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[9] Selected analytical and spectroscopic data for the new complexes: Complex **2**, elemental analysis (%) calcd for $C_{42}H_{24}N_6O_{18}I_2Ir_6{\cdot}0.5(C_6H_{14})$: C 22.99, H 1.33, N 3.57; found: C 23.12, H 1.39, N 3.49; IR (Nujol): $\tilde{\nu}=2101$ (sh), 2079 (s), 2061 (sh), 2042 (s), 2023 (sh), 2007 cm^{-1} (sh) (CO); ^1H NMR ([D$_8$]toluene, −50 °C): $\delta=9.74$ (dd, $J=6.3$, 1.8 Hz, 2H), 9.68 (d, $J=6.3$ Hz, 2H), 9.56 (dd, $J=6.3$, 1.8 Hz, 2H), 6.58 (td, $J=8.4$, 2.1 Hz, 2H), 6.49 (m, 4H), 6.35 (td, $J=7.2$, 1.5 Hz, 2H), 6.17 (d, $J=8.4$ Hz, 2H), 6.10 (d, $J=8.1$ Hz, 2H), 5.98 (td, $J=7.2$, 1.3 Hz, 2H), 5.69 ppm (m, 4H). Complex **3**-HH; elemental analysis (%) calcd for $C_{14}H_8N_2O_6I_2Ir_2$: C 17.92, H 0.86, N 2.98; found: C 18.17, H 1.03, N 2.89; IR (toluene): $\tilde{\nu}=2123$ (s), 2095 (m), 2071 (s), 2050 cm^{-1} (w) (CO); ^1H NMR (C_6D_6, 23 °C): $\delta=8.90$ (ddd, $J=6.6$, 1.8, 0.6 Hz, 2H), 6.34 (ddd, $J=8.7$, 6.6, 1.8 Hz, 2H), 6.22 (ddd, $J=8.7$, 1.2, 0.6 Hz, 2H), 5.61 ppm (td, $J=6.6$, 1.2, 0.6 Hz, 2H). Complex **3**-HT; elemental analysis (%) calcd for $C_{14}H_8N_2O_6I_2Ir_2$: C 17.92, H 0.86, N 2.98; found: C 18.07, H 0.96, N 2.91; IR (toluene): $\tilde{\nu}=2123$ (s), 2096 (m), 2070 cm^{-1} (s) (CO); ^1H NMR (C_6D_6, 23 °C): $\delta=9.30$ (dd, $J=6.6$, 1.8 Hz, 2H), 6.35 (ddd, $J=8.7$, 6.6, 1.8 Hz, 2H), 6.19 (dd, $J=8.7$, 1.5 Hz, 2H), 5.67 ppm (td, $J=6.6$, 1.5 Hz, 2H).
[10] a) Crystal data for **2**·0.5(C_6H_{14}): $C_{42}H_{24}I_2Ir_6N_6O_{18}{\cdot}0.5(C_6H_{14})$, $M_r=2350.76$, laminar crystal ($0.09\times0.035\times0.008$ mm), triclinic, space group $P\bar{1}$, $a=14.2642(18)$, $b=20.927(3)$, $c=21.153(3)$ Å, $\alpha=68.369(2)$, $\beta=81.169(2)$, $\gamma=82.126(2)$°, $V=5777.8(14)$ Å^{-3}, $Z=4$, $\rho_{calcd}=2.702$ g cm^{-3}, $F(000)=4220$, $T=100(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å, $\mu=14.905$ mm^{-1}). Data collected with a Bruker SMART APEX CCD diffractometer. Of 49364 measured reflections (2θ: 5–50°, ω scans 0.3°), 20135 were unique ($R_{int}=0.0892$); a multi-scan absorption correction was applied (SADABS program) with min./max. transmission factors of 0.455/0.825. Structure solved by Patterson and difference-Fourier maps; refined using SHELXTL. Two independent complex molecules and disordered hexane solvent were found in the asymmetric unit. Final agreement factors were $R1=0.0660$ (10409 observed reflections, $F^2>4\sigma(F^2)$) and $wR2=0.1912$; data/restrains/parameters 20135/309/1381; GOF = 0.970. Largest peak and hole in the final difference map 2.912 and −2.980 e Å^{-3}. The limited quality of the structural data (also the merging and agreement factors) should be necessarily associated to the very small dimensions of the crystal, and to the associated diffracting weakness. b) CCDC-191178 (**2**) and CCDC-191179 (**3**-HH) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).
[11] Crystal data for **3**-HH·0.25(C_7H_8)·0.25(C_6H_{14}): $C_{14}H_8I_2Ir_2N_2O_6{\cdot}0.25(C_7H_8){\cdot}0.25(C_6H_{14})$, $M_r=983.00$, triclinic, space group $P\bar{1}$, $a=11.9579(12)$, $b=12.6320(13)$, $c=16.2249(16)$ Å, $\alpha=104.439(2)$, $\beta=99.257(2)$, $\gamma=93.659(2)$°, $V=2328.6(4)$ Å^{-3}, $Z=4$, $\rho_{calcd}=2.804$ g cm^{-3}, $F(000)=1756$, $T=100(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å, $\mu=14.103$ mm^{-1}). Data collected as described for **2** with a prismatic block ($0.27\times0.25\times0.09$ mm). Of 27550 measured reflections (2θ: 5–54°, ω scans 0.3°), 10076 were unique ($R_{int}=0.0360$); a multi-scan absorption correction was performed (SADABS program) with min./max. transmission factors of 0.092/0.244. Structure solution and refinement as described for **2**. Two independent complex molecules and disordered toluene and hexane solvents were found in the asymmetric unit. Final agreement factors were $R1=0.0279$ (9002 observed reflections) and $wR2=0.0638$. Data/restrains/parameters 10076/37/518; GOF = 1.051. Largest peak and hole in the final difference map 1.652 and −1.107 e Å^{-3}.[10b]
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Nanoporous Coordination Polymers

Nanoporous Lanthanide–Copper(II) Coordination Polymers: Syntheses and Crystal Structures of $[\{M_2(Cu_3(iminodiacetate)_6)\}{\cdot}8H_2O]_n$ (M = La, Nd, Eu)**

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Designing and constructing three-dimensional (3D) coordination polymers with well-defined pores is of current interest for the creation of new zeolite-type materials with potential applications in catalysis, gas storage, chemical separation, and ion exchange.[1–3] Up to now, a great many porous three-dimensional coordination polymers have been synthesized and characterized.[4–6] However, the synthetic focus in this rapidly expanding area of research has been centered on monometallic porous coordination polymers,[1–6] while the chemistry, as well as the synthetic strategy toward porous heterometallic coordination polymers has received much less attention.[7–9]

It is well known that heterometallic coordination polymers have potentially interesting physical properties, such as conductivity or magnetic ordering, that result from interactions between two distinct metal centers connected by a suitable linker.[10,11] Moreover, the structural preference of different metal centers in a mixed-metal system often leads to a broader palette of polymer structural motifs than can be achieved with monometallic systems, and thus makes the obtained structures more diverse.[7a] In particular, the incorporation of different metals may enhance the catalytic properties of the coordination polymers. By using this approach, we now report the syntheses and crystal structures of three 3D lanthanide–transition metal coordination polymers of the form $[\{M_2(Cu_3(iminodiacetate)_6)\}{\cdot}8H_2O]_n$, where M = La (**1**),Nd (**2**), and Eu (**3**). Investigation of the thermal

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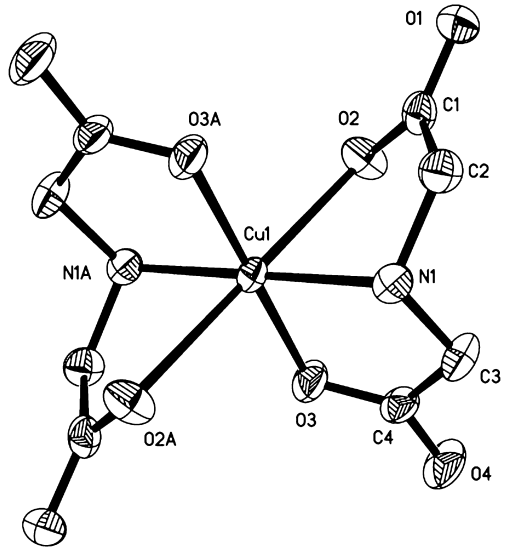

Figure 1. ORTEP diagram of the metalloligand.

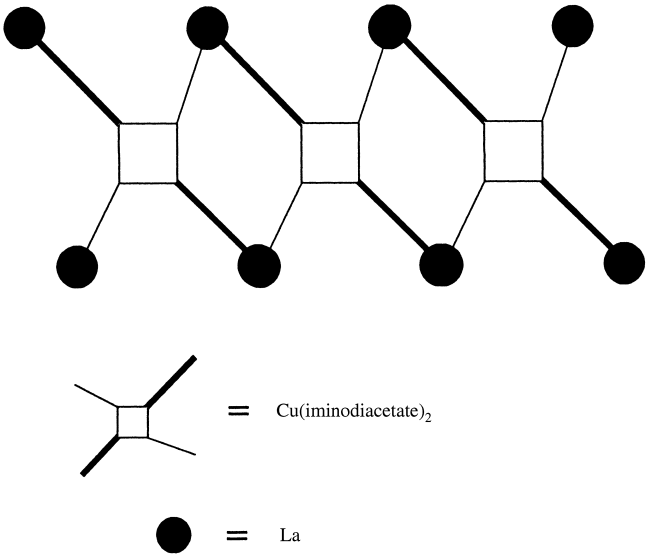

Figure 2. A schematic of the infinite band-like structure, with Cu(iminodiacetate)$_2$ anions connected to La^{III} ions. The bold lines represent carboxylate groups of iminodiactate units that bind to a La^{III} ion in a bidentate fashion, while the narrow lines represent carboxylate groups that exhibit a monodentate binding mode.

stability of the coordination polymers shows that their frameworks retained their stability when the guest molecules were removed.

The synthetic strategy of this study is to use a metalloligand to construct the coordination polymers.[7a,12] As shown in Figure 1, the iminodiacetate anions form complexes with copper(II) centers, in which four noncoordinated oxygen atoms can act as potential donors for other metal ions. If these donors do coordinate with another metal ion, an assembly process will occur, which leads to the formation of a heterometallic coordination polymer.

Compounds **1**, **2**, and **3** were obtained by the reaction of $LaCl_3 \cdot 9H_2O$, $NdCl_3 \cdot 9H_2O$, or $EuCl_3 \cdot 9H_2O$, respectively, with a mixture of iminodiacetic acid and $Cu(NO_3)_2 \cdot 3H_2O$ in a 2:6:3 molar ratio in aqueous solution, at a pH value of 5–6. X-ray diffraction analysis[13] reveals that the three compounds are isomorphous. In **1**, the copper(II) ion is chelated by two iminoacetate ligands to form the metalloligand (Figure 1), which acts as a tetradentate ligand, with each of the uncoordinated oxygen atoms coordinating to one La(III) ion, which leads to the formation of an infinite band-like structure, as illustrated in Figure 2. Connection of the bands in C_3 symmetry through sharing La^{III} ions gives rise to an edge-shared 3D structure with a chair-shaped hexagonal channel along the crystallographic *c* axis, as shown in Figure 3. Each channel in **1** is formed by six CuO_4N_2 polyhedra and six LaO_9 polyhedra. The diameter of the hexagonal channels is 16.8 Å, with lattice water molecules located within the channels. To the best of our knowledge, the pores in **1** are the largest among heterometallic coordination polymers reported to date.

Each copper(II) ion in **1** is six-coordinated in a distorted octahedral geometry by four oxygen atoms and two nitrogen atoms from iminoacetate ligands, while each La^{III} ion is nine-coordinated through interactions with carboxylate groups from six metalloligands; three ligands exhibit bidentate chelation, while the remaining three chelate in a monodentate fashion. The bond lengths of Cu–N, Cu–O, and La–O are 2.022(3), 1.960(3)–2.373(3), and 2.449(3)–2.775(3) Å, respectively, which is comparable to those bonds found in the lanthanide–copper(II)–iminoacetate complex previously reported.[14] The shortest Cu···Cu, Cu···La, and La···La separations in **1** are 6.370, 4.640, and 7.461 Å, respectively.

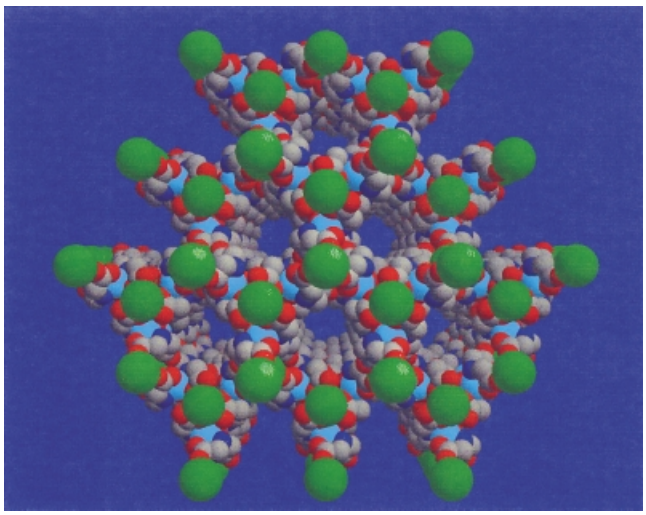

Figure 3. Space-filling representation of the 3D structure of **1**, viewed along the crystallographic *c* axis. La: green, Cu: cyan, O: red, N: deep blue and C: grey.

The crystal structures of **2** and **3** are very similar to that of **1**. In **2**, the Cu–N bond length is 2.009(3) Å, while the length of the Cu–O bonds range from 1.950(3) to 2.378(2) Å, and the Nd–O bond lengths are between 2.397(2) and 2.741(3) Å. The shortest Cu···Cu, Cu···Nd, and Nd···Nd distances are 6.071, 4.594, and 7.335 Å, respectively, slightly shorter than those of

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1. In **3**, the Cu–N bond length is 2.019(3) Å, while the Cu–O bond lengths range from 1.952(2) to 2.401(3) Å, and the Eu–O bond lengths of between 2.339(3)–2.721(3) Å. The shortest Cu···Cu, Cu···Eu, and Eu···Eu distances are 6.064, 4.552, and 7.264 Å, respectively, slightly shorter than those of **2**.

Owing to the similarity of the structures for **1**, **2,** and **3**, compound **1** was selected for thermogravimetric analysis (TGA) to examine the thermal stability of the complexes. The TGA curve for **1** (Figure 4) displays an initial weight loss of 11.16% between 50 and 141.6 °C, which corresponds to the loss of lattice water molecules. Between 141.6 and 300 °C, **1** shows no weight loss, which is an indication of its stability up to 300 °C, comparable to that of $[Zn_4O(O_2C{-}C_6H_4{-}CO_2)]_n$ (300 °C),[1e] and significantly higher than for $[Cu_3(TMA)_2(H_2O)_3]_n$ (240 °C, TMA = benzene-1,3,5-tricarboxylate)[2a], and $[Cu_3(BTB)_2(H_2O)_2]_n$ (250 °C, BTB = 4,4′,4″-benzene-1,3,5-triyl-tribenzocarboxylate).[3a] The higher thermal stability of **1** is mainly attributed to the coordination of cooper(II) ions, which solidifies the flexible organic ligand.

In light of the results of the TGA study of **1**, we decided to investigate the crystal structures of samples that had been heated to 200 °C overnight under reduced pressure. Although TGA proved such samples to be anhydrous, they were extremely hygroscopic and, thus, the structure of an anhydrous sample of **1** could not be obtained. However, we were able to collect and fully analyze data from structures of **1** that were reloaded with water (hereafter named **1a**) and **3** (hereafter named **3a**). Structural characterization[13] reveals that the frameworks of **1a** and **3a** are very similar to that of **1** and **3**, respectively, but the number of water molecules in **1a** and **3a** is significantly less than that in **1** and **3**; both structures now only containing five lattice water molecules per polymer unit.

Interestingly, the TGA of **1a** (Figure 4) shows that the dehydration temperature for the reloaded water molecules in **1a** (approximately 100 °C) is much lower than that in **1** (approximately 150 °C). Crystal structure analysis reveals that the significant difference in dehydration temperature between the two samples can be attributed to different arrangements of the water molecules in **1** and **1a**. The O2W and O3W

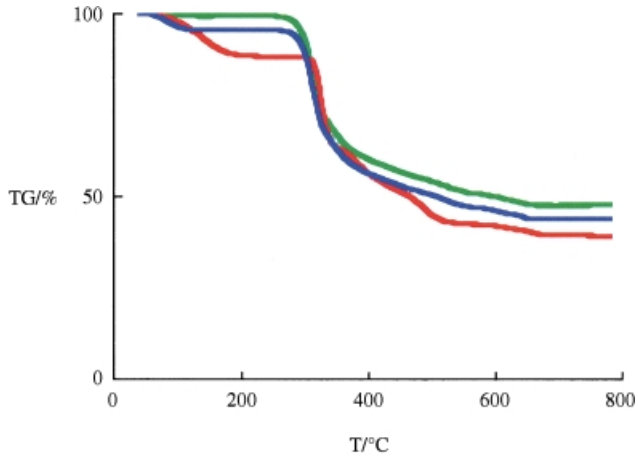

Figure 4. TGA curves for **1** (red), guest-free **1** (green), and **1a** (blue).

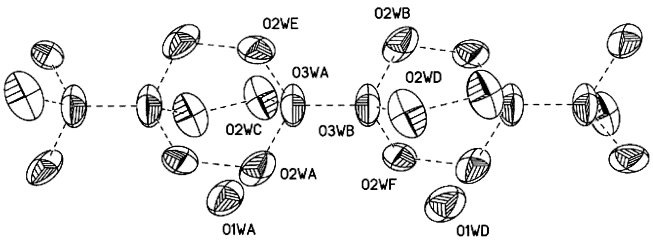

Figure 5. An ORTEP plot showing the Chinese-lanternlike water cluster in **1**.

lattice water molecules in **1** form a Chinese-lanternlike water cluster through water–water hydrogen bonds (Figure 5), with the O1W water molecules forming weak hydrogen bonds with the oxygen atoms of carboxylate groups. In contrast, the lattice water molecules in **1a** are hydrogen-bonded only to oxygen atoms of carboxylate groups; there are no water–water hydrogen bonds observed, as a consequence of the O2W water molecules being absent in the structure of **1a**.

In conclusion, we have reported the crystal structures and thermal properties of three nanoporous 3D lanthanide–copper(II) coordination polymers. Since the coordination polymers possess high thermal and structural stability, they may be promising materials for applications in catalysis, separation, gas storage, and molecular recognition. Investigations of molecular recognition, as well as potential catalytic properties of the materials are underway.

Experimental Section

1: An aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.36 g, 1.5 mmol) was added to an aqueous solution of iminodiacetic acid (0.40 g, 3.0 mmol). After the pH value of the mixture had been adjusted to approximately 6, an aqueous solution of $LaCl_3$ (1.0 mmol) was added. The resulting mixture was allowed to stand in air at room temperature for one week. Blue hexagonal column-shaped crystals of **1** suitable for X-ray crystallography were obtained in 83% yield. Compounds **2** and **3** were prepared in a similar way to **1**, except that $NdCl_3$ and $EuCl_3$ were used instead of $LaCl_3$.

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[13] X-ray crystal structure analysis: The data were collected at 293(2) K on a CAD4 diffractometer ($Mo_{K\alpha}$ radiation; $\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXTL Version 5.10) and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Crystal data for $[C_{24}H_{46}Cu_3La_2N_6O_{32}]_n$ (**1**): $0.50 \times 0.40 \times 0.40$ mm, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 13.4713(19)$, $c = 14.922(3)$ Å, $\gamma = 120°$, $V = 2345.3(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.958$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.223$ mm^{-1}, $M_W = 1398.98$. Of the 2615 reflections measured ($2 < 2\theta < 56$), 1708 symmetry-independent reflections were used to solve the structure. Based on these data and 108 refined parameters, $R_1 = 0.0410$ (all data), $wR_2 = 0.0757$, GOF (F^2) = 1.111. Crystal data for $[C_{24}H_{46}Cu_3Nd_2N_6O_{32}]_n$ (**2**): $0.52 \times 0.40 \times 0.40$ mm, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 13.4027(19)$, $c = 14.669(3)$ Å, $\gamma = 120°$, $V = 2282.0(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.019$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.699$ mm^{-1}, $M_W = 1409.64$. Of the 1854 reflections measured ($2 < 2\theta < 56$), 1189 symmetry-independent reflections were used to solve the structure. Based on these data and 114 refined parameters, $R_1 = 0.0642$ (all data), $wR_2 = 0.0870$, and GOF (F^2) = 1.011. Crystal data for $[C_{24}H_{46}Cu_3Eu_2N_6O_{32}]_n$ (**3**): $0.33 \times 0.18 \times 0.17$ mm, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 13.306(5)$, $c = 14.528(5)$ Å, $\gamma = 120°$, $V = 2227.6(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.101$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 4.291$ mm^{-1}, $M_W = 1425.08$. Of the 1533 reflections measured ($2 < 2\theta < 56$), 1468 symmetry-independent reflections were used to solve the structure. Based on these data and 107 refined parameters, $R_1 = 0.0497$ (all data), $wR_2 = 0.1143$, GOF (F^2) = 1.127. Crystal data for $[C_{24}H_{38}Cu_3La_2N_6O_{29}]_n$ (**1a**): $0.32 \times 0.24 \times 0.22$ mm, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 13.5588(3)$, $c = 14.9986(6)$ Å, $\gamma = 120°$, $V = 2387.94(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.857$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.157$ mm^{-1}, $M_W = 1344.98$. Of the 9010 reflections measured ($2 < 2\theta < 56$), 1721 symmetry-independent reflections were used to solve the structure. Based on these data and 100 refined parameters, $R_1 = 0.1017$ (all data), $wR_2 = 0.2352$, GOF (F^2) = 1.155. Crystal data for $[C_{24}H_{38}Cu_3Eu_2N_6O_{29}]_n$ (**3a**): $0.30 \times 0.22 \times 0.20$ mm, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 13.3031(2)$, $c = 14.5660(3)$ Å, $\gamma = 120°$, $V = 2232.42(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.025$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 4.273$ mm^{-1}, $M_W = 1369.08$. Of the 9618 reflections measured ($2 < 2\theta < 48$), 1170 symmetry-independent reflections were used to solve the structure. Based on these data and 107 refined parameters, $R_1 = 0.0359$ (all data), $wR_2 = 0.0881$, GOF (F^2) = 1.091. CCDC-193487–193491 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

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Protein-Protein Interactions

Design and Application of an α-Helix-Mimetic Scaffold Based on an Oligoamide-Foldamer Strategy: Antagonism of the Bak BH3/Bcl-xL Complex**

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The design of low-molecular-weight ligands (< 750 Da) that recognize protein surfaces and subsequently disrupt protein–protein interactions is an area of intense research.[1] Current strategies for identifying small-molecule protein-surface antagonists primarily involve the use of combinatorial methods.

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