Crystal Structure and $^{113}_{48}Cd$ N.M.R. Spectrum of Di-μ-chloro-dichlorobis-(6-mercaptopurine)diaquodicadmium(II)

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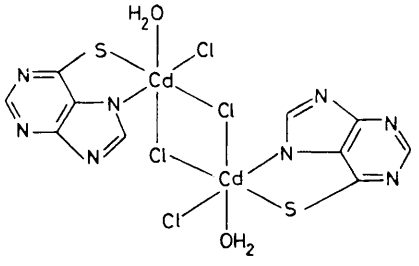
Summary The ^{113}Cd n.m.r. spectrum of di-μ-chloro-dichlorobis-(6-mercaptopurine)diaquodicadmium(II) has been observed and the crystal structure determined to consist of dimers with relatively long Cd–S and Cd–N(7) distances.

^{113}Cd N.M.R. spectroscopy has considerable potential as a probe of polypeptide and polynucleotide structures, particularly when cadmium can be used as a replacement for naturally occurring divalent metal ions such as Ca^{2+} and Mg^{2+}. The utility of this probe would also be enhanced by coupling the observations with ^{13}C n.m.r. spectroscopy.

However, a current drawback to the use of ^{113}Cd n.m.r. spectroscopy for these situations is the lack of crystal structure data for appropriate Cd complexes for which solution n.m.r. spectra can be observed. In addition, it is not clear whether or not Cd has a specific site preference in nucleotides. For example, in purine nucleotides crystal structure evidence indicates that Cd^{2+} binds to phosphate oxygen as well as purine base to give a complicated three-dimensional structure.[1-4] As a first step, we decided to examine a situation where the likelihood of specific binding was the best, *i.e.*, a sulphur-containing purine. 6-Mercaptopurine was our choice, not only because it contains a sulphur ligand, but also because it can be incorporated into DNA. We report here the preparation, crystal structure, and ^{113}Cd n.m.r. spectrum of the title compound.



(1)

Compound (**1**) was prepared by heating 6-mercaptopurine monohydrate (5 mmol; Aldrich) and $CdCl_2 \cdot 2\frac{1}{2} H_2O$ (3 mmol; Allied) in 100 ml of 0·2 M HCl at 70 °C for 3 h. Diffraction-quality crystals grew after *ca.* 2 days of controlled evaporation of the resulting solution. *Crystal* data: $[Cd(SN_4C_5H_4)Cl_2H_2O]_2$; triclinic, space group $P\bar{1}$, $a = 10{\cdot}447(1)$, $b = 8{\cdot}026(1)$, $c = 6{\cdot}735(1)$ Å, $\alpha = 96{\cdot}41(1)$, $\beta = 101{\cdot}88(1)$, $\gamma = 74{\cdot}01(1)°$, $Z = 1$, $D_c = 2{\cdot}21$ g cm^{-3}, $D_M = 2{\cdot}22(2)$ g cm^{-3}, with Mo-K_α radiation, $\lambda = 0{\cdot}71068$ Å and $\mu = 27{\cdot}1$ cm^{-1}. No absorption corrections were made for this refinement, but one will be made for the final refinement. A total of 4582 *hkl* reflections were measured of which 2662 had $I \geqslant 2\sigma(I)$ and were used for structure solution and refinement. The structure was solved by standard heavy atom methods. The current R is 0·0475 and the weighted R is 0·0525 from a full-matrix least-squares refinement including anisotropic temperature factors for non-hydrogen atoms and fixed hydrogen atom position and isotropic temperature factors.[5]†

The ^{113}Cd n.m.r. spectrum was measured at room temperature in $(CD_3)_2SO$ at a concentration of 0·085 M in monomer in an 18 mm tube, using a highly modified Varian XL100-15 n.m.r. spectrometer.[6]

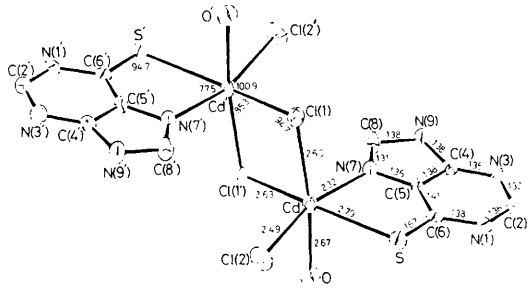


FIGURE. An ORTEP[5] plot of the structure of di-μ-chloro-dichlorobis-(6-mercaptopurine)diaquodicadmium(II) with major distances and angles. The maximum e.s.d.'s are: Cd–Cl, Cd–S, ± 0·003 Å; Cd–O, Cd–N, ± 0·006 Å; C–C, C–N ± 0·01 Å: angles X–Cd–Y ± 0·1°. N–C–N *etc.* ± 0·3°. The centre of the dimer is a crystallographic centre of symmetry. The hydrogen atoms are not shown for clarity.

The structure may be most simply described as a centrosymmetric dimer of 6-mercaptopurine–$CdCl_2 \cdot H_2O$ with bridging Cd–Cl–Cd bonds separated by more or less normal van der Waals interatomic distances; see Figure. The Cd^{2+} co-ordination sphere is approximately octahedral with the bridging chlorines occupying an axial and an equatorial site, the non-bridging Cl filling an equatorial site, the water molecule being at the remaining axial site, and the S and N(7) of the purine ring completing the co-ordination sphere in adjacent equatorial sites. The Cd–Cl(2) distance of 2·494(3) Å is appropriate for a normal Cd–Cl single bond and the bridging Cd–Cl distances are elongated by 0·1 Å or more. Both the Cd–S and Cd–N(7) distances are rather long when compared to the expected 2·52 and 2·18 Å, respectively. The Cd–S interaction was expected but the Cd–N(7) was not.

A strong (3 : 1 signal to noise ratio) ^{113}Cd n.m.r. signal was observed within 6 h (*ca.* 50,000 transients) with a 10,000 Hz sweep width from a natural abundance ^{113}Cd sample. The line width at half peak height was *ca.* 20 Hz. The peak was actually an asymmetric doublet with a peak separation of *ca.* 5 Hz. We attribute this feature to an equilibrium mixture of isomers in solution. The peak was at 554 p.p.m. downfield (increasing deshielding) from 0·1 M $Cd(ClO_4)_2$ in D_2O–H_2O (50 : 50 v/v). The ^{113}Cd resonance of Cd bound to sulphur would be expected at *ca.* 600 p.p.m. downfield from the resonance for $CdClO_4 \cdot 6H_2O$.[6-8]

This structure and ^{113}Cd n.m.r. spectrum are the first reported of a cadmium mercaptopurine complex and are the first step in the establishment of ^{113}Cd n.m.r. spectroscopy as a probe of polynucleotides.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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