Abstract: The synthesis and crystal structure of the one-dimensional coordination polymer, [Cd(spar)$_2$]$_n$$\cdot$$n$(H$_2$O), are described, where spar$^-$ is the sparflroxacin anion, C$_{19}$H$_{21}$N$_4$O$_3$F$_2$$^-$. The Cd$^{2+}$ ion is bonded to four spar$^-$ ligands: Two O,O-chelate with their β-keto carboxylate groupings and two are monodentate-bound through a carboxylate O atom, to result in a distorted CdO$_6$ octahedral coordination geometry. The bridging ligands lead to [100] polymeric chains in the crystal and N–H···O hydrogen bonds and possible weak aromatic π–π stacking interactions help to consolidate the structure. Crystal data: C$_{38}$H$_{44}$CdF$_4$N$_8$O$_7$, $M_r = 913.21$, triclinic, $P\bar{1}$ (No. 2), $Z = 2$, $a = 9.2256(4)$ Å, $b = 12.8767(5)$ Å, $c = 17.4297(7)$ Å, $\alpha = 89.505(2)$$^\circ$, $\beta = 85.062(2)$$^\circ$, $\gamma = 70.757(2)$$^\circ$, $V = 1947.20(14)$ Å$^3$, $R(F) = 0.036$, $wR(F^2) = 0.082$.

Keywords: one-dimensional coordination polymer; sparflroxacin; cadmium

1. Introduction

Sparflroxacin (C$_{19}$H$_{22}$NaO$_3$F$_2$; Hspar; systematic name: 5-amino-1-cyclopropyl-7-[(3$R^*$,5$S^*$) (3,5-dimethylpiperazin-1-yl)-6,8-difluoro-4-oxoquinoline-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\textsubscript{19}H\textsubscript{22}N\textsubscript{4}O\textsubscript{3}F\textsubscript{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\textsubscript{2}spar\textsuperscript{+} 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)\textsubscript{2}]\textsubscript{n}·n(H\textsubscript{2}O), (I).

2. Results and Discussion

2.1. Crystal Structure of [Cd(spar)\textsubscript{2}]\textsubscript{n}·nH\textsubscript{2}O (I)

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

The metal ion in 1 is coordinated by two bidentate spar\textsuperscript{−} 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\textsuperscript{−} 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\textsubscript{6} polyhedron (Table 1, Figure 3), with the monodentate O-atoms in 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\textdegree 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)\textdegree.
Figure 2. The asymmetric unit of 1 (50% displacement ellipsoids), expanded to show the complete \(\text{Cd}^{2+}\) 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 \(\text{Cd}^{2+}\) 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.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd1–O4</td>
<td>2.264(2)</td>
<td>Cd1–O1*</td>
<td>2.269(2)</td>
<td>Cd1–O5&quot;</td>
<td>2.280(2)</td>
</tr>
<tr>
<td>Cd1–O5&quot;</td>
<td>2.280(2)</td>
<td>Cd1–O2</td>
<td>2.292(2)</td>
<td>Cd1–O6&quot;</td>
<td>2.304(2)</td>
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<tr>
<td>O4–Cd1–O1*</td>
<td>87.58(8)</td>
<td>O4–Cd1–O5&quot;</td>
<td>90.75(8)</td>
<td>O1&quot;–Cd1–O5&quot;</td>
<td>102.81(8)</td>
</tr>
<tr>
<td>O1&quot;–Cd1–O5&quot;</td>
<td>98.16(7)</td>
<td>O4–Cd1–O2</td>
<td>104.12(8)</td>
<td>O5&quot;–Cd1–O2</td>
<td>154.76(7)</td>
</tr>
<tr>
<td>O4–Cd1–O6&quot;</td>
<td>164.30(7)</td>
<td>O1&quot;–Cd1–O6&quot;</td>
<td>100.15(8)</td>
<td>O2–Cd1–O6&quot;</td>
<td>88.40(8)</td>
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<tr>
<td>O5&quot;–Cd1–O6&quot;</td>
<td>74.28(8)</td>
<td>O2–Cd1–O6&quot;</td>
<td>88.40(8)</td>
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<td></td>
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<tr>
<td>O4–Cd1–O3</td>
<td>92.27(7)</td>
<td>O1&quot;–Cd1–O3</td>
<td>170.82(8)</td>
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<tr>
<td>O5&quot;–Cd1–O3</td>
<td>86.37(7)</td>
<td>O2–Cd1–O3</td>
<td>72.97(7)</td>
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<tr>
<td>O6&quot;–Cd1–O3</td>
<td>82.26(8)</td>
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</tbody>
</table>

Symmetry codes: * 2 – x, 1 – y, 1 – z; " 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–Cq (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 (3R*,5S*) 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.

<table>
<thead>
<tr>
<th>Bond</th>
<th>D–H</th>
<th>H···A</th>
<th>D···A</th>
<th>D–H···A angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–H1A···O1 iii</td>
<td>0.86</td>
<td>2.33</td>
<td>3.021(3)</td>
<td>138</td>
</tr>
<tr>
<td>N1–H1B···O3</td>
<td>0.86</td>
<td>1.96</td>
<td>2.598(3)</td>
<td>130</td>
</tr>
<tr>
<td>N1–H1B···O5</td>
<td>0.86</td>
<td>2.35</td>
<td>3.061(3)</td>
<td>141</td>
</tr>
<tr>
<td>N5–H5A···O4 iii</td>
<td>0.86</td>
<td>2.59</td>
<td>3.221(3)</td>
<td>131</td>
</tr>
<tr>
<td>N5–H5B···O6</td>
<td>0.86</td>
<td>1.98</td>
<td>2.609(3)</td>
<td>129</td>
</tr>
</tbody>
</table>

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 –CO2 asymmetric and symmetric stretches, respectively.

3. Experimental Section

3.1. Synthesis and Characterization

A mixture of cadmium acetate trihydrate (0.25 mmol), sparflonaxin (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_{4}N_{8}O_{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 > 2σ(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_{4}N_{8}O_{7}, M_r = 913.21, triclinic, P ̅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° ≤ 2θ ≤ 50.0°; −10 ≤ h ≤ 10, −15 ≤ k ≤ 15, −20 ≤ l ≤ 20), R_{int} = 0.039, 6848 merged reflections, 6225 with I > 2σ(I), 541 variable parameters, R(F) = 0.036, wR(F^2) = 0.082, min./max. ∆ρ = −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)_2·4H_2O (Henro = enroflaxacin; C_{19}H_{22}N_{3}O_{3}F), in which isolated binuclear complexes occur and the metal coordination geometry is a CdO_6 trigonal prism [5]. In [Cd(cipro)_2]_2·2.5nH_2O (Hcipro = ciprofloxacin; C_{17}H_{18}FN_{3}O_{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_2·4H_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].
References


5. An, Z.; Gao, J.; Harrison, W.T.A. Two binuclear complexes containing the enrofloxacinate anion: Cd$_2$(C$_{19}$H$_{21}$N$_3$O$_3$F)$_4$(H$_2$O)$_2$$·$4H$_2$O and Pb$_2$(C$_{19}$H$_{21}$N$_3$O$_3$F)$_4$$·$4H$_2$O. *J. Coord. Chem.* **2010**, *63*, 3871–3879.


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