Pyridyl-thiazoles as a new class of ligand for metallosupramolecular chemistry: formation of double and triple helicates with Cu(II)

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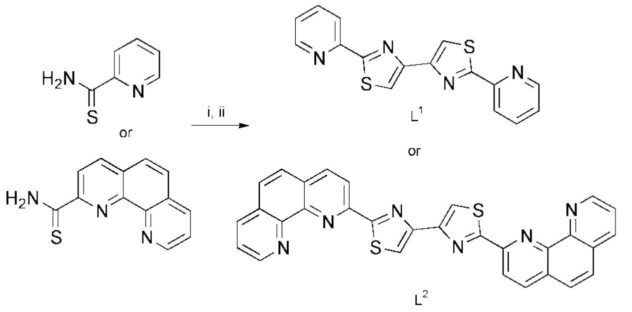
Reaction of either 1,10-phenanthroline-2-thioamide or pyridine-2-thioamide with 1,4-dibromobutane-2,3-dione affords the novel thiazole-containing polydentate ligands L^1 and L^2, respectively; these ligands form dinuclear double and triple helicate architectures, respectively, with Cu^{2+}.

Studies on the assembly of double and triple helicate complexes have been a major area of supramolecular coordination chemistry for the last 15 years. Helicate complexes have elegantly illustrated how the specific formation of architecturally complex assemblies are directed by the interplay between relatively simple parameters such as the stereoelectronic preference of the metal ion and the disposition of binding sites in the ligand.[1]

Many helicates are derived from ligands which are obviously partitioned into distinct binding sites, as exemplified by (i) the bis-catecholate ligands of Albrecht which form dinuclear triple helicates with various octahedral M(IV) ions;[2] (ii) the poly-bipyridyl ligands of Lehn and coworkers which form multinuclear double helicates with pseudo-tetrahedral Cu(I) and Ag(I);[3] and (iii) the bisterdentate ligands of Piguet and coworkers which afford triple helicates with nine-coordinate lanthanide(III) ions.[4] In contrast to these are the well-studied linear oligopyridines, whose partition into distinct metal-ion binding domains is controlled by the preference of the metal ion.[5] Thus, 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine (spy) splits into two terdentate domains to give dinuclear double helicates with metals such as Cd(II) which are six-coordinate, but splits into three bidentate domains to give trinuclear double helicates with metals such as Cu(I) which prefer to be pseudo-tetrahedral. Similarly 2,2′:6′2″:6″,2‴-quaterpyridine (qpy) can act as a simple tetradentate chelate in many mononuclear complexes,[6,7] or split into a '3 + 1'-dentate arrangement in octahedral $[Fe(qpy)_2]^{2+}$ in which qpy behaves as a terdentate ligand,[8] or split into a '2 + 2'-dentate arrangement in dinuclear double helicates with Cu(I) and Ag(I).[7] It is clear that the versatility of these ligands arises from their ability to adopt a wide variety of different coordination modes.

Here, we describe the preparation of a new class of ligand, containing chelating pyridyl-thiazolyl fragments, for the assembly of helicates. There are two features that make these of particular interest. Firstly, they are very simple to prepare and are readily available in far higher quantities than the analogous polypyridines; in this respect they are like the pyridyl/imine chelates of Hannon *et al.*[9] The thiazole unit is particularly easy to introduce into polydentate ligands and a number of metal complexes (but no helicates) of thiazole-based ligands have been prepared.[10] Secondly, unlike their polypyridyl analogues, these ligands naturally partition themselves into distinct binding domains because of the inability of the two adjacent thiazolyl units to chelate to the same metal: thus a substantial twist arises in the backbone of the coordinated ligand at this point.

The new ligands L^1 and L^2 are easily prepared as the bishydrobromide salts in good yield by reaction of 2 equivalents of the corresponding thioamide (2-pyridylthioamide and 1,10-phenanthroline-2-thioamide, respectively) with 1,4-dibromobutane-2,3-dione in methanol (Scheme 1).† Subsequent neutralization gives the free-base ligands. Reaction of L^1 with 2 equivalents of $Cu(PF_6)_2$ in Me_2CO gives, after precipitation in an atmosphere of ethyl acetate, a green crystalline material for which electrospray mass spectrometry and elemental analysis suggested a formula of $[Cu_2(L^1)_3](PF_6)_4$ **1**. This formulation was confirmed by X-ray crystallography, which shows two Cu(II) ions co-ordinated by three bridging ligands L^1 in a triple helical arrangement (Fig. 1).‡ Each of the Cu centres has a pseudo-octahedral coordination geometry (bite angles 77.0–79.6°, Cu–N distances 2.028–2.228 Å), formed by coordination of three thiazole-pyridyl bidentate units with each



Scheme 1 *Reagents and conditions:* i, $(COCH_2Br)_2$, MeOH; ii, $NH_3(aq)$.

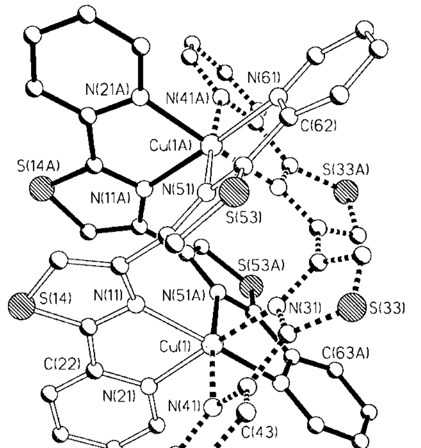


Fig. 1 Crystal structure of the complex cation of $\mathbf{1}\cdot 4Me_2CO$. Selected bond distances (Å) and angles (°): Cu(1)–N(21) 2.028(8), Cu(1)–N(31) 2.056(7), Cu(1)–N(11) 2.187(8), Cu(1)–N(41) 2.192(8), Cu(1)–N(61A) 2.171(8), Cu(1)–N(51A) 2.219(8); N(21)–Cu(1)–N(31) 171.5(3), N(21)–Cu(1)–N(61) 96.7(3), N(31)–Cu(1)–N(61) 87.2(3), N(21)–Cu(1)–N(11) 79.2(3), N(31)–Cu(1)–N(11) 97.1(3), N(61)–Cu(1)–N(11) 175.4(3), N(21)–Cu(1)–N(41) 92.9(3), N(31)–Cu(1)–N(41) 79.1(3), N(61)–Cu(1)–N(41) 97.8(3), N(11)–Cu(1)–N(41) 84.8(3), N(21)–Cu(1)–N(51) 86.8(3), N(31)–Cu(1)–N(51) 101.4(3), N(61)–Cu(1)–N(51) 76.8(3), N(11)–Cu(1)–N(51) 100.5(3), N(41)–Cu(1)–N(51) 174.5(3).

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ligand twisted about the bond between the two thiazole rings. Although the coordination geometry is somewhat irregular, there is no obvious Jahn–Teller distortion axis. The structure is stabilized by extensive aromatic π-stacking interactions between overlapping, near-parallel fragments of adjacent ligand, as emphasized in the space-filling picture (Fig. 2).

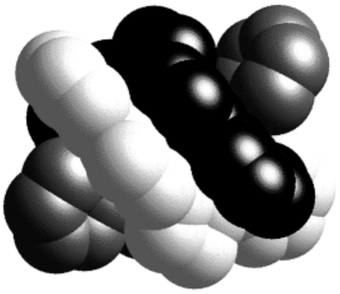

Fig. 2 Space-filling representation of the triple helicate **1**.

The formation of a triple helicate is in interesting contrast to the mononuclear complexes in which qpy acts as a simple equatorial tetradentate chelate.[6,7] In qpy this coordination mode is facilitated by the fact that each chelate ring has a bite angle appropriate for coordination to a single metal ion. In L^1, this is not the case; the two five-membered thiazolyl rings cannot chelate as the N atoms of the two five-membered rings are not sufficiently convergent, so the ligand naturally partitions into two bidentate pyridyl/thiazolyl units with a twist in the ligand backbone between them. The result is a dinuclear triple helicate instead of a simple mononuclear complex.

Reaction of L^2 with $Cu(ClO_4)_2$ in MeCN gives the double-helical complex $[Cu_2(L^2)_2](ClO_4)_4$ **2**.‡ Each of the copper centres is pseudo-octahedral, coordinated by two thiazolyl-phenanthroline tridentate units [bite angles 74.2–98.7°, Cu–N distances 1.967–2.312 Å], with each ligand again twisted about the inter-thiazole bond (Fig. 3) for the same reason as before.

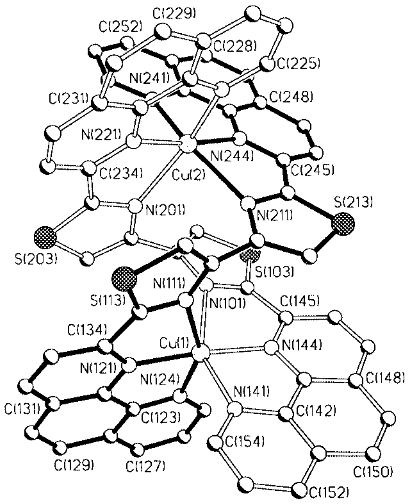

Fig. 3 Crystal structure of the complex cation of **2**·8MeCN·H_2O. Selected bond distances (Å) and angles (°): Cu(1)–N(121) 1.972(11), Cu(1)–N(144) 1.987(11), Cu(1)–N(124) 2.111(12), Cu(1)–N(141) 2.138(13), Cu(1)–N(111) 2.226(12), Cu(1)–N(101) 2.311(13); N(121)–Cu(1)–N(144) 173.9(5), N(121)–Cu(1)–N(124) 79.3(5), N(144)–Cu(1)–N(124) 95.6(5), N(121)–Cu(1)–N(141) 98.7(5), N(144)–Cu(1)–N(141) 79.2(5), N(124)–Cu(1)–N(141) 102.1(5), N(121)–Cu(1)–N(111) 76.3(5), N(144)–Cu(1)–N(111) 109.3(5), N(124)–Cu(1)–N(111) 154.1(4), N(141)–Cu(1)–N(111) 90.0(4), N(121)–Cu(1)–N(101) 108.7(5), N(144)–Cu(1)–N(101) 74.3(5), N(124)–Cu(1)–N(101) 91.1(5), N(141)–Cu(1)–N(101) 151.4(4), N(111)–Cu(1)–N(101) 88.8(4). Cu(2)–N(244) 1.965(12), Cu(2)–N(221) 1.968(12), Cu(2)–N(241) 2.129(14), Cu(2)–N(224) 2.148(11), Cu(2)–N(201) 2.258(12), Cu(2)–N(211) 2.299(13); N(244)–Cu(2)–N(221) 173.6(5), N(244)–Cu(2)–N(241) 79.5(5), N(221)–Cu(2)–N(241) 98.2(5), N(244)–Cu(2)–N(224) 96.3(5), N(221)–Cu(2)–N(224) 78.4(5), N(241)–Cu(2)–N(224) 105.3(5), N(244)–Cu(2)–N(201) 110.7(5), N(221)–Cu(2)–N(201) 75.2(5), N(241)–Cu(2)–N(201) 88.8(5), N(224)–Cu(2)–N(201) 151.6(5), N(244)–Cu(2)–N(211) 74.7(5), N(221)–Cu(2)–N(211) 108.6(5), N(241)–Cu(2)–N(211) 151.6(5), N(224)–Cu(2)–N(211) 89.3(4), N(201)–Cu(2)–N(211) 89.3(4).

In conclusion, we have demonstrated that polydentate ligands containing two central thiazolyl units are easy to prepare, and are very effective at forming double and/or triple helicates because of the way they naturally partition into two separate binding domains.[11] This method for preparing large polydentate ligands not only allows significant quantities to be produced but can also be readily extended to the preparation of a wide variety of ligands whose size, shape and functionality can be changed with ease.

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Notes and references

† L^1: yield: 80%. EI mass spectrum: *m/z* 322 (75, M^+). δ_H[300 MHz, $(CD_3)_2SO$]: 8.68 (1H, d, pyridyl H), 8.26 (1H, d, pyridyl H), 8.24 (1H, s, thiazole H), 8.23 (1H, t, pyridyl H), 7.55 (1H, t, pyridyl H). Found: C, 59.5; H, 2.8; N, 16.9. $C_{16}H_{10}N_4S_2$ requires C, 59.6; H, 3.1; N, 17.4%. L^2: yield: 50%. EI mass spectrum: *m/z* 524 (80, M^+). Found: C, 60.4; H, 3.7; N, 12.8. $C_{30}H_{16}N_5S_2\cdot 2(CH_3)_2SO$ requires C, 60.0; H, 4.1; N, 12.3%. The ^1H NMR spectrum was not obtained owing to the poor solubility of L^2 in common organic solvents. $[Cu_2(L^1)_3(PF_6)_4]$ **1** electrospray MS: *m/z* 1401 $[Cu_2(L^1)_3(PF_6)_2H_2O]$. Found: C, 33.7; H, 2.0; N, 10.0. $C_{48}H_{30}N_{12}S_6Cu_2P_4F_{24}$ requires C, 33.9; H, 1.9; N, 10.5%. $[Cu_2(L^2)_2(ClO_4)_4]$ **2**: electrospray MS: *m/z* 1473 $[Cu_2(L^2)_2(ClO_4)_3]$, 686 $[Cu_2(L^2)_2(ClO_4)_2]$. Found: C, 46.4; H, 2.1; N, 10.2. $C_{60}H_{32}N_{12}S_4Cu_2Cl_4O_{16}$ requires C, 45.8; H, 2.0; N, 10.7%.

‡ *Crystal data*: for $C_{48}H_{30}N_{12}S_6Cu_2P_4F_{24}\cdot 4(CH_3)_2CO$ (**1**·4Me$_2$CO): M = 1906.5, monoclinic, space group $C2/c$, a = 13.9497(14), b = 23.133(2), c = 22.485(2) Å, β = 99.792(2) °, U = 7150.3(12) Å^3, Z = 4, D_c = 1.771 Mg m^{-3}, μ(Mo-Kα) = 0.980 mm^{-1}, $F(000)$ = 3840, T = 173 K, 6291 independent reflections with $2\theta < 50°$. Refinement of 505 parameters with 59 restraints converged at final $R1$ = 0.0886, $wR2$ = 0.2807. The complex cation lies on a C_2 axis such that only half of it is crystallographically unique.

For $C_{60}H_{32}Cu_2Cl_4N_{12}O_{16}S_4\cdot 8CH_3CN\cdot H_2O$ (**2**·8MeCN·H_2O): M = 1920.5, triclinic, space group $P1$, a = 13.4641(13), b = 15.0528(15), c = 21.859(2) Å, α = 80.685(2), β = 81.242(2), γ = 77.288(2)°, U = 4233.1(7) Å^3, Z = 2, D_c = 1.507 Mg m^{-3}, μ(Mo-Kα) = 0.806 cm^{-1}, $F(000)$ = 1960, T = 173 K, 7887 independent reflections with $2\theta < 40°$. Refinement of 677 parameters with 8 restraints converged at final $R1$ = 0.0984, $wR2$ = 0.2884.

X-Ray measurements were made using a Bruker SMART CCD area-detector diffractometer; structure solution SHELXTL program system version 5.1, 1998. In both cases the complexes (**1** and **2**) crystallise as racemates, with equal numbers of opposite enantiomers in the achiral unit cell.

CCDC 182/1712. See http://www.rsc.org/suppdata/cc/b0/b004319m/ for crystallographic files in .cif format.

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