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Two Unprecedented Entangled Metal–Olsalazine Complexes with Coexistence of 2D → 3D Polycatenation and *meso*-Helix

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Rational self-assembly of the anti-inflammatory drug olsalazine (H_4osa) with a cobalt salt in the presence of linear bidentate ligands yields two novel metal–drug complexes [Co(H_2osa)(bpp)] (**1**) and [Co_2(osa)$(bpy)_2(H_2O)_4$] (**2**) [bpp = 1,3-bis(4-pyridyl)propane, bpy = 4,4′-bipyridine]. Their structures were determined by single-crystal X-ray diffraction and further characterized by elemental analysis, IR spectroscopy, X-ray powder diffraction, and thermogravimetric analysis (TGA). Compound **1** displays a new 2D → 3D parallel polycatenation of undulating (4,4) layers, whereas **2** exhibits an unusual 2D → 3D inclined polycatenation of (6,3) layers. To the best of our knowledge, they represent the first examples of metal–drug complexes that have both polycatenane and *meso*-helix characteristics. The magnetic properties of **1** and **2** have been studied by measuring their magnetic susceptibility in the temperature range of 2–300 K.

Introduction

Current interest in the crystal engineering of coordination polymer frameworks not only stems from their tremendous potential applications in porous materials, optical devices, magnetism, microelectronics, and heterogeneous catalysis, but also from their intriguing variety of molecular architectures and topologies.[1,2] An important subject in this field is the design and synthesis of helical metal–organic frameworks and the exploration of their potential utilities in enantioselective separation, asymmetric catalysis, and nonlinear optics.[1c,3,4] Helical structures, which are ubiquitous in nature, have attracted intense interest from chemists,[1c,4–6] and many helical coordination polymers have been prepared and discussed in several excellent reviews.[4a–4e] In contrast, metal–drug complexes with helical characteristics are rare, although many drugs possess modified pharmacological and toxicological properties administered in the form of metal complexes,[7] and the resulting helical metal–drug complexes are particularly important both in coordination chemistry and biochemistry.[1i,8–11] To the best of our knowledge, no metal–drug complex containing *meso*-helices has been reported to date, implying a new challenging issue in coordination chemistry.

On the other hand, considerable efforts have recently been invested in the design and synthesis of entangled networks. Entanglements, which are common in biology as seen in catenanes, rotaxanes, and molecular knots, have captured much attention due to their intrinsic aesthetic appeal and complicated topological structures.[1e–1h,12,13] Interpenetrating nets, which can be considered as polymeric analogues of catenanes and rotaxanes, are now becoming increasingly common, and many fascinating structures have been constructed and discussed in comprehensive reviews by Robson, Batten, Ciani, Proserpio, and their coworkers.[1e–1h,13] Apart from interpenetrating nets, particular attention has recently been turning to another burgeoning subclass described as polycatenates, which differ from interpenetrating nets in that the whole catenated array shows an increased dimensionality with respect to that of the constituent motifs, and each individual motif is not catenated with all the others in the array.[1f,13a] Furthermore, interest in these compounds is increasingly heightened by their potential applications ranging from sensor devices to drug delivery vehicles.[14,15] Unfortunately, metal–drug complexes with polycatenate character are extremely rare,[1f,13a] and therefore, the search for viable routes to construct polycatenated metal–drug complexes is still a great challenge for synthetic chemists.

In an attempt to construct polycatenated metal–drug complexes, we chose the anti-inflammatory drug olsalazine {H_4osa = 3,3′-azo[bis(6-hydroxybenzoic acid)]} and two linear bidentate ligands, 1,3-bis(4-pyridyl)propane (bpp)

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and 4,4′-bipyridine (bpy), based on the following considerations: (i) olsalazine, as a long flexible dicarboxylato ligand, has the potential to produce unique interwoven motifs, thanks to its varied conformations (Scheme S1) and geometries;[5d,14a,16,17d] (ii) olsalazine has been widely used to prevent and treat inflammatory bowel diseases, such as ulcerative colitis;[17] (iii) bpp and bpy, as two long, linear ditopic N-donor ligands with little steric hindrance, are good candidates for the assembly of versatile entangled structures, mainly because of their propensity to form large voids or corrugates.[1f,15c,16a,18,19] In view of these points, we have performed many experiments, and these efforts have led to the isolation of the first entangled metal–olsalazine complexes, namely [Co(H_2osa)(bpp)] (**1**) and [Co_2(osa)$(bpy)_2$$(H_2O)_4$] (**2**), which exhibit both polycatenane and *meso*-helical character.

Results and Discussion

Crystal Structures

Single-crystal X-ray diffraction analysis reveals that **1** is an intriguing 3D polycatenated metal–olsalazine complex containing *meso*-helices. The crystallographically independent Co atom exhibits a distorted tetrahedral geometry (Figure 1) and is coordinated by two nitrogen atoms of two bpp ligands and two oxygen atoms from two H_2osa ligands. The H_2osa acts as a bidentate ligand; two carboxylic groups adopt a monodentate mode to connect with two Co atoms (Scheme S2a). On the basis of these coordination modes, all the Co centers are linked by H_2osa and bpp bridging ligands (Scheme S2b) to generate a 2D wavelike (4,4) (or 4^4-sql) layer with large parallelogrammic windows (12.27 × 14.84 Å, Figures 2 and S2a). To the best of our knowledge, no metal–olsalazine complex with 4^4-sql topology has been reported to date. Such an undulating sheet with large square pores offers an ideal opportunity for polycatenation. As shown in Figure 3, each sheet is catenated in a parallel fashion with its two nearest neighbor sheets (one above and one below) to give rise to an intriguing 2D → 3D parallel polycatenation of 4^4-sql layers. According to the notation suggested by Ciani and coworkers,[1f] the "degree of catenation" (Doc) here is equal to 2. To date, the 2D → 3D parallel polycatenation of (4,4) layers is extremely rare, as evidenced in a recent review.[1f] To the best of our knowledge, only a limited number of examples of 2D → 3D parallel polycatenation with (4,4) nets have been reported to date.[21–24] In addition, the 2D layer of **1** contains a single-stranded *meso*-helix (Figure 4) that is built from H_2osa ligands that bridge between the Co centers running along the [$12\bar{1}$] direction with a pitch of 25.596 Å. To date, *meso*-helical molecules are still quite uncommon, and only a few *meso*-helical coordination polymers have been characterized.[11,12a]

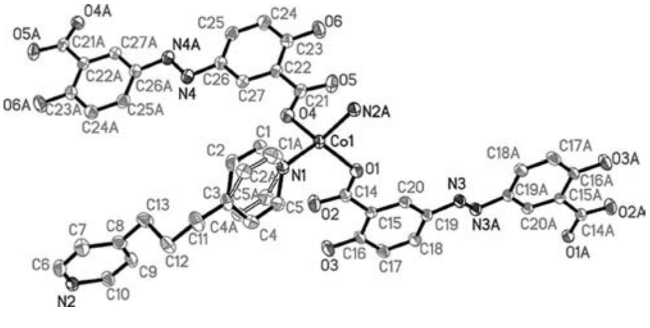

Figure 1. ORTEP diagram showing the coordination environment for the Co atom in **1**.

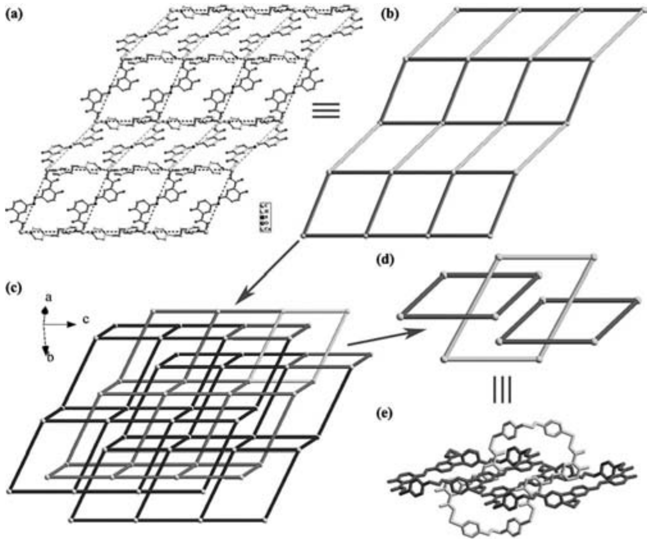

Figure 2. (a) Perspective and (b) schematic views of the 2D wavelike (4,4) layer in **1**. (c) Schematic view of the parallel polycatenation in **1** and the topological links of the windows [(d), (e)].

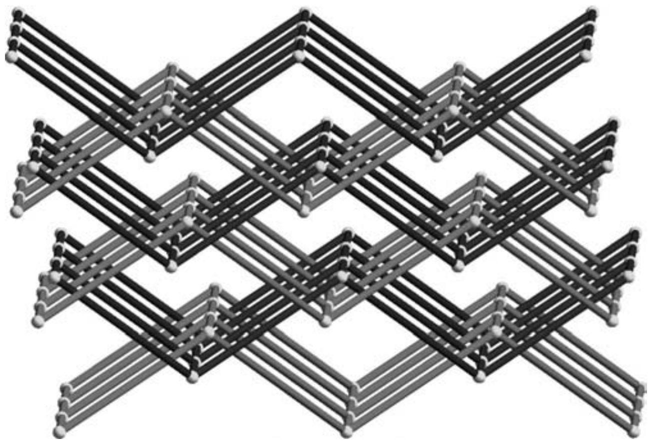

Figure 3. Schematic representation of 2D → 3D parallel polycatenation of the (4,4) layers in **1**.

When the rigid N-containing ligand bpy, which is shorter than bpp, was used instead of bpp, an unusual 2D → 3D inclined polycatenation of (6,3) layers is formed in **2**. The distorted octahedral cobalt center of **2** is coordinated by one carboxyl oxygen atom and one hydroxy oxygen atom from one osa ligand, two nitrogen atoms from two bpy ligands and two aqua ligands (Figure 5). Unlike that in compound **1**, the osa ligand in **2** acts as a tetradentate bridging

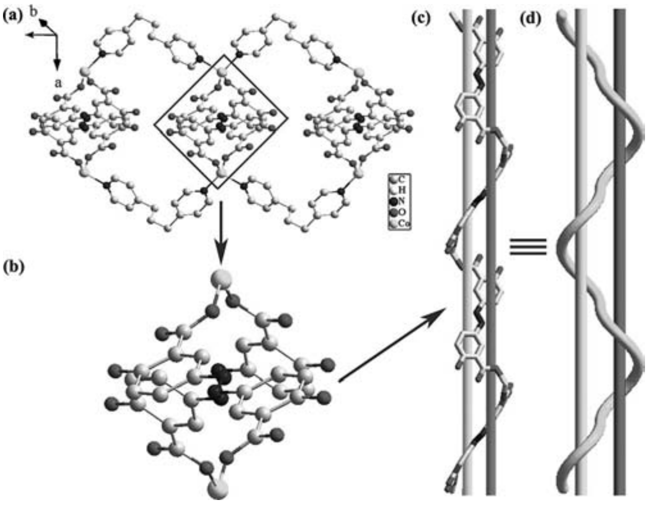

Figure 4. (a), (b) Side views of the single-stranded *meso*-helix in a 2D layer. (c) Perspective and (d) schematic views of the *meso*-helix.

ligand. Each osa ligand chelates two Co^{2+} ions using hydroxy and carboxyl oxygen atoms of the salicylic groups (Scheme S2c). Based on these connection modes, each Co center, which acts as a three-connected node, is connected to three others through one osa and two bpy ligands to generate a 2D (6,3) (or 6^3-hcb) net of large hexagonal windows (14.164 × 11.478 × 11.554 Å, Figures 6 and S2). As far as we know, such an unusual 2D metal–olsalazine complex with 6^3-hcb topology has not been reported to date. Similar to **1**, the open space within each sheet leads to polycatenation. Unlike **1**, however, the layers in **2** are distributed along two different directions, [111] and $[1\bar{1}1]$, to afford two sets of layers in parallel–parallel arrangements. Interestingly, these two sets of layers are interlocked in such a way that each window is catenated with four other windows from two distinct inclined layers [Doc = (2/2)], thus giving a graceful 2D → 3D inclined polycatenated array (Figures 7, 8 and S3) with an angle between two inclined (6,3) layers of 31.3°. The inclined catenation of the polymeric motifs represents a new type of supramolecular entanglement that has been recognized only recently.[1f,13a] To date, examples of 2D → 3D inclined polycatenation based on (6,3) layers are still rare as evidenced in a recent review by Ciani.[1f] The oldest example exhibiting a 2D → 3D inclined

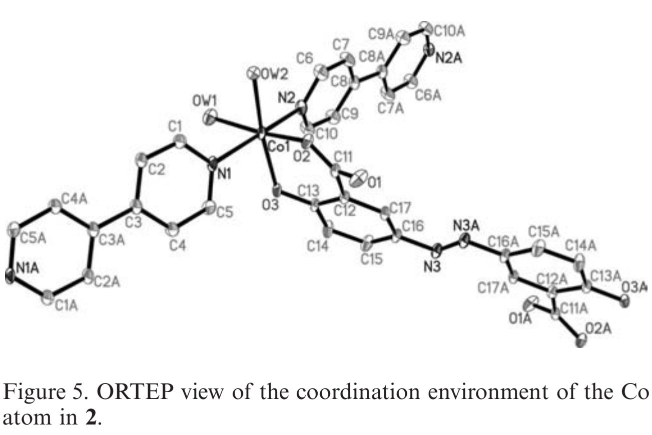

Figure 5. ORTEP view of the coordination environment of the Co atom in **2**.

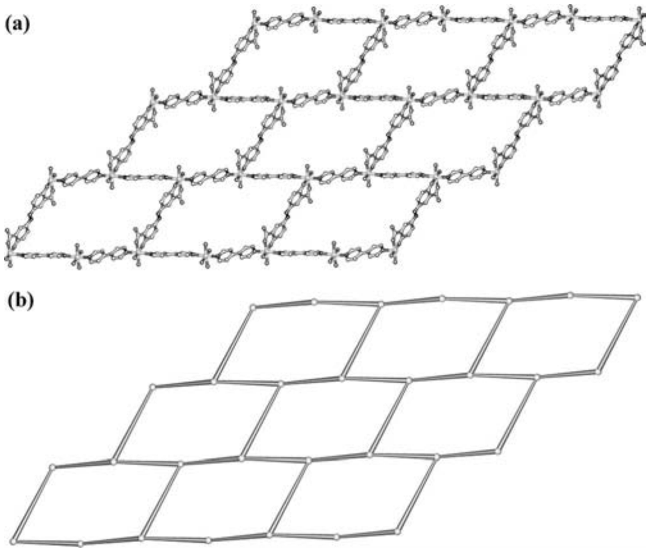

Figure 6. (a) Perspective and (b) schematic views of the 2D (6,3) layer in **2**.

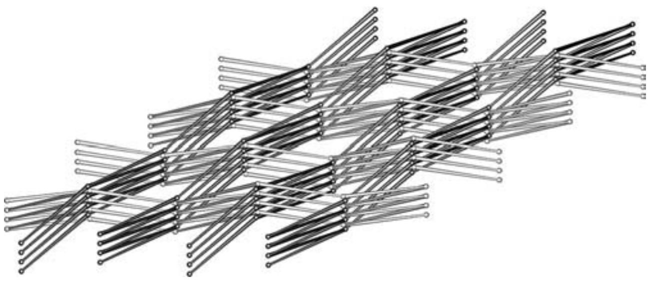

Figure 7. Schematic representation of 2D → 3D inclined polycatenation of the (6,3) layers in **2**.

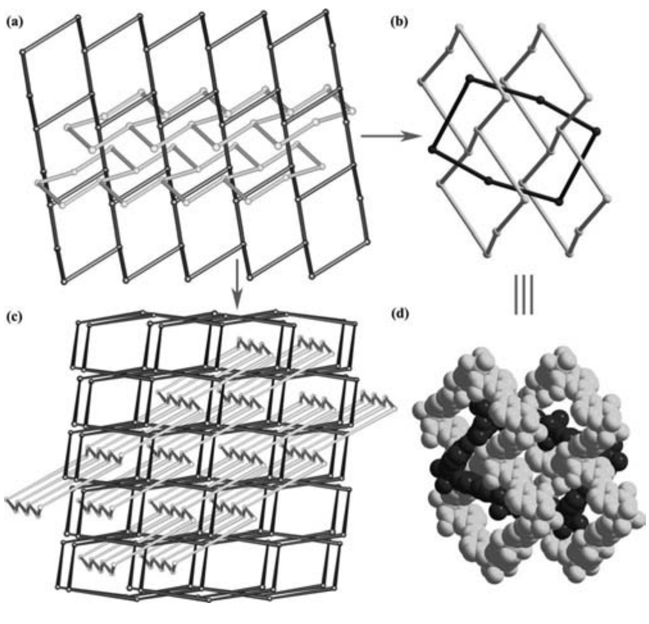

Figure 8. (a), (c) Schematic views of mutually inclined polycatenated (6,3) layer motifs in **2**. (b), (d) Schematic and space-filling presentations of the six-membered windows in one layer catenated by four others from two independent layers.

polycatenation of (6,3) layers was described by Zaworotko et al. in 1994.[25] Interestingly, the two inclined sets of (6,3) layers are crosslinked by strong hydrogen-bonding interactions [OW2···O1 2.697(4) Å and OW2···O3 2.717(4) Å] to generate a (3,6)-connected 3D self-penetrating network (Figure 9) with an unprecedented $(6^3)(6^{15})$ topology (the first symbol is for the OW2 ligand and the second for the Co atom). The self-catenation of the six-membered smallest topological rings by other six-membered smallest rings is illustrated in Figure 9. Similar to **1**, **2** also contains a single-stranded *meso*-helix (Figure 10). Unlike that in **1**, the *meso*-helix in **2** is constructed by osa and bpy ligands bridged between the Co centers, which is extended along the $[\bar{1}10]$ direction with a period of 21.877 Å.

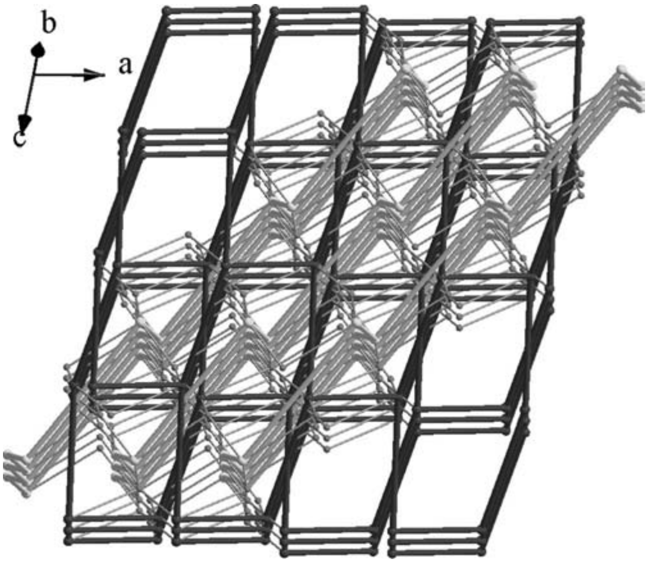

Figure 9. The (3,6)-connected 3D self-penetrating network derived from crosslinked polycatenated 2D (6,3) layers.

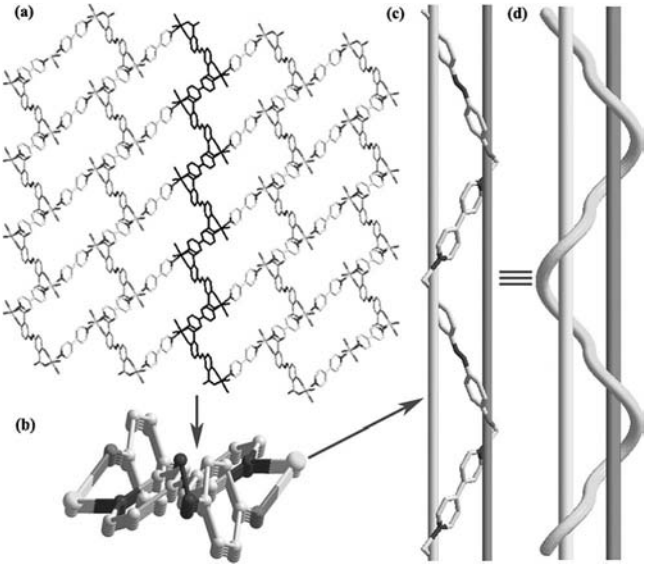

Figure 10. Top (a), side (b), perspective (c), and schematic (d) views of the single-stranded *meso*-helix in **2**.

Thermal Properties and X-ray Powder Diffraction

In order to examine the thermal stability of the two compounds, TGA was carried out for **1** and **2**. TGA showed that **1** possesses high thermal stability and does not decompose until 320 °C (Figure S5a). The first weight loss starts at 320 °C and continues up to 1000 °C, which corresponds to the decomposition of bpp and H_2osa ligands. The total weight loss of 83.71% is slightly less than that calculated (86.56%) if the final product is assumed to be CoO. In the differential scanning calorimetry (DSC) curve of **1**, the endothermic peaks at 390 and 420 °C, as well as the exothermic peaks at 493, 547, and 855 °C are attributed to the decomposition of the bpp and H_2osa ligands. The TGA curve of **2** (Figure S5b) exhibits three weight loss stages in the temperature ranges of 200–370 (27.13%), 370–520 (17.99%), and 520–695 °C (35.96%), all assigned to the decomposition of coordinated water molecules, bpy, and osa ligands. The residue is CoO. The total weight loss (81.08%) is in good agreement with the calculated value (81.28%). In the DSC curve of **2**, the endothermic peaks at 250 °C correspond with the release of coordinated water molecules. The endothermic peaks at 652 and 819 °C, as well as the exothermic peaks at 448 and 726 °C are attributed to the decomposition of the bpy and osa ligands.

In order to check the phase purity of the two compounds, X-ray powder diffraction (XRPD) patterns of **1** and **2** were recorded at room temperature (Figures S6 and S7). Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the crystalline powder samples.

Magnetic Properties

The temperature dependence of the magnetic susceptibilities for **1** and **2** were measured in the temperature range of 2–300 K at a direct current field of 1.0 kOe. For **1**, the $\chi_M T$ value of 2.34 $cm^3 K mol^{-1}$ at 300 K is much higher than the spin-only value of 1.88 $cm^3 K mol^{-1}$ expected for an isolated tetrahedral Co^{II} ion ($S = {}^3/_2$, taking $g = 2$; Figure 11a), which can be ascribed to the orbital contribution to the magnetic moment of Co^{II}.[26,27] With decreasing temperature, the $\chi_M T$ product remains roughly constant from 300 K to 50 K, and then decreases on further cooling, which is attributed to the zero-field splitting (ZFS). The Curie–Weiss fitting of $1/\chi_M$ in the temperature range of 2–300 K gives a good result with $C = 2.33$ $cm^3 K mol^{-1}$ and $\theta = -1.57$ K.

For **2**, the $\chi_M T$ value of 6.28 $cm^3 K mol^{-1}$ at 300 K is also much higher than the spin-only value of 3.75 $cm K mol^{-1}$ for two isolated octahedral Co^{II} ions ($S = {}^3/_2$, taking $g = 2$; Figure 11b), which can be ascribed to the strong orbital contribution to the magnetic moment of Co^{II}.[26,27] The $1/\chi_M$ vs. T plot above 21 K follows the Curie–Weiss law with $C = 6.67$ $cm^3 K mol^{-1}$ and $\theta = -18.64$ K. In the octahedral coordination geometry of Co^{II}, the ground state is a ${}^4T_{1g}$

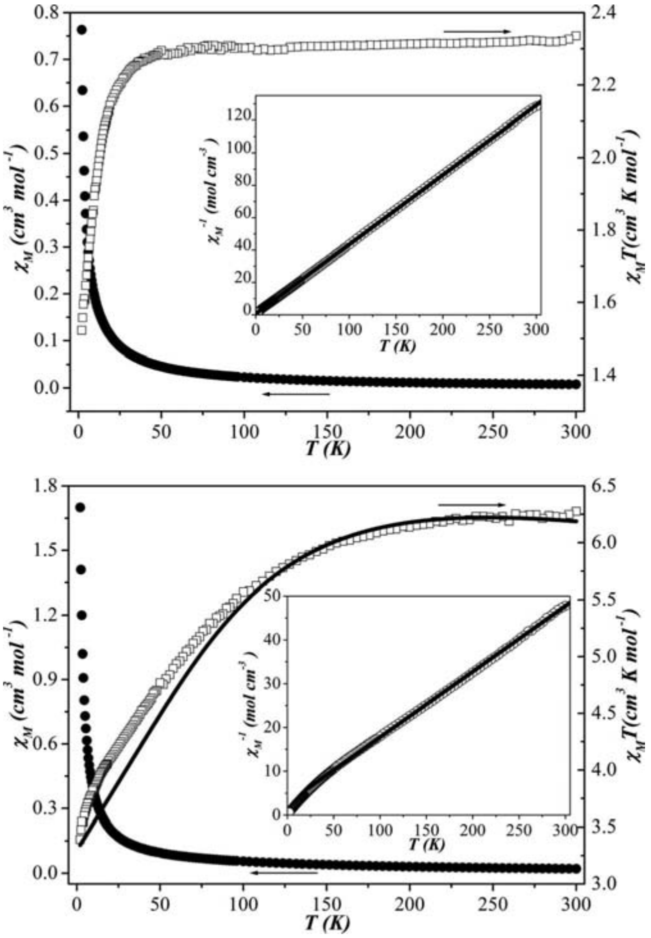

Figure 11. Thermal variation of χ_M and $\chi_M T$ for compounds **1** (a) and **2** (b). The solid line is the fitting of the data; see the text for the fitting parameters. Inset: Plot of thermal variation of χ_M^{-1} for the respective compound.

term for $S = {}^3/_2$. Taking into account an axial distortion of the Co^{II} ion, the triplet $^4T_{1g}$ ground state would split into $^4A_2$ and ^4E levels. For the low temperature state, Abraham and Price have found an effective $S = {}^1/_2$ and a $g_{av} = {}^{13}/_3$, consistent with the EPR spectra of several cobalt salts.[26] For the reasons of spin–orbit coupling and/or crystal field effect and/or ZFS, the $\chi_M T$ value decreased to 3.39 cm^3 K mol^{-1} at 2 K, which is in good agreement with two Co^{II} ions with effective $S = {}^1/_2$ and a $g_{av} = {}^{13}/_3$ (2×1.76 cm^3 K mol^{-1} = 3.52 cm^3 K mol^{-1}). Taking the spin–orbit coupling and the crystal field effect into account, fitting the $\chi_M T$ by the magnetic formulae [Equations (1a)–(1c)] for an isolated mononuclear Co^{II} complex in a strictly octahedral symmetry (O_h) is applied.[28] The best fit gives λ = –136 cm^{-1} and α = 1.29 [λ represents the spin–orbit coupling parameter; the α parameter is defined as the product of two other parameters κ and A ($\alpha = \kappa A$) that, having a different nature, are responsible for the orbital reduction]. Both parameters are comparable to the reported values.[28] The deviation of the fitted curve from the experimental data at low temperature suggests the ZFS effect still plays a role.

$$\chi_M T = \frac{N\beta^2}{k}\frac{F_1}{F_2} \tag{1a}$$

$$\begin{aligned} F_1 = {} & \frac{7\lambda}{5kT}(3-\alpha)^2 + \frac{12(2+\alpha)^2}{25\alpha} \\ & + \left[\frac{2\lambda}{45kT}(11-2\alpha)^2 + \frac{176(2+\alpha)^2}{675\alpha}\right]\exp\left(-\frac{5\alpha\lambda}{2kT}\right) \\ & + \left[\frac{\lambda}{9kT}(5+\alpha)^2 + \frac{20(2+\alpha)^2}{27\alpha}\right]\exp\left(-\frac{4\alpha\lambda}{kT}\right) \end{aligned} \tag{1b}$$

$$F_2 = \frac{\lambda}{kT}\left[3 + 2\exp\left(-\frac{5\alpha\lambda}{2kT}\right) + \exp\left(-\frac{4\alpha\lambda}{kT}\right)\right] \tag{1c}$$

Conclusions

We have successfully prepared the first two polycatenated metal–olsalazine complexes by appropriately combining long, linear bidentate N-donor ligands with the anti-inflammatory drug olsalazine, which show parallel and inclined interlocking modes, respectively. The successful isolation of both compounds not only provides unprecedented examples in the realm of metal–olsalazine complexes, but also indicates that the contemporary use of long N-containing ligands and olsalazine is a feasible route for the construction of entangled metal–drug complexes, thus opening new possibilities for the design of metal–drug complexes with particular functions in the near future.

Experimental Section

Materials and General Methods: All chemicals were purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. Co was determined by a tps-7000 Plasma-Spec (I) inductively coupled plasma atomic emission spectrometer (ICP-AES). IR spectra were recorded in the range of 400–4000 cm^{-1} with a Bio-Rad FTS-185 FTIR Spectrophotometer by using KBr pellets. TG analyses were performed with a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. XRPD data were recorded with an X-ray diffractometer (device type: XD-3 for **1** and Bruker D8 Advance for **2**) by using Cu-K_α radiation. Variable-temperature magnetic susceptibility data were obtained with a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range of 2–300 K with an applied field of 1 kG.

Syntheses

[Co(H$_2$osa)(bpp)] (1): A mixture of $CoCl_2 \cdot 6H_2O$ (71.4 mg, 0.3 mmol), bpp (59.5 mg, 0.3 mmol), Na$_2$H$_2$osa (69.24 mg, 0.2 mmol), and distilled water (8 mL) was stirred in air for 30 min, then transferred to and sealed in an 18 mL Teflon-lined autoclave, which was heated at 120 °C for 5 d. After slow cooling to the room temperature, dark purple crystals of **1** were collected by filtration, washed with distilled water, and dried at ambient temperature (yield: 58 % based on Co). $C_{27}H_{22}CoN_4O_6$ (557.43): calcd. C 58.18, H 3.98, N 10.05, Co 10.57; found C 58.41, H 3.79, N 10.27, Co 10.36. IR (KBr pellet): $\tilde{\nu}$ = 3419 (m), 3061 (w), 2947 (w), 2928 (w), 2862 (w), 2770 (w), 2360 (m), 2339 (w), 1950 (w), 1621 (s), 1569 (m), 1504 (w), 1477 (m), 1432 (s), 1390 (s), 1368 (w), 1297 (s), 1252 (s), 1186 (s), 1130 (w), 1070 (m), 1027 (m), 978 (w), 926 (m), 850 (s), 814 (s), 791 (s), 725 (w), 682 (s), 616 (m), 591 (s), 527 (s), 469 (m), 450 (w) cm^{-1}.

[Co_2(osa)(bpy)$_2$(H_2O)$_4$] (2): A mixture of Co(OAc)·$4H_2O$ (124.54 mg, 0.5 mmol), bpy (78.10 mg, 0.5 mmol), Na_2H_2osa (69.24 mg, 0.25 mmol), and distilled water (8 mL) was stirred in air for 30 min, then transferred to and sealed in an 18 mL Teflon-lined autoclave, which was heated at 120 °C for 5 d. After slow cooling to the room temperature, dark purple crystals of **2** were collected by filtration, washed with distilled water, and dried at ambient temperature (yield: 42% based on Co). $C_{34}H_{30}Co_2N_6O_{10}$ (800.51): calcd. C 51.01, H 3.78, N 10.50, Co 14.72; found C 51.22, H 3.61, N 10.28, Co 14.94. IR (KBr): $\tilde{\nu}$ = 3591 (s), 3424 (m), 3114 (w), 2921 (w), 2852 (w), 1645 (m), 1587 (s), 1585 (w), 1533 (w), 1470 (s), 1420 (w), 1395 (m), 1313 (s), 1286 (m), 1257 (w), 1215 (s), 1193 (s), 1137 (m), 1110 (w), 1074 (w), 1061 (w), 1041 (w), 1001 (w), 953 (w), 935 (w), 837 (m), 813 (s), 794 (w), 726 (m), 623 (s), 582 (m), 523 (m), 471 (s) cm^{-1}.

X-ray Crystallography: Suitable single crystals with dimensions of 0.49 × 0.42 × 0.36 mm for **1** and 0.43 × 0.35 × 0.32 mm for **2** were glued to a glass fiber. Diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer with Mo-K_α monochromated radiation (λ = 0.71073 Å) at 293 K. Absorption corrections were applied by using the multiscan technique. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 software.[20] All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference Fourier maps. Selected bond lengths for **1** and **2** are listed in Table 1. A summary of crystal data and structure refinement for compounds **1** and **2** is provided in Table 2. CCDC-807878 (for **1**) and -808127 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**.[a]

Compound **1**			
Co(1)–O(4)	1.9229(19)	Co(1)–N(1)	2.041(2)
Co(1)–O(1)	1.9454(17)	Co(1)–N(2)#1	2.060(2)
O(4)–Co(1)–O(1)	120.45(9)	O(4)–Co(1)–N(2)#1	113.92(8)
O(4)–Co(1)–N(1)	100.66(9)	O(1)–Co(1)–N(2)#1	94.65(8)
O(1)–Co(1)–N(1)	118.06(8)	N(1)–Co(1)–N(2) #1	109.38(9)
Compound 2			
Co(1)–O(2)	2.034(3)	Co(1)–O(3)	2.055(2)
Co(1)-OW2	2.093(3)	Co(1)-OW1	2.140(3)
Co(1)–N(1)	2.208(3)	Co(1)–N(2)	2.223(3)
O(2)–Co(1)–O(3)	88.94(11)	O(2)–Co(1)–OW2	83.05(11)
O(3)–Co(1)–OW2	171.69(11)	O(2)–Co(1)–OW1	168.25(11)
O(3)–Co(1)–OW1	101.31(10)	OW2–Co(1)-OW1	86.89(11)
O(2)–Co(1)–N(1)	90.27(12)	O(3)–Co(1)–N(1)	89.42(11)
OW2–Co(1)–N(1)	92.82(12)	OW1–Co(1)–N(1)	84.16(12)
O(2)–Co(1)–N(2)	98.76(12)	O(3)–Co(1)–N(2)	86.11(11)
OW2–Co(1)–N(2)	92.90(12)	OW1–Co(1)–N(2)	87.77(12)
N(1)–Co(1)–N(2)	169.83(13)		

[a] Symmetry transformations used to generate equivalent atoms; for **1**: #1 $x, y, z + 1$; #2 $x, y, z - 1$; #3 $-x, -y, -z$; #4 $-x + 1, -y + 2, -z - 1$; for **2**: #1 $-x, -y + 1, -z + 2$; #2 $-x + 1, -y, -z + 2$; #3 $-x + 1, -y + 1, -z + 1$.

Table 2. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{27}H_{22}CoN_4O_6$	$C_{34}H_{30}Co_2N_6O_{10}$
F_w	557.42	800.50
T [K]	293(2)	293 (2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	9.795(2)	7.8567(11)
b [Å]	10.861(2)	20.417(3)
c [Å]	12.270(3)	10.1979(14)
α [°]	90.32(3)	90
β [°]	98.96(3))	102.525(10)
γ [°]	104.09(3)	90
V [Å^3]	1249.3(4)	1596.9(4)
Z	2	2
Dc [g/cm^3]	1.482	1.665
μ [mm^{-1}]	0.738	1.111
R_1[a] [$I > 2\sigma(I)$]	0.0414	0.0685
wR_2[b] [$I > 2\sigma(I)$]	0.0948	0.1773
R_1 (all data)	0.0610	0.0797
wR_2 (all data)	0.1053	0.1874

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Supporting Information (see footnote on the first page of this article): TG–DSC curves, XRPD patterns, IR spectra, and additional plots of the structures.

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