

Hydrogen bonding in calcium–tri-fluoromethanesulfonate–1,3-di-4-pyridylurea–methanol (1/2/2/4)

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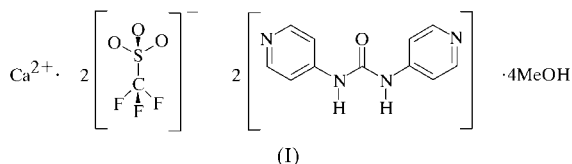
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The structure of the supramolecular complex calcium–tri-fluoromethanesulfonate–1,3-di-4-pyridylurea–methanol (1/2/2/4), $\text{Ca}^{2+} \cdot 2\text{CF}_3\text{SO}_3^- \cdot 2\text{C}_{11}\text{H}_{10}\text{N}_4\text{O} \cdot 4\text{CH}_4\text{O}$, is presented. The Ca^{2+} ion lies on an inversion centre and is octahedrally coordinated by four methanol molecules and two trifluoromethanesulfonate counter-ions. The molecular packing is dominated by hydrogen-bonded sheets in the (110) plane which contain $R_4^1(32)$ rings; in these rings, significant π – π interactions are observed between inversion-related 1,3-di-4-pyridylurea molecules.

Comment

Functional supramolecular architectures as constitutionally dynamic adaptive materials have emerged as a major field in supramolecular chemistry geared towards the design of self-organizing nanosystems of increasing complexity (Lehn, 2000*a,b*, 2002; Funeriu *et al.*, 2001). The self-assembly of different entities is based both on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and on complexed ions reading out the structural information through the algorithm defined by their recognition geometry. Of special interest are so-called hereon–heteroditopic ligand systems containing different binding units that can combine to form different superstructures according to the specific interaction involved (Funeriu *et al.*, 2001).

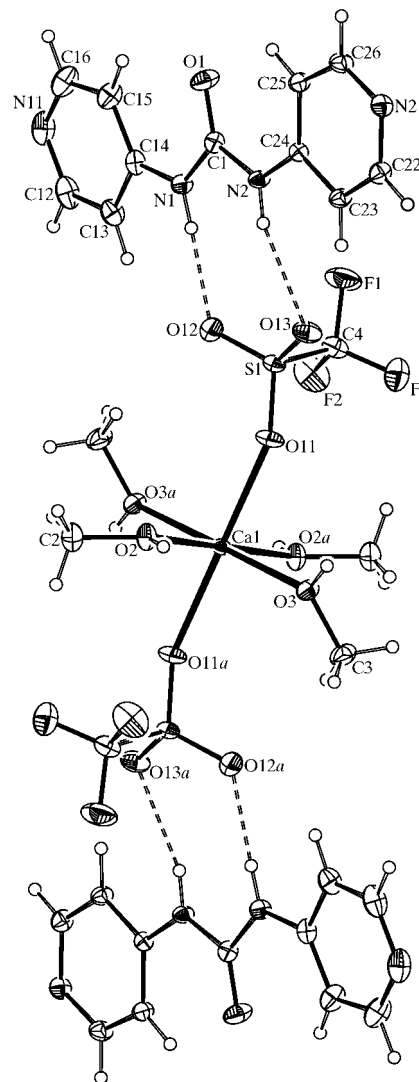


We consider in this context the 1,3-di-4-pyridylurea ligand, *L*, in which the available urea and pyridine moieties are covalently linked. We reasoned that, by an appropriate choice of these binding units and of a specific metal salt, we could obtain, under specific conditions, a supramolecular structure

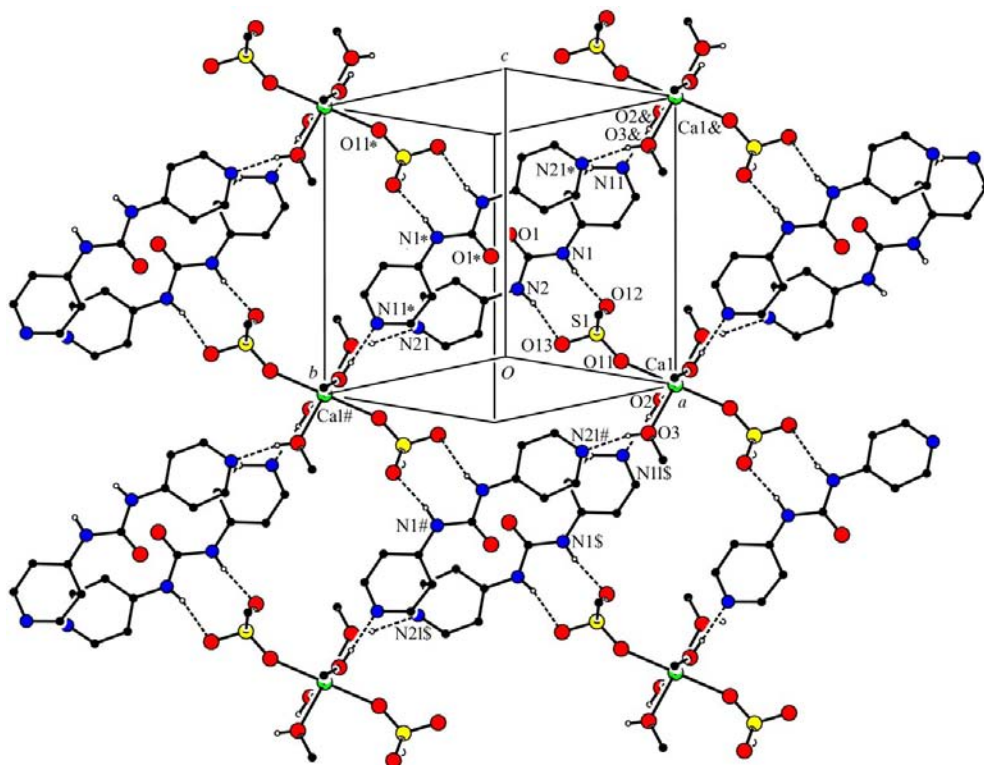
(output device). The different interaction types (subprograms) involved are: (a) pyridine–metal coordination (Scudder *et al.*, 1999; Lu *et al.*, 2001), (b) metal–anion association (coordination), (c) urea–anion complexation (Scheerder *et al.*, 1996) and (d) urea head-to-tail association (Etter, 1990). These interactions combine either in an independent way (linear combination) or by a crossover with interference between the individual subprograms.

The structure of the complex, (I), of *L* with $\text{CaTf}_2 \cdot (\text{methanol})_4$ ($\text{Tf}^- = \text{CF}_3\text{SO}_3^-$, triflate) was determined from a crystal obtained from a methanol/diisopropyl ether (1:1) solution at room temperature. This complex proves to be an intriguing coordination polymer with a novel architecture and results from the crossover of the simultaneous independent trifluoromethanesulfonate–urea and trifluoromethanesulfonate– Ca^{2+} complexation subprograms.

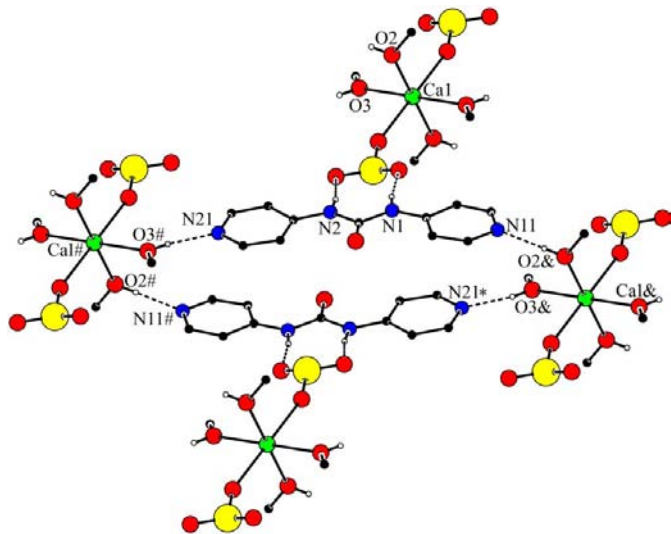
The molecular structure of (I) is presented in Fig. 1. The unit cell contains two *L* ligands, one Ca^{2+} ion on an inversion


Figure 1

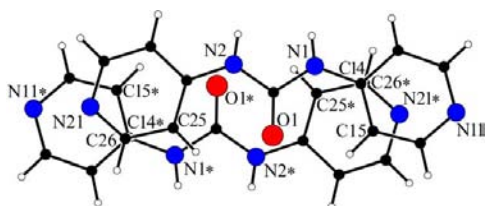
The structure of (I), showing displacement ellipsoids at the 30% probability level. [Symmetry code: (a) $2 - x, -y, -z$.]

**Figure 2**

A view of part of the (110) sheet structure. For clarity, F atoms of the CF_3 moieties and H atoms not involved in hydrogen bonding are not shown. [Symmetry codes: (*) $1 - x, 1 - y, 1 - z$; (\$) $x, y, -1 + z$; (#) $1 - x, 1 - y, -z$; (&) $x, y, 1 + z$.]

**Figure 3**

A detailed view of the $R_4^4(32)$ ring. For clarity, H atoms not involved in hydrogen bonding and the CF_3 moieties are not shown. The symmetry codes are as in Fig. 2.

**Figure 4**

A view normal to the best plane through the L ligand, showing ring overlap. The symmetry code is as in Fig. 2.

centre, two trifluoromethanesulfonate (Tf^-) counter-ions and four methanol molecules. The unique L ligand has an almost planar conformation; the angle between the two pyridyl rings is $4.28(10)^\circ$. Two inversion-related Tf^- ions are coordinated to the Ca^{2+} ion and the octahedral coordination at Ca^{2+} is completed by two pairs of inversion-related methanol molecules; pertinent dimensions are given in Table 1. The inversion-related L ligands are linked to the Tf^- ion by pairs of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, as shown in Fig. 1; hydrogen-bond geometry details are given in Table 2. Possibly assisting the retention of this structure are $\text{C}-\text{H} \cdots \text{O}$ contacts (Table 2) between $\text{C}3-\text{H}3\text{A}$ and $\text{O}12$ at $(2 - x, -y, -z)$.

The crystal structure contains sheets of molecules lying in the (110) plane (Fig. 2). A feature of this sheet structure is the $R_4^4(32)$ (Bernstein *et al.*, 1995) hydrogen-bonded ring system, which is shown in more detail in Fig. 3. Infinite chains are thus generated which are further linked to yield the sheet structure by $\text{Tf}^- - \text{Ca}^{2+} - \text{Tf}^-$ moieties. The $R_4^4(32)$ ring is stabilized by significant $\pi-\pi$ interactions between inversion-related L ligands; details of the overlap are shown in Fig. 4, where the shortest intermolecular $\text{C} \cdots \text{C}$ distance is $3.388(2) \text{ \AA}$ between $\text{C}14$ and $\text{C}26$ at $(1 - x, 1 - y, 1 - z)$.

Experimental

A solution of L (20 mg, 0.09 mmol) in methanol (1 ml) was added to a solution of CaTf_2 (17.6 mg, 0.09 mmol) in methanol (1 ml) and the mixture was heated for 2 h at 333 K. Single crystals of the LCaTf_2 complex were obtained by slow diffusion of diisopropyl ether as non-solvent into the resulting methanol solution at room temperature.

Crystal data

$\text{Ca}^{2+} \cdot 2\text{CF}_3\text{O}_3\text{S}^- \cdot 2\text{C}_{11}\text{H}_{10}\text{N}_4\text{O} \cdot 4\text{CH}_4\text{O}$	$Z = 1$
$M_r = 894.84$	$D_x = 1.497 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.157 (1) \text{ \AA}$	Cell parameters from 4175 reflections
$b = 9.768 (1) \text{ \AA}$	$\theta = 1.8\text{--}23.2^\circ$
$c = 11.366 (2) \text{ \AA}$	$\mu = 0.36 \text{ mm}^{-1}$
$\alpha = 98.95 (1)^\circ$	$T = 173 \text{ K}$
$\beta = 97.14 (1)^\circ$	Prism, colourless
$\gamma = 94.03 (1)^\circ$	$0.30 \times 0.30 \times 0.25 \text{ mm}$
$V = 992.3 (2) \text{ \AA}^3$	

Data collection

Xcalibur CCD diffractometer	2931 reflections with $I > 2\sigma(I)$
Area-detector scans	$R_{\text{int}} = 0.030$
Absorption correction: Gaussian (Schwarzenbach & Flack, 1991)	$\theta_{\text{max}} = 28.5^\circ$
$T_{\text{min}} = 0.900$, $T_{\text{max}} = 0.910$	$h = -13 \rightarrow 12$
17 908 measured reflections	$k = -12 \rightarrow 13$
5013 independent reflections	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.023P)^2]$
$R(F) = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 0.70$	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
6255 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
264 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0018 (4)

Table 1

Selected interatomic distances (\AA).

Ca1—O2	2.3384 (11)	N1—C1	1.3834 (18)
Ca1—O3	2.3215 (11)	N1—C14	1.3913 (19)
Ca1—O11	2.3521 (11)	N2—C1	1.3731 (19)
O1—C1	1.2160 (18)	N2—C24	1.3996 (18)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H \cdots A$	$D\text{--}H$	$H \cdots A$	$D \cdots A$	$D\text{--}H \cdots A$
N1—H1 \cdots O12	0.86	2.01	2.8608 (18)	170
N2—H2A \cdots O13	0.86	2.27	3.1025 (17)	163
C3—H3A \cdots O12 ⁱ	0.96	2.52	3.316 (2)	140
O2—H2 \cdots N11 ⁱⁱ	0.82	1.87	2.6891 (18)	179
O3—H3 \cdots N21 ⁱⁱⁱ	0.82	1.92	2.7250 (16)	167

Symmetry codes: (i) $2 - x, -y, -z$; (ii) $x, y, z - 1$; (iii) $1 - x, 1 - y, -z$.

For simplicity, the atoms were positioned in the cell so that the $\pi\text{--}\pi$ interaction was between molecules of the ligand L related by the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. All H atoms were located in difference maps and subsequently allowed for as riding atoms, with C—H = 0.93 and 0.96 \AA , N—H = 0.86 \AA and O—H = 0.82 \AA .

Data collection: *Crysalis CCD* (Oxford Diffraction, 2002); cell refinement: *Crysalis RED* (Oxford Diffraction, 2002); data reduction: *Crysalis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001), *SHELXL97* (Sheldrick, 1997) and *WinGX* (Version 1.64.05; Farrugia, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1212). Services for accessing these data are described at the back of the journal.

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