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Mixed-anion complexes with a bipyrazolyl ligand. A new entry to a realm of three-dimensional five-connected coordination topologies†

Vira V. Ponomarova,[a] Vasiliy V. Komarchuk,[a] Ishtvan Boldog,[a] Alexander N. Chernega,[b] Joachim Sieler[c] and Konstantin V. Domasevitch*[a]

[a] *Inorganic Chemistry Department, Kiev University, Volodimirska Street 64, Kiev 01033, Ukraine. E-mail: dk@anorgchemie.univ.kiev.ua*
[b] *Institute of Organic Chemistry, Murmanskaya St. 4, Kiev 253660, Ukraine*
[c] *Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leipzig, Germany*

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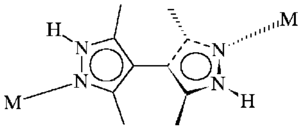
Cross-linking of corrugated square grid coordination layers by anionic bridging groups generates five-connected coordination networks; the 3D topologies of mixed-anion cobalt(II) and nickel(II) complexes with a tetramethyl-substituted 4,4′-bipyrazolyl ligand are supported by μ-SO_4^{2-} functions and exist as neutral or cationic five-connected arrays involving additional terminal (NCS^-) or non-coordinated (NO_3^-, ClO_4^-) groups.

The modular, or multicomponent, approach to crystal design has developed rapidly in recent years, and has resulted in the engineering of a range of metal–organic polymers based upon multiconnected metal ions and organic bridging ligands (connectors).[1] Dimensionality of the resulting modular structures as well as inherent properties of their topology of practical interest (*e.g.* porosity, chirality) originate in connectivity of a single point and mutual spatial alignment of the links. A wide range of transition metal ions and spacer ligands easily produces different three- and four-connected topologies, but networks of higher connectivity remain rather rare.[2–4] We report an approach for the generation of a five-connected network topology without the need for metal ions with high coordination numbers.[2]

The most simple and symmetric variant of five-connected topologies, a body-centered tetragonal (bct) net, has recently been observed for a La^{3+}–4,4′-bipyridine–*N*,*N*′-dioxide network.[2] This net may be viewed as a set of successively interlinked 2D four-connected layers that loosely possess a puckered structure.[5] This key geometrical feature of a ‘2D building block’ may be easily engineered considering the structure of the organic connectors themselves. Thus the 3,3′,5,5′-tetramethyl-substituted 4,4′-bipyrazolyl ligand (4,4′-bpz) is an angular bridging unit (two planar pyrazolyl fragments are related by *ca.* 60–80°)[6] that supports non-collinear orientation of two N–M vectors and facilitates corrugation of coordination layers $[M(4,4'\text{-bpz})_2]_n$.[7] The flexible geometry of such a square grid network greatly favors a close disposition for the pairs of metal atoms from successive layers and their effective interlinking by additional organic or inorganic connectors.



4,4'-bpz

This appears to be a common feature of mixed-anion metal complexes with 4,4’-bipyrazolyl ligands.‡ The three-dimensional structure of the isomorphous sulfate–perchlorate (nitrate) complexes $[M_2(4,4'\text{-bpz})_4(H_2O)_2\{SO_4\}](X)_2\cdot H_2O$ (M = Co, X = ClO_4, **1**; M = Ni, X = NO_3, **2**)§ is generated by cross-linking of the 2D square grid coordination layers $[M(4,4'\text{-bpz})_2]_n$ by μ-SO_4 anions (Fig. 1). This 3D structure exists as a distorted five-connected bct net, 4/5 of the links of which are bridging 4,4′-bpz molecules and 1/5 are bridging sulfate groups (M–M 9.89 and 6.56 Å, respectively). The coordination environment of the metal atoms includes four nitrogen atoms of μ-bipyrazolyl ligands in an equatorial plane [M–N: 2.092(3) Å, **1**; 2.084(8) Å, **2**] and oxygen atoms of the μ-SO_4 ligand and terminal water molecule in axial positions [M–O 2.092(3)–2.146(4) Å]. The angular structure of the organic connectors (interplanar angle 77.4°) supports the corrugated structure for the $[M(4,4'\text{-bpz})_2]_n$ layers.

The overall 3D linkage thus uses only half of the axial functionality from the corrugated ‘2D building block’ $[M(4,4'\text{-bpz})_2]_n$ which is contrary to the linkage pattern of known ‘pillared’ structures, *cf.* $Zn(4,4'\text{-bipy})_2SiF_6$.[4] These axial positions that remain not involved in the overall 3D linkage allow further functionalization of the structure. The use of additional anionic groups with greater affinity for transition metal ions may lead to the formation of a genuine porous array in which an

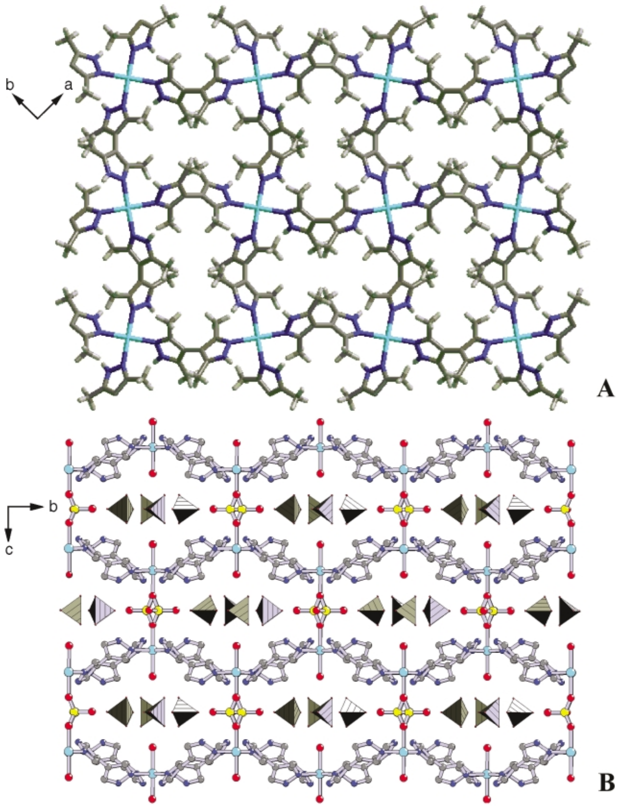


Fig. 1 Square grid coordination layers $[Co(4,4'\text{-bpz})_2]_n$ in structure **1** (A) and their interconnection by μ-SO_4 groups (B). Bridging sulfate groups are disordered over a four-fold axis and non-coordinated perchlorate anions, presented as tetrahedra, are situated in the cavities of the network.

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† Electronic supplementary information (ESI) available: crystal structure determination and refinement details for **1**–**4**. See http://www.rsc.org/suppdata/cc/b1/b110599j/

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anionic group, instead of a water molecule for **1** and **2**, will occupy the second axial side at the metal ion. This situation is clearly illustrated by the structure of isomorphous Co(II) **3** and Ni(II) **4** sulfate–thiocyanate complexes $[M_2(4,4'\text{-bpz})_4\{SO_4\}\{NCS\}_2]\cdot2CH_3OH\cdot2CHCl_3$ (Fig. 2). Each metal ion has an octahedral environment and coordinates four pyrazole nitrogen atoms, and two axial positions are occupied by μ-SO_4 and terminal NCS groups. The resulting neutral five-connected network incorporates one methanol and one chloroform molecule per metal atom. 2D nets $[M(4,4'\text{-bpz})_2]_n$ are corrugated, each of their quadrangular meshes having a cyclobutane conformation with an interplanar angle of *ca.* 49° (29° for **1** and **2**). This clearly indicates that 3D topology of this type cannot be generated with linear rod-like connectors of a 4,4′-bipyridine type, that remain as yet to be the most common and usual in crystal engineering.[1,4,8]

The shortest circuits of the network adopted around each metal center are the same as for structures **1** and **2** and include four quadrangles and six hexagons. However, topologies of these structures and bct network are quite different and may be discussed in terms of supramolecular isomers.[1] Both topologies are uninodal nets that have the same vertex symbol $(4\cdot4\cdot4\cdot4\cdot6\cdot6\cdot6_5\cdot6_5\cdot6_5\cdot6_5)$,[5] but the coordination sequences of these nets differ after the third neighbours: 5, 16, 33, 58 for **1** and **2**, and 5, 16, 34, 60 for **3** and **4**. This difference is parallel to the one observed between four-connected diamond and lonsdaleite topologies.[5] For **3** and **4** the sulfate groups bridge zigzag ribbons of metal atoms from successive square grid layers, and within a single metal–organic quadrangle three metal atoms are bound, through a sulfate bridge, to neighbours from the same layer (upper or lower). This network topology is unprecedented and was not predicted by Wells.[9] Both 3D architectures may be related as different modes of space tiling by square pyramids sharing the vertices (which are at the midpoints of M–M links) (Fig. 3).

Our results provide wide possibilities for the generation of novel five-connected topologies that may be anticipated for a number of transition metal ions, organic and inorganic bridging groups. This approach implies well known and predictable coordination geometry around the metal atom and conformational features of organic bridging groups that allow the desired geometry for the network subunit of lower connectivity to be designed separately.

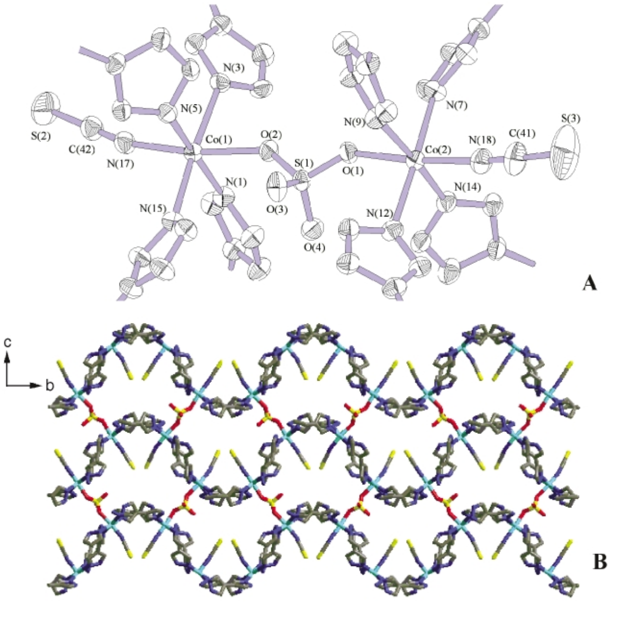

Fig. 2 (A) Functions of bridging SO_4 and terminal NCS ligands in structure **3** (methyl groups are omitted for clarity). (B) Interconnection of corrugated coordination layers $[Co(4,4'\text{-bpz})_2]_n$ by sulfate anions.

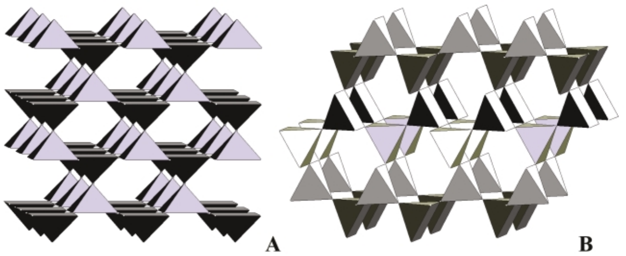

Fig. 3 Representation of overall 3D connectivities and their representation as space tiling by square pyramids sharing the vertices in **1** and **2** (A), and **3** and **4** (B).

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Notes and references

‡ Mixed-anion complexes **1**–**4** were prepared using a similar procedure which employed metal perchlorate (nitrate, thiocyanate) and metal sulfate. In a typical synthesis, a solution of 0.092 g (0.25 mmol) of $Co(ClO_4)_2\cdot6H_2O$ and 0.070 g (0.25 mmol) of $CoSO_4\cdot7H_2O$ in 5 ml methanol was layered over a solution of 0.190 g (1.0 mmol) of 4,4′-bpz in 5 ml methanol and 5 ml chloroform. Slow interdiffusion of the layers afforded crystallization of the pink-red sulfate–perchlorate complex $[Co_2(4,4'\text{-bpz})_4(H_2O)_2\{SO_4\}](ClO_4)_2\cdot H_2O$ **1** (yield: 0.215 g, 70%).

§ Crystallographic measurements were made at 223 K using a SMART CCD Siemens diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). *Crystal data*: for $[Co_2(4,4'\text{-bpz})_4(H_2O)_2\{SO_4\}](ClO_4)_2\cdot H_2O$ **1**: $C_{40}H_{62}Cl_2Co_2N_{16}O_{15}S$, $M = 1227.88$, tetragonal, space group $P4/mnc$ (no. 128), $a = 13.7588(9)$, $c = 16.726(1)$ Å, $U = 3166.3(4)$ Å^3, $Z = 2$, $\mu = 7.08$ cm^{-1}, θ_{max} 28.9°, 2070 unique data, $R1 = 0.044$.

For $[Ni_2(4,4'\text{-bpz})_4(H_2O)_2\{SO_4\}](NO_3)_2\cdot H_2O$ **2**: $C_{40}H_{62}N_{18}Ni_2O_{13}S$, $M = 1152.56$, tetragonal, space group $P4/mnc$ (no. 128), $a = 13.654(1)$, $c = 16.477(2)$ Å, $U = 3071.9(5)$ Å^3, $Z = 2$, $\mu = 7.13$ cm^{-1}, θ_{max} 27.1°, 1129 unique data, $R1 = 0.080$.

For $[Co_2(4,4'\text{-bpz})_4\{SO_4\}\{NCS\}_2]\cdot2CH_3OH\cdot2CHCl_3$ **3**: $C_{46}H_{66}Cl_6Co_2N_{18}O_6S_3$, $M = 1393.91$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 13.699(2)$, $b = 21.594(3)$, $c = 22.220(3)$ Å, $U = 6573(2)$ Å^3, $Z = 4$, $\mu = 9.01$ cm^{-1}, θ_{max} 28.3°, 14 262 unique data, $R1 = 0.055$.

For $[Ni_2(4,4'\text{-bpz})_4\{SO_4\}\{NCS\}_2]\cdot2CH_3OH\cdot2CHCl_3$ **4**: $C_{46}H_{66}Cl_6N_{18}Ni_2O_6S_3$, $M = 1393.47$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 13.625(1)$, $b = 21.376(2)$, $c = 22.072(2)$ Å, $U = 6429(1)$ Å^3, $Z = 4$, $\mu = 9.91$ cm^{-1}, θ_{max} 27.0°, 15 614 unique data, $R1 = 0.049$.

CCDC reference numbers 175727–175730. See http://www.rsc.org/suppdata/cc/b1/b110599j/ for crystallographic data in CIF or other electronic format.

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