Short Note

A One-Dimensional Coordination Polymer Constructed from Cadmium(II) Cations and Sparfloxacinate Anions

Zhe An [1], Jing Gao [2] and William T. A. Harrison [3],*

[1] School of Chemistry and Life Science, Guangdong University of Petrochemical Technology, Maoming 525000, China; E-Mail: anzhe6409@sina.com

[2] Department of Pharmacy, Mudanjiang Medical University, Heilongjiang 157011, China; E-Mail: gaojing_mmu@163.com

[3] Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, UK

* Author to whom correspondence should be addressed; E-Mail: w.harrison@abdn.ac.uk; Tel.: +44-1224-272897; Fax: +44-1224-272921.

Abstract: The synthesis and crystal structure of the one-dimensional coordination polymer, $[Cd(spar)_2]_n \cdot n(H_2O)$, are described, where $spar^-$ is the sparfloxacinate anion, $C_{19}H_{21}N_4O_3F_2^-$. The Cd^{2+} ion is bonded to four $spar^-$ ligands: Two O,O-chelate with their β-keto carboxylate groupings and two are monodentate-bound through a carboxylate O atom, to result in a distorted CdO_6 octahedral coordination geometry. The bridging ligands lead to [100] polymeric chains in the crystal and N–H···O hydrogen bonds and possible weak aromatic π–π stacking interactions help to consolidate the structure. Crystal data: $C_{38}H_{44}CdF_4N_8O_7$, $M_r = 913.21$, triclinic, $P\bar{1}$ (No. 2), $Z = 2$, $a = 9.2256(4)$ Å, $b = 12.8767(5)$ Å, $c = 17.4297(7)$ Å, $\alpha = 89.505(2)°$, $\beta = 85.062(2)°$, $\gamma = 70.757(2)°$, $V = 1947.20(14)$ Å^3, $R(F) = 0.036$, $wR(F^2) = 0.082$.

Keywords: one-dimensional coordination polymer; sparfloxacin; cadmium

1. Introduction

Sparfloxacin ($C_{19}H_{22}N_4O_3F_2$; Hspar; systematic name: 5-amino-1-cyclopropyl-7-[(3R^*,5S^*)(3,5-dimethylpiperazin-1-yl]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid), is a quinolone derivative (Figure 1) [1] with significant antibiotic properties [2,3], although ironically, the effectiveness of

Hspar and related compounds in treating infections appear to promote the subsequent colonization by "super bugs" such as MRSA [4]. Our own interest in this class of compounds, along with that of others, is focused on their potential as multi-dentate and bridging ligands in the construction of new complexes [5] and coordination polymers [6,7].

Figure 1. Chemical scheme for sparfloxacin ($C_{19}H_{22}N_4O_3F_2$).
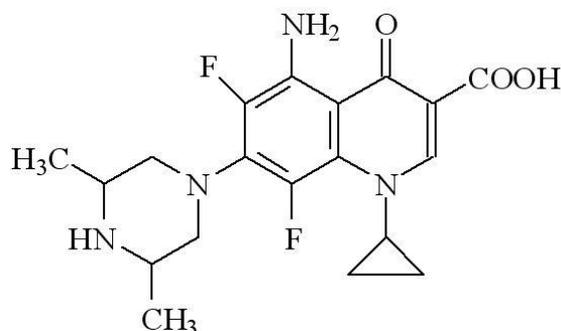
The crystal structure of the hydrated, zwitterionic molecule of Hspar has been reported [8] and its hydrate polymorphism demonstrated, which may have important pharmacological consequences [9]. A molecular salt of the H_2spar^+ cation with sulfate counter-ions is known [10]. The crystal structures of its anionic complexes with nickel [11], copper [12,13] and zinc [14] have been reported. As an extension of these studies, we now describe the hydrothermal synthesis and crystal structure of the polymeric title compound, $[Cd(spar)_2]_n \cdot n(H_2O)$, (**1**).

2. Results and Discussion

### 2.1. Crystal Structure of $[Cd(spar)_2]_n \cdot nH_2O$ (**1**)

Compound **1** is a one-dimensional coordination polymer: The asymmetric unit contains a Cd^{2+} cation, two mono-anionic $spar^-$ ligands and a disordered water molecule of crystallisation (Figure 2).

The metal ion in **1** is coordinated by two bidentate $spar^-$ anions, with the ketone O-atom and its *syn*-carboxylate O atom (O3 and O2, respectively, in the C1-containing ion and O6 and O5, respectively, in the C20-ion) serving as the donors, which generates a six-membered chelate ring in each case. The metal coordination sphere is completed by two monodentate-O bonded $spar^-$ species: In each case the carboxylate O-atom anti to the ketone O-atom is involved. Together, these lead to a moderately distorted octahedral geometry for the CdO_6 polyhedron (Table 1, Figure 3), with the monodentate O-atoms is a *cis* disposition. The mean Cd–O separation is 2.293 Å, the angular variance [15] for the O–Cd–O bond angles is 105.2° and the bond-valence-sum (BVS) for the metal ion, calculated by the Brown–Altermatt formalism [16], is 2.11 (expected value = 2.00). The –O2–C1–C2–C3–O3–Cd1– six-membered chelate ring approximates to a distorted half-chair, with O2 and Cd1 displaced by 0.320(5) Å and −0.702(7) Å, respectively, from the plane of the other four atoms (r.m.s. deviation = 0.026 Å). The –O5–C20–C21–C22–O6–Cd1– ring can be described in the same way, with O5 and Cd1 displaced by 0.190(5) Å and −1.013(7) Å, respectively, from the other atoms (r.m.s. deviation = 0.008 Å). The dihedral angle between the near-planar segments of the chelate rings is 32.0(3)°.

Figure 2. The asymmetric unit of **1** (50% displacement ellipsoids), expanded to show the complete Cd²⁺ coordination sphere. Hydrogen bonds are shown as double-dashed lines and the minor disorder components of the piperazine rings of the ligands and the disordered, uncoordinated water molecule are omitted for clarity. See Table 1 for symmetry codes.
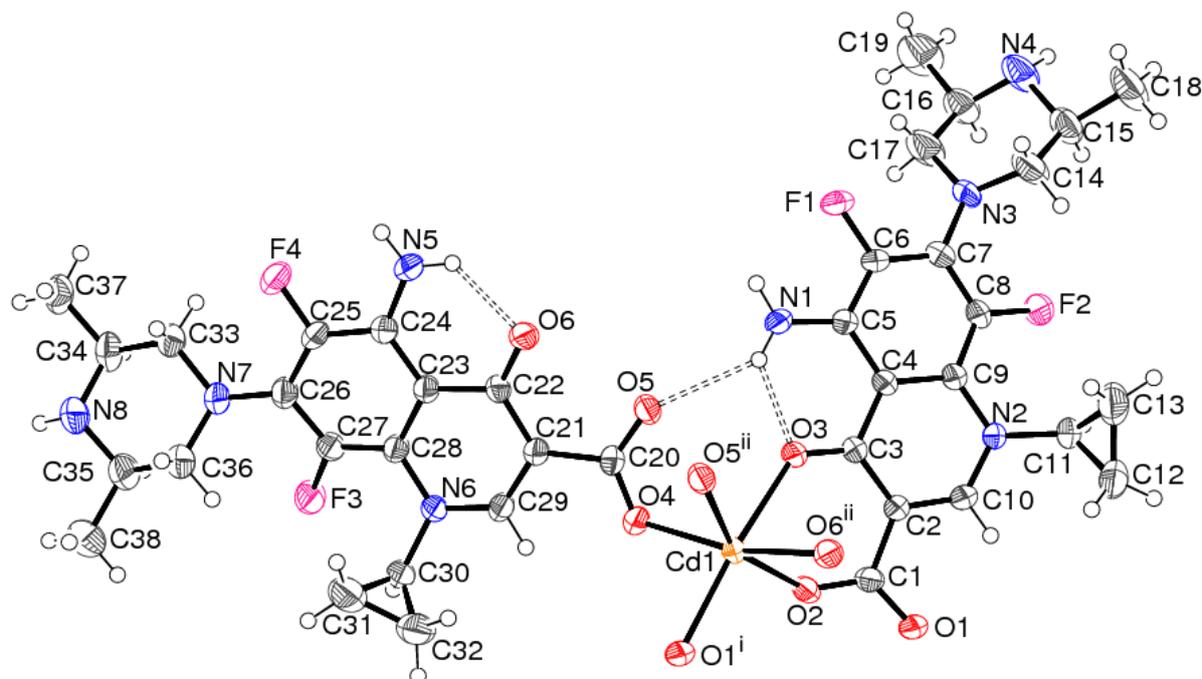
Figure 3. Detail of **1** showing the coordination geometry of the Cd²⁺ ion (50% displacement ellipsoids for Cd and O). The octahedral edges are shown as open lines and the C atoms of the chelate rings are shown as spheres. See Table 1 for symmetry codes.
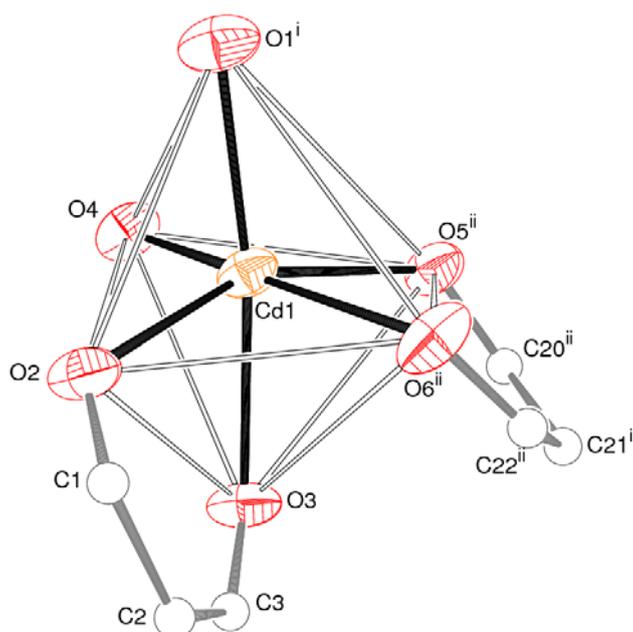
Table 1. Selected geometrical data (Å,°) for **1**.

Cd1–O4	2.264(2)	Cd1–O1 ⁱ	2.269(2)
Cd1–O5 ⁱⁱ	2.280(2)	Cd1–O2	2.292(2)
Cd1–O6 ⁱⁱ	2.304(2)	Cd1–O3	2.3466(19)
O4–Cd1–O1 ⁱ	87.58(8)	O4–Cd1–O5 ⁱⁱ	90.75(8)
O1 ⁱ–Cd1–O5 ⁱⁱ	102.81(8)	O4–Cd1–O2	104.12(8)
O1 ⁱ–Cd1–O2	98.16(7)	O5 ⁱⁱ–Cd1–O2	154.76(7)
O4–Cd1–O6 ⁱⁱ	164.30(7)	O1 ⁱ–Cd1–O6 ⁱⁱ	100.15(8)
O5 ⁱⁱ–Cd1–O6 ⁱⁱ	74.28(8)	O2–Cd1–O6 ⁱⁱ	88.40(8)
O4–Cd1–O3	92.27(7)	O1 ⁱ–Cd1–O3	170.82(8)
O5 ⁱⁱ–Cd1–O3	86.37(7)	O2–Cd1–O3	72.97(7)
O6 ⁱⁱ–Cd1–O3	82.26(8)		

Symmetry codes: ⁱ 2 − *x*, 1 − *y*, 1 − *z*; ⁱⁱ 1 − *x*, 1 − *y*, 1 − *z*.

The important geometrical features of the first spar⁻ anion (containing C1) are as follows: The C1–O1 and C1–O2 bond lengths of 1.266(4) Å and 1.250(3) Å, respectively, are typical for a delocalised carboxylate group and the dihedral angle between C1/O1/O2 and the adjacent N2-containing ring (r.m.s. deviation = 0.051 Å) is 11.5(5)°. The dihedral angle between the cyclopropane ring and the N2 ring is 66.4(2)°. The dihedral angle between the N2 ring and the C5 ring (r.m.s. deviation = 0.021 Å), which are fused at the C4–C9 bond, is 7.50(15)°, indicating a significant puckering to the quinolone system. The piperazine ring adopts a typical chair conformation with the N–C$_q$ (q = quinolone) bond in an equatorial orientation. Its geometry is complicated by disorder of the C atoms bearing the terminal methyl groups over two orientations, in a 0.766(10):0.234(10) ratio, but both of these maintain the (3*R**,5*S**) relative configurations of these stereogenic atoms.

The second spar⁻ anion (containing C20) has a broadly similar geometry: The C20–O4 and C20–O5 bond lengths are 1.273(3) Å and 1.250(3) Å, respectively, and the dihedral angle between C20/O4/O5 and the N6 ring (r.m.s. deviation = 0.037°) is 4.0(4)°. The dihedral angle between the N6 ring and the pendent three-membered ring is 73.5(2)°. The N6 and C24 rings (r.m.s. deviation for the latter = 0.041 Å), fused at the C23–C28 bond, are tilted by 4.38(16)°. The piperazine ring in the second anion shows the same type of positional disorder as the first, in a 0.908(8):0.092(8) ratio for the two orientations.

The extended structure of **1** features polymeric chains in the [100] direction (Figure 4), such that each spar⁻ anion links two cadmium metal ions. Adjacent metal ions are fused via eight-membered loops, generated by crystallographic inversion symmetry.

Figure 4. Fragment of a [100] polymeric chain in **1** showing only the O atoms and linking C atoms of the ligands (50% displacement ellipsoids; symmetry codes as in Table 1). The bonds of the C1 and C20 spar$^-$ anions are colored mint and plum, respectively.
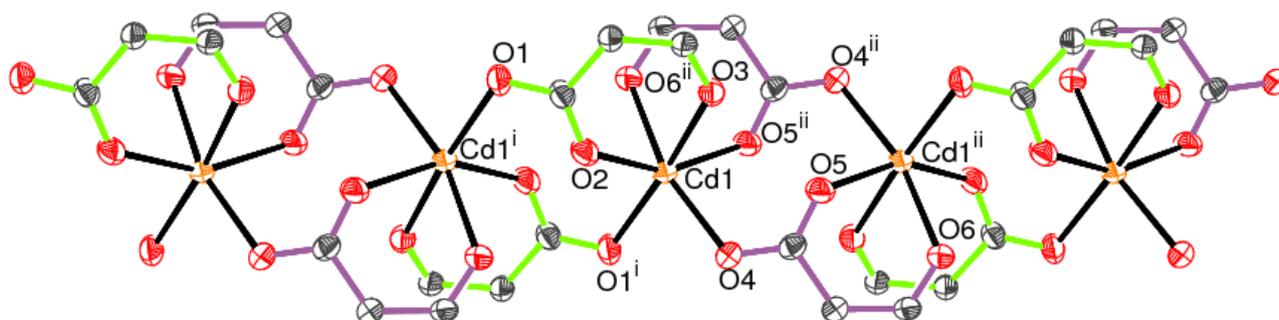
To complete the structure of **1**, several N–H⋯O hydrogen bonds occur of varying strengths, including a bifurcated N–H⋯(O,O) link (Table 2). All of these bonds are intra-chain interactions. It is notable that neither of the piperazine H atoms (attached to N4 and N8) participates in a hydrogen bond, perhaps due in part to the steric crowding of the two adjacent methyl groups. Weak aromatic π–π stacking (centroid–centroid separation = 3.7164(17) Å between the N6 and C24 rings) might also play some role in consolidating the structure of **1**.

Table 2. Hydrogen-Bond geometries for **1**.

N1–H1A⋯O1 [iii]	0.86	2.33	3.021(3)	138
N1–H1B⋯O3	0.86	1.96	2.598(3)	130
N1–H1B⋯O5	0.86	2.35	3.061(3)	141
N5–H5A⋯O4 [iii]	0.86	2.59	3.221(3)	131
N5–H5B⋯O6	0.86	1.98	2.609(3)	129

The four columns specify the *D*–H, H⋯*A* and *D*⋯*A* separations (Å) and the *D*–H⋯*A* angle (°), respectively. Symmetry code: [iii] $x - 1, y, z$.

2.2. Spectroscopy

By analogy with data from related compounds [9], the 1629 cm^{-1} band is assigned as a C=O(pyridone) stretch and the 1570 cm^{-1} and 1364 cm^{-1} signals correspond to the carboxylate –CO$_2$ asymmetric and symmetric stretches, respectively.

3. Experimental Section

3.1. Synthesis and Characterization

A mixture of cadmium acetate trihydrate (0.25 mmol), sparfloxacin (0.5 mmol), 1,4-benzenedicarboxylic acid (0.25 mmol), sodium hydroxide (1 mmol), and water (15 mL) was stirred for 30 min at room temperature. The mixture was then transferred to a 25-mL Teflon-lined reactor and heated to 423 K for 72 h under autogenous pressure. Upon cooling, colorless prisms of **1** were recovered from the reaction mixture by vacuum filtration. The role of the 1,4-benzenedicarboxylic acid in the synthesis is unknown, but it has not proved possible to prepare **1** if it is not present.

Elemental analysis: calc (%) for $C_{38}H_{44}CdF_4N_8O_7$: C 49.98, H 4.86, N 12.27; found (%): C 49.76, H 4.49, N 12.04. IR (cm^{-1}, KBr): 3450 (br, m), 1629 (s), 1570 (s), 1449 (s), 1364 (w), 1290 (s).

3.2. Single-Crystal Data Collection and Analysis

The single-crystal data for **1** (colorless prism 0.20 × 0.20 × 0.18 mm) were collected using a Bruker APEX II CCD diffractometer (graphite monochromated MoKα radiation, λ = 0.71073 Å) at room temperature. Data reduction with SAINT [17] then proceeded and the structure was solved by direct methods with SHELXS-97 [18]. The resulting atomic model was developed and refined against $|F|^2$ with SHELXL-97 [18] and the "observed data" threshold for calculating the $R(F)$ residuals was set as $I > 2\sigma(I)$. The C-bound H atoms were placed in idealised locations (C–H = 0.93–0.98 Å) and refined as riding atoms. The N-bound H atoms were located in difference maps: Those attached to N1 and N5 were relocated to idealised locations (N–H = 0.86 Å) and refined as riding and those attached to N4 and N8 were refined as riding in their as-found relative locations. Due to the disorder of the piperazine rings, the location of the N4 and N8 H atoms are perhaps less certain, although they appeared reasonably distinctly in difference maps. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied as appropriate. The H atoms associated with the disordered water molecule could not be located; based on geometrical considerations, one of the water molecules may form a hydrogen bond to N4. The structural model was analysed and validated with PLATON [19] and full refinement details are given in the deposited cif.

Crystal data for **1**: $C_{38}H_{44}CdF_4N_8O_7$, M_r = 913.21, triclinic, $P\bar{1}$ (No. 2), Z = 2, a = 9.2256(4) Å, b = 12.8767(5) Å, c = 17.4297(7) Å, α = 89.505(2)°, β = 85.062(2)°, γ = 70.757(2)°, V = 1947.20(14) Å^3, $F(000)$ = 936, T = 296(2) K, ρ_{calc} = 1.558 g·cm^{-3}, μ = 0.640 mm^{-1}, 27884 reflections recorded ($3.4° \leq 2\theta \leq 50.0°$; $-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$), R_{Int} = 0.039, 6848 merged reflections, 6225 with $I > 2\sigma(I)$, 541 variable parameters, $R(F)$ = 0.036, $wR(F^2)$ = 0.082, min./max. $\Delta\rho$ = $-0.58/0.46$ e Å^{-3}. Cambridge Structural Database deposition number: CCDC-888200.

4. Conclusions

The synthesis and crystal structure of the title one-dimensional coordination polymer have been described, in which the metal atom adopts a distorted octahedral geometry arising from its coordination by two O,O-bidentate and two O-monodentate spar$^-$ anions. The linkages in the polymeric chain are centrosymmetric eight-membered rings. The structure of **1** is completely different to that of $Cd_2(enro)_4(H_2O)_2\cdot 4H_2O$ (Henro = enroflaxacin; $C_{19}H_{22}N_3O_3F$), in which isolated binuclear complexes occur and the metal coordination geometry is a CdO_6 trigonal prism [5]. In $[Cd(cipro)_2]_n\cdot 2.5nH_2O$ (Hcipro = ciprofloxacin; $C_{17}H_{18}FN_3O_4$) [6], the Cd^{2+} ion is coordinated by O,O-bidentate and N_p-bonded (p = piperazine) cipro$^-$ ions to generate a coordination network containing *trans*-CdN_2O_4 octahedra. Conversely, $Cd(Hcipro)_2Cl_2\cdot 4H_2O$ is a mononuclear complex containing O,O-bidentate neutral, zwitterionic Hcipro molecules and two charge-balancing chloride ions to generate *trans*-$CdCl_2O_4$ octahedra [20].

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