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An Adduct of Magnesium Sulfate with a Member of the Quinolone Family (Ciprofloxacin)

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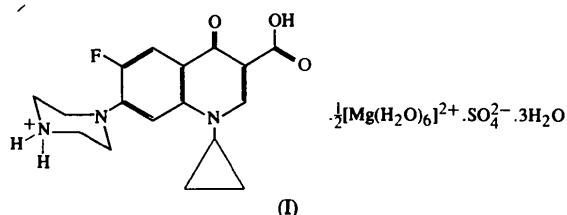
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Abstract

In the title compound, 4-(3-carboxy-1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-quinolinyl)-1-piperazinium-magnesium hexahydrate-sulfate-water (1/0.5/1/3), (C₁₇H₁₉FN₃O₃)[Mg(H₂O)₆]_{0.5}SO₄·3H₂O, the Mg²⁺ ion lies on a twofold axis and adopts a nearly regular octahedral geometry. The quinolone is protonated at the terminal N atom of the piperazine residue. The H atom of the carboxylic acid group is hydrogen bonded to the carbonyl O atom, thus preventing the bonding of the metal to this part of the molecule.

Comment

The title quinolone, ciprofloxacin [cf; 1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline-carboxylic acid] is a fluoroquinolone antibacterial agent with a wide spectrum of activity. It is known that the absorption of all quinolones appears to be significantly reduced by magnesium and aluminium antacids. Several other cations interact in a similar manner and the cause is probably chelation between the quinolone and the metal ion (Polk, 1989; Kara, Hasinoff, McKay & Campbell, 1991). Only a few crystal structures between quinolones and different metal ions (Ag⁺, Co²⁺, Cu²⁺) have been published (Baenzinger, Fox & Modak, 1986; Chulvi, Muñoz, Perelló, Ortiz, Arriortua, Via, Urtiaga, Amigó & Ochando, 1991; Turel, Leban & Bukovec, 1994; Turel, Gruber, Leban & Bukovec, 1996). Our aim has been to prepare a compound of the magnesium-ciprofloxacin system and examine the bonding mode of the ciprofloxacin molecule, and we have thus prepared the title compound, (I), and determined its crystal structure.



The unit cell of (I) contains [Mg(H₂O)₆]²⁺, SO₄²⁻ and (cfH)⁺ ions [(cfH)⁺ is protonated ciprofloxacin], and water molecules (Fig. 1). The Mg²⁺ ion, lying on the twofold axis, is coordinated by six water molecules and adopts a nearly regular octahedral geometry. Marked preference for oxygen ligands is typical of magnesium (Black, Huang & Cowan, 1994). All Mg—O distances are similar [2.040 (4)–2.063 (5) Å] and only small discrepancies in the O—Mg—O angles from ideal values were observed, in agreement with other structures containing [Mg(H₂O)₆]²⁺ ions (Ledesert & Monier, 1982; Griffith, Skapski & West, 1982). The tetrahedral sulfate(VI) ions are isolated and the S—O distances, as well as the O—S—O angles, are close to expected values. The role and appearance of the quinolone molecule is similar to those already reported for quinolone-halometalate compounds (Turel, Gruber, Leban & Bukovec, 1996; Turel, Leban, Bukovec & Klintschar, 1996; Turel, Leban & Bukovec, 1996). Ciprofloxacin is protonated at the terminal N24 atom of the piperazine residue. The H atom of the carboxylic acid group is hydrogen bonded to the carbonyl O1 atom (Table 3), thus preventing the metal bonding to this part of the molecule and so it appears that water molecules are coordinated to magnesium. The longer C9—N1 [1.401 (7) Å] and shorter C2—N1 [1.337 (7) Å] bond lengths are typical for these molecules (Wallis, Gahan, Charles & Hambley, 1994). There are also water molecules lying between the distinct layers in the structure which participate in the hydrogen-bonding network.

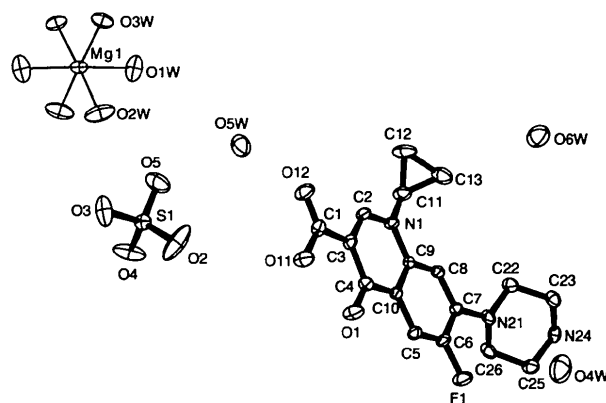


Fig. 1. ORTEP (Johnson, 1971) view of the title molecule with the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms have omitted for clarity.

Experimental

Crystals suitable for the single-crystal diffraction work were prepared by dissolving ciprofloxacin in hydrochloric acid. Magnesium sulfate(VI) was added to the solution and a white precipitate formed after 1 d. Crystals grew from the saturated aqueous solution of the precipitate when it was kept in a closed ethanol chamber. The density D_m was measured by flotation in chlorobenzene/CCl₄ solution.

Crystal data

(C₁₇H₁₉FN₃O₃)[Mg-(H₂O)₆]_{0.5}SO₄·3H₂O*M_r* = 548.66

Monoclinic

*C*2/*c**a* = 13.273 (3) Å*b* = 9.692 (2) Å*c* = 38.608 (8) Å

β = 99.19 (3)°

V = 4902.9 (18) Å³*Z* = 8*D_x* = 1.487 Mg m⁻³*D_m* = 1.48 (5) Mg m⁻³

Data collection

Modified Stoe diffractometer

Fixed ω = 1.2° scans

Absorption correction:

none

3835 measured reflections

3200 independent reflections

1710 observed reflections

[*I* > 2σ(*I*)]*R_{int}* = 0.055

Refinement

Refinement on *F*²*R*(*F*) = 0.0600*wR*(*F*²) = 0.1695*S* = 1.048

3183 reflections

360 parameters

Only coordinates of H atoms refined

 $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 12.0673P]$ where $P = (F_o^2 + 2F_c^2)/3$ Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10–13°

μ = 0.222 mm⁻¹*T* = 298 (2) K

Plate

0.40 × 0.21 × 0.15 mm

Colourless

N21	0.0855 (4)	0.6457 (5)	0.12678 (11)	0.0380 (13)
C22	0.0716 (5)	0.5400 (6)	0.15213 (14)	0.042 (2)
C23	0.1207 (5)	0.5867 (7)	0.18777 (15)	0.043 (2)
N24	0.0800 (3)	0.7221 (5)	0.19746 (11)	0.0371 (13)
C25	0.0892 (5)	0.8277 (6)	0.17024 (15)	0.045 (2)
C26	0.0391 (5)	0.7758 (6)	0.13519 (15)	0.045 (2)
N1	0.0617 (4)	0.3063 (5)	0.03321 (12)	0.0324 (12)
C8	0.0646 (4)	0.4807 (6)	0.07891 (14)	0.0321 (14)
O12	0.1442 (4)	0.1791 (5)	-0.06152 (12)	0.0554 (13)
C1	0.1620 (5)	0.2963 (7)	-0.0510 (2)	0.039 (2)
C11	0.0017 (5)	0.2145 (6)	0.0529 (2)	0.048 (2)
C13	0.0514 (6)	0.1518 (7)	0.0856 (2)	0.066 (2)
C12	0.0198 (7)	0.0652 (7)	0.0526 (2)	0.072 (2)
C6	0.1421 (5)	0.6975 (6)	0.07160 (15)	0.036 (2)

Table 2. Selected geometric parameters (Å, °)

S1—O2	1.418 (5)	C3—C2	1.372 (8)
S1—O5	1.436 (5)	C3—C4	1.419 (8)
S1—O3	1.455 (4)	C3—C1	1.462 (8)
S1—O4	1.461 (5)	C2—N1	1.337 (7)
Mg1—O1W ^a	2.040 (4)	C10—C5	1.405 (8)
Mg1—O1W	2.040 (4)	C10—C4	1.437 (7)
Mg1—O3W	2.061 (4)	C5—C6	1.350 (8)
Mg1—O3W ^a	2.061 (4)	N21—C22	1.449 (7)
Mg1—O2W ^a	2.063 (5)	N21—C26	1.463 (7)
Mg1—O2W	2.063 (5)	C22—C23	1.495 (8)
F1—C6	1.349 (6)	C23—N24	1.490 (7)
O1—C4	1.270 (6)	N24—C25	1.486 (7)
C9—C10	1.393 (7)	C25—C26	1.496 (8)
C9—N1	1.401 (7)	N1—C11	1.482 (7)
C9—C8	1.402 (7)	O12—C1	1.217 (7)
O11—C1	1.329 (7)	C11—C13	1.460 (9)
C7—C8	1.371 (8)	C11—C12	1.467 (9)
C7—N21	1.385 (7)	C13—C12	1.527 (10)
C7—C6	1.418 (8)		
O2—S1—O5	111.7 (4)	O1—C4—C3	121.6 (5)
O2—S1—O3	109.2 (3)	O1—C4—C10	121.4 (5)
O5—S1—O3	108.9 (3)	C3—C4—C10	117.0 (5)
O2—S1—O4	110.6 (4)	C6—C5—C10	120.4 (6)
O5—S1—O4	106.9 (3)	C7—N21—C22	119.5 (5)
O3—S1—O4	109.5 (3)	C7—N21—C26	122.3 (5)
O1W ^a —Mg1—O1W	177.7 (4)	C22—N21—C26	110.9 (4)
O1W ^a —Mg1—O3W	90.9 (2)	N21—C22—C23	108.9 (5)
O1W—Mg1—O3W	90.7 (2)	N24—C23—C22	112.1 (5)
O3W—Mg1—O3W ^a	92.4 (3)	C25—N24—C23	110.8 (4)
O1W—Mg1—O2W ^a	86.2 (2)	N24—C25—C26	109.5 (5)
O3W—Mg1—O2W ^a	176.9 (2)	N21—C26—C25	110.4 (5)
O1W—Mg1—O2W	92.2 (2)	C2—N1—C9	120.2 (5)
O3W—Mg1—O2W	87.3 (2)	C2—N1—C11	120.6 (5)
O2W ^a —Mg1—O2W	93.1 (3)	C9—N1—C11	119.0 (5)
C10—C9—N1	118.7 (5)	C7—C8—C9	121.6 (5)
C10—C9—C8	120.3 (5)	O12—C1—O11	120.2 (6)
N1—C9—C8	121.0 (5)	O12—C1—C3	124.2 (6)
C8—C7—N21	123.3 (5)	O11—C1—C3	115.5 (6)
C8—C7—C6	116.8 (5)	C13—C11—C12	62.9 (5)
N21—C7—C6	119.5 (5)	C13—C11—N1	119.1 (6)
C2—C3—C4	119.3 (5)	C12—C11—N1	119.0 (6)
C2—C3—C1	119.7 (6)	C11—C13—C12	58.8 (5)
C4—C3—C1	121.0 (6)	C11—C12—C13	58.3 (4)
N1—C2—C3	123.5 (5)	F1—C6—C5	118.7 (5)
C9—C10—C5	118.2 (5)	F1—C6—C7	118.5 (5)
C9—C10—C4	121.2 (5)	C5—C6—C7	122.6 (6)
C5—C10—C4	120.5 (5)		

Symmetry code: (i) -*x*, *y*, -½ - *z*.Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S1	0.18769 (12)	0.2503 (2)	-0.20909 (4)	0.0369 (4)
O2	0.2770 (3)	0.3027 (7)	-0.1881 (2)	0.112 (2)
O3	0.2121 (3)	0.2078 (6)	-0.24295 (11)	0.074 (2)
O4	0.1076 (4)	0.3552 (5)	-0.2143 (2)	0.082 (2)
O5	0.1470 (4)	0.1341 (5)	-0.19282 (14)	0.078 (2)
Mg1	0	-0.2328 (3)	-1/4	0.0356 (7)
O1W	0.0271 (3)	-0.2286 (7)	-0.30054 (12)	0.070 (2)
O2W	-0.1137 (4)	-0.0864 (5)	-0.2602 (2)	0.080 (2)
O3W	-0.1118 (3)	-0.3800 (4)	-0.26292 (12)	0.0489 (12)
O4W	0.3837 (4)	0.7474 (7)	0.1425 (2)	0.104 (2)
O5W	0.1843 (5)	0.0196 (6)	-0.12390 (13)	0.083 (2)
O6W	0.2867 (4)	0.0014 (6)	0.14041 (14)	0.085 (2)
F1	0.1745 (3)	0.8216 (4)	0.08478 (9)	0.0570 (11)
O1	0.2087 (4)	0.5672 (4)	-0.02498 (11)	0.0550 (13)
C9	0.0877 (4)	0.4386 (6)	0.04634 (14)	0.0283 (13)
O11	0.2058 (4)	0.3859 (5)	-0.06995 (11)	0.0544 (13)
C7	0.0927 (4)	0.6080 (6)	0.09264 (14)	0.0317 (14)
C3	0.1367 (4)	0.3496 (6)	-0.01798 (14)	0.0329 (14)
C2	0.0841 (4)	0.2679 (6)	0.00205 (15)	0.0349 (14)
C10	0.1364 (4)	0.5285 (6)	0.02624 (14)	0.0287 (14)
C4	0.1631 (4)	0.4861 (6)	-0.00679 (15)	0.0323 (14)
C5	0.1635 (4)	0.6601 (6)	0.03990 (15)	0.0360 (15)

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1WA...O2 ⁱ	0.95 (3)	1.79 (2)	2.722 (6)	166 (8)
O1W—H1WB...O4W ⁱⁱ	0.95 (4)	1.76 (2)	2.675 (7)	163 (7)
O2W—H2WA...O5 ⁱⁱⁱ	0.95 (6)	1.86 (2)	2.791 (7)	166 (7)
O3W—H3WA...O3 ^{iv}	0.95 (4)	1.78 (1)	2.712 (6)	169 (5)
O3W—H3WB...O4 ^v	0.95 (4)	1.79 (2)	2.716 (6)	165 (6)
O4W—H4WA...O5W ^{vi}	0.95 (5)	1.88 (3)	2.796 (9)	163 (9)
O4W—H4WB...O6W ^{vii}	0.95 (6)	1.88 (3)	2.774 (9)	157 (8)
O5W—H5WA...O12	0.95 (6)	2.03 (1)	2.980 (7)	176 (6)

O5W—H5WB···O5	0.95 (5)	1.96 (3)	2.853 (7)	157 (7)
O6W—H6WA···O11 ^{vi}	0.95 (7)	2.10 (5)	2.948 (7)	149 (8)
N24—H24A···O4 ^{viii}	1.12 (1)	1.69 (1)	2.776 (6)	161 (1)
N24—H24B···O3 ^{ix}	1.07 (2)	1.69 (1)	2.746 (6)	167 (1)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $-x, y, -\frac{1}{2} - z$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (v) $-x, y - 1, -\frac{1}{2} - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (vii) $x, 1 + y, z$; (viii) $-x, 1 - y, -z$; (ix) $x, 1 - y, \frac{1}{2} + z$.

All H atoms were found in the difference electron-density map. The H atoms of (cfH)⁺ were included in the refinement at calculated positions, whereas the H atoms of the water molecules were refined with the O—H and H···H distances restrained (*DFIX* in *SHELXL93*; Sheldrick, 1993) to 0.95 (1) and 1.50 (2) Å, respectively. For all H atoms, the values of the isotropic displacement parameters were taken as 1.5 times the value of the attached heavy atom. The rather high value of the final *R* factor is due to the slight decomposition of the crystal during data collection. In addition to the computer programs mentioned below, *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *PLUTON* (Spek, 1991) were used for data processing and the final interpretation of the structural geometry. Calculations were performed on a PC 486 computer.

Data collection: local program (Kratky, 1993). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971) and *PLUTON*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1358). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(tetraphenylphosphonium) Decatelluriumtantalide Dimethylformamide (1/1), a Tetraphenylphosphonium Salt of TaTe_{10}^{3-}

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Abstract

The TaTe_{10}^{3-} anion of the title compound, $(\text{C}_{24}\text{H}_{20}\text{P})_3\text{[TaTe}_{10}]\cdot\text{C}_3\text{H}_7\text{NO}$, consists of an extended 'birdcage' of Te atoms containing an interstitial Ta atom. The Ta atom is seven-coordinate, with Ta—Te distances ranging from 2.753 (3) to 2.870 (3) Å, arranged in a distorted capped trigonal prism geometry.

Comment

The title compound, (I), is isomorphous with that of the niobium derivative (Flomer & Kolis, 1988). The geometric parameters of the two structures are identical within experimental error. In addition to the anion, the structure contains three tetraphenylphosphonium cations

