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Hydantoin Derivatives as Spacers for Crystal Engineering in the Chemistry of Heavy Alkali Metal Ions: Synthesis and Crystal Structure of Layered $(CsLOH)_\infty$ (L = 5,5-Dimethyl-4-oxoimidazolidine-2-thione)

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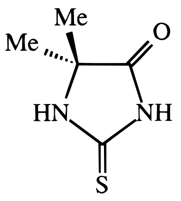
In an attempt to prepare the cesium salt of the monoanion of the hydantoin derivative, 5,5-dimethyl-4-oxoimidazolidine-2-thione (L)[1]



(L)

crystals of formula $(CsLOH)_\infty$ suitable for X-ray crystal structure determination[2] were obtained. A view of the structure of $(CsLOH)_\infty$ seen along [010] is shown in Figure 1. The polymeric complex consists of layers with thickness $c/2$ stacked along [001] and separated by normal van der Waals contacts. A view of a single layer is shown in Figure 2, where the methyls have been omitted. The figure also shows the coordination environment around the alkaline ion. Each cesium atom displays an 8-fold coordination with four different L molecules and three OH^- groups as surrounding ligands. One L molecule is coordinated through the sulfur and a nitrogen atom, a second L molecule through the sulfur and the remaining two ligands through the oxygen. Each ligand molecule displays three donor atoms toward the alkaline ion: a nitrogen atom, the oxygen atom, which bridges two Cs atoms separated by 4.832 Å, and the sulfur atom bridging two Cs atoms almost aligned along [010], with a Cs···Cs distance of 5.122 Å. The hydroxo groups are triply bridging three cesium ions.

The bond lengths of the imidazolidine ring in $(CsLOH)_\infty$ are reported in Table 1 together with the calculated values of free L.[3] In the same Table the corresponding values observed in the charge-transfer adduct between L and diiodine (**1**)[4] and in 2-thiohydantoin (4-oxoimidazolidine-2-thione, **2**)[5] are reported for comparison. The main differences between the calculated bond lengths and those observed in $(CsLOH)_\infty$ are found in the C(2)−S(6) and C(4)−O(7) bonds, which are appreciably lengthened in the latter compound, as a consequence of the interaction of the oxygen and sulfur atoms with the cesium ions.

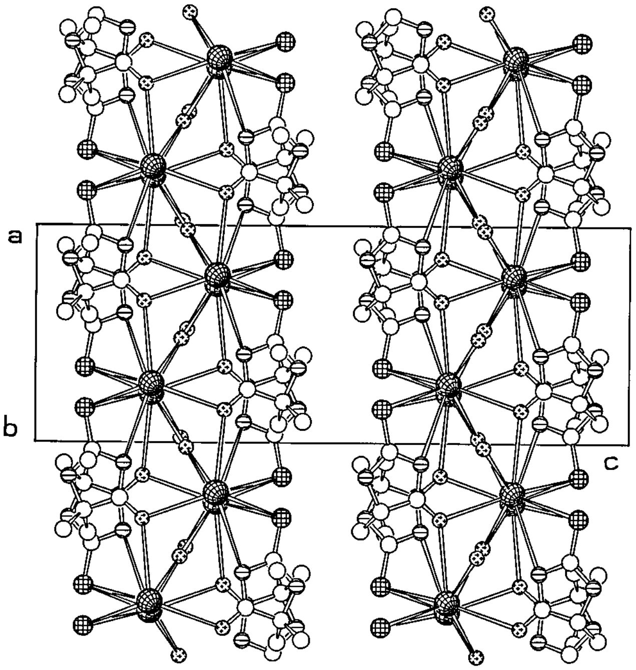


Figure 1. Crystal packing of $(CsLOH)_\infty$ seen along [010].

Infrared spectroscopy agrees with the structural data, since the $\nu(C{=}O)$ stretching frequency shifts from 1745 to 1627 sbr cm^{-1} on passing from L to $(CsLOH)_\infty$, as a consequence of the C=O lengthening upon coordination, while the $\nu(NH)$ shifts from 3179 sbr to 3220 sbr cm^{-1}. The spectrum of $(CsLOH)_\infty$ also shows a strong neat absorption at 3458 cm^{-1} attributable to triply bridging OH^- groups.

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(1) 5,5-Dimethyl-4-oxoimidazolidine-2-thione was reacted with CsOH in H_2O/2-propanol (1:1 vol). By slow evaporation of the solvent, crystals with elemental analysis corresponding to $C_5H_8CsN_2O_2S$ were obtained.

(2) Crystal data for $(CsLOH)_\infty$: $C_5H_8CsN_2O_2S$, $M = 293.10$, orthorhombic, space group *Pbca* (No. 61), $a = 8.300(2)$ Å, $b = 10.221(1)$ Å, $c = 22.673(6)$ Å, $U = 1923.3(9)$ Å^3, $Z = 8$, F(000) = 1112, $D_c = 2.024$ g cm^{-3}, μ(Mo Kα) = 39.9 cm^{-1}. The structure was solved by Patterson and Fourier methods and refined using 1837 observed reflections [$I > 3\sigma(I)$] to $R = 0.025$ and $Rw = 0.041$.

(3) Ab initio SCF calculations with geometry optimization and frequency calculation were performed in the 6-311G** basis set [(a) Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Curtis, L. A.; McGrath, M. P.; Blandeau, J.-P.; Davis, N. E.; Binning, R. C., Jr.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104] with Gaussian 94W. (c) *Gaussian 94*, Revision D.1; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, **1995**. Full geometry optimization was performed with conventional Gaussian default convergence criteria from a starting geometry obtained at AM1 level. (d) Dewar, M.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4499. (e) Davis, L. P.; Guidry, R. M.; Williams, J. R.; Dewar, M. J.; Rzepa, H. S. *J. Comput. Chem.* **1981**, *2*, 433.

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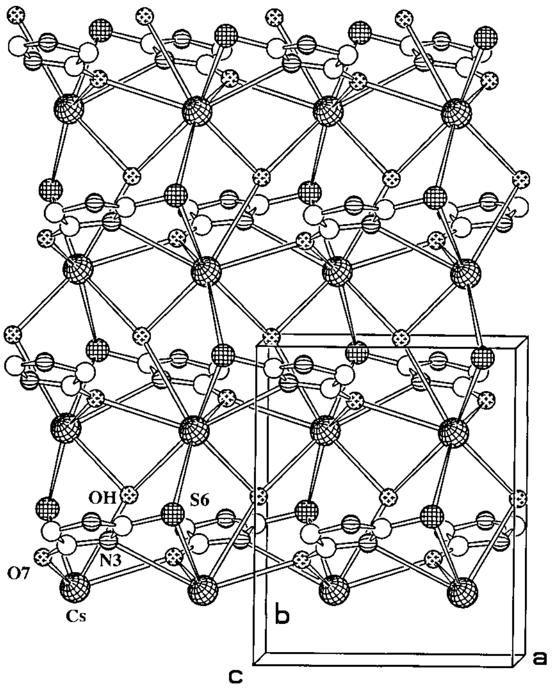

Figure 2. Crystal packing of $(CsLOH)_\infty$ seen almost along [001]. Relevant interatomic distances (Å) are Cs−S(6) 3.710(1), Cs−S(6) (1/2-*x*, 1/2+*y*, *z*) 3.659(1), Cs−OH 3.642(2), Cs−OH (1/2-*x*, *y* −1/2, *z*) 3.157(2), Cs−OH (1-*x*, *y* −1/2,1/2- *z*) 3.257(2), Cs−O(7) (3/2-*x*, 1/2+*y*, *z*) 3.327(2), Cs−O(7) (1-*x*, 1/2+*y*, 1/2-*z*) 3.114(2), Cs−N(3) (1/2-*x*, 1/2+*y*, *z*) 3.567(2).

Table 1. Calculated Bond Lengths (Å)[a] of L Compared with Experimental Values Found in $(CsLOH)_\infty$ and in Its 1:1 Charge-Transfer Adduct with Diiodine (**1**) and in 2-Thiohydantoin (= 4-oxoimidazolidine-2-thione, **2**)

	L[b]	$(CsLOH)_\infty$	**1**	**2**
N(1)−C(2)	1.330	1.333(2)	1.317(3)	1.325(2)
C(2)−S(6)	1.656	1.691(2)	1.673(3)	1.648(2)
C(2)−N(3)	1.368	1.367(2)	1.372(4)	1.378(2)
N(3)−C(4)	1.373	1.349(3)	1.375(4)	1.349(2)
C(4)−O(7)	1.180	1.244(3)	1.211(4)	1.222(3)
C(4)−C(5)	1.528	1.522(3)	1.514(4)	1.502(2)
C(5)−N(1)	1.458	1.459(3)	1.477(4)	1.442(3)
ref	this work	this work	4	5

[a] The numbering scheme proceeds according to crystal data labels. [b] Calculated values (see text).

CP-MAS ^{13}C NMR spectra,[6] recorded for L and $(CsLOH)_\infty$, show an appreciable deshielding of C=O and C=S in the coordinated L and a splitting of the signal due to the methyl groups, in agreement with the different contacts of the two methyls. According to the results of the crystal data, the CP-MAS ^{133}Cs NMR spectrum shows a unique peak at 103.2 ppm (referred to $Cs^+(aq)$ at infinite dilution), which is a common value for Cs^+ salts.[7]

It is interesting to compare the present structure with those of $CsOH{\cdot}nH_2O$ (n = 1, 2, and 3).[8,9] The crystals of the monohydrate are made up of anionic layers of $[H_3O_2^-]$, connected by layers of cesium ions;[8] in the di- and trihydrates, layers, in which hydrogen-bonded anionic water structure forms four-, five-, and seven-membered rings in $CsOH{\cdot}2H_2O$ and four-, five-, and six-membered rings in $CsOH{\cdot}3H_2O$, are linked together by H_2O molecules and Cs^+ ions to give three-dimensional structures.[9] In the present case, the structure of $(CsLOH)_\infty$ is made up of layers of CsOH sandwiched between layers of L. This structure represents a unique case, in which each 5,5-dimethyl-4-oxo-imidazolidine-2-thione ligand acts as a polyhaptic molecule toward four different Cs^+ ions. While alkali metal ion complexes with polydentate ligands, particularly crown ethers and criptands, are quite common,[10] to our knowledge no similar examples are reported in the literature.

The present case could be considered a new example of molecular crystal engineering based on noncovalent interactions. In fact crystal engineering so far has mainly been focused on the use of suitable organic molecules as building blocks of multi-dimensional arrays and networks by supramolecular hydrogen bond interactions.[11] Recently, analogous attention is being focused on the design and control of polymeric metal complexes with polydentate ligands.[12] In the present case, an organic multidentate molecule induces a drastic modification in the inorganic networks observed in $CsOH{\cdot}nH_2O$, which are mainly determined by hydrogen bonds. The effect is that of obtaining a layered structure of CsOH when water is substituted by L. The use of poorly coordinating organic ligands as modifying agents of crystal structures opens new perspectives in the crystal engineering of alkali metal hydroxides.

Supporting Information Available: Tables giving crystal data and details of the structure determination, fractional atomic coordinates, general displacement parameter expressions, bond lengths, bond angles, anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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(6) ^{13}C NMR CP-MAS spectra were obtained on a Varian Unity 400 spectrometer operating at 100.5 MHz; the ^{13}C chemical shifts were calibrated indirectly through the adamantane peaks (δ 38.3, 29.2) relative to $SiMe_4$. ^{133}Cs NMR CP-MAS spectra at 52.4 MHz were referenced to external CsCl (δ 232.0) relative to $Cs^+(aq)$ at infinite dilution. The ^{13}C signals of L in $(CsLOH)_\infty$ are the following (in parentheses the corresponding values of pure L): 198.3 (182) for C=O, 194.4 (181) for C=S, 64.2 (64.8) for C(5), and 25.9 and 23.1 (25.3) for the methyl groups bonded to C(5).

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