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Pinwheel motifs: formation of unusual homo- and hetero-nuclear aggregates *via* bridging thiolates†

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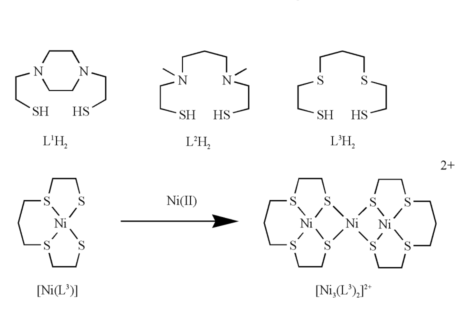
The homohexanuclear complexes $[Ni_2\{Ni(L^1)\}_4](BF_4)_4\cdot MeCN$, 1, $[Pd_2\{Pd(L^2)\}_4](BF_4)_4$, 2, and the heteropentanuclear aggregate $[Cu_2\{Ni(L^3)\}_3](PF_6)_2$, 3, all adopt a 'pinwheel' type structural motif *via* thiolate bridging between square-planar Ni(II) or Pd(II) and between trigonal planar Cu(I) centres, respectively.

Aggregation through bridging of thiolate donors is well established, with Jicha and Busch[1] being the first to report the formation of trinuclear species such as $[Ni_3(L^3)_2]^{2+}$ in which two mononuclear fragments $[Ni(L^3)]$ bind to a third Ni(II) centre to give the corresponding linear trinuclear species (Scheme 1). This work has been extended, and the formation of linear trinuclear complexes with Ni(II)[2–5] and larger aggregates with a range of transition metal ions[6] has now been established. We have recently reported the use of metal-carboxylates as metallo-ligands for the synthesis of unusual aggregates,[7] and were interested in developing further the chemistry of metal-dithiolates as functional metallo-ligands.[8] Furthermore, the development of new controls in the formation of dithiolate-bridged complexes is of importance to the synthesis of new structural models for a range of Ni, Cu and Zn-containing metalloenzymes,[8,9] particularly with recent interest in biosites containing thiolate bridged Ni–Cu centres.[10] We report herein the synthesis and structural characterisation of unusual, discrete aggregates formed from metallo-polythiolate ligands utilising variation of ligand bite angles and choice of metal centres to control the observed assemblies.

Reaction of L^1H_2 with a stoichiometric amount of $[Ni(H_2O)_6](BF_4)_2$ in MeCN yields a deep red complex $[Ni_2\{Ni(L^1)\}_4](BF_4)_4$, **1**, upon addition of excess Et_2O. Complex **1**‡ crystallises in the unusual cubic space group *I*432 of which there are only six examples in the Cambridge Structural Database.§ The structure of **1** (Figure 1) confirms§ a highly unusual hexanuclear arrangement consisting of six Ni(II) cations and four ligands. Each of the four ligands is bound to a Ni(II) cation with the internal chelate bond angles close to the ideal value of 90° for a square-planar complex. However, the bond angle N(1)–Ni(1)–N(4) 77.3(5)° is far more strained and distorted from the ideal value due to the constraints imposed upon the polychelate by the piperazine ring. Significantly, this leads to an expansion in the S(1)–Ni(1)–S(4) angle to 103.02(15)°, which opens out the bite angle of the two thiolate donors for subsequent binding to further Ni(II) centres. The two sulfur donors, S(1) and S(4), from each of the four $[Ni(L^1)]$ units bind, therefore, not to one other metal centre as expected by analogy with Scheme 1,[2–5] but to *two* further Ni(II) cations to give an overall "pinwheel-like" thiolate-bridged hexanuclear structure with crystallographically imposed C_4 symmetry. The Ni···Ni separation along the central axle is 3.024(7) Å and the two NiS_4 planes about this axle are twisted by 32.2° with respect to one another. The expansion of the S(1)–Ni(1)–S(4) angle in **1** to 103.02(15)° is a critical feature of this system, and significantly, the alternative linear trimeric species of the type $[Ni_3(L)_2]^{2+}$ show analogous S–Ni–S angles of 82.8(1),[2] 85.77(4),[3] 84.0(2)[4] and 81.2(1)°.[5] The opening out of the S–Ni–S angle, therefore, appears to destabilise the formation of $[Ni_3(L)_2]^{2+}$ and leads to the observed alternative mode of aggregation.

Variable temperature ^1H NMR studies on **1** indicate that there are no fluxional processes in solution. Further evidence is provided by the ^{13}C NMR spectrum which exhibits signals for four carbon environments: at 31.04 and 61.22 ppm attributed to the two carbon atoms on the pendant arms of the ligand, and at 58.02 and 53.85 ppm for the carbon atoms on the piperazine backbone. The two different signals observed for the piperazine carbon atoms arise because the 'pinwheel-like' motif leads to one half of the ring lying *syn* and the other half *anti* with respect to the central binuclear Ni core and the unbound S-lone pairs (Figure 1). This also suggests the complex stays intact as a hexanuclear entity in solution. **1** shows only an irreversible reduction at −0.65V *vs* Ag/AgCl.

Reaction of L^2H_2 with $[Pd(MeCN)_4](BF_4)_4$ in MeCN yields a yellow solid, $[Pd_2\{Pd(L^2)\}_4](BF_4)_4$, **2**,‡ upon addition of excess Et_2O. The complex **2**§ (Figure 2) is also hexanuclear involving square planar Pd(II), analogous to **1**, with crystallographically imposed inversion symmetry. The chelate S–Pd–S bite angles in **2** involved in binding to the central Pd(II) cations are 90.6(2)° to Pd(1) and Pd(1B), 89.8(2)° to Pd(3) and Pd(3B), significantly larger than the chelating bite angles observed in the Ni(II) trinuclear species (Scheme).[2–5] Thus, the gain in conformational freedom with the more flexible ligand (L^2H_2) is counteracted by the increase in the size of the metal ion,



Scheme 1

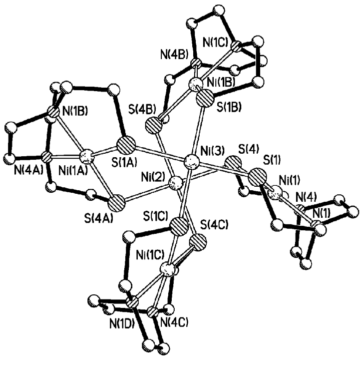


Fig. 1 View of the cationic structure in $[Ni_2\{Ni(L^1)_4\}](BF_4)_4.MeCN$ **1** with numbering scheme adopted.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b303851c/

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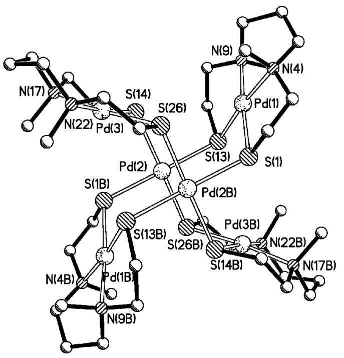

Fig. 2 View of the cationic structure in $[Pd_2\{Pd(L^2)_4\}](BF_4)_4$ **2** with numbering scheme adopted.

restricting the orientation of the sulfur lone pairs and leading to the formation of the hexanuclear rather than a trinuclear complex. The PdS_4 units about the Pd···Pd axle are co-planar (Pd···Pd = 3.089, 3.100 Å), while variable temperature ^1H NMR spectral studies of **2** suggest the complex to be non-fluxional in solution.

Reaction of $[Ni(L^3)]$ with one equivalent of $[Cu(MeCN)_4]PF_6$ in CH_2Cl_2 yields a dark solid $[Cu_2\{Ni(L^3)\}_3](PF_6)_2$, **3**.‡ The structure of the major [72.5(3)%] disorder component§ shows a pentanuclear aggregate with crystallographically imposed mirror symmetry (Figure 3) consisting of three neutral $[Ni(L^3)]$ units and two Cu(I) centres. Each of the three ligands binds to a square planar Ni(II) cation with all chelate angles at the Ni(II) very close to 90°, and the bite angle for the S–Ni–S bite moiety involved in binding to the Cu(I) centres being 90.6(2), 92.1(2), 91.1(2)° to Ni(1), Ni(2) and Ni(3), respectively. This notwithstanding, the two sulfur atoms from each of the three $[Ni(L^3)]$ units bind to two Cu(I) cations, such that each Cu(I) occupies a near perfect trigonal planar environment with a Cu···Cu separation of 2.983(6) Å, giving, as in **1** and **2**, an overall "pinwheel-like" thiolate-bridged heteronuclear structure. The formation of **3** can be ascribed to the tendency of the Cu(I) centres to adopt an open trigonal planar stereochemistry with observed S–Cu–S angles of 120.3(2), 120.4(2) and 119.2(2)°.

The structures of **1, 2** and **3** are related in that they all adopt a "pinwheel-type" structural motif around a binuclear central core. The degree of aggregation observed, however, is determined by the constraints imposed by the stereochemical preferences of the metal ions and the demands of the bite angles of the metal-thiolate ligands. Structures of this type using thiolate complexes as metallo-ligands are relatively rare,[6] especially with labile first row metal ions such as Ni(II) and Cu(I).[11] Significantly, dithiolate bridged Ni–Cu complexes have relevance to the recently reported Ni–Cu site discovered at the active site of carbon monoxide dehydrogenase/acetyl-CoA synthase.[10] Current work is aimed at developing this chemistry further with other metal-ligand fragments and to direct this synthetic strategy towards the modelling of biosites.

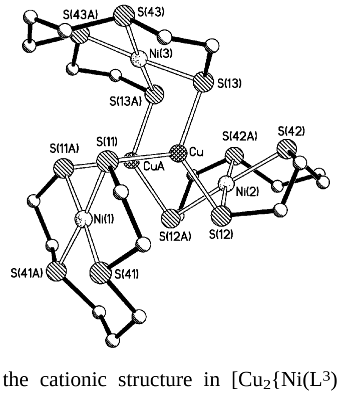

Fig. 3 View of the cationic structure in $[Cu_2\{Ni(L^3)_3\}](PF_6)_2$ **3** with numbering scheme adopted.

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Notes and references

‡ All ligands and complexes were characterised by elemental analysis, nmr and ir spectroscopy and mass spectrometry where appropriate. See the ESI for details.

§ *Crystal data for* **1**. $C_{34}H_{65}B_4F_{16}N_9Ni_6S_8$, M = 1555.93, cubic, a = 25.796(5) Å, U = 17166(6) Å^3, T = 220(2) K, space group $I432$ (No. 211), Z = 12, D_c = 1.806 g cm^{-3}, μ(Mo–$K\alpha$) = 2.316 mm^{-1}, 1899 unique reflections measured (R_{int} 0.094) and used in all calculations. Final R_1 [1422 $I \geq 2\sigma(I)$] = 0.066 and wR(all F^2) was 0.129. CCDC 207885.

Crystal data for **2**: $C_{44}H_{92}B_4F_{16}N_{12}Pd_6S_8$, M = 2031.42, triclinic, a = 11.594(5), b = 13.393(6), c = 25.598(11) Å, α = 77.182(7), β = 89.969(8), γ = 76.473(7)°, U = 3763(3) Å^3, T = 150(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ = 1.704 mm^{-1}, 24288 reflection measured, 16451 unique (R_{int} = 0.091). Final R_1 [6448 $I \geq 2\sigma(I)$] = 0.095, wR_2 (all data) = 0.288. CCDC 207886.

Crystal data for 3. $C_{17}H_{34}Cu_2F_{12}Ni_3P_2S_{12}$, M = 1216.32, orthorhombic, a = 17.466(3), b = 22.546(7), c = 12.156(7) Å, U = 4787(3) Å^3, T = 150(2) K, space group $Pnma$ (No. 62), Z = 4, D_c = 1.688 g cm^{-3}, μ(Mo–$K\alpha$) = 2.683 mm^{-1}, 4324 unique reflections measured (R_{int} 0.024) and used in all calculations. Final R_1 [2788 $I \geq 2\sigma(I)$] = 0.127 and wR(all F^2) was 0.354. CCDC 207887. See http://www.rsc.org/suppdata/cc/b3/b303851c/ for crystallographic data in .cif or other electronic format. See ESI for a listing of the six other structures determined in the rare space group $I432$.

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