonal pyramidal in which the basal plane of the pyramid is provided by the O(1) and O(3) siloxide atoms and the THF O(4) donor center. This otherwise trigonal coordination of the potassium center is little disrupted through a further longer contact (2.840(2) Å) to O(2) of the siloxide ligand which bridges the two cobalt centers of the dimer. This Co-O(2) bond length is slightly elongated (2.002(4) Å) in comparison to the Co-O(1) and Co-O(3) contacts provided by the other unique siloxide ligands (1.913(3) and 1.914(3) Å respectively) which engage in μ^2-bridging interactions between the cobalt and potassium centers.

Addition of a single equivalent of TMEDA during the synthesis of the triorganosiloxide complexes (**2** – **4**) was found to prevent the retention of potassium in the structure and oligomerization in the solid state. The triphenylsiloxide **4** (Figure 2) crystallized as bright blue blocks in the chiral monoclinic $P2_1$ space group, with two identical molecules in the unit cell.

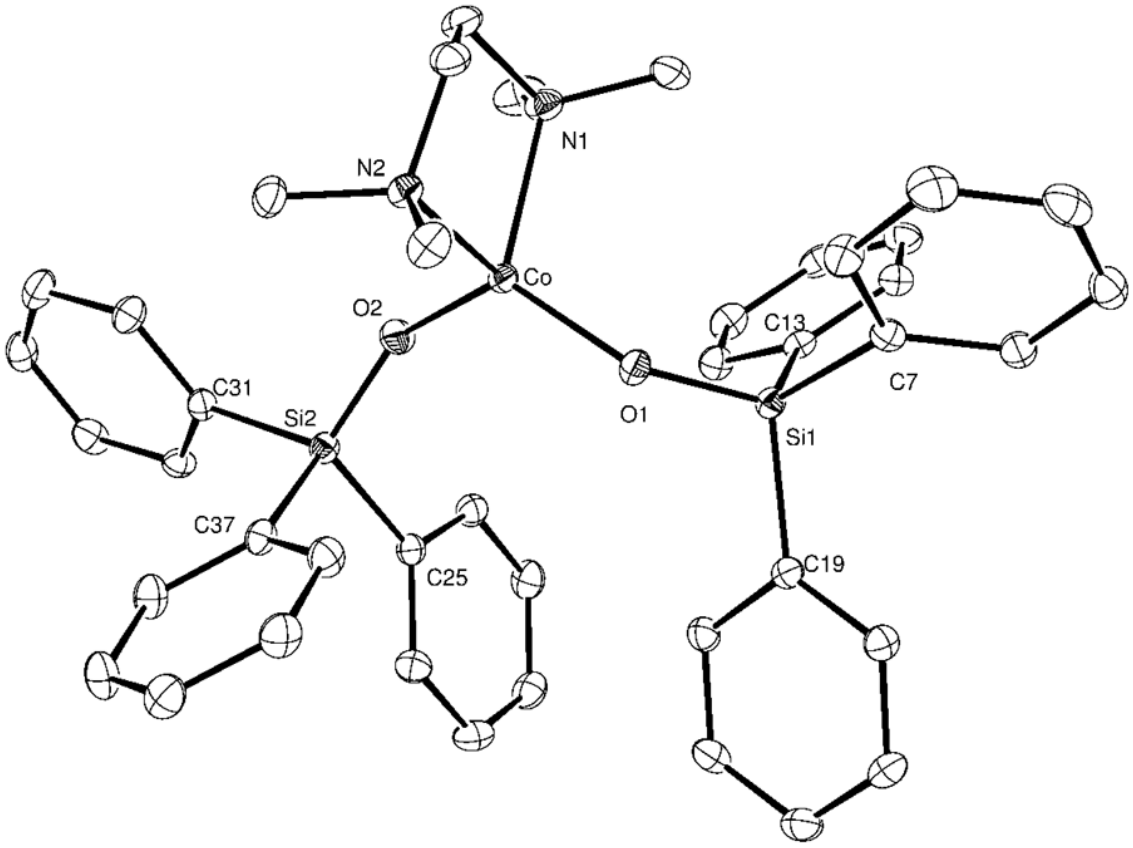


Figure 2: ORTEP representation of compound **4**. Thermal ellipsoids presented at 30% probability. Hydrogen atoms are omitted for clarity.

The structure of **4** comprises a four-coordinate cobalt center in which the coordination sphere is provided by two terminal triphenylsiloxides and a chelating, bidentate TMEDA ligand. A lack of rotational freedom along the central Si-O-Co-O-Si unit gives chirality to the molecule in the solid state and in this case, the crystal structure is optically pure. As a consequence of the terminal disposition of the siloxide ligands, the Co-O bond lengths (Co-O(1), 1.8758(11); Co-O(2), 1.8793(11) Å) of **4** are more comparable to the terminal Co-O distances (1.858(3) and 1.845(4) Å) in Power's dimeric homoleptic species **III** than the exclusively bridging Co-O interactions of the 'ate' complex **1**.[10a] The angles around the Co(II) center are enforced by the narrow bite angle of the TMEDA donor (N(1)-Co-N(2) = 86.43(5)°) and the steric repulsion of the bulky triphenylsiloxides (O(1)-Co-O(2) = 124.56(5)°).

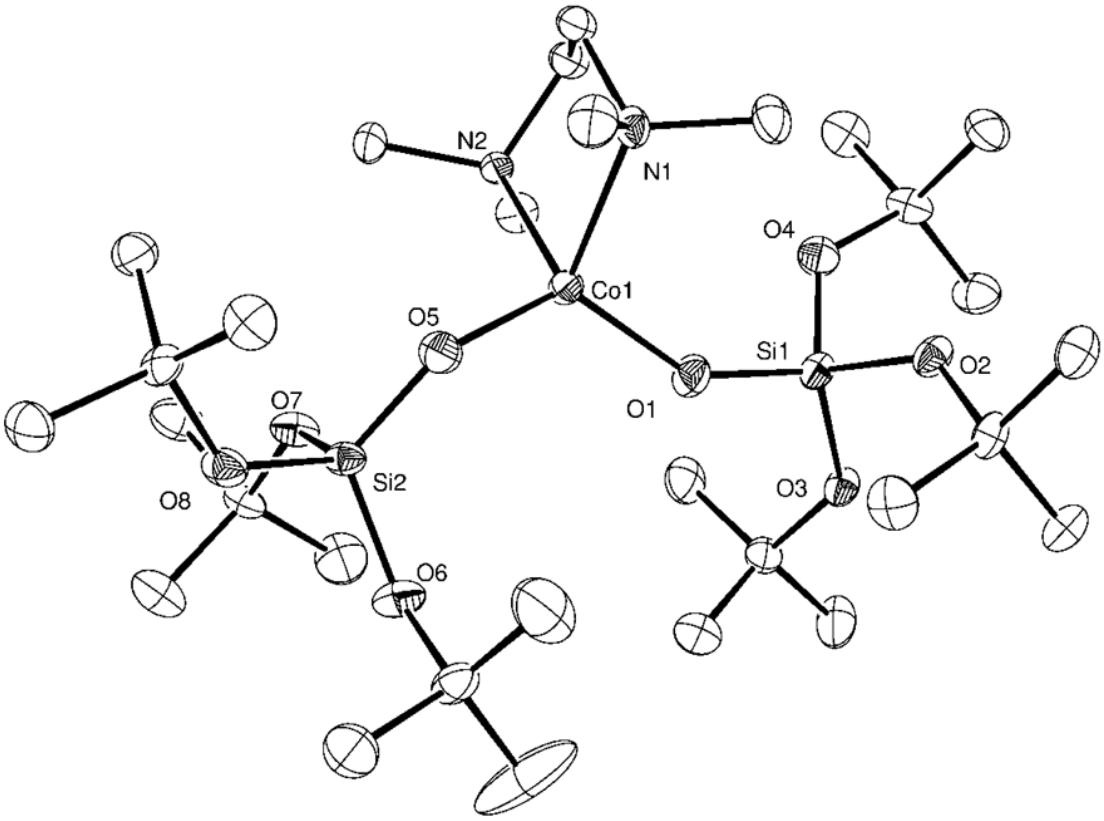


Figure 3: ORTEP representation of the Co(1)-containing unit in the structure of compound **5**. Thermal ellipsoids presented at 50 % probability. Hydrogen atoms and *tert*-butyl methyl carbon atoms are omitted for clarity.

The addition of chelating *N*-donor ligands was also found to enforce a monomeric constitution for the alkoxysiloxide Co(II) complexes, **5** – **8**. The TMEDA adduct, compound **5**, which crystallized as dark blue blocks, was shown to display an analogous coordination mode to **4** despite the further potential *O*-donor ability of the oxygen-rich siloxide ligands (Figure 3). Compound **5** crystallized in the monoclinic $P2_1/a$ space group in an unusually large unit cell with an asymmetric unit consisting of a cluster of 4 similar but non-identical molecules. Torsion along the line of the SiO-Co-OSi axis shows that the *tert*-butoxide groups again crystallize in a staggered arrangement to minimise intramolecular interactions with endemic chirality leading to a crystalline racemate enforced in the solid state. Although the Co-O bond lengths occupy a range of values because of the 4 similar, independent molecules in the asymmetric unit, each molecule exhibits one short Co-O bond (mean(Co-O)$_{short}$ = 1.866 Å) and one longer Co-O bond (mean(Co-O)$_{long}$ = 1.893 Å). This asymmetry

in the solid state is effected by the staggered conformation and resultant steric inequivalence of the siloxide ligands.

X-ray diffraction analysis of the grass-green needles of the 2,2-bipyridine adduct **6** revealed a similar monomeric constitution (Figure 4). In common with the structure inferred for Tilley's analogous 4,4'-di-*tert*-Bu-bipy derivative **II**,[7n] the cobalt atom of **6** resides in a tetrahedral coordination environment provided by two terminal siloxides and a chelating 2,2-bipyridine molecule. In contrast to the structures of both compounds **4** and **5**, the Co-O bond lengths of in **6** are effectively identical. These distances (1.872(4) and 1.864(4) Å) are comparable to the shorter bond lengths observed in the structure of **5** and are possibly a reflection of the lower steric demands of the more two-dimensional 2,2-bipyridine ligand. Pairs of molecules associate through a π-stacking interaction of parallel 2,2-bipyridine units with a centroid-centroid distance of 3.669 Å.

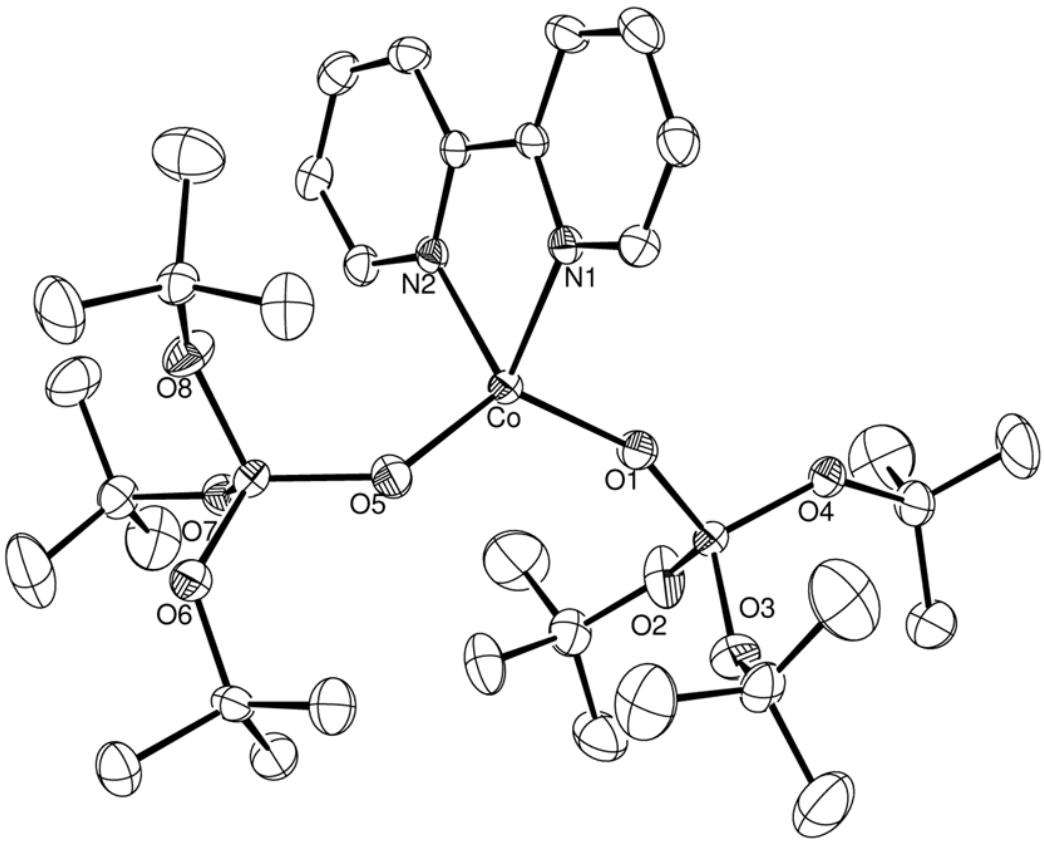


Figure 4: ORTEP representation of compound **6**. Thermal ellipsoids are presented at 25 % probability. Hydrogen atoms and *tert*-butyl methyl carbon atoms are omitted for clarity.

The crystal structure of the dark purple PMDETA adduct (**7**) revealed that cobalt sits in a 5-coordinate geometry comprising the two terminal siloxide ligands and all three *N*-donors of the amine ligand (Figure 5). An analysis of the bond angles surrounding cobalt provides a tau value, $\tau = 0.38$, indicating a structure that is intermediate between the extremes of square-based pyramidal and trigonal bipyramidal, but favouring the former geometry.[12] The Co-O bond lengths differ according to their disposition with respect to the N(2)-donor of the PMDETA ligand. The O(5)-bound siloxide, which effects an approximate *transoid* disposition (N(2)-Co-O(5) 158.05(5)^{o}) with respect to N(2), displays a considerable elongation (Co-O(5), 1.9526(10) Å) in comparison to the O(1)-containing siloxide unit (Co-O(1), 1.9147(10) Å) and occupies what is effectively the apical position of the square pyramidal array.

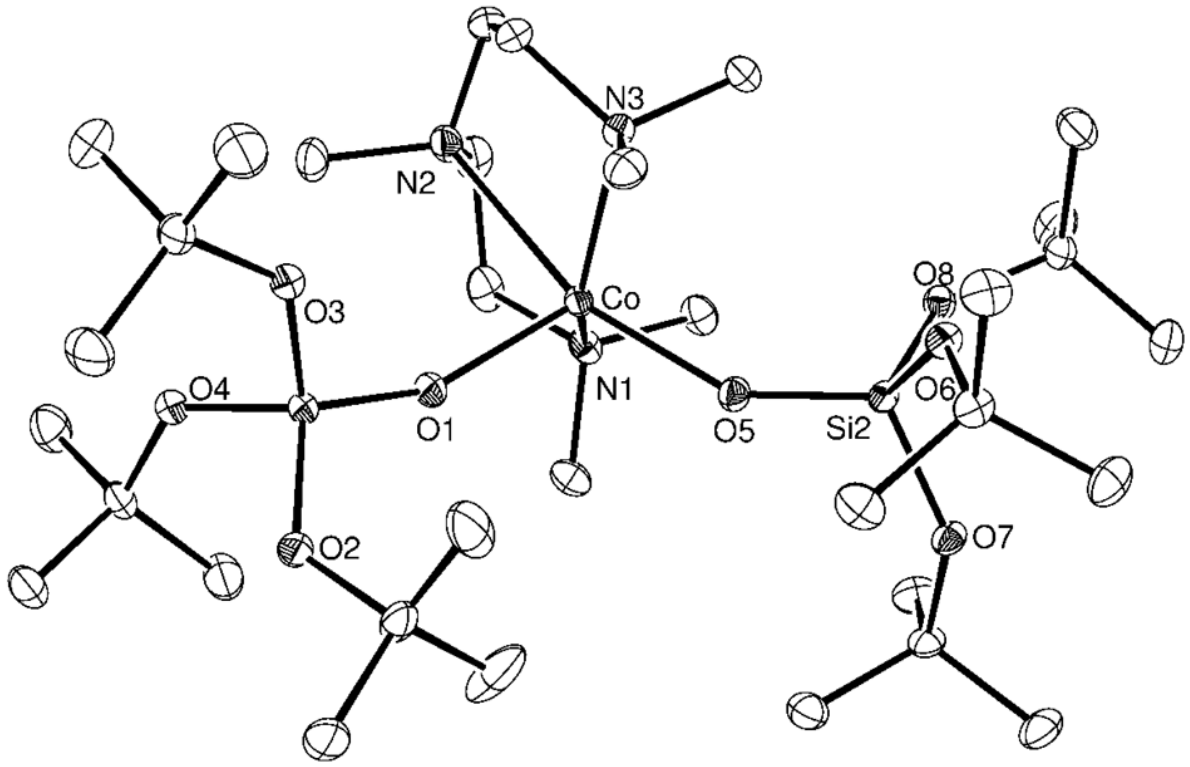


Figure 5: ORTEP representation of compound **7**. Thermal ellipsoids are presented at 25 % probability. Hydrogen atoms and *tert*-butyl methyl carbon atoms are omitted for clarity.

While all attempts to synthesise a 4-coordinate mono-ethylenediamine (en) complex analogous to compounds **6** and **7** were unsuccessful, the six-coordinate bis-(en) complex **8** was readily synthesized through addition of two equivalents of the amine ligand. Although

solutions of compound **8** decomposed on exposure to air, the pale grey/brown rod-like crystals displayed moderate air and moisture stability in the solid state. Single-crystal X-ray-diffraction analysis of these crystals evidenced an octahedral cobalt complex with mutually *trans* terminal siloxide ligands (O(1)-Co(1)-O(5) 174.88(5); O(9)-Co(2)-O(13) 174.83(5)^{o}) and two equivalents of en providing the equatorial plane of the cobalt coordination sphere. The molecules are arranged in pairs with an approximate orthogonal disposition between the individual cobalt-containing entities as the result of four co-lateral hydrogen-bonds which occur between the *N*-bound hydrogen atoms of the equatorial en ligands and the axial oxygens of an adjacent molecule (Figure 6). The Co-O bond lengths (Co(1)-O(1) 2.0721(13); Co(1)-O(5) 2.0786(13); Co(1)-O(9) 2.0676(14); Co(1)-O(13) 2.0774(14) Å) are significantly longer than those observed in the four- or five-coordinate compounds discussed previously as a consequence of the higher coordination number at cobalt.

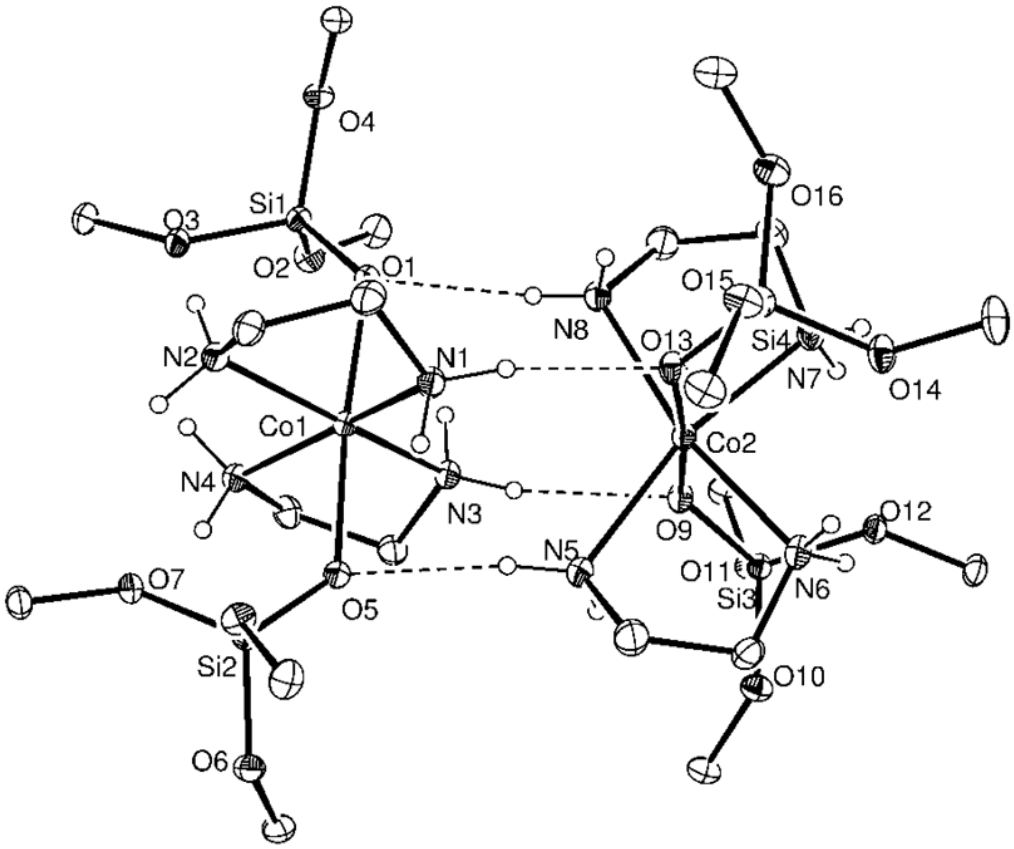


Figure 6: ORTEP representation of the hydrogen-bonded dimer comprising the asymmetric unit of compound **8**. Ellipsoids are presented at 25 % probability. Hydrogen atoms except those bonded to N(1)–N(8) and *tert*-butyl methyl carbons are omitted for clarity.

Table 1: X-ray Crystallographic Data for Compounds **1**, **4**, **5**, **6**, **7** and **8**

	1	**4**	**5**	**6**	**7**	**8**
Empirical Formula	$C_{22}H_{53}CoKO_4Si_3$	$C_{42}H_{46}CoN_2O_2Si_2$	$C_{30}H_{70}CoN_2Si_2$	$C_{143}H_{256}Co_4N_8O_{32}Si_8$	$C_{62}H_{154}Co_2N_8O_{16}Si_4$	$C_{33}H_{77}CoN_3O_8Si_2$
FW ($g.mol^{-1}$)	331.552	725.92	701.99	3060.00	1498.15	759.09
Crystal System	Monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space Group	$P\,2_1/n$	$P\,2_1$	$P\,2_1/a$	$P\,n\,a\,a$	$P\bar{1}$	$P\,2_1$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	16.2290(2)	9.77130(10)	18.6530(2)	9.96910(10)	14.1585(3)	9.2429(2)
b (Å)	13.6030(3)	18.2644(3)	30.8820(3)	26.4142(3)	16.7348(2)	16.9014(3)
c (Å)	14.0630(3)	10.8943(2)	29.4370(4)	32.9842(4)	18.6851(4)	14.3981(2)
α (^{o})	90	90	90	90	86.7150(10)	90
β (^{o})	90.000(1)	102.5240(10)	104.0890(10)	90	83.6600(10)	100.3390(10)
γ (^{o})	90	90	90	90	85.0640(10)	90
Density (Mgm^{-3})	1.019	1.27	1.134	1.17	1.136	1.139
Z	2	2	16	2	2	2
μ (Mo Kα) (mm^{-1})	0.825	0.553	0.517	0.496	0.491	0.486
Reflections Collected	48330	41460	81229	74149	85388	46728
Independent Reflections	7083	10954	31042	7644	19842	12827
R_{int}	0.039	0.0407	0.0965	0.1051	0.0533	0.0337
R_1 .wR_2 $[I>2\sigma(I)]$	0.1135, 0.2847	0.0328, 0.0660	0.0768, 0.1549	0.0777, 0.1976	0.0401, 0.0896	0.0310, 0.0661
R indices (all data)	0.1245, 0.2918	0.0441, 0.0702	0.1365, 0.1773	0.1254, 0.2262	0.0666, 0.1021	0.0409, 0.0689

Table 2: Selected Bond Lengths (Å) for Compounds **1**, **4**, **5**, **6**, **7** and **8**

	1	**4**	**5**	**6**	**7**	**8**
Co-O(1)	1.906(4)	1.8793(11)	1.862(3)	1.871(4)	1.9147(10)	2.0721(13)
Co-O(5)	2.036(4)[a]	1.8758(11)[a]	1.894(4)	1.864(4)	1.9526(10)	2.0786(13)
Si(1)-O(1)	1.610(6)	1.5969(12)	1.590(4)	1.543(4)	1.5717(11)	1.5743(14)
Si(2)-O(5)	1.528(19)[b]	1.5905(12)[b]	1.573(4)	1.605(4)	1.5753(10)	1.5744(14)
Co-N(1)	-	2.1158(15)	2.127(4)	2.069(4)	2.1765(13)	2.2058(18)
Co-N(2)	-	2.1113(14)	2.108(4)	2.077(4)	2.1672(13)[c]	2.1823(17)

[a] Co-O(5); [b] Si(2)-O(2); [c] Co-N(3)

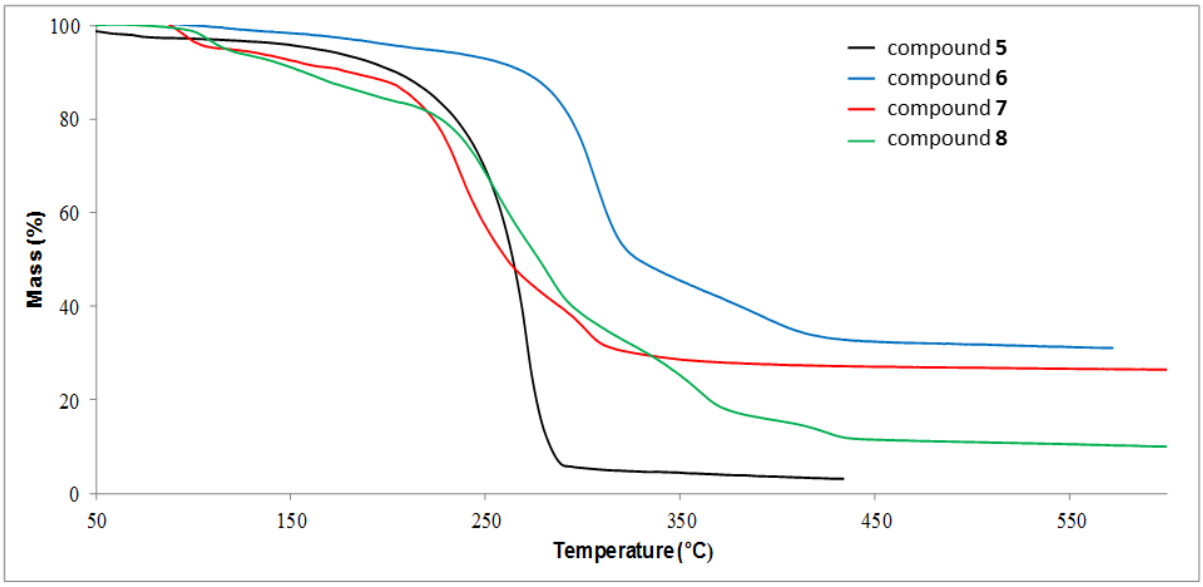
Table 3: Selected Bond Lengths for Compounds **1**, **4**, **5**, **6**, **7** and **8**

	1	**4**	**5**	**6**	**7**	**8**
O(1)-Co-O(5)	104.69((19)[a]	124.56(5)[a]	124.84(16)	122.73(17)	111.71(5)	174.88(5)
N(1)-Co-N(2)	-	86.43(5)	86.06(17)	79.19(16)	135.44(5)[d]	78.72(7)
N(1)-Co-O(1)	-	115.38(6)	111.24(16)	103.81(17)	103.50(5)	93.44(6)
N(2)-Co-O(5)	-	109.93(5)[c]	112.02(16)	110.40(16)	97.67(4)[e]	95.05(6)
Co-O(1)-Si(1)	155.1(4)	141.13(7)	146.3(2)	157.7(3)	154.04(7)	130.27(8)
Co-O(5)-Si(2)	126.4(5)[b]	141.89(8)[b]	129.1(2)	133.4(2)	150.23(7)	132.44(8)

[a] O(1)-Co-O(2); [b] Co-O(5)-Si(2); [c] N(2)-Co-O(2); [d] N(1)-Co-N(3); [e] N(3)-Co-O(5)

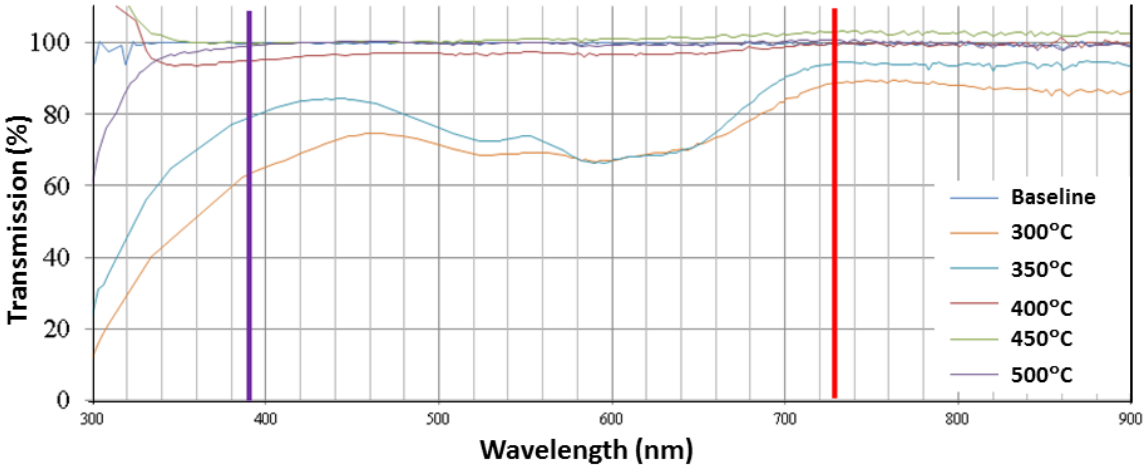
Materials Chemistry: Compounds **2** - **8** were studied by thermogravimetric analysis (TGA) under an inert N_2 atmosphere. Whereas the triphenylsiloxide species **4** displayed notable thermal stability at temperatures up to 250°C, partial decomposition and some evidence for whole-molecule volatility was observed for the trialkylsiloxide derivatives **2** and **3** at temperatures above 130°C. In both of these latter cases, however, the mass loss events were observed to occur gradually and over temperature ranges in excess of 200°C while the ultimate residual masses could not be correlated with any meaningful stoichiometric component of the precursor molecules. In contrast, and in common with the observations of Tilley and co-workers,[7] the onset of decomposition of each of the tris-(*tert*-butoxy)siloxide complexes **5** – **8** was found occur to at significantly reduced temperatures (Figure 7)**.** While the thermolyses of compounds **6** and **7** occurred as multi-step processes which resulted in residual masses in excess of that calculated for $CoSi_2O_5$ (**6**$_{calc}$ 32% ; **7**$_{calc}$ 27%), compound **5** evidenced a more controlled and continuous mass loss from approximately 80°C which accelerated at temperatures higher than 190°C. Although the final residual mass (6% *versus* 27.8% for $CoSi_2O_5$) for **5** is indicative of considerable thermal stability and whole molecule volatility, an inflection point observed in the differential of the TGA curve at 280°C suggested that TMEDA decomplexation and complex decomposition were also significant at temperatures approaching 300°C.

Figure 7: TGA of the cobalt tri-*tert*-butoxysiloxide complexes **5** - **8**.



Compound **5** was selected for CVD trials as a result of its less complex thermal behavior. Although apparent material loss by sublimation indicates that compound **5** is likely to be applicable to direct low-pressure vapour phase delivery, a combination of high solubility and potentially higher mass transport and deposition rates led us to employ aerosol-assisted chemical vapour deposition (AACVD) for film growth studies onto glass microscope slide substrates.[13] Films were grown from an aerosol of compound **5** dissolved in dried, degassed toluene (12.5 gL^{-1}) and transported to the reactor chamber in a N_2 carrier gas at a rate of 0.3 $Lmin^{-1}$. The Scotch-tape test was performed after each deposition to confirm film adherence to the substrate and all films can be assumed to have passed unless otherwise stated. As illustrated by the UV/Vis spectra (Figure 8), depositions at 300, 350 and 400°C provided transparent films which were deep blue in colour, whereas the films were colorless for depositions at 450 and 500°C. The depositions at 300 and 350°C displayed distinct absorptions in the visible range at approximate wavelengths of 535, 595 and 647 nm and into the near IR range. These maxima translate to absorption in the red, orange and yellow regions, leading to expression of a visually discernible purple/blue color. While various bulk crystalline cobalt oxide phases have been described in yellow-orange, black and green forms,[14] pure CoO displays a range of absorptions from 600 – 900 nm with λ_{max} values at 601 to 772 nm.[15] Absorption by CoO in the near IR at 826 nm is also observed due to charge carrier absorption, affording semiconductor ability to the oxide. The absence of these features in the UV/vis spectra, along with a complete absence of any evidence for crystallinity by PXRD, of the deposited films leads us to surmise that the colors observed in the samples prepared at temperatures of 400°C and below arise from the incorporation of cobalt color centers dispersed within an effectively amorphous silica matrix.

Figure 8: UV/Visible spectra of thin-films deposited from precursor **5**; [Co{OSi(OtBu)$_3$}$_2$.TMEDA]



The films were subjected to microscopic analysis by SEM. A plan view captured at 50,000x magnification of a blue film deposited at 350°C is shown in Figure 9a. This shows a continuous surface morphology consisting of small, almost circular features some of which appear to be agglomerations of smaller particles. The 80° tilt view of the same region (Figure 9b) illustrates that, despite this textured surface, the film is solid and continuous with respect to the glass substrate. Figure 9c provides a cross sectional view and allows an estimation of the maximum film thickness of approximately 102 nm. The EDS spectrum acquired for this same region is shown in Figure 9d confirming the presence of cobalt along with silicon, carbon and other elements which can be attributed to the glass substrate.

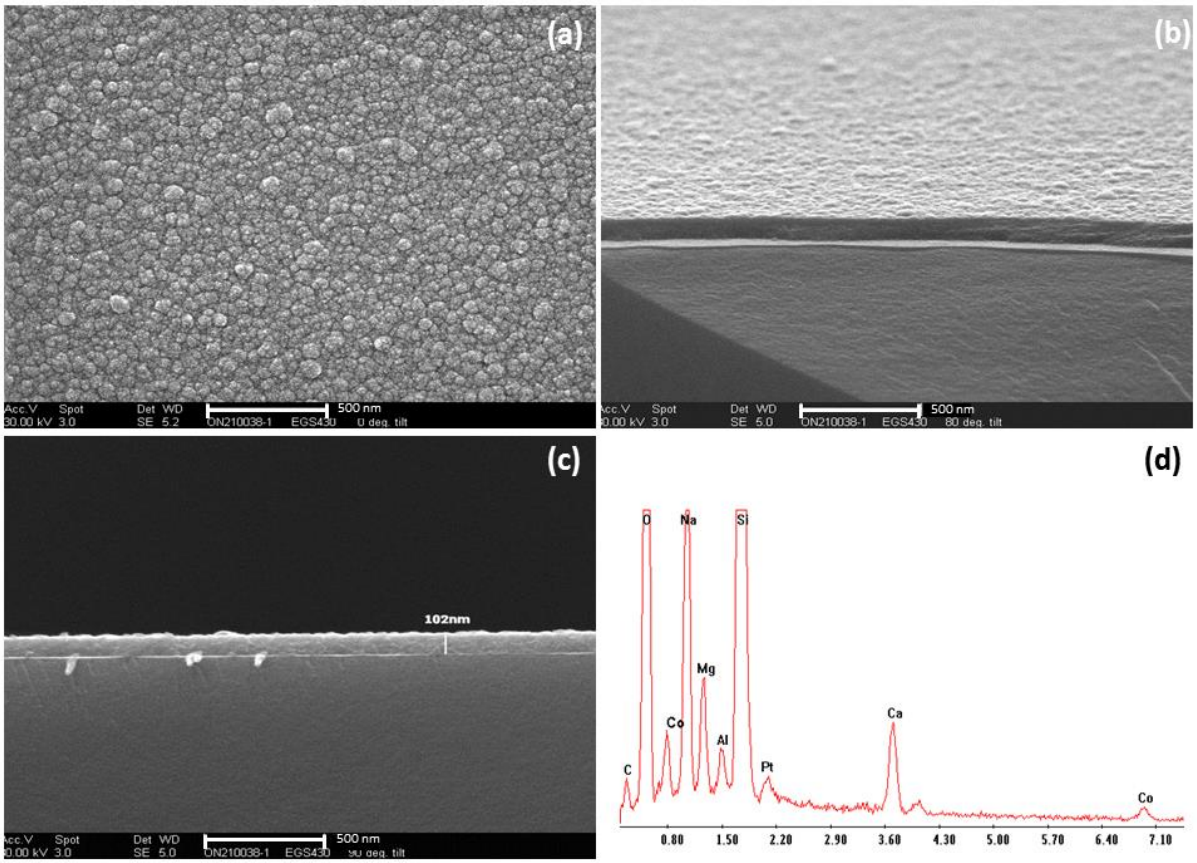
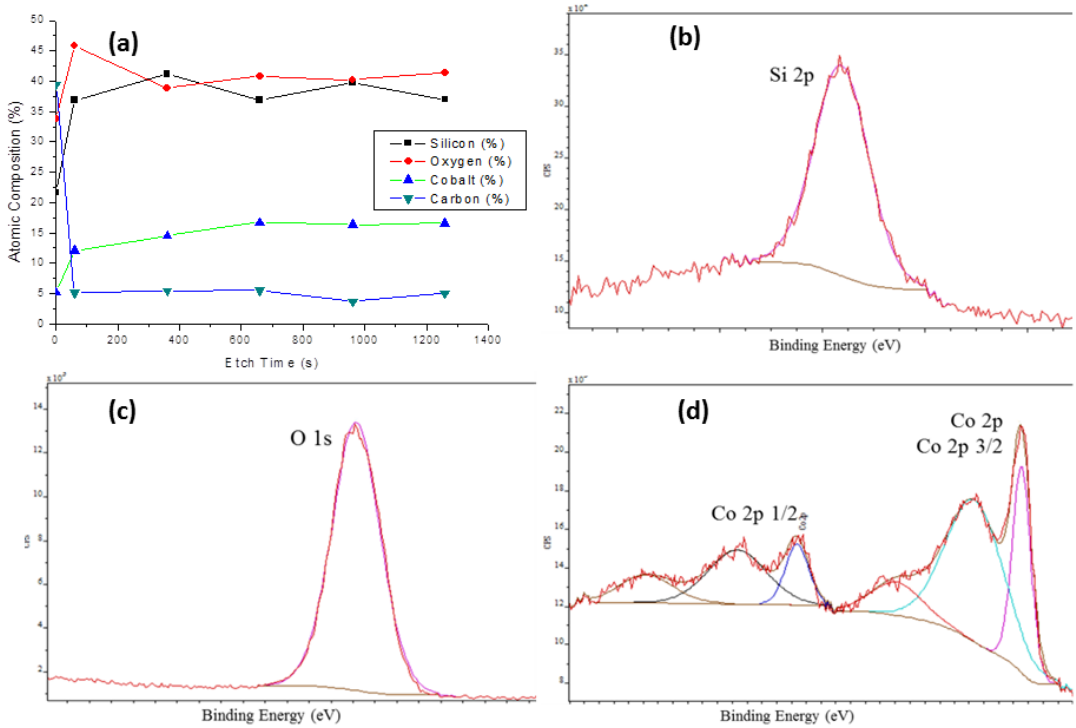


Figure 9: (a) SEM plan view image of the blue region of a film grown at 350^{oC}, taken at 50,000x magnification; (b) SEM 80° tilt view taken at 50,000x magnification; (c) 90° tilt view taken at 50,000x magnification; (d) EDS analysis of the same blue film grown at 350°C.

Whereas the FTIR spectra of the colorless films deposited at 450 and 500°C revealed distinctive and wide absorption bands at 850 cm^{-1}, characteristic of silica υ(Si-O) bending vibrations, the samples deposited at lower temperatures displayed a significant shift of this SiO_2 absorption from 850 to 823 cm^{-1}, suggesting an interruption of the intimate SiO_2 structure with an incorporated component such as cobalt.[16]

Figure 10: (a) Quantitative, elemental depth profiling by XPS of a blue film deposited at 350°C from compound **5** onto glass. Analysis of key peaks at 660s etch time: (b) Si_{2p}; (c) O_{1s}; (d) Co_{2p}. Shirley baselines, simulated distributions and distribution combinations calculated using CasaXPS.



A film grown at 350°C was analyzed by depth-profiling X-ray photoelectron spectroscopy (XPS) (Figure 10a), confirming the ability of compound **5** to deposit a binary metal-doped silicon oxide under anaerobic conditions. The atomic compositions of cobalt, silicon, oxygen and carbon were measured and compared at each etch depth and therefore through the bulk of the material. The high percentage of carbon observed prior to argon ion etching was not representative of the bulk of the material and was, thus, ascribed to atmospheric, surface contamination. This feature decreased rapidly upon etching while the cobalt, silicon and oxygen content increased to stable concentrations from 360 s etching time. The etching did not pass beyond the total depth of the film as no sodium or calcium were

detected, and within the bulk of the film, the Si:Co ratio of 2:1 was representative of the stoichiometry of the compound **5**. The spectrum acquired at an etch time of 660 s was studied in detail to deduce the oxidation states of the elements in the film. While the Si_{2p} and O_{1s} signals were well represented by the simulated distribution of single peaks (indicative of a true metal silicate) (Figures 10b/10c), the Co 2p emission was more complex. Whereas the exclusive maintenance of the single cobalt(II) oxidation state of the precursor **5** would result in two peaks split by approximately 15 eV, the observed Co_{2p} and $Co_{2p3/2}$ emissions were best simulated as three superimposed binding energies (Figure 10d). We suggest that this latter observation indicates that, while the precursor delivers exclusively Co(II), a proportion of the transition metal centers undergo disproportionation to provide a distribution of cobalt oxidation states throughout the silica matrix.

Conclusion

Cobalt(II) complexes derived from the tris(*tert*-butoxy)siloxide ligand have been found to be suitable single-source precursors for the deposition of aesthetically attractive blue cobalt-silicon oxide composite thin films by AACVD at 300 – 400 °C. The films have been analyzed by PXRD, SEM, EDS and XPS. Microscopic analysis evidenced the formation of granular but homogeneous and continuous films, which displayed absorption maxima between 530 – 640 nm, leading to the expression of the blue coloration. Although XPS analysis revealed that the bulk compositions were reflective of the cobalt, silicon and oxygen stoichiometry of the molecular precursor complex, analysis of the Co_{2p} and $Co_{2p3/2}$ emissions was indicative of some level of disproportionation of the precursor Co(II) under the AACVD conditions.

General Synthetic Experimental Procedures

All reactions were carried out under an argon atmosphere using standard Schlenk line and glovebox techniques in an MBraun Labmaster glovebox at O_2, H_2O < 2.5 ppm. NMR experiments were conducted in Youngs tap NMR tubes prepared and sealed in the glovebox under argon. All NMR spectra were acquired on a Bruker 300 Ultrashield™ spectrometer for ^1H (300 MHz), ^{13}C (75.48 MHz), at room temperature. $^1H/^{13}C$ NMR spectra were referenced using residual solvent resonances. Elemental analyses were performed by Stephen Boyer of London Metropolitan Enterprises. Solvents for air- and moisture-sensitive reactions were provided by an Innovative Technology Solvent Purification System, or dried/degassed

manually according to established laboratory procedures. C_6D_6 was purchased from Fluorochem and dried/degassed over molten potassium prior to vacuum transfer into a sealed ampule and storage in the glovebox under argon. All reagents were purchased and used as received with the exceptions of tris(*tert*-butoxy)silanol and potassium hexamethyldisilazide which were synthesized by literature procedures.[18] All amines and pyridine were dried over CaH_2 and distilled before use. Thermogravimetric analyses were performed using a Perkin Elmer TGA 4000™ quartz microbalance instrument and spectra were analysed using PYRIS Version 10.1 Instrument managing and analysis software. Samples were sealed into pre-weighed aluminium pans and unless stated otherwise, TGAs were run using a standardised method. Under a continuous furnace purge rate of 20 mLmin^{-1} of N_2, the furnace was heated to an initiation temperature of 30 ^{o}C, at which point mass measurements were recorded every 10 s. Temperature was increased at a ramp-rate of 5 ^{o}C min^{-1} until a pre-designated maximum temperature. Mass was recalculated back to a measure of percentage, according to the initial mass of the sample.

[Co(OSiMe$_2$^{t}Bu)$_2$.TMEDA], 2: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.99 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.65 g / 5.0 mmol) in THF (20 mL) at -60 ^{o}C and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution with a KCl precipitate. To the stirred solution of [Co{N(SiMe$_3$)$_2$}$_2$] (40 mL) was added a solution of Me$_2$^{t}BuSiOH (1.32 g / 1.57 mL / 10.0 mmol) in THF (20 mL) and stirred for 30 minutes, followed by TMEDA (0.58 g / 0.75 mL / 5.0 mmol).. The mixture was stirred for 4 hours giving a bright blue solution and the volatiles removed *in vacuo*. The residue was redissolved in hexane (30 mL) and filtered by cannula to remove KCl. Volatiles were removed *in vacuo* leaving a waxy blue / purple residue. Poor quality crystals were afforded in high yield on standing at room temperature. Yield: 68%. m.p. 68°C. Anal. Calcd. for $C_{18}H_{46}CoN_2O_2Si_2$ (437.67) C = 49.90 %, H = 10.59 %, N = 6.40 %. Found C = 49.77 %, H = 10.68 %, N = 6.51 %.

[Co(OSiEt$_3$)$_2$.TMEDA], 3: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.99 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.65 g / 5.0 mmol) in THF (20 mL) at -60 ^{o}C and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution with a KCl precipitate. To the stirred solution of [Co{N(SiMe$_3$)$_2$}$_2$] (40 mL) was added a

solution of triethylsilanol (1.11 g / 10.0 mmol) in THF (20 mL) and stirred for 30 minutes, followed by TMEDA (0.58 g / 0.75 mL / 5.0 mmol). The mixture was stirred for 4 hours giving a bright blue solution and the volatiles removed *in vacuo*. The residue was redissolved into hexane (30 mL) and filtered by cannula to remove KCl. Volatiles were removed *in vacuo* leaving a waxy blue residue. Yield: 72 %. m.p. not observed below 300 ^{o}C. Despite repeated attempts, an analytically pure microanalysis could not be obtained for this compound.

[Co(OSiPh$_3$)$_2$.TMEDA], 4: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.599 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.65 g / 5.0 mmol) in THF (20 mL) at -60 ^{o}C and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution with a KCl precipitate. To the stirred solution of [Co{N(SiMe$_3$)$_2$}$_2$] (40 mL) was added a solution of triphenylsilanol (2.76 g / 10.0 mmol) in THF (20 mL) and stirred for 30 minutes, followed by TMEDA (0.58 g / 0.75 mL / 5.0 mmol). The mixture was stirred for 4 hours giving a bright blue solution and the volatiles removed *in vacuo*. The residue was redissolved into toluene (30 mL) and filtered by cannula to remove KCl. Successive concentration, cooling and decantation of the solution afforded light blue block crystals in a high yield. Yield: 86 %. m.p. 207 ^{o}C. Anal. Calcd. for $C_{42}H_{46}CoN_2O_2Si_2$ (725.93) C = 69.49%, H = 6.39 %, N = 3.86 %. Found C = 69.40 %, H = 6.48 %, N = 4.01 %.

[Co{OSi(O^{t}Bu)$_3$}$_2$.TMEDA], 5: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.99 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.64 g / 5.0 mmol) in THF (20 mL) at -60 ^{o}C and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution with a KCl precipitate. To the stirred solution of [Co{N(SiMe$_3$)$_2$}$_2$] (40 mL) was added a solution of tris(*tert*-butoxy)silanol (2.64 g / 10.0 mmol) in THF (20 mL) and stirred for 30 minutes, followed by TMEDA (0.58 g / 0.75 mL / 5.0 mmol). The mixture was stirred for 4 hours giving a bright blue solution and the volatiles removed *in vacuo*. The residue was redissolved into hexane and filtered by cannula to remove KCl. Hexane was removed *in vacuo* and toluene (20 mL) added to dissolve the product. Successive concentration, cooling and decantation of the solution afforded bright blue block crystals in a high yield. Yield: 92%. m.p. 96 – 99 ^{o}C. Anal. Calcd. for $C_{30}H_{70}CoN_2O_8Si_2$ (701.99) C = 51.33 %, H = 10.05 %, N = 3.99 %. Found C = 51.29 %, H = 10.01 %, N = 3.96 %.

[Co{OSi(O^{t}Bu)$_3$}$_2$.2,2-bipy], 6: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.99 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.65 g / 5.0 mmol) in THF (20 mL) at -60 ^oC and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution with a KCl precipitate. To the stirred solution of [Co{N(SiMe$_3$)$_2$}$_2$] (40 mL) was added a solution of tris(*tert*-butoxy)silanol (2.64 g / 10. mmol) in THF (20 mL) and stirred for 30 minutes, followed by a solution of 2,2-bipyridine (0.78 g / 5.0 mmol) in toluene (10 mL). The solution was stirred for a further 30 minutes followed by removal of volatiles *in vacuo*. Solids were redissolved into toluene and the solution filtered by cannula to remove KCl. The dark green solution was reduced to ~5 mL and 25 mL of hexane was added to precipitate a fibrous, microcrystalline product in high yield, isolated by decantation. Large, X-ray quality crystals were produced by the slow cooling of a solution of the product (10 mL / 50:50, toluene:hexane) from ~60 ^oC to 0 ^oC. Yield: 93 %. m.p. 216 - 217 ^oC. Anal. Calcd. For $C_{34}H_{62}CoN_2O_8Si_2$ (741.97) C = 55.04 %, H = 8.42 %, N = 3.78 %. Found. C = 55.12 %, H = 8.53 %, N = 4.01 %.

[Co{OSi(O^{t}Bu)$_3$}$_2$.PMDETA], 7: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.99 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.65 g / 5.0 mmol) in THF (20 mL) at -60 ^oC and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution with a KCl precipitate. To the stirred solution of [Co{N(SiMe$_3$)$_2$}$_2$] (40 mL) was added a solution of tris(*tert*-butoxy)silanol (2.64 g / 10.0 mmol) in THF (20 mL) and stirred for 30 minutes, followed by PMDETA (1.04 mL / 0.87 g / 5.0 mmol). The mixture was stirred for 4 hours giving a bright purple solution and filtered by cannula to remove KCl. Successive concentration, cooling and decantation of the solution afforded dark purple needle-like crystals in a good yield. Yield: 80 %. m.p. 94 ^oC. Anal. Calcd. for $C_{33}H_{77}CoN_3O_8Si_2$ (759.08) C = 52.21 %, H = 10.22 %, N = 5.54 %. Found C = 52.12 %, H = 10.18 %, N = 5.49 %.

[Co{OSi(O^{t}Bu)$_3$}$_2$.2en], 8: [Co{N(SiMe$_3$)$_2$}$_2$] was synthesized *in situ* in a THF solution (40 mL) by the addition of a solution of KN(SiMe$_3$)$_2$ (1.99 g / 10.0 mmol) in THF (20 mL) to a stirring suspension of $CoCl_2$ (0.65 g / 5.0 mmol) in THF (20 mL) at -60 ^oC and allowed to warm to room temperature. Stirring was continued for 24 hrs to give a dark green solution

with a KCl precipitate. To the stirred solution of $[Co\{N(SiMe_3)_2\}_2]$ (40 mL) was added a solution of tris(*tert*-butoxy)silanol (2.64 g / 10.0 mmol) in THF (20 mL) and stirred for 30 minutes, followed by two equivalents of ethylenediamine (0.67 mL / 0.60 g / 10.0 mmol). The mixture was stirred for 4 hours giving a very pale pink solution and the volatiles removed *in vacuo*. The residue was redissolved into hexane and filtered by cannula to remove KCl. Hexane was removed *in vacuo* and toluene (20 mL) added to dissolve the product. Successive concentration, cooling and decantation of the solution afforded near-colorless needles in a good yield. Yield: 78 %. m.p. 135 ^{o}C. Anal. Calcd. for $C_{28}H_{70}CoN_4O_8Si_2$ (705.98) C = 47.64 %, H = 9.99 %, N = 7.94 %. Found. C = 47.58 %, H = 10.03 %, N = 8.12 %.

AACVD Experiments

Cobalt-silicon oxide films were prepared by aerosol-assisted CVD, (AACVD) in a cold-walled reactor (Electro Gas System Reactor). Glass microscope slides cut into 1/3s were chosen as substrates and prepared for deposition by the standardised cleaning procedure: substrates were sonicated in iso-propanol for 15 minutes, deionized water for 15 minutes and stored in fresh iso-propanol. Substrates were left to evaporate dry, ready for use. Substrates were placed on a heated graphite attenuator and heated to 400 ^{o}C under a 2 $Lmin^{-1}$ flow of N_2 to purge the reactor for 5 minutes. After purging, the substrate thermostat was adjusted to the desired deposition temperature and allowed to equilibrate. The N_2 flow rate was reduced to 0.3 $Lmin^{-1}$ and the precursor was introduced to the deposition chamber in a ultrasonically nebulized aerosol solution in toluene (12.5 gL^{-1}). All depositions were conducted for 25 minutes, starting when the vaporiser was activated. N_2 flow was maintained by an electronic mass-flow controller, and substrate temperature was measured and controlled by a platinum thermocouple positioned inside the graphite attenuator.

UV/Visible spectroscopy was performed using a Varian 50 Probe UV/Vis Spectrophotometer, in an "in-house-engineered" flat-plate mode. Spectra were measured at wavelengths from 900 – 300 nm, at a rate of 10 nm s^{-1}, and data was analysed using Varian Cary WnUV software. FTIR spectra were measured on a Perkin Elmer Spectrum 100, reflectance Fourier-transform infra-red spectrometer. SEM and EDS analysis was performed at Pilkington Labs by Mr Mike Baines. Specimens were prepared for examination in plan-view and cross section by mounting onto aluminium stubs. Loosely bound contamination was removed using a "Dust-Off" compressed gas aerosol. The cleaned specimens were coated with a thin layer of platinum (to provide a uniform conductive surface) and examined using a

scanning electron microscope (SEM) equipped with the energy dispersive spectroscopy (EDS) technique. X-ray Photoelectron Spectroscopy was performed at the National XPS service at Cardiff University by David Morgan. Samples were analysed as received (no cleaning procedures) on a Kratos Axis Ultra-DLD XPS system. All experimental data was analysed using CasaXPS software, developed by Neal Fairley.

Single-crystal X-ray Diffraction Analysis

Single-crystal X-ray diffraction analysis was performed at 150 K on a single-crystal FR590 Nonius Kappa CCD diffractometer, equipped with an Oxford Cryosystem, using graphite-monochromated Mo Kα radiation (λ =0.71073 Å). Data were processed using Nonius Software. Crystal parameters and details on data collection, solution and refinement of all the complexes are presented in supplementary data. Structure solution, followed by full-matrix least-squares refinement, was performed using the XSEED or WINGX-1.70 suite of programs. The structure of compound **1** was refined taking pseudo-merohedral twinning, 180.0 degree rotation about 100 direct lattice direction, into account. Additionally, the THF ligand and one siloxyl group connected to O3 were found to be disordered in the ratio 1:1. All disordred atoms were refined using bond lengths restraints and C13A C15 C17A were refined using ADP restraints. The A-Alert: 'Coordinates do not Form a Properly Connected Set' is consequence of the hydrogen atoms placed onto calculated positions for the THF ligand. The asymmetric unit of compound **6** contains one Co complex and one solvent molecule of toluene which has an occupation factor of 25% only. One t-Bu group attached to O2 shows rotational disorder in the ratio of 60:40 and the solvent molecule lies on a two-fold axis. In order to idealize bond lengths and angles the whole toluene molecule had to be constrained using the rigid group contraint AFIX 66. All solvent atoms have been refined isotropically with the same displacement parameters. The asymmetric unit of compound **8** contains two cobalt complexes and one solvent molecule of hexane. All -NH_2 hydrogen atoms have been located in the difference Fourier map and freely refined apart from N-H5C which has been restrained. The solvent molecule was refined using a split atom model for atoms C20-C60. The ratio of the disorder is 66:34. ADPs for atoms pairs of C20 C40 and C60 have been equalised.

Supplementary Information Available

CCDC 999835-999840 contain the supplementary crystallographic data for compounds **1**, **4**, **5**, **6**, **7** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Single-Source AACVD of Composite Cobalt-Silicon Oxide Thin Films

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Cobalt(II) siloxide complexes are employed as single-source precursors for the aerosol-assisted CVD of thin films with bulk compositions reflecting the cobalt, silicon and oxygen stoichiometry of the molecular precursor complex.