Assembly of Dicobalt(III) Complexes Incorporating Di-μ-thiophenolate Moieties

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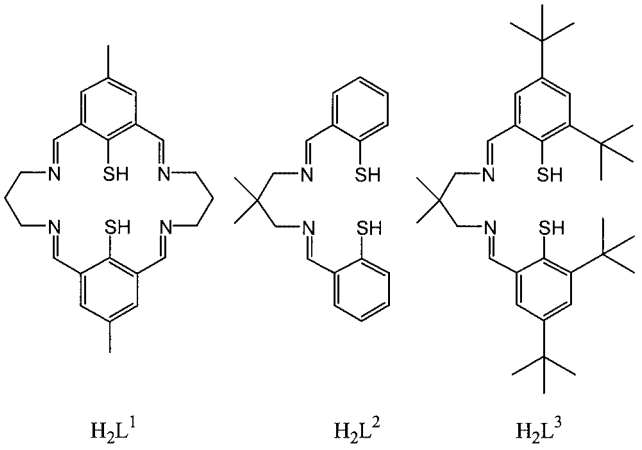
The dinuclear $[Co^{III}Co^{III}]$ complexes $[Co_2(L^1)(\mu\text{-OAc})(OAc)(NH_3)](PF_6)_2$ and $[(Co_2(L^2)_2(\mu\text{-OAc})](PF_6)$, incorporating the rare $Co(\mu\text{-SR})_2Co$ moiety associated with Schiff-base co-ligands, are protected by bridging μ-OAc^- units situated within a domed cavity formed by the complexes; increasing the steric bulk of the ligand, as in $[L^3]^{2-}$, affords the mononuclear species $[Co(L^3)(OAc)]$.

Homo- and heterodimetallic complexes occur in a number of metalloenzymes, and increasing efforts have been directed towards the synthesis of compartmental macrocycles capable of mimicking their structural, spectroscopic and chemical properties.[1] Compartmental macrocyclic ligands derived from 2,6-dicarbonylphenols offer a stable framework for binding two metal cations in close proximity via a bridging phenolate, and may also be designed to incorporate unsymmetrical compartments and coordinating pendant groups.[1,2] We[3,4] and others[5,6] have developed synthetic strategies to thiophenolate macrocyclic analogues that stabilise the dinuclear dithiolate fragment within the macrocyclic core. The incorporation, however, of highly redox-active $Co^{II/III}$ centres into such coordination frameworks remains relatively rare.[7] We describe herein for the first time the synthesis and characterisation of two di-μ-thiolato dimetallic Co^{III} complexes, $[Co_2(L^1)(\mu\text{-OAc})(OAc)(NH_3)](PF_6)_2$ and $[Co_2(L^2)_2(\mu\text{-OAc})](PF_6)$, incorporating the macrocyclic ($[L^1]^{2-}$) and corresponding open-chain ($[L^2]^{2-}$) ligands, respectively. Interestingly and significantly, both complexes show novel coordination modes with very similar core structures at the metal centres. The complexes incorporate a pyramidal stereochemistry at the bridging thiolate donors, with the nonplanar, domed conformation of the ligand set affording a hydrophobic pocket for OAc^- binding.

Template reactions of Co^{II} and Co^{III} salts with 2,6-diformyl-4-methylthiophenol and 1,3-diaminopropane under a range of conditions generally do not afford the metal complexes in a pure, tractable form. Higher yields of up to 60% can be obtained, however, by transmetallation reactions of the analogous Zn^{II} complex. Thus, reaction of $[Zn_2(L^1)(OAc)](PF_6)$[3] with $Co(OAc)_2{\cdot}4H_2O$ in MeCN in the presence of NH_4PF_6 under aerobic conditions affords a red diamagnetic solid that precipitates from the reaction mixture. The IR spectrum of this product confirms the presence of both PF_6^- and OAc^- anions, with absorptions at 3353 and 3302 cm^{-1} indicating the presence of ammonia in the product. A broad signal (δ = 3.3−3.6 ppm), which exchanges with D_2O, in the ^1H NMR spectrum (CD_3CN) further supports the presence of coordinated NH_3. As the integral of this signal accounts for only one molecule of ammonia per macrocycle, the coordination at the two Co^{III} ions is, therefore, expected to be different. This hypothesis is supported by both ^1H and ^{13}C NMR spectroscopy, each of which shows two signals for the C(H)=N groups, at δ =



Scheme 1

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8.22 and 8.28 ppm and at δ = 168 and 171 ppm, respectively. Asymmetry is also observed for the $N-CH_2$ groups of the macrocyclic ligand. The ^1H NMR spectrum also confirms the presence of two nonequivalent acetate anions, with signals at δ = 0.77 and 2.03 ppm. The chemical shift for the former appears rather low, but such upfield shielding can occur when an acetate ion is located close to an aromatic ring current, as in calixarenes that bind guest molecules within a hydrophobic pocket.[8] Therefore, we interpret the upfield shift for the OAc^- signal as a strong indication that it is located within the macrocyclic hydrophobic pocket.

The solid-state structure of $[Co_2(L^1)(\mu\text{-OAc})(OAc)(NH_3)](PF_6)_2$ is entirely consistent with the structure proposed in solution. The molecular structure (Figure 1) shows two octahedral Co^{III} centres, each bound to the N_2S_2 donor set provided by the macrocyclic ligand and to a bridging acetate ion. The coordination sphere of one Co^{III} centre is completed by a monodentate acetate ion while the remaining site on the other centre is occupied by an NH_3 molecule. The macrocyclic ligand adopts a folded conformation, with the bridging acetate ion located within the cleft of the macrocycle. Because of its domed shape, the cleft can be de-

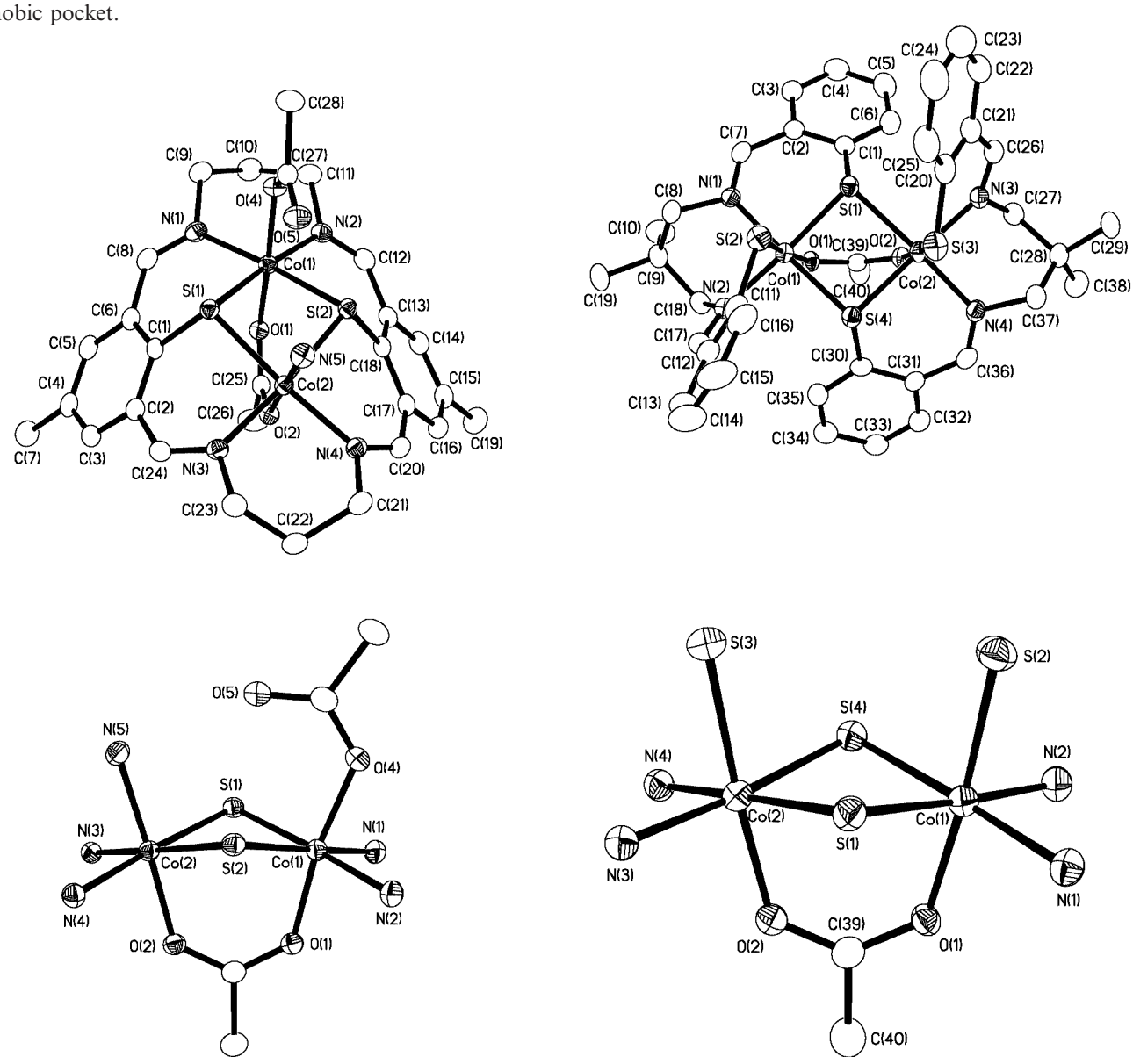

Figure 1. Two views of the structure of $[Co_2(L^1)(\mu\text{-OAc})(OAc)(NH_3)]^{2+}$ with displacement ellipsoids drawn at 50% probability: (top) a general view showing the atom numbering scheme; hydrogen atoms and PF_6^- anions are omitted for clarity; (bottom) a view of the metal coordination sphere; Co(1)···Co(2) 3.1750(5), Co(1)−O(1) 1.9181(16), Co(1)−O(4) 1.8968(17); Co(1)−N(1) 1.976(2), Co(1)−N(2) 1.975(2), Co(1)−S(1) 2.2239(6), Co(1)−S(2) 2.2216(6), Co(2)−O(2) 1.9202(16), Co(2)−N(5) 1.961(2), Co(2)−N(3) 1.975(2), Co(2)−N(4) 1.9792(19), Co(2)−S(1) 2.2399(6), Co(2)−S(2) 2.2416(6) Å

Figure 2. Two views of the structure of $[(Co_2(L^2)_2(\mu\text{-OAc})]^+$ cation with displacement ellipsoids drawn at 50% probability: (top) a general view showing the atom numbering scheme; hydrogen atoms and PF_6^- anions are omitted for clarity; (bottom) a view of the metal coordination sphere; Co(1)···Co(2) 3.2074(8), Co(1)−O(1) 1.967(3), Co(1)−N(1) 1.974(3), Co(1)−N(2) 1.974(3), Co(1)−S(1) 2.2306(11), Co(1)−S(2) 2.2284(12), Co(1)−S(4) 2.2806(11), Co(2)−N(3) 1.958(3), Co(2)−N(4) 1.969(3), Co(2)−O(2) 1.986(3), Co(2)−S(3) 2.2267(12), Co(2)−S(4) 2.2501(11), Co(2)−S(1) 2.2666(11) Å

scribed by two dihedral angles, one between the two aromatic rings (97°), the other between the N_2S_2 planes (144)° (Figure 1). Cyclic voltammetry of $[Co_2L(\mu\text{-}OAc)(OAc)(NH_3)](PF_6)_2$ displays two reversible one-electron reductions (confirmed by coulometry) in MeCN (0.3 M $^nBu_4NPF_6$, C electrode, 293 K) at $E_{1/2} = -0.76$ and -0.96 V vs. Fc^+/Fc, assigned to the formation of $[Co^{III}Co^{II}]$ and $[Co^{II}Co^{II}]$ species, respectively.

Transmetallation of $[Zn(L^2)]$ with $Co(OAc)_2{\cdot}4H_2O$ in the presence of NH_4PF_6 affords a Co^{III} complex, the IR spectrum of which confirms the presence of both PF_6^- and OAc^- anions. ^1H NMR spectroscopy in CD_3CN indicates asymmetry in the complex and shows two signals for the C(H)=N groups at δ = 8.23 and 7.74 ppm, as well as two signals for the methyl groups at δ = 1.16 and 1.07 ppm. The signal belonging to the OAc^- anion can be observed at δ = 1.10 ppm and, as previously noted for $[Co_2L(\mu\text{-}OAc)(OAc)(NH_3)](PF_6)_2$, this upfield shift suggests the anion is exposed to an aromatic ring current.

The single-crystal X-ray structure of $[Co_2(L^2)_2(\mu\text{-}OAc)]PF_6$ (Figure 2) is in agreement with the spectroscopic data observed in solution, suggesting that the dinuclear structure is stable in solution, even in coordinating solvents such as MeCN. Although both metal ions exhibit the same coordination environment, the *cis* configuration adopted by the tetradentate ligand accounts for the various signals observed in the ^1H NMR spectrum. The overall structures of $[Co_2(L^2)_2(\mu\text{-}OAc)]PF_6$ and $[Co_2(L^1)(\mu\text{-}OAc)(OAc)(NH_3)](PF_6)_2$ are similar. The angle of the cleft defined by the aromatic rings is only 1° wider in the former and the N_2S_2 planes in $[Co_2(L^2)_2(\mu\text{-}OAc)]PF_6$ make an angle of 154°. As suggested by ^1H NMR spectroscopic data, an acetate anion is situated within this cleft. Cyclic voltammetry of $[Co_2(L^2)_2(\mu\text{-}OAc)]PF_6$ gives rise to only irreversible redox processes, reflecting the loss of redox stability on going from the macrocyclic chelate $[L^1]^{2-}$ to the polychelate $[L^2]^{2-}$, even though the resultant complexes have very similar coordination spheres.

Interestingly, reaction of $[Zn(L^3)]$ with $Co(AcO)_2{\cdot}4H_2O$ in $CHCl_3$ affords the corresponding *mononuclear* complex $[Co(L^3)(OAc)]$ (Figure 3), which shows octahedral coordination at Co^{III} with the OAc^- anion binding as a *cis*-chelate. The ligand $[L^3]^{2-}$ binds to the metal centre in a folded manner, the inherent steric hindrance of the ligand inhibiting the formation of dinuclear complex products. This observation is further confirmed by the formation of mononuclear complexes of $[L^3]^{2-}$ and related hindered ligands with square-planar Ni^{II}, Cu^{II} and Pd^{II}, and tetrahedral Zn^{II}.

Our current work seeks to examine the redox properties of these and related thiolate-bridged complexes and to develop new synthetic routes to heterodinuclear complexes.

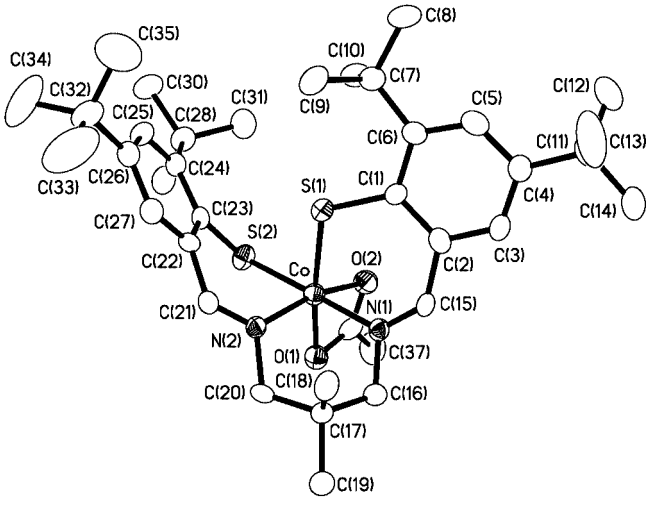

Figure 3. A view of the structure of $[Co(L^3)(OAc)]$ showing atom numbering, with displacement ellipsoids drawn at 50% probability; hydrogen atoms are omitted for clarity; Co−N(1) 1.953(5), Co−N(2) 1.886(5), Co−O(1) 2.023(4), Co−O(2) 1.992(4), Co−S(1) 2.201(2), Co−S(2) 2.231(2) Å

Experimental Section

X-ray Crystal Analysis: Crystal data for $[Co_2(L^1)(\mu\text{-}OAc)(OAc)(NH_3)](PF_6)_2{\cdot}3CH_3NO_2$: $C_{31}H_{44}Co_2F_{12}N_8O_{10}P_2S_2$ (M = 1160.66), triclinic, $P\bar{1}$, a = 11.7767(9), b = 14.8953(11), c = 15.1242(12) Å, α = 62.866(1), β = 82.093(1), γ = 74.901(1)°, V = 2279.0(3) Å^3, Z = 2, T = 150(2) K, $\rho_{calcd.}$ = 1.691 g cm^{-3}, $F(000)$ = 1180, μ(Mo-K_α) = 0.999 mm^{-1}, 10536 unique reflections measured, 621 variables, R_1 = 0.0380 [8575; $I > 2\sigma(I)$], $wR(F^2)$ = 0.107. Crystal data for $[(Co_2(L^2)_2(\mu\text{-}OAc)](PF_6)_2{\cdot}0.5CH_3CN$: $C_{41}H_{44.5}Co_2F_6N_{4.5}O_2PS_4$ (M = 1023.38), monoclinic, $P2_1/n$, a = 17.732(2), b = 10.5918(12), c = 23.506(2) Å, β = 97.187(2)°, V = 4380.0(14) Å^3, Z = 4, T = 150(2) K, $\rho_{calcd.}$ = 1.552 g cm^{-3}, $F(000)$ = 2100, μ(Mo-K_α) = 1.052 mm^{-1}, 10100 unique reflections measured, 561 variables, R_1 = 0.0523 [6840; $I > 2\sigma(I)$], $wR(F^2)$ = 0.1235. Crystal data for $[Co(L^3)(OAc)]{\cdot}0.5CHCl_3{\cdot}7/18(Et_2O)$: $C_{37}H_{55}CoN_2S_2{\cdot}0.5CHCl_3{\cdot}7/18(Et_2O)$ (M = 771.38), monoclinic, $C2/c$, a = 30.077(4), b = 12.519(2), c = 22.960(3) Å, β = 100.371(3)°, V = 8505(3) Å^3, Z = 8, T = 150(2) K, $\rho_{calcd.}$ = 1.205 g cm^{-3}, $F(000)$ = 3291, μ(Mo-K_α) = 0.630 mm^{-1}, 7937 unique reflections measured, 438 variables, R_1 = 0.0600 [2619; $I > 2\sigma(I)$], $wR(F^2)$ = 0.149. CCDC-200957, -200958 and -200959 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of $[Co_2(L^1)(\mu\text{-}OAc)(OAc)(NH_3)](PF_6)_2$: $Co(OAc)_2{\cdot}4H_2O$ (0.05 g, 0.2 mmol) in MeOH (5 mL) was added to a solution of $[Zn_2(L^1)(OAc)]PF_6$ (0.077 g, 0.1 mmol) in MeOH (25 mL). The resulting red solution was heated under reflux for 1 h and then NH_4PF_6 (0.074 g, 0.4 mmol) was added. The resultant solution was heated under reflux for a further 1 h, after which time a red precipitate was observed. This precipitate was filtered and washed with cold MeOH and diethyl ether (0.059 g, 60% yield). $C_{28}H_{35}Co_2F_{12}N_5O_4P_2S_2$ (977.5): calcd. C 34.39, H 3.58, N 7.16; found C 34.60, H 3.52, N 7.13. MS (ES^+): m/z = 335 $[Co_2L(OAc)_2]^{2+}$. ^1H NMR (CD_3CN): δ = 8.28 (s, 2 H, CH=N), 8.22 (s, 2 H, CH=N), 4.57 (t, J = 13 Hz, 2 H, NCH_2) 4.22 (m, 4 H, NCH_2), 3.98 (d, J = 13 Hz, 2 H, NCH_2), 3.43 (br., 3 H, NH_3), 2.3−2.7 (m, 4 H, CCH_2C), 2.23 (s, 6 H, Ar-CH_3), 2.03 (s, 3 H, CH_3CO_2), 0.77 (s, 3 H, CH_3CO_2) ppm. ^{13}C NMR (CD_3CN): δ = 186.5 (CH_3CO_2), 180.0 (CH_3CO_2), 171.3 (C=N), 168.4 (C=N), 140.3 (ArC), 138.8 (ArC),

138.7 (ArC), 134.4 (ArC), 134.0 (ArC), 125.9 (ArC), 62.7 (NCH_2), 60.8 (NCH_2), 28.2 (CCH_2C), 27.8 (CCH_2C), 23.0 (CH_3CO_2), 20.8 (CH_3CO_2), 19.6 (CH_3-Ar) ppm. IR (KBr): $\tilde{\nu}$ = 3353 m, 3302 m, 3132 w, 2939 w, 1628 s, 1606 m, 1567 w, 1529 w, 1434 s, 1378 m, 1320 s, 1299 m, 1127 w, 1074 m, 955 w, 934 w, 842 vs, 740 w, 585 w, 621 w, 558 s cm^{-1}. For $Co^{III}Co^{III}$ complex: λ_{max} = 540 nm (ε = 1822 M^{-1} cm^{-1}), 430 (2933). For $Co^{III}Co^{II}$ complex: λ_{max} = 534 nm (ε = 1822 M^{-1} cm^{-1}).

Synthesis of $[Co_2(L^2)_2(\mu\text{-AcO})]PF_6$: A solution of $Co(AcO)_2{\cdot}4H_2O$ (0.027 g, 0.11 mmol) in MeOH (5 mL) was added to a solution of $[Zn(L^2)]$ (0.040 g, 0.1 mmol) in $CHCl_3$ (20 mL) The yellow solution immediately changed colour to become deep red and then slowly became ill-defined red-brown. After heating the resulting solution under reflux for 20 min, NH_4PF_6 (0.163 g, 1.0 mmol) in MeOH (5 mL) was added. After a few minutes, a brownish precipitate was obtained, which was washed with MeOH and diethyl ether (0.039 g, 80% yield). This product can be recrystallised from MeCN/diethyl ether. Single crystals suitable for X-ray analysis were obtained by this procedure. $C_{40}H_{43}Co_2F_6N_4O_2PS_4$ (1002.9): calcd. C 47.90, H 4.32, N 5.59; found C 47.86, H 4.22, N 5.57. MS (FAB^+, 3-NOBA): *m/z* = 399, 858; (ES^+): *m/z* = 857 $[(C_{19}H_{20}N_2S_2Co)_2CH_3CO_2]^+$, 399 $[C_{19}H_{20}N_2S_2Co]^+$. IR (KBr): $\tilde{\nu}$ = 3053 w, 2934 w, 2873 w, 1636 m, 1615 s, 1583 m, 1515 m, 1470 m, 1410 s, 1371 w, 1342 w, 1303 m, 1255 w, 1225 m, 1186 w, 1080 w, 1087 w, 1027 m, 839 vs, 679 w, 755 s cm^{-1}. ^1H NMR (CD_3CN): δ = 8.23 (s, 1 H, CH=N), 7.93 (d, *J* = 7.7 Hz, 1 H, Ar), 7.75 (s, 1 H, CH=N), 7.25−7.48 (m, 6 H, Ar), 7.18 (t, *J* = 7.4 Hz, 1 H, Ar), 5.01 (d, *J* = 11.1 Hz, 1 H, NCH_2), 4.47 (d, *J* = 11.5 Hz, 1 H, NCH_2), 3.59 (d, *J* = 11.1 Hz, 1 H, NCH_2), 3.11 (d, *J* = 11.5 Hz, 1 H, NCH_2), 1.16 (s, 3 H, CCH_3), 1.10 (s, 3 H, CO_2CH_3), 1.07 (s, 3 H, CCH_3).

Synthesis of $[Co(L^3)(AcO)]$: A solution of $Co(AcO)_2{\cdot}4H_2O$ (0.0271 g, 0.11 mmol) in MeOH (3 mL) was added to a solution of $[Zn(L^3)]$ (0.063 g, 0.1 mmol) in $CHCl_3$ (20 mL). The solution was stirred at 40 °C for 10 min, the resulting red-brown solution was concentrated to dryness and then the green residue was washed with MeOH and recrystallised from $CHCl_3$/diethyl ether (0.27 g, 40% yield). Single crystals were obtained by diffusion of ether into a $CHCl_3$ solution. $C_{37}H_{57}CoN_2O_3S_2$ (700.92): calcd. C 63.40, H 8.20, N 4.00; found C 63.43, H 7.90, N 4.01. MS (ES^+): *m/z* = 623 ($C_{35}H_{52}N_2S_2Co$ = $[Co(L^3)]^+$ requires 623). IR (KBr): $\tilde{\nu}$ = 2955 s, 2904 w, 2868 w, 1623 s, 1516 s, 1470 s, 1393 m, 1357 m, 1265 m, 1198 w, 1152 m, 1060 w, 947 m, 760 m, 681 m cm^{-1}. This compound is unstable towards oxidation, as the ligand can be oxidised when the compound is heated under reflux for longer periods of time in solvents such as ethyl acetate or chloroform. Thus, increases in *m/z* by 16 or 32 units indicate the gain of one or two atoms of oxygen [MS (ES^+): *m/z* = 639 and 655]. A deep-red colour in solution is associated with oxidation of the ligand.

Acknowledgments

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