X-Ray crystal structures of copper(II) and cobalt(II) complexes with Schiff base ligands. Reactivity towards dioxygen

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Copper(II) and cobalt(II) Schiff base complexes with derivatives of the pentadentate ligand bis(salicylideneimino-3-propyl)amine [H₂salDPT] have been prepared. The X-ray crystal structures of the copper(II) complexes Cu[salDPT] and Cu[sal(n-propyltrimethylsilyl)DPT] were determined and revealed five-coordination at the metal centre in both cases. The 1 : 1 dioxygen adduct of Co[sal(n-propyltrimethylsilyl)DPT] was also isolated and its X-ray molecular structure determined.

Introduction

Cobalt(II) Schiff base complexes have been known for a long time to undergo reversible coordination of the dioxygen ligand in solution.[1] However, these complexes suffer like other dioxygen carriers in solution from oxidative degradation.[2] Therefore, the heterogenisation of dioxygen reactive carriers was one of the strategies that has been investigated to overcome these problems. Among the various kinds of solid supports, a silica matrix was considered for the immobilization of Schiff base derivatives.[3–7] This was achieved through the formation of a covalent bond between a chloro propyl group grafted onto a MCM-41 silica and the amino group of a pentadentate ligand[3,6] or through coordinate bond formation between the metal centre of the Schiff base complex and a ligand covalently bonded to the silica matrix.[5,7] Both routes present some drawbacks. The anchorage of the pentadentate ligand by the first route was poor. In the second route the attachment of the Schiff base complexes *via* a coordinate bond can give rise to leaching.

A very simple way to obtain a Co(II) Schiff base complex supported on silica could consist in the grafting of the Co[sal-(n-propyltrimethoxysilyl)DPT] complex **2a[Co]** (Scheme 1). Such a complex can be easily prepared by substitution of the amino group of the pentadentate ligand bis(salicylideneimino-3-propyl)amine [H₂salDPT] by the propyltrimethoxysilyl group.

Since it was observed that a five-coordinate Schiff base ligand is necessary for binding dioxygen,[8–14] it was of importance to know if the substitution of the amino group still allowed the coordination of the nitrogen donor atom on the metal centre in **2a[M]**. It is worth noting that only a few single crystal X-ray analyses of pentadentate Schiff base complexes have been reported in the literature[9–12] whereas the study of compounds capable of reversibly binding dioxygen has attracted much interest. This is probably due to the instability of such compounds and the difficulties in getting crystals suitable for X-ray structure determination.

In this paper, we describe and compare the X-ray structures of the copper(II) complexes with pentadentate Schiff base **1[Cu]** and **2b[Cu]** (Scheme 1) with the aim of pointing out the influence of the substitution of the amino group on the metal centre
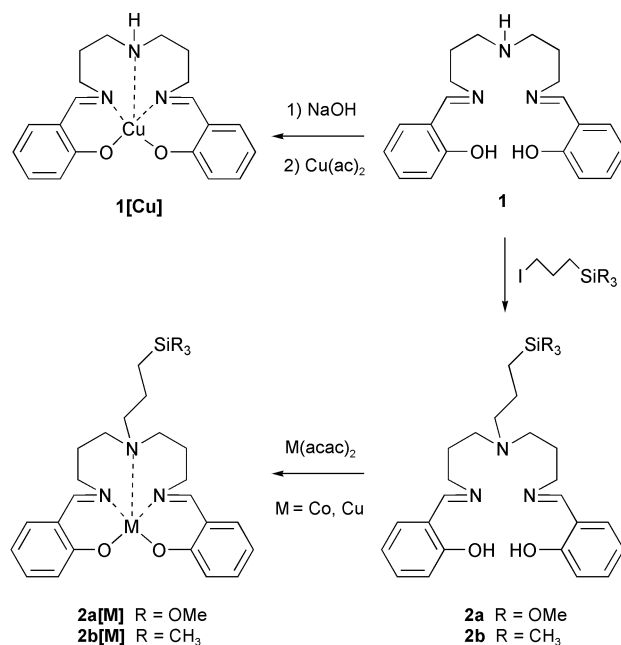
Scheme 1

coordination in the complex **2b[Cu]**. The X-ray molecular structure of **2b[Co]O₂** was also determined and revealed the formation of a 1 : 1 dioxygen adduct, showing thus that tertiary nitrogen in the pentadentate ligand does not prevent dioxygen binding to **2b[Co]**.

Results and discussion

Bond lengths and angles from the crystal structure determinations can be found in Table 1, whereas the details of the determinations themselves are given in Table 2.

Synthesis and X-ray structure of 1[Cu]

The pentadentate Schiff base bis(salicylidenimino-3-propyl)-amine [H₂salDPT] **1**[15] was obtained by condensation of

Table 1 Selected interatomic distances (Å) and bond angles (°) for **1[Cu]**, **2b[Cu]**, and **2b[Co]O$_2$**, M refers to the cation. τ is the trigonality index (see text)

	1[Cu]	2b[Cu]	2b[Co]O$_2$		1[Cu]	2b[Cu]	2b[Co]O$_2$
M–O(1)	1.968(5)	1.945(4)	1.902(6)	N(2)–M–N(1)	179.0(3)	174.3(2)	176.7(7)
M–O(2)	1.970(5)	1.960(3)	1.937(5)	O(2)–M–O(1)	148.2(2)	143.8(2)	175.2(8)
M–N(1)	1.961(5)	1.951(4)	1.853(5)	τ	0.513	0.508	0.025
M–N(2)	1.959(5)	1.966(4)	1.894(7)	N(2)–M–O(1)	89.4(2)	91.6(2)	90.1(9)
M–N(3)	2.253(5)	2.374(3)	2.119(8)	N(1)–M–N(3)	90.8(3)	86.7(2)	87.7(9)
M–O(34)			1.956(7)	N(2)–M–N(3)	89.2(2)	87.7(2)	89.8(8)
O(34)–O(35)			1.201(7)	O(36)–O(34)–O(35)			120(1)
O(34)–O(36)			1.142(5)	N(3)–Co–O(34)			178.7(9)
				N(2)–Co–O(34)			91.1(9)

bis(aminopropyl)amine with 2 equivalents of 2-hydroxy-benzaldehyde in 98% yield. The copper(II) complex of the bis-(salicylidenimino-3-propyl)amine named **1[Cu]** was prepared according to the method described by Calvin and co-workers [16] (Scheme 1). **1[Cu]** was purified by recrystallization in hot toluene from which crystals suitable for X-ray structure analysis were grown. The unit cell corresponds to one **1[Cu]** and one solvent molecule (toluene). The ORTEP drawing of **1[Cu]** without solvent is displayed in Fig. 1.
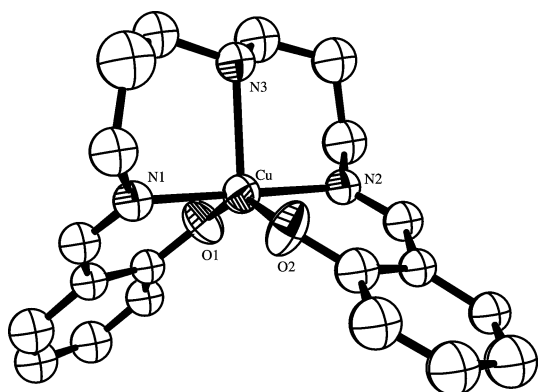
Fig. 1 ORTEP [23]-plot of **1[Cu]** without solvent molecule.

The structure of **1[Cu]** clearly shows that the metal centre of this complex is five-coordinate. The three nitrogen and the two oxygen atoms of the pentadentate ligand are arranged in a distorted trigonal bipyramidal environment. They coordinate the copper atom with N(2)–Cu–O(1), N(1)–Cu–N(3) and N(2)–Cu–N(3) angles of 89.4, 90.8 and 89.2°, respectively. The two imino groups are in apical positions with a N(1)–Cu–N(2) angle of 179.0(3)°. The main deviations from a regular trigonal bipyramid are in the equatorial angles O(2)–Cu–O(1), N(3)–Cu–O(1) and N(3)–Cu–O(2), which are respectively 148.2, 105.4 and 106.4°. The amino group is coordinated to the copper atom with a N(3)–Cu bond length of 2.253 Å. The remaining four bond lengths around the metal centre are shorter (Cu–O(1) 1.968, Cu–O(2) 1.970, Cu–N(1) 1.961 and Cu–N(2) 1.959 Å).

Synthesis and characterization of 2b[Cu] and 2b[Co]

The N-substituted Schiff base **2a** bearing the hydrolysable trimethoxysilyl group was prepared by treating **1** with an MeCN solution containing one equivalent of 3-iodopropyl-trimethoxylsilane in 98% yield (Scheme 1). Subsequent complexation was achieved by an exchange reaction in MeOH between **2a** and a stoichiometric amount of Cu(acac)$_2$ to yield **2a[Cu]** in 96% yield. **2a[Co]** was prepared in exactly the same way using Co(acac)$_2$. It is worth mentioning that the compound **2a[Cu]** could not be obtained by treatment of **1[Cu]** with 3-iodopropyl-trimethoxylsilane. This result is in agreement with the X-ray structure analysis of **1[Cu]**, which revealed that the amino group is coordinated to the metal centre, rendering nucleophilic substitution impossible. All attempts to get crystals from **2a[Cu]** and **2a[Co]** failed, due to their high solubility in common solvents. Therefore, we prepared **2b** by reaction of **1** with 3-iodopropyl-trimethylsilane.[17] **2b** was characterized by elemental analysis, NMR and mass spectroscopy (see Experimental section). **2b[Cu]** and **2b[Co]** were then obtained in almost quantitative yield by reaction of **2b** with respectively Cu(acac)$_2$ and Co(acac)$_2$. Crystals of **2b[Cu]** suitable for X-ray structure analysis were grown from pyridine solution.

Crystal structure of 2b[Cu]

The ORTEP diagram for **2b[Cu]** is shown in Fig. 2. The coordination geometry around the cobalt atom is essentially identical to that found in the structure of **1[Cu]**. The metal centre is also penta-coordinated: the three nitrogen and the two oxygen atoms of the pentadentate ligand are arranged in a distorted trigonal bipyramidal environment, as for **1[Cu]**, the two imino groups also being in apical positions with N(2)–Cu–O(1), N(1)–Cu–N(3) and N(2)–Cu–N(3) angles being respectively 91.6, 86.7 and 87.7°. The main deviations from a regular trigonal bipyramid are in the same range as for **1[Cu]**, the equatorial angles O(1)–Cu–O(2), O(1)–Cu–N(3) and O(2)–Cu–N(3) being 143.8, 105.0 and 111.2°, respectively. The Cu coordination for this structure could also be described as distorted square pyramidal. It is worth noting that the bond length between metal centre and the tertiary amino group [Cu–N(3) = 2.374 Å] is a little longer than the corresponding bond length between the metal centre and the secondary amino group in **1[Cu]** [Cu–N(3) = 2.253 Å]. Thus, in spite of the substitution, the nitrogen atom of the tertiary amino group remains in the coordination sphere of the metal centre.
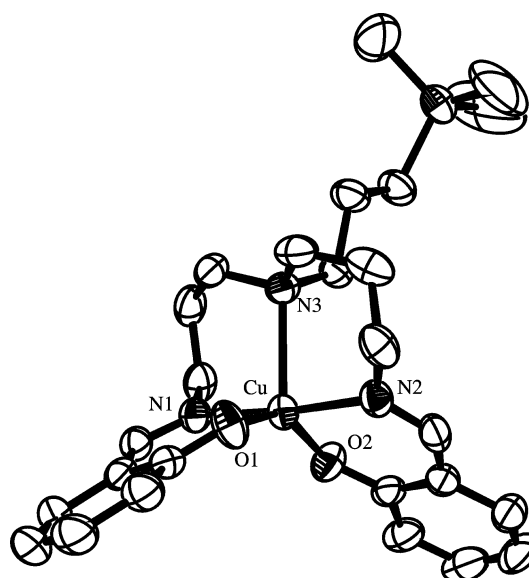
Fig. 2 ORTEP-plot of **2b[Cu]**.

Crystal structure of 2b[Co]O$_2$

2b[Co] was recrystallized from hot benzonitrile giving brown dark crystals suitable for X-ray analysis. The ORTEP diagram

for **2b[Co]O$_2$** is shown in Fig. 3. The molecular structure of **2b[Co]O$_2$** revealed the formation of a 1 : 1 dioxygen adduct of **2b[Co]** during the recrystallization in air as the complexation of **2b** was done under argon. The coordination geometry around the cobalt atom can be described in terms of an octahedron in which five coordinating positions are occupied by the three nitrogen atoms and the two oxygen atoms as for **2b[Cu]**, and the sixth position opposed to the tertiary amino group (N(3)–Co–O(34) 178.8°), is occupied by a dioxygen molecule, bound in a bent end-on fashion. The dioxygen molecule shows a twofold statistical disorder (see Crystallography section), the O(34)–O(35)–O(36) plane almost bisecting the angles N(1)–Co–O(1) and N(2)–Co–O(2). The dioxygen O(34)–O(35) distance [average 1.20 Å] is in the same range as in the dioxygen molecule (1.216 Å). This structure is very similar to that of [N,N′-(3,3′-dipropylmethylaminebis(salicylideneamin-ato)]cobalt(II) in which the amino group is substituted by a methyl group.[10] Indeed, in this last complex, the bond length between the cobalt and the nitrogen atom of the tertiary amino group is 2.09 Å[10] while it is 2.119 Å for **2b[Co]O$_2$** [Co–N(3) = 2.119 Å]. The structure of **2b[Co]O$_2$** can also be compared to that of Co(bzacen)(pyridine)O$_2$ (bzacen = N,N′-ethylene-bis(benzoylacetoniminide)) in which the coordination about cobalt is also approximately octahedral.[11] Indeed, the bond length beween Co and the nitrogen of the pyridine is 2.02 Å and the O–O distance is 1.26 Å which is close to the value observed in **2b[Co]O$_2$**.
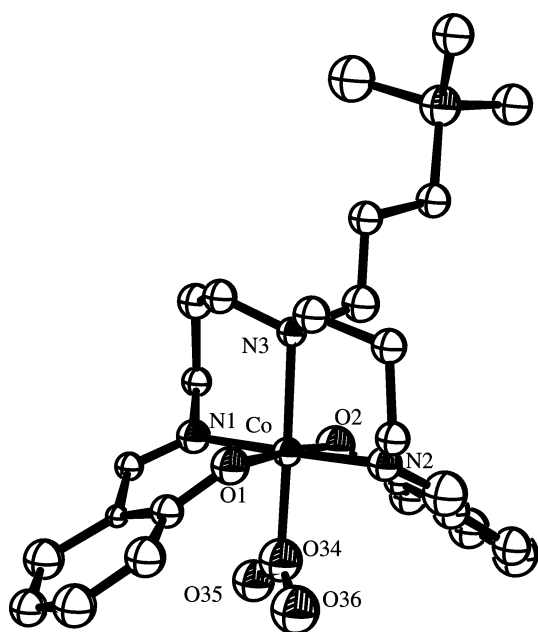

Fig. 3 ORTEP-plot of **2b[Co]O$_2$**.

Comparison of the crystal structures of 1[Cu], 2b[Cu], and 2b[Co]O$_2$

An angular structural parameter, τ, can be defined that serves as an index of trigonality.[18] It is defined as the ratio of the difference of the two basal angles N(1)–M–N(2) and O(1)–M–O(2) and 60. For pure square-pyramidal geometry τ is 0, whereas τ is 1 for an ideal trigonal-bipyramidal geometry. The two structures **1[Cu]** and **2b[Cu]** compare well: they have τ parameters equal to 0.513 and 0.508, respectively (Table 1). The τ parameter of **2b[Co]O$_2$**, without taking into account the dioxygen adduct, approaches 0, indicating that the angular geometry is close to square-pyramidal. The real coordination is, however, octahedral, due to the presence of O(34). Intermolecular hydrogen bonding in the structures of **1[Cu]** and **2b[Cu]** is very weak. The data for **2b[Co]O$_2$** are not of sufficient quality to assess the intermolecular bonding inter-actions.

Conclusion

In conclusion, we have shown that the complex Cu[sal-(n-propyl-trimethylsilyl)DPT] **2b[Cu]** is penta-coordinated. We have isolated crystals suitable for X-ray analysis of a dioxygen adduct of Co[sal(n-propyl-trimethylsilyl)DPT], **2b[Co]O$_2$**, formed during the recrystallisation in air of **2b[Co]**. This proves the great affinity of **2b[Co]** for dioxygen. This complex can be formally described as a Co^{III} superoxo complex. This suggests that grafting of the corresponding complex Co[sal(n-propyltrimethoxysilyl)DPT] **2a[Co]** onto a silica matrix deserves to be investigated and could be a good candidate for dioxygen binding.

Experimental

All manipulations were carried out with standard high-vacuum and Schlenk techniques. Solvents were dried and distilled just before use. 2-Hydroxybenzaldehyde, 3,3′-diaminodipropyl-amine, Cu(acac)$_2$ and Co(acac)$_2$ were purchased from Acros organics. IR data were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer. Melting points (mp) were measured with a Buchi B-540 apparatus and are uncorrected. The solution NMR spectra were recorded on a Bruker AC-200 (^{29}Si), Bruker DPX-200 (^{1}H and ^{13}C). Chemical shifts (δ, ppm) were refer-enced to Me$_4$Si (^{1}H, ^{13}C, ^{29}Si). The abbreviations used are s for singlet, d for doublet, dd for double doublet, t for triplet, q for quartet, sept for septet and m for multiplet. FAB mass spectra [matrix, m-nitrobenzyl alcohol (NBA)] were recorded on a JEOL JMS-D3000 spectrometer. Elemental analyses were carried out by the Service Central de Micro-Analyse du CNRS, Lyon.

Synthesis

2a. A mixture of **1** (20.0 g, 59 mmol), K$_2$CO$_3$ (16.2 g, 118 mmol) and 3-iodopropyl-trimethoxysilane (17.1 g, 59 mmol) in MeCN (80 mL) was heated under reflux for 22 hours under an argon atmosphere. The solvent was removed in vacuo and 100 mL of pentane were added to precipitate the salts. The precipitate was filtered off and washed with pentane (2 × 30 mL). Evaporation of pentane gave 29.0 g (58 mmol, 98%) of **2a** as an orange oil. ^{1}H NMR (δ, 200 MHz, CDCl$_3$) 0.62 (m, 2H, CH$_2$Si), 1.54 (m, 2H, CH$_2$), 1.79 (m, 4H, CH$_2$), 2.46 (m, 6H, CH$_2$N), 3.54 (m, 4H, CH$_2$N=; 9H, MeO), 6.78–7.30 (m, 8H, Ar + 2OH), 8.29 (s, 2H, Ar). ^{13}C NMR (δ, 50 MHz, CDCl$_3$) 7.1, 20.6, 29.0, 50.9, 51.8, 57.3, 57.8, 117.3, 118.8, 119.2, 131.6, 132.4, 161.7, 165.3. ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −41.4 (s). ^{15}N NMR (δ, 40 MHz, CDCl$_3$) −82.7 (s, imines), -343.2 (s, amine). MS (FAB+, NBA): m/z = 502 [(M + H)$^+$, 25], 367 [(M − (CH$_2$Si(OMe)$_3$)$^+$, 13], 121[(Si(OMe)$_3$)$^+$, 100]. IR (cm^{-1}, CCl$_4$): 3052 (ν C$_{sp2}$–H); 2940–2839 (ν C$_{sp3}$–H); 1633 (ν C=N); 1582 (ν C=C); 1150–1050 (ν Si–OMe); 757 (δ C$_{sp2}$–H). Anal. calcd. for C$_{26}$H$_{39}$N$_3$O$_5$Si: C, 62.25; H, 7.83; N, 8.38; Si, 5.60. Found: C, 62.13; H, 7.82; N, 8.66; Si, 6.35%.

2a[Cu]. To a solution of **2a** (15.9 g, 32.0 mmol) in MeOH (40 mL) was added dropwise a hot solution of Cu(acac)$_2$ (8.3 g, 32.0 mmol) in MeOH (300 mL). The green mixture was heated under reflux for 2 hours. The solvent was removed in vacuo and 500 mL of THF were added. After one hour of stirring the complex precipitated. The precipitate was then filtered off and washed with pentane to give 17.3 g (30.7 mmol, 96%) of **2a[Cu]** as a green powder; mp = 213 °C (decomp.). MS (FAB+, NBA): m/z = 563 [(M + H)$^+$, 100], 441 [(M − (Si(OMe)$_3$))$^+$, 17], 401 [(M − ((CH$_2$)$_3$Si(OMe)$_3$)$^+$, 13], 121 [(Si(OMe)$_3$)$^+$, 42]. IR (cm^{-1}, KBr): 3080 (ν C$_{sp2}$–H); 2938–2836 (ν C$_{sp3}$–H); 1632 (ν C=N); 1599 (ν C=C); 1150–1080 (ν Si–OMe); 756 (δ C$_{sp2}$–H). Anal. calcd. for C$_{26}$H$_{37}$N$_3$O$_5$SiCu: C, 55.45; H, 6.62; N, 7.46; Si, 4.99; Cu, 11.28. Found: C, 55.94; H, 6.66; N, 6.82; Si, 5.30; Cu, 10.60%.

	1[Cu]	**2b[Cu]**	**2b[Co]O₂**
Formula	$C_{27}H_{31}CuN_3O_2$	$C_{26}H_{37}CuN_3O_2Si$	$C_{26}H_{37}CoN_3O_4Si$
M	493.10	515.23	542.62
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2cb$ (no. 32)	$I2/a$ (no. 15)
$a/\text{Å}$	10.895(2)	6.881(1)	13.137(3)
$b/\text{Å}$	16.911(2)	13.389(3)	15.949(5)
$c/\text{Å}$	13.142(4)	30.349(4)	58.548(8)
$\alpha/°$	90	90	90
$\beta/°$	90.94(2)	90	92.79(2)
$\gamma/°$	90	90	90
$U/\text{Å}^3$	2421.0(9)	2796.0(8)	12253(1)
Z	4	4	16
μ/mm^{-1}	0.931	0.849	0.626
T/K	295	295	295
Total reflections	4065	10515	21365
Independent reflections	3861	4948	10788
Reflections with $I>2\sigma(I)$	971	3494	3944
$R1^a$, $wR2^a$	0.2894, 0.1055	0.0606, 0.0897	
$R1^b$, $wR2^b$	0.0518, 0.0839	0.0380, 0.0761	0.01722, 0.01830

[a] Refinements were performed on all reflections (F^2) by minimizing $wR2$, except for **2b[Co]O₂**. [b] Conventional R-factors $R1$ and $wR2$ calculated with only 'observed' reflections are given for comparison.

2a[Co]. To a solution of **2a** (4.15 g, 8.27 mmol) in MeOH (10 mL) was added dropwise a hot solution of Co(acac)₂ (2.13 g, 8.27 mmol) in MeOH (100 mL). The brown mixture was heated under reflux for one night. The solvent was removed *in vacuo* and 200 mL of pentane were added. The precipitate was then filtered off and washed with pentane to give 4.40 g (7.94 mmol, 96%) of **2a[Co]** as a brown powder; mp = 166 °C (decomp.). MS (FAB+, NBA): $m/z = 558$ [(M + H)⁺, 100], 396 [(M + H)⁺ − ((CH₂)₃Si(OMe)₃), 18], 121 [(Si(OMe)₃)⁺, 22]. IR (cm⁻¹, KBr): 3080–3020 (ν C$_{sp2}$–H); 2932–2834 (ν C$_{sp3}$–H); 1632 (ν C=N); 1594 (ν C=C); 1150–1081 (ν Si–OMe); 756 (δ C$_{sp2}$–H). Anal. calcd. for $C_{26}H_{37}N_3O_5SiCo$: C, 55.90; H, 6.67; N, 7.52; Si, 5.03; Co, 10.55. Found: C, 55.47; H, 6.51; N, 6.65; Si, 4.90; Co, 8.95%.

2b. A mixture of **1** (6.0 g, 17.0 mmol), K₂CO₃ (4.90 g, 35 mmol) and 3-iodopropyl-trimethylsilane (4.3 g, 17.0 mmol) in MeCN (40 mL) was heated under reflux for 8 hours. The solvent was removed *in vacuo* and 50 mL of pentane were added to precipitate the salts. The precipitate was filtered off and washed with pentane (2 × 30 mL). Evaporation of pentane gave 7.5 g (16.5 mmol, 97%) of **2b** as a yellow oil. ¹H NMR (δ, 200 MHz, CDCl₃) 0.02 (s, 9H, SiMe₃); 0.51 (m, 2H, CH₂Si); 1.49 (m, 2H, CH₂); 1.85 (m, 4H, CH₂); 2.50 (m, 6H, CH₂N); 3.64 (m, 4H, CH₂N=); 6.88–7.32 (m, 8H, Ar + 2OH); 8.37 (s, 2H, Ar). ¹³C NMR (δ, 50 MHz, CDCl₃) 0.01; 14.72; 22.02; 28.97; 51.92; 57.76; 57.87; 117.28; 119.22; 119.49; 131.53; 132.45; 161.74; 165.26. ²⁹Si NMR (δ, 40 MHz, CDCl₃) 1.77 (s). MS (FAB+, NBA): $m/z = 454$ [(M + H⁺), 5]; 73 [(SiMe₃)⁺, 100]. IR (cm⁻¹, oil): 3063–3008 (ν C$_{sp2}$–H); 2954–2812 (ν C$_{sp3}$–H); 1632 (ν C=N); 1583 (ν C=C); 837 (ν Si–Me); 755 (δ C$_{sp2}$–H). Anal. calcd. for $C_{26}H_{39}N_3O_2Si$: C, 68.83; H, 8.66; N, 9.26; Si, 6.19. Found: C, 67.68; H, 8.43; N, 9.39; Si, 7.20%.

2b[Cu]. To a solution of **2b** (3.23 g, 7.1 mmol) in MeOH (10 mL) was added a hot solution of Cu(acac)₂ (1.86 g, 7.1 mmol) in MeOH (150 mL). The mixture was heated under reflux for 3 hours. The solvent was removed *in vacuo* and 150 mL of pentane were added to precipitate the complex. The precipitate was then filtered off and recrystallized from pyridine to give 3.31 g (6.4 mmol, 90%) of **2b[Cu]** as green crystals; mp = 158–160 °C. MS (FAB+, NBA): $m/z = 515$ [(M + H)⁺, 68]; 73 [(SiMe₃)⁺, 100]. IR (cm⁻¹, KBr): 3074–3020 (ν C$_{sp2}$–H); 2942–2867 (ν C$_{sp3}$–H); 1632 (ν C=N); 1600 (ν C=C); 842 (ν Si–Me); 755 (δ C$_{sp2}$–H). Anal. calcd. for $C_{26}H_{37}O_2N_3SiCu$: C, 60.61; H,

7.24; N, 8.15; Si, 5.45; Cu, 12.33. Found: C, 60.60; H, 6.87; N, 8.07; Si, 5.12; Cu, 11.76%.

2b[Co]. This synthesis was carried out with dry-argon techniques. To a solution of **2b** (2.70 g, 6.06 mmol) in MeOH (10 mL) was added dropwise a hot solution of Co(acac)₂ (1.56 g, 6.06 mmol) in MeOH (40 mL). The mixture was heated under reflux for 4 hours. The solvent was removed *in vacuo* and 150 mL of pentane were added to precipitate the complex. The brown precipitate was then filtered off and recrystallized from benzonitrile to give 2.78 g (5.4 mmol, 90%) of **2b[Co]O₂** as brown dark crystals; mp = 124.3–124.7 °C. MS (FAB+, NBA): $m/z = 511$ [(M + H)⁺, 20]; 73 [(SiMe₃)⁺, 100]. IR (cm⁻¹, KBr): 3080–3020 (ν C$_{sp2}$–H); 2954–2878 (ν C$_{sp3}$–H); 1632 (ν C=N); 1594 (ν C=C); 842 (ν Si–Me); 755 (δ C$_{sp2}$–H). Anal. calcd. for $C_{26}H_{37}O_2N_3SiCo\cdot O_2$: C, 57.55; H, 6.87; N, 7.74; Si, 5.18; Co, 10.86. Found: C, 57.65; H, 6.78; N, 7.85; Si, 5.35; Co, 10.58%.

Crystallography

The details of the X-ray structure determinations are given in Table 2. The diffraction data for **1[Cu]** and **2b[Cu]** were collected on an Enraf-Nonius CAD4 and a Siemens P3 diffractometer, respectively, both in the θ–2θ mode with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS 86[19] and SIR92[20] for **1[Cu]** and **2b[Cu]**, respectively), and refined using SHELXL 93[21] and CRYSTALS[22] for **1[Cu]** and **2b[Cu]** respectively. Hydrogens atoms were located from difference Fourier maps but not refined. Data for different crystals of **2b[Co]O₂** were collected as well on the Siemens P3 diffractometer, but appeared to be each time of poor quality. Direct methods from SIR92[19] gave for each data set however one well defined molecule, which is shown in Fig. 3, and two similar molecules approximately related by a local inversion centre at (0,1/4,0) and with equal occupation probablities of 0.5. The refinement of the well-defined molecule proceeded smoothly, including the disordered dioxygen group (O(34)–O(35)–O(36) with occupation probablities of O(35) and O(36) equal to 0.50), but the refinement of the two molecules related by the local inversion centre appeared to be impossible even after applying heavy constraints and restraints, the R agreement factor being stuck at about 20%. Thus although the inter-molecular arrangement could only be approximately determined, the intra-molecular arrangement was easily found.

CCDC reference numbers 207478 (for **1[Cu]**), 207479 (for **2b[Cu]**) and 213845 (for **2b[Co]O₂**).

See http://www.rsc.org/suppdata/dt/b3/b304032a/ for crystallographic data in CIF or other electronic format.

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