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Controlled crystallization of mixed-ligand complexes of 1,3-bis(4-pyridyl)propane-*N*,*N*′-dioxide with metal(II) thiocyanates: isostructurality in coordination networks bearing different mono- and di-nuclear nodes†‡

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The new flexible spacer ligand 1,3-bis(4-pyridyl)propane-*N*,*N*′-dioxide forms three classes of isomorphous compounds with metal(II) thiocyanates at controlled ligand–metal molar ratios, and its μ$_3$-*O*,*O*,*O*′ mode leads to a pair of coordination networks having the same (4, 4) topological characteristics but different mono- and di-nuclear nodes.

Much effort is devoted to the design and controlled crystallization of coordination polymers with potential application as catalytic, conductive, luminescent, magnetic, spin-transition, non-linear optical, and/or nanoporous materials.[1,2] It is well established that the coordination network assembly process can be affected by the choice of metal ions, counter anions, co-existing neutral ligands, temperature, pH, and solvents used for crystallization.[3–10] In some instances, two or more complexes of different composition can be obtained merely by manipulating the ligand–metal molar ratio.[11–13] A widely applicable strategy using poly(*N*-oxide) ligands as linkers for constructing polymeric metal-organic networks of f-block metals has been developed.[14–16] Based on the "node and spacer" methodology, we have synthesized a new di-*N*-oxide ligand, namely 1,3-bis(4-pyridyl)propane-*N*,*N*′-dioxide (L), and used it to generate a series of divalent transition metal mixed-ligand complexes $[\mathrm{ML(H_2O)(SCN)_2}]_\infty$ (M = Co (**1**), Cd (**2**), Mn (**3**), Zn (**4**)), $[\mathrm{ML_2(SCN)_2}]_\infty$ (M = Co (**5**), Cd (**6**)) and $[\mathrm{ML_2(H_2O)_2(SCN)_2}]$ (M = Mn (**7**), Zn (**8**)) under controlled crystallization conditions at different ligand–metal molar ratios.§ Three coordination modes of this type of linear bifunctional, dipyridine di-*N*-oxide ligands are known: terminal monodentate,[15a] μ-*O*,*O*′ (*i.e.* end-to-end bidentate),[15b–d] and μ$_4$-*O*,*O*,*O*′,*O*′.[16] Here we report two new coordination modes that have been anticipated but not found before, namely the μ$_3$-*O*,*O*,*O*′ tridentate mode in **1**, **3** and **4**, and the μ-*O*,*O* (*i.e.* terminal bridging bidentate) mode in **2**.¶

In preparing the corresponding pairs of compounds (**1**, **5**) and (**2**, **6**), when the initial molar ratio L : M was set at 1 : 1, compound **1** and **2** were obtained, respectively. When L : M was changed to 2 : 1, **1** together with **5**, or **2** with **6**, were obtained in the same preparation with **1** or **2** crystallizing out first from the mother liquor. With a further increase in L : M, compound **5** or **6** became the major product. When L : M reached 6 : 1 and beyond, compound **5** or **6** was the only product. These results indicate that the formation of both **1** and **5**, or **2** and **6**, in the same reaction vessel depends primarily on the molar ratio of L : M.

In the solid state, L occupies a site of symmetry *m* with one pyridyl ring orthogonal to the rest of the molecule. The crystal structure consists of a stacking of corrugated sheets consolidated by intermolecular C–H···O hydrogen bonding between adjacent pyridyl rings (structure plots are given in the ESI‡).

In the crystal structure of compound **1**, each Co(II) ion is located in a distorted octahedral environment, being surrounded by two *cis* *N*-bonded thiocyanate anions, an aqua ligand, and three facial oxygen atoms from adjacent L ligands. The independent L ligand acts in the μ$_3$-*O*,*O*,*O*′ mode, with one terminal *N*-oxide bridging two Co(II) ions to form a centrosymmetric $\mathrm{Co_2O_2}$ ring, and the other bound to a Co(II) ion of an adjacent $\mathrm{Co_2O_2}$ ring, thus generating an undulated layer perforated by centrosymmetric 56-membered S-shaped rings (Fig. 1a). Within each macrocyclic ring, π–π interaction exists between a pair of parallel pyridyl rings at a distance of 3.62 Å between the centers. In compound **5**, with a L : Co(II) composition of 2 : 1, each Co(II) ion lies in a distorted octahedral, centrosymmetric site, being surrounded by two *trans* *N*-bonded thiocyanate anions and four oxygen atoms of adjacent L ligands. Both independent L ligands act in the end-to-end bidentate mode to connect the Co(II) ions, generating an analogous layer structure exhibiting (4, 4) net topology and 56-membered rings, but the nodes are mononuclear and the center-to-center separation between the parallel pyridyl rings is increased to 6.21 Å (Fig. 1b). Notably, if the pair of metal ions in each $\mathrm{Co_2O_2}$ ring in **1** coalesces into one, the coordination framework is converted into that of **5**, the only difference being

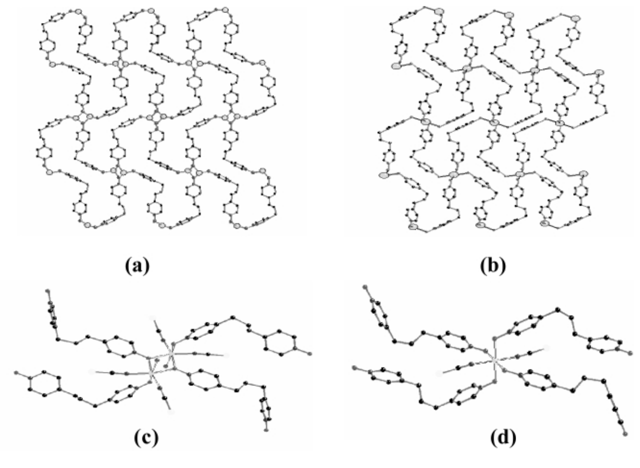

Fig. 1 (a) Two-dimensional coordination network with 56-membered S-shaped rings and dinuclear nodes in complex **1** viewed along the *c* axis. (b) Analogous (4, 4) net with 56-membered rings and mononuclear nodes in complex **5** viewed along the *a* axis. Hydrogen atoms, *N*-bonded thiocyantate ligands and water molecules are omitted for clarity. (c) The binuclear node in complex **1**. (d) The mononuclear node in comples **5**.

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† Dedicated to Professor Khi-Rui Tsai (also known as Cai Qirui) on the occasion of his 90th birthday.

‡ Electronic supplementary information (ESI) available: synthesis of compounds **1–8**, TGA analysis results of **1** and **5**, and structural details with additional figures. See http://www.rsc.org/suppdata/cc/b3/b307604k/

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the dispositions (*cis vs. trans*) of the thiocyanate ligands and the presence of the additional aqua ligand in **1**. Subsequent TGA measurements conducted on **1** and **5** revealed that except for the loss of the aqua ligand in **1**, the two-dimensional frameworks of both compounds have similar thermal stability. Compound **6** is isomorphous to **5** with Cd(II) replacing Co(II).

Compound **2** has the same stoichiometry and asymmetric unit as **1** but exhibits an entirely different crystal structure. In this compound, the L ligand acts in the μ–*O*,*O* mode with one *N*-oxide group bridging two Cd(II) ions, leading to a centrosymmetric dinuclear Cd_2O_2 ring. The adjacent Cd_2O_2 rings are connected by two centrosymmetrically related μ–*N*,*S* thiocyanate ligands[17] to generate an infinite chain (Fig. 2). Such chains are then further connected through hydrogen bonds between the aqua ligand and the terminal *N*-oxide group, generating a three-dimensional network.

In preparing the corresponding pairs (**3**, **7**) and (**4**, **8**), compounds **3** and **4** were obtained as scaly crystals, respectively, when the molar ratio L : M was kept at 1 : 1. When L : M became higher, **3** and **7**, or **4** and **8** were obtained from the same mother liquor with **3** or **4** crystallizing out first. However, even when L : M reached 10 : 1, **7** or **8** (block-like crystals, easily separated from **3** or **4**) was not obtainable as the only product, though the yield improved steadily with increasing L : M.

Compound **3** and **4** are both isomorphous to **1**. In the isomorphous pair **7** and **8**, the metal center located at an inversion center is coordinated by pairs of monodentate L ligands, aqua ligands and *N*-bonded thiocyanate ions.[17] The second *N*-oxide group of L forms two acceptor hydrogen bonds with the aqua ligands of two adjacent metal centers, leading to a three-dimensional network (Fig. 3).

In summary, a new flexible spacer ligand L has been synthesized and shown to exhibit versatile coordination behavior toward transition metal(II) thiocyanates, yielding eight mixed-ligand complexes by manipulating the ligand-to-metal molar ratio. The pair of compounds **1** and **5** provides an unprecedented example of isostructurality in coordination networks exhibiting different nodal characteristics that can be selectively generated by shifting the position of equilibrium.

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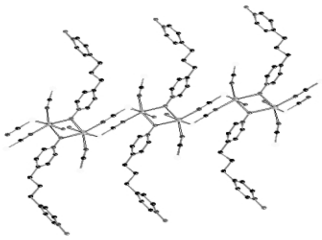

Fig. 2 An infinite chain in compex **2** with dinuclear centers bridged by μ–*N*,*S* thiocyanate ligands.

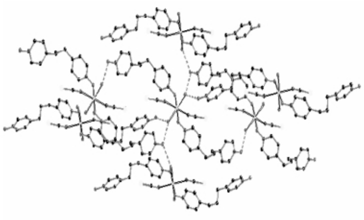

Fig. 3 Hydrogen-bonded three-dimensional network in compound **7** and **8** (hydrogen atoms are omitted for clarity).

Notes and references

§ Synthesis of 1,3-bis(4-pyridyl)propane-*N*,*N*′-dioxide, L. A mixture of 4,4′-trimethylenedipyridine (10 g, 50.3 mmol), acetic acid (40 ml), and 35% hydrogen peroxide (20 ml) was heated at 70–80 °C for 3 h. An additional portion of hydrogen peroxide (15 ml) was added, and heating was continued for a further 9 h. The excess acetic acid and water were removed under vacuum, then water (20 ml) was introduced, and the mixture was concentrated to dryness under vacuum. Acetone (150 ml) was added to the remaining oil to yield a pale-yellow precipitate, which was filtered off and washed twice with hot acetone to remove unreacted 4,4′-trimethylenedipyridine. The crude product was re-crystallized in ethanol to give 9 g of ligand L. Yield 77.5%. Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17%. Found C, 67.61; H, 6.14; N, 12.16%. IR (KBr, cm^{-1}): 3387*m*, 3092*m*, 3046*m*, 3003*m*, 2928*w*, 1688*w*, 1489*s*, 1452*m*, 1228*s*, 1109*w*, 1034*w*, 857*m*, 818*w*, 760*m*, 723*w*, 648*w*, 561*w*. ^1H NMR (300 MHz, D_2O): δ 7.97–8.00 (4H, m, py-2,6), 7.24 (4H, d, J = 6.6Hz, py-3,5), 2.56 (4H, t, J = 7.5Hz, py–CH_2–), 1.803–1.853 (2H, m, py–C–CH_2–C–py).

¶ *Crystal data*: ligand L, orthorhombic, space group *Pnma*, with a = 9.159(2), b = 7.799(1), c = 16.794(3) Å, Z = 4, 1548 unique Mo$K\alpha$ reflections (R_{int} = 0.0260), R_1 = 0.0440, wR_2 = 0.1434 for 1134 observed reflections [$I > 2\sigma(I)$]. Compound **1**, monoclinic, space group $P2_1/c$, with a = 12.510(7), b = 12.446(7), c = 13.185(8) Å, β = 114.40(1)°, Z = 4, 4556 unique Mo$K\alpha$ reflections (R_{int} = 0.0496), R_1 = 0.0403, wR_2 = 0.1086 for 3202 observed reflections [$I > 2\sigma(I)$]. Compound **2**, monoclinic, space group $P2_1/c$, with a = 15.375(2), b = 14.926(2), c = 8.1696(8)Å, β = 91.079(2)°, Z = 4, 4514 unique Mo$K\alpha$ reflections (R_{int} = 0.0289), R_1 = 0.0326, wR_2 = 0.0877 for 3785 observed reflections [$I > 2\sigma(I)$]. Compound **5**, monoclinic, space group $P2_1/c$, with a = 6.925(1), b = 22.460(5), c = 9.688(2) Å, β = 98.24(3)°, Z = 2, 2633 unique Mo$K\alpha$ reflections (R_{int} = 0.0271), R_1 = 0.0471, wR_2 = 0.1332 for 1873 observed reflections [$I > 2\sigma(I)$]. Compound **7**, monoclinic, space group $P2_1/c$, with a = 12.773(3), b = 14.033(3), c = 8.734(2) Å, β = 94.66(3)°, Z = 2, 2760 unique Mo$K\alpha$ reflections (R_{int} = 0.0355), R_1 = 0.0374, wR_2 = 0.1047 for 2138 observed reflections [$I > 2\sigma(I)$].

CCDC 214073–214081. See http://www.rsc.org/suppdata/cc/b3/b307604k/ for crystallographic data in .cif or other electronic format.

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