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Can 4,4′-bipyridine *N*,*N’*-dioxide play the same important role as 4,4′-bipyridine in the construction of metal coordination networks and crystal engineering?†

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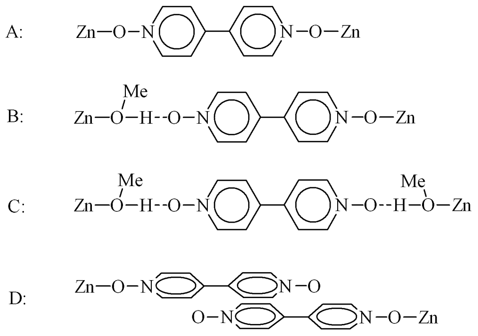
Various binding modes of 4,4′-bipyridine *N*,*N*′-dioxide (L) for crystal engineering are demonstrated in the complexes $[Zn(MeOH)_2L_3](SiF_6)\cdot 3MeOH$ and $[ZnL_6](NO_3)_2$, which include examples of M–L coordination bonds, hydrogen-bonding and π–π stacking interactions.

4,4′-Bipyridine and its analogues containing two 4-pyridyl donor units have been found to be useful bridging ligands in the construction of inorganic networks and crystal engineering, and this has resulted in a plethora of extended assemblies including helical networks and diamondoid, honeycomb, square-grid, ribbon, grid, T-shaped, ladder, brick wall and octahedral frameworks.[1,2] We demonstrated recently the use of 4,4′-bipyridine *N*,*N*′-dioxide (L) in the construction of lanthanide coordination polymers with unusual 2- or 3-D networks.[3] We now extend this work to d-block elements and confirm that L and related *N*-oxide ligands have enormous potential for the construction of unusual networks incorporating these metal ions. We report herein two Zn(II) complexes, $[Zn(MeOH)_2L_3](SiF_6)\cdot 3MeOH$ **1** and $[ZnL_6](NO_3)_2$ **2**, which contain *four* different connection modes of L *via* M–L coordination, hydrogen-bonding and π–π interactions. While **1** has a 3-D open-framework structure whose large pores accommodate methanol solvent molecules, **2** is a mononuclear complex which forms 2-D layers *via* extensive π–π stacking interactions.

Compounds **1** and **2** were prepared by mixing methanolic solutions of $Zn(SiF_6)$ or $Zn(NO_3)_2$, respectively, and 4,4′-bipyridine *N*,*N*′-dioxide.‡ Crystals of **1** were found to be unstable in air and decayed quickly *via* solvent loss. X-Ray analysis of **1** confirms a polymeric structure based on networks of six-coordinate Zn(II) centres linked by 4,4′-pyridine *N*,*N’*-dioxide ligands.§ The Zn(II) ions have an octahedral environment provided by four oxygen atoms from four different *N*-oxide ligands and two others from coordinated molecules of MeOH. The 4,4′-bipyridine *N*,*N*′-dioxide ligands bridge metal centres directly or through combinations of M–L coordination and hydrogen bonds in three distinct fashions A (A′), B and C as shown in Scheme 1 and Fig. 1. The 4,4′-bipyridine *N*,*N*′-dioxide ligands therefore sustain a 3D framework structure through *four* different linkages. If coordination bonds (A or A′) are taken into account alone the structure can be considered as having a two-dimensional brick-wall (6,3) topology. Linkages of type A and A′ propagate along the *a* and *b* axes, respectively, and are chemically equivalent but crystallographically different, the latter having an inversion centre at its midpoint. Ligand A is slightly bent, with the two pyridyl rings twisted by 17.9° and bridging two Zn(II) centres separated by 12.7 Å. Ligand A′ is planar by symmetry and bridges two Zn(II) centres lying 12.3 Å apart. Ligands adopting connection mode C modify the two-dimensional framework by joining the nodes at the centres of the long sides of the rectangle (*i.e.* across the centre of the "brick" in the brick-wall structure) to form a square grid network of (4,4) topology. Strong hydrogen-bonding is confirmed by the short O···O separation [2.571(7) Å] within the O–H···O unit in mode C. Ligands involved in connection mode B [O···O separation 2.652(6) Å] join sheets to build up a 3-D open network with channels of dimensions 10.2 × 14.2 Å extending along the *c* axis (Fig. 2).



Scheme 1 Modes of connection observed in compounds **1** and **2**.

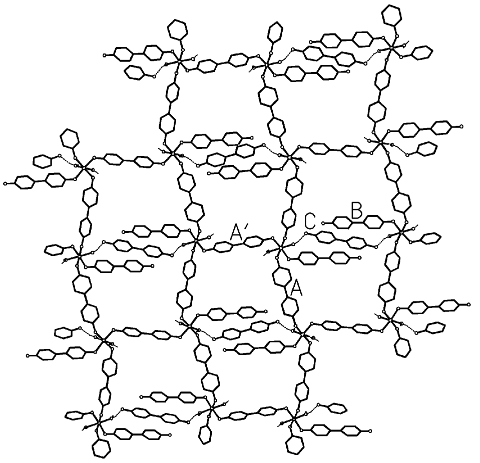


Fig. 1 View of the sheet observed in compound **1**. The $[SiF_6]^{2-}$ anion, methanol solvent molecules and hydrogen atoms are omitted for clarity.

4,4′-Bipyridine and its analogues containing two 4-pyridyl donor units can also adopt these coordination modes when forming complexes with either lanthanide[4,5] or d-block metals[6] but no examples of all three modes occurring in the same compound have been reported previously. The coexistence of three coordination modes for such a bidentate ligand is unique and indicates a real versatility in coordinative behaviour for *N*-oxide ligands.

Compound **2** is composed of discrete $[ZnL_6]^{2+}$ cations and uncoordinated nitrate anions. The Zn(II) centres are octahedral with a ZnO_6 environment, the six oxygen donors being derived from six different terminal 4,4′-bipyridine *N*,*N*′-dioxide ligands. The Zn(II) centre occupies a crystallographic inversion centre which results in three crystallographically independent ligands

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† Electronic supplementary information (ESI) available: molecualr structures and labelling schemes for complexes **1** and **2**. See http://www.rsc.org/suppdata/cc/b0/b006679f/

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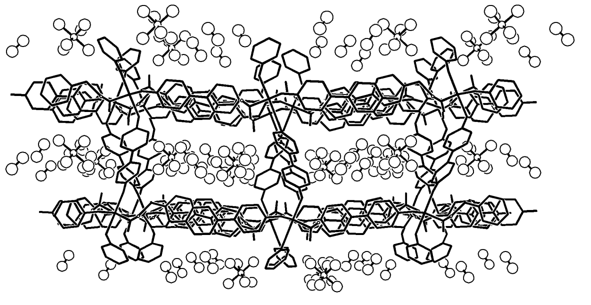

Fig. 2 View of the channels in compound **1**. Methanol solvent molecules and anions are highlighted by large open cycles. Hydrogen atoms are omitted for clarity.

with Zn–O bond lengths falling in the range 2.063(3)–2.109(3) Å, typical for Zn(II) complexes of pyridine *N*-oxide.[7] The pyridyl rings within each of these ligands are twisted with respect to each other, the twist angles ranging from 13.0 to 28.5°. To our knowledge this is the first example of a mononuclear complex of the 4,4′-bipyridine *N*,*N*′-dioxide ligand, which normally acts as a bridge between metal ions, either though M–L coordination or hydrogen bonds.[3]

Although all six 4,4′-bipyridine *N*,*N*′-dioxide ligands act as terminal ligands and the complex is mononuclear, an overall layered polymeric structure is observed for **2** *via* intermolecular π–π interactions. π–π Interactions have been used previously for the construction of coordination networks from discrete molecules,[8] but the mode found here is unique (Fig. 3). The six ligands are distributed alternatively in two planes around the Zn(II) centre so that the molecule has approximate D_{3h} symmetry. Each complex cation is involved in six ligand-to-ligand π–π interactions (mode D, Scheme 1) with six adjacent coplanar molecules to give an unprecedented (3,6) two-dimensional sheet. The plane/centroid distances for these π–π interactions are in the range 3.27–3.39 Å. It is important to note that the use of 4,4′-bipyridine *N*,*N*′-dioxide is crucial here; not only do the reduced steric requirements of the *N*,*N*′-dioxide ligand, compared with 4,4′-bipyridine, allow coordination of six ligands around the metal centre, but the angle subtended at the O-donor (the Zn–O–N bond angles for **2** range from 124.4 to 129.2°) is necessary to allow the construction of the two-dimensional sheet. These differences between donors based on bipyridine and those derived from bipyridine *N*,*N*′-dioxide are crucial to the differing roles they can play in coordination polymer chemistry.

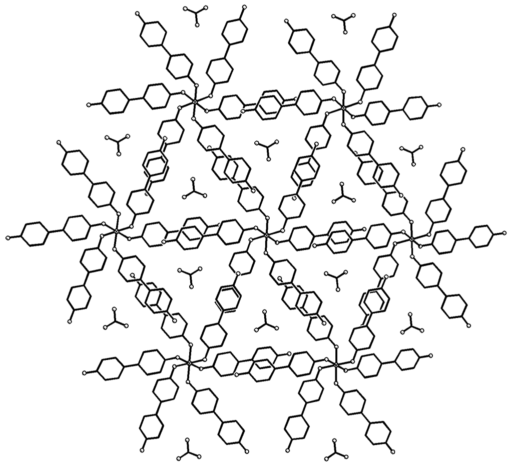

Fig. 3 View of the layer structure of (3,6) topology formed *via* π–π interactions in compound **2**. Hydrogen atoms are omitted for clarity.

Furthermore, comparison of the structures of **1** and **2** gives insight into the templating role of the anion in the construction of coordination polymer networks.[9] Thus for example in **2**, the nitrate anion appears to template the formation of a network of trigonal symmetry (Fig. 3) of specific stoichiometry. Efficient space-filling enables dense-packing to leave small trigonal holes that accommodate nitrate anions. Significantly, the formation of compound **2** is independent of M : L ratio, and is obtained even when a ratio of M : L ratio of 1 : 2 is used. The influence of the anion, therefore, appears significant enough to influence the oberved coordination of the bridging ligand and stoichiometry of the product isolated. Current works seeks to investigate further the binding of *N*-oxide ligands to d-, f-block and other elements.

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Notes and references

‡ Preparation of [Zn(MeOH)$_2$L$_3$](SiF$_6$)·3MeOH **1**: 4,4′-bipyridine *N*,*N*′-dioxide (22 mg, 0.10 mmol) in MeOH (6 cm^3) was carefully mixed with a solution of ZnSiF$_6$·6H$_2$O (21 mg, 0.05 mmol) in MeOH (6 cm^3). The reaction gave a colourless crystalline product after several days. [ZnL$_6$](NO$_3$)$_2$ **2** was prepared similarly replacing ZnSiF$_6$·6H$_2$O with Zn(NO$_3$)$_2$·6H$_2$O, colourless crystals growing over several days.

§ *Crystal data*: for **1**: $C_{35}H_{44}F_6N_6O_{11}SiZn$, $M = 932.22$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.174(3)$, $b = 28.313(5)$, $c = 13.865(4)$ Å, $\beta = 92.06\ (3)°$, $U = 3991(2)$ Å^3, $T = 150(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.74 mm^{-1}. 7821 unique reflections of which 5277 with $F_o > 4\sigma(F_o)$. Final $R1$ [$I > 2\sigma(I)$] = 0.083, $wR2$ (all data) = 0.166.

For **2**: $C_{60}H_{48}N_{14}O_{18}Zn$, $M = 1318.49$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.8202(9)$, $b = 11.6805(10)$, $c = 14.006(2)$ Å, $\alpha = 104.589(6)$, $\beta = 96.265(6)$, $\gamma = 99.082(6)°$, $U = 1326.1(3)$ Å^3, $T = 150(2)$ K, $Z = 1$, μ(Mo-Kα) = 0.55 mm^{-1}. 6140 unique reflections ($R_{int} = 0.099$) of which 3378 with $F_o > 4\sigma(F_o)$. Final $R1$ [$I > 2\sigma(I)$] = 0.069, $wR2$ (all data) = 0.146.

CCDC 182/1795. See http://www.rsc.org/suppdata/cc/b0/b006679f/ for crystallographic files in .cif format.

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