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Redetermination of (6*R*,7*S*,9*S*,11*S*)-(−)-sparteinium monoperchlorate

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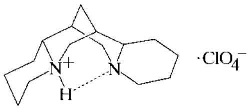
The structure of the title compound, $C_{15}H_{27}N_2^+\cdot ClO_4^-$, consists of a monoprotonated sparteinium cation and a perchlorate anion. The two tertiary N atoms of the cation, one perchlorate O atom and a H atom form a bifurcated hydrogen bond, the four hydrogen-bonding atoms being nearly in the same plane.

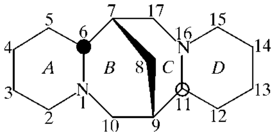
Comment

The crystal structure of sparteinium monoperchlorate, (I), has been determined previously (Borovyak *et al.*, 1973). However, the refinement of the structure was not complete and the structural data collected were very limited; the H-atom and ClO_4^- positions were not determined. We redetermined the crystal structure of (I) for two reasons: (i) there is a need for the complete and well refined crystal structure of (−)-sparteine in order to understand the structural features of many previously reported metal sparteine complexes (Kim *et al.*, 2001; Kuroda & Mason, 1979; Lee *et al.*, 1998, 2000, 2002; Lopez *et al.*, 1998; Motevalli *et al.*, 1993) and (ii) compound (I) has attracted research attention and has been intensively utilized in medicinal chemistry (Cady *et al.*, 1977) and asymmetric synthesis (Beak *et al.*, 1996; Kretchmer, 1972; Mason & Peacock, 1973).



(I)

The neutral dialkaloid sparteine structure is composed of four rings, two of which (*A* and *B*, see *Scheme* below) form a double-chair *trans*-quinolizidine system, which is relatively resistant to conformational–configurational change upon protonation. However, the second system of rings (*C* and *D*) is much more susceptible to inversion on an N-donor atom (N16), and inversion may occur in a *trans*-boat–chair or *cis*-double-chair conformation. The outer rings (*A* and *D*) are directed upward (*cis*) or downward (*trans*) with respect to the methylene bridge, *i.e.* the H atoms on C6 and C11 are in *trans*–*trans* or *cis*–*cis* positions, respectively. The conformation and configuration of the spartenium cation in (I) was found to be the same as reported previously (Borovyak *et al.*, 1973).



Based on ^{13}C NMR and IR studies, Boczon & Koziol (1997) suggested that sparteine and its isomers and derivatives can undergo conformational–configurational rearrangements in solution. It is well known that, in the case of the monoprotonated base, *viz.* $C_{15}H_{27}N_2^+$, in solution, a tautomeric equilibrium takes place, with the contributions of cations $N1^+—H1\cdots N16$ and $N1\cdots H1—N16^+$ being in the ratio 1:1.25 (Boczon & Koziol, 1997). However, in the solid state, the H atom bonds to atom N1 and the compound crystallizes exclusively in the $N1—H1\cdots N16$ tautomeric form (Fig. 1 and Table 1). The H atom also interacts with perchlorate atom O2 to form a rare three-centered hydrogen bond (bifurcated hydrogen bonding), as shown in Fig. 1. The four hydrogen-bonding atoms (N1, N16, H1 and O2) are nearly in the same plane; the sum of the three angles $N1—H1\cdots N16$, $N1—H1\cdots O2$ and $N16\cdots H1\cdots O2$ is approximately 358°. Atom H1 on protonated atom N1 is axial relative to rings *A* and *B*, as is usually observed (Boczon & Koziol, 1997). The $N1\cdots N16$ distance is 2.755 (5) Å, which is considerably less than the sum of the van der Waals radii of 3.16 Å and confirms the participation of the two N atoms in a bifurcated intramolecular hydrogen bond (Table 2).

The (−)-sparteine conformation in metal(II) (−)-sparteine complexes is almost identical to the conformations in free and monoprotonated (−)-sparteine. In the metal complexes, there is a relationship between the N—*M*—N bite angle and *M*—N distance, *i.e.* the N—*M*—N bite angle decreases as the *M*—N

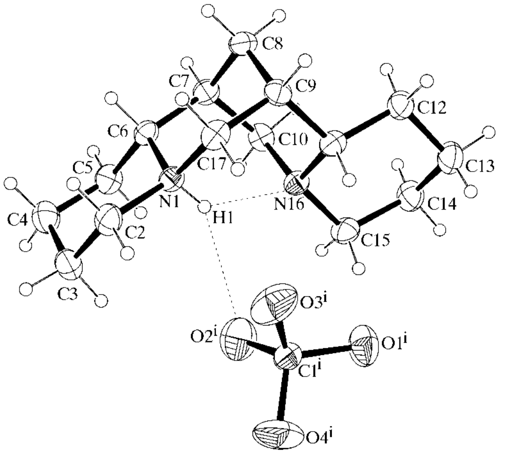


Figure 1
A view (Farrugia, 1997) showing the atom labelling and the hydrogen bonding (dashed lines) in (I); ellipsoids are at the 30% probability level [symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$].

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bond length increases and *vice versa* (Lee *et al.*, 2002). In fact, the N—*M*—N bite angle in metal(II) (−)-sparteine complexes affects the N···N distance of the coordinated (−)-sparteine ligand. The N1···N16 distance in (I) is shorter than corresponding distances observed in the metal complexes due to the intramolecular N—H···N hydrogen bond and the cation size.

Experimental

The precursor complex [Cu($C_{15}H_{26}N_2$)(ClO_4)$_2$] was prepared by mixing a solution of copper(II) perchlorate in ethanol–triethylorthoformate (3:1 *v*/*v*) with a stoichiometric amount of (−)-*l*-sparteine, *viz*. (6*R*,7*S*,9*S*,11*S*)-$C_{15}H_{26}N_2$. The resulting dark-blue solution was added to a stoichiometric amount of potassium fluoride. CuF_2 salts immediately precipitated and were removed from the solution by filtration. Single crystals of (I) were obtained by slow evaporation of the solution at room temperature. Analysis calculated for $C_{15}H_{27}ClN_2O_4$: C 53.81, H 8.13, N 8.37%; found: C 53.63, H 8.00, N 8.34%.

Crystal data

$C_{15}H_{27}N_2^+\cdot ClO_4^-$
$M_r = 334.84$
Orthorhombic, $P2_12_12_1$
$a = 8.029$ (2) Å
$b = 13.4196$ (16) Å
$c = 15.3094$ (16) Å
$V = 1649.6$ (5) Å^3
$Z = 4$
$D_x = 1.348$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 11.3–14.1°$
$\mu = 0.25$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.33 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.887$, $T_{\max} = 0.926$
2438 measured reflections
2402 independent reflections
1559 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 10$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 300 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.128$
$S = 1.02$
2402 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.3075P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 232 Friedel pairs
Flack parameter = 0.00 (13)

The positional parameters of the H atoms were calculated geometrically (C—H = 0.96–0.98 Å) and these atoms were constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(CH and CH$_2$). The H atom on N1 was located in a difference map and refined isotropically.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.500 (5)	N16—C17	1.469 (5)
N1—C6	1.512 (5)	Cl—O1	1.423 (3)
N1—C10	1.506 (5)	Cl—O2	1.423 (4)
N16—C11	1.475 (5)	Cl—O3	1.439 (4)
N16—C15	1.479 (5)	Cl—O4	1.406 (4)
C2—N1—C6	112.2 (3)	C11—N16—C17	112.7 (3)
C2—N1—C10	109.9 (3)	C15—N16—C17	113.0 (3)
C6—N1—C10	112.2 (3)	C7—C8—C9	107.5 (4)
C11—N16—C15	110.8 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2$^{\rm i}$	0.84 (4)	2.54 (4)	3.155 (6)	130 (4)
N1—H1···N16	0.84 (4)	2.13 (5)	2.755 (5)	131 (4)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1088). Services for accessing these data are described at the back of the journal.

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