Inorganica Chimica Acta, 203 (1993) 93–95

Short Communication

A thiouracil–Ca^{2+} complex containing two tautomeric forms of the thiouracilyl anion: synthesis and crystal structure of $[(\text{thiouracilyl})_2Ca\cdot 2DMSO\cdot H_2O]_2$

F. Adele Banbury, Matthew G. Davidson, Andrew J. Edwards, Maria-Isabel Lopez Solera, Paul R. Raithby, Ronald Snaith, Dietmar Stalke and Dominic S. Wright*

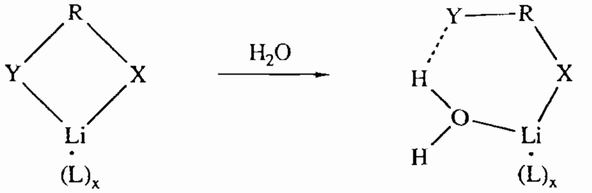
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (UK)

(Received April 1, 1992; revised July 30, 1992)

Abstract

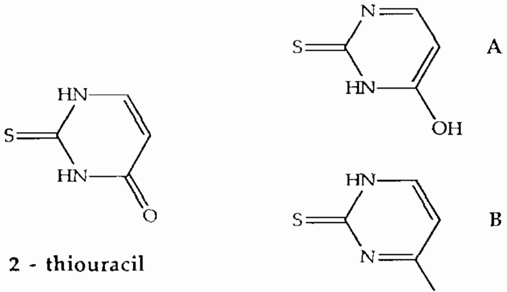
A DMSO solution of 2-thiouracil dissolves $Ca(OH)_2$ to give $[(\text{thiouracilyl})_2Ca\cdot 2DMSO\cdot H_2O]_n$ (**1**), a solution of which will in turn dissolve solid $PtCl_2$. **1** is dimeric ($n=2$) in the solid, and the presence of two tautomers of the thiouracilyl anion (one terminal on Ca, one bridging) allows every electronegative centre not used in bonding to calcium to be used in an intricate system of intra- and intermolecular hydrogen bonding.

We have shown that water can be incorporated into certain lithiated organic molecules, becoming coordinated to the lithium without causing hydrolysis [1]. The key feature is that a chelate complex of type $(Y\text{–}R\text{–}XLi\cdot xL)_n$ (X, Y drawn from N, O, S; L a Lewis base, e.g. HMPA, $O=P(NMe_2)_3$) accommodates added water by displacement of the side-arm Y, which then stabilises this H_2O by hydrogen-bonding to it (eqn. (1)).



(1)

More recently, a direct route to aqua complexes, including those of Group 2 metals [2], assembles H_2O by reacting toluene solutions of Y–R–XH ‘acids’ (notably, 2-mercaptobenzoxazole, OxSH, $C_6H_4O\cdot C(=S)NH$) with solid metal hydroxides (e.g. LiOH, NaOH; $M(OH)_2$, M = Ca, Sr, Ba). All such results suggested that metal salts ($^{\delta+}MZ_n{}^{\delta-}$) might, like $^{\delta+}H_2O^{\delta-}$, be captured by such displaceable side-arm chelate complexes. This idea was in part substantiated in that a solution of $(OxS)_2Ca\cdot 2HMPA$ dissolves solid $PtCl_2$ to give $[(HMPA)_3Ca\cdot(\mu_2\text{-}Cl)_3\cdot Ca(HMPA)_3]^+\cdot[Pt(OxS)_4\cdot CaCl]^-$ [3] and solid $HgCl_2$ to give $[(OxS)CaCl\cdot 2HMPA]_2\cdot(OxS)_2Ca\cdot(HgCl_2)_2$ [4]. These findings were potentially of biochemical interest since the natural ‘bases’ in DNA and RNA (A, T, G, C, U) are themselves type Y–R–XH organic ‘acids’. However, the $(OxS)_2Ca\cdot 2HMPA$ complex noted above is not a viable precursor for any biochemical studies since (i) OxSH is not a natural base, and (ii) HMPA is highly toxic. Thus we have studied, and now report on, a more realistic system employing (i) 2-thiouracil (see Scheme 1) as the organic precursor (uracil itself is rather insoluble in common solvents), and (ii) dimethyl sulfoxide (DMSO, $Me_2S=O$), which is non-toxic, as the Lewis base. These react with solid $Ca(OH)_2$ to give $[(\text{thiouracilyl})_2Ca\cdot 2DMSO\cdot H_2O]_n$ (**1**), a dimer ($n=2$) in the solid. A solution of **1** dissolves solid $PtCl_2$.



2 - thiouracil

Scheme 1.

A hot solution of thiouracil in DMSO dissolves solid $Ca(OH)_2$ and, from the resulting solution, colourless crystals of **1** can be isolated in high yield (see ‘Experimental’). X-ray crystallography shows that solid **1** is a dimer (Fig. 1). The structure is derived formally from hydroxy tautomers of thiouracil (Scheme 1: **A**, **B**). Each Ca^{2+} ion in the dimer is seven-coordinate, with pseudo-pentagonal bipyramidal geometry (a coordination number and geometry not observed before for calcium with simple (non-protein) ligands [5]). Six attachments are to oxygen centres: to two DMSO oxygen atoms (mean of Ca–O(2) and Ca–O(3) distances 2.324(4) Å), to one H_2O (Ca–O(1), 2.366(3) Å), to O of a terminal thiouracilyl anion (Ca–O(4), 2.343(3) Å), and to the O centres of two μ_2 anions (Ca–O(5A),

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

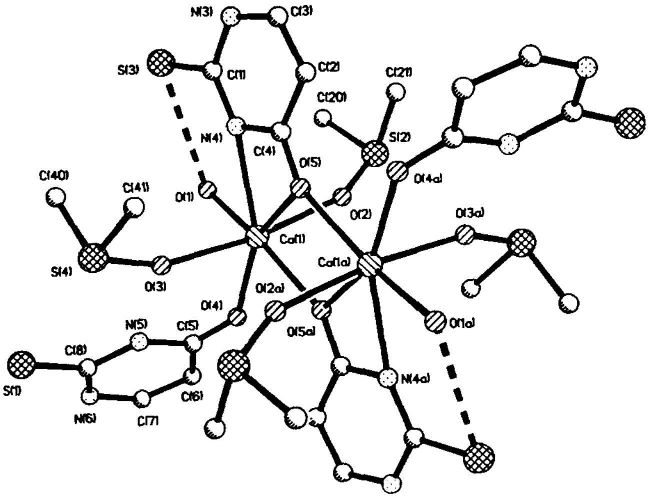


Fig. 1. The molecular structure of **1** showing the atom numbering scheme. H atoms have been omitted for clarity, and only one orientation of the disordered DMSO ligand is shown.

2.361(3) and Ca–O(5) 2.482(3) Å). The seventh contact is to the N atom of one of these bridging anions (Ca–N(4) 2.557(4) Å). There are no Ca–S contacts, the S atoms of all four anions being displaced from the Ca^{2+} ions due to the presence of one H_2O and two DMSO molecules at each end of the structure. However, the S atoms of the bridging anions do hydrogen-bond to one H atom of their respective terminal H_2O molecules (S(3)...H(10), 2.263(5); S(3)...O(1), 3.203(5) Å) [6].

The intermolecular hydrogen-bonding found within **1** is of particular interest. The molecular structure is designed superbly so as to maximise such bonding, using all the electronegative centres (N, O, S) and all the N- and O-attached H atoms. Two hydroxy tautomers of the thiouracilyl anion are present: deprotonated **A** (see Scheme 1) is terminal on Ca, and deprotonated **B** is bridging. Considering one half of $(\mathbf{1})_2$, the periphery of each half has an N atom (N(6), within **A**-H) and an NH group (N(3)H(3), within **B**-H). Atom N(6) hydrogen-bonds to the second H of an H_2O ligand (H(11), that not involved in intramolecular bonding to S) in a nearby molecule (N(6)...H(11), 1.801(5); N(6)...O(1), 2.746(5) Å). The group N(3)H(3) bonds to the displaced S of a terminal anion (S(1), that not involved in intramolecular bonding to H_2O) in a nearby molecule (S(1)...H(3), 2.386(5); S(1)...N(3), 3.274(5) Å). There is then left, in each half of $(\mathbf{1})_2$, just one unused electronegative centre, namely the inward-pointing NH group (N(5)H(5)) of a terminal anion. This group hydrogen-bonds, intramolecularly, to an O atom of one of the DMSO ligands (O(3)...H(5), 1.895(5); O(3)...N(5), 2.816(5) Å). Overall, the structure of **1** contains an unusual number and variety of hydrogen-bonded combinations: OH...S, OH...N, NH...S and NH...O.

Reacting a DMSO solution of **1** with solid $PtCl_2$ results in dissolution of the solid. Addition of toluene/alcohol precipitates a gold-coloured powder, **2**, which appears to be the simple adduct $(\mathbf{1})_2 \cdot PtCl_2$ (see 'Experimental'). This adduct is soluble in water, and attempts are being made to grow crystals of **2** from this and from other solvents.

Experimental

1. Solid $Ca(OH)_2$ (0.74 g, 10 mmol) was added to a solution of 2-thiouracil (2.56 g, 20 mmol) in DMSO (20 ml) under nitrogen. On heating at 100 °C for 2 h all the solid dissolved. Addition of toluene/alcohol (40 ml/20 ml), followed by slow cooling, gave a large crop of colourless cubic crystals, identified as **1** (yield 87%; m.p. 134–136 °C). *Anal.* Calc. for **1**, $C_{12}H_{20}CaN_4O_5S_4$: C, 30.8; H, 4.3; N, 12.0. Found: C, 30.7; H, 4.3; N, 11.6%. ^1H NMR (d_6-DMSO, 25 °C, 250 MHz): δ 10.8 (broad s, 2H, N*H*), 7.44 (d, 2H, C*H*), 5.56 (d, 2H, C*H*), 3.4 (broad s, 2H, H_2O), 2.54 (s, 12H, two DMSO); cf. ^1H NMR of 2-thiouracil (same conditions): δ 12.3 (broad s, 2H, N*H*), 7.40 (d, 1H, C*H*), 5.41 (d, 1H, C*H*).

2. Solid $PtCl_2$ (0.27 g, 1 mmol) was added to a solution of **1** (0.94 g, 2 mmol) in DMSO (5 ml) under nitrogen. All of the solid dissolved. Addition of toluene: alcohol (10 ml:10 ml) caused precipitation of a gold-coloured powder, provisionally identified as **2**, i.e. $(\mathbf{1})_2 \cdot PtCl_2$ (yield 62%; decomp. > 300 °C to a black powder). *Anal.* Calc. for **2**, $C_{24}H_{40}Ca_2Cl_2N_8O_{10}PtS_8$: C, 24.0; H, 3.3; N, 9.3. Found: C, 24.0; H, 3.0; N, 9.6%. The ^1H NMR shows the presence of thiouracil anions, DMSO, and H_2O in the same ratio as in **1** (i.e. 2:2:1 ligands, 6:12:2 protons).

Crystal data for **1**: [(thiouracilyl)$_2$Ca·2DMSO·H$_2$O]$_2$, $C_{24}H_{40}Ca_2N_8O_{10}S_8$, $M = 931.2$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.140(2)$, $b = 13.357(2)$, $c = 19.060(4)$ Å, $\beta = 98.07(2)°$, $U = 2051.8(7)$ Å^3, $T = 120$ K, $Z = 2$ (dimer), $D_c = 1.507$ g cm^{-3}, $F(000) = 964$, μ(Mo Kα) $= 7.42$ cm^{-1}. 2925 Intensity data ($2\theta_{max} = 45.0°$) recorded on a Stoe four-circle diffractometer using graphite monochromated Mo Kα radiation and averaged to give 2148 unique reflections with $F > 4\sigma(F)$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares to $R = 0.051$ with the ordered non-hydrogen atoms anisotropic; H atoms were placed on the ordered C atoms and allowed to ride with C–H 0.96 Å. The two water hydrogens were located directly and refined freely. One DMSO ligand was severely disordered and was modelled with five positions for the sulfur atom.

Supplementary material

The atomic coordinates, bond lengths and angles, and thermal parameters for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW.

Acknowledgements

We thank the SERC (Ph.D. quota award to F.A.B.), the SERC and the Associated Octel Co. Ltd. (CASE award to M.G.D.), and the DAAD, Nato Scholarship (D.S.) for financial support. Thanks are also given to the Universidad Autónoma de Madrid and the Comunidad Autónoma de Madrid for funding and study leave (M.-I.L.S.). All of the work described is being patented by the Associated Octel Co. Ltd.

References

1 (a) D. Barr, P. R. Raithby, P. v. R. Schleyer, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, (1990) 643; (b) D. R. Armstrong, D. Barr, P. R. Raithby, R. Snaith, D. S. Wright and P. v. R. Schleyer, *Inorg. Chim. Acta, 185* (1991) 163.

2 P. Mikulcik, P. R. Raithby, R. Snaith and D. S. Wright, *Angew. Chem., 103* (1991) 452; *Angew. Chem., Int. Ed. Engl., 30* (1991) 428.

3 M. G. Davidson, P. R. Raithby, R. Snaith, D. Stalke and D. S. Wright, *Angew. Chem., 103* (1991) 1696; *Angew. Chem., Int. Ed. Engl., 30* (1991) 1648.

4 M. G. Davidson, S. C. Llewellyn, M.-I. Lopez Solera, P. R. Raithby, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, (1992) 573.

5 (a) N. S. Poonia and A. V. Bajaj, *Coord. Chem. Rev., 87* (1988) 55, a review of the structures of Group 2 complexes; (b) Search of the Cambridge Crystallographic Data base.

6 (a) W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids,* Benjamin, New York 1968; (b) J. Emsley, *J. Chem. Soc. Rev., 9* (1980) 91.