Anions of Dithiouracil and Trithiocyanuric Acid as Bridges in Polynuclear Titanium(III) Metallocenes: the *X*-Ray Crystal Structure of Pyrimidine-2,4-dithiolatobis[bis(η^5-methylcyclopentadienyl)titanium(III)]

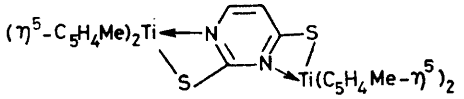
By David R. Corbin, Lynn C. Francesconi, David N. Hendrickson,* and Galen D. Stucky*

(School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801)

Summary The preparation and magnetic properties are reported for five compounds which incorporate the anions of 2,4-dithiouracil, 2-thiouracil, 4,6-dithiopyrimidine, 4,6-dihydroxypyrimidine, or trithiocyanuric acid as chelating bridges between bis(methylcyclopentadienyl)-titanium(III) units; the single crystal structure of pyrimidine-2,4-dithiolatobis[bis(η^5-methylcyclopentadienyl)-titanium(III)] is reported.

There has been considerable recent interest in the modes in which metal ions interact with nucleic-acid constituents such as pyrimidine.[1,2] In the case of three copper(II) complexes, the neutral cytosine ligand has been shown to co-ordinate to the metal with atom N(3). The exocyclic oxygen O(2) is then involved in a weak interaction (Cu–O *ca.* 2·8 Å) with the copper(II) ion.[3] The thyminato anion has been shown[4] to co-ordinate to copper(II) only with atom N(1). The only reported example where a pyrimidine type molecule was shown to act as a bidentate ligand is for the second-row transition metal complex bis(pyrimidine-2-thiolato)bis(triphenylphosphine)ruthenium(II).[5] There is no reported compound where either cytosine, thymine, or uracil chelates to a first-row transition metal ion. The ability to bond with normally inert compounds and the great reactivity of titanium metallocenes,[6] and our recent indirect evidence[7] of chelation of bis(cyclopentadienyl)-titanium species by the anions of uracil and cyanuric acid led to the present study. We here report the preparation of several new $\mathrm{Ti^{III}(\eta^5\text{-}MeC_5H_4)_2}$ compounds with chelated anionic pyrimidine ligands. The results of an *X*-ray crystal structure of the dithiouracil compound are also reported together with unusual magnetic susceptibility and e.s.r. results for several of the compounds.

Five new compounds were prepared by treating, under helium, a tetrahydrofuran (THF) solution of the pyrimidine and sodium sand with bis(methylcyclopentadienyl)titanium monochloride. Microcrystalline products were isolated after several days of heating (*ca.* 50 °C) and stirring. The reaction with 2,4-dithiouracil ($\mathrm{H_2}$dtura), 2-thiouracil ($\mathrm{H_2}$tura), 4,6-dimercaptopyrimidine ($\mathrm{H_2}$dtpyr), and 4,6-dihydroxypyrimidine ($\mathrm{H_2}$dhpyr) gave the binuclear complexes $[\{(\eta^5\text{-}\mathrm{MeC_5H_4})_2\mathrm{Ti}\}_2(\mathrm{dtura})]$ (I), $[\{(\eta^5\text{-}\mathrm{MeC_5H_4})_2\mathrm{Ti}\}_2(\mathrm{tura})]$, $[\{(\eta^5\text{-}\mathrm{MeC_5H_4})_2\mathrm{Ti}\}_2(\mathrm{dtpyr})]$, and $[\{(\eta^5\text{-}\mathrm{MeC_5H_4})_2\mathrm{Ti}\}_2(\mathrm{dhpyr})]$, respectively. The trinuclear complex $[\{(\eta^5\mathrm{MeC_5H_4})_2\mathrm{Ti}\}_3(\mathrm{ttcyn})]$ was obtained from the reaction with trithiocyanuric acid ($\mathrm{H_3}$ttcyn). All the complexes were found to be air-sensitive and exhibited mass spectra with intense molecular ion peaks.



(I)

The single-crystal *X*-ray structure of $[\{(\eta^5\text{-}\mathrm{MeC_5H_4})_2\mathrm{Ti}\}_2(\mathrm{dtura})]$ was solved ($R = 0{\cdot}085$, $R_w = 0{\cdot}056$) with anisotropic thermal parameters for all non-hydrogen atoms using 1444 observed reflections collected on a Picker four-circle diffractometer: space group *Pbca*; $a = 16{\cdot}910(17)$, $b = 22{\cdot}218(18)$, $c = 13{\cdot}934(10)$ Å, $D_m = 1{\cdot}37(1)$, $D_c = 1{\cdot}41$ g cm^{-3}, $Z = 8$. The structure of the binuclear complex is illustrated in the Figure.† The dianion of 2,4-dithiouracil is planar and chelates two $(\eta^5\text{-MeC}_5H_4)_2Ti^{III}$ units leading to an intramolecular Ti–Ti distance in the non-centrosymmetric binuclear complex of 6·075(2) Å. The two titanium ions are nearly coplanar with the dithiouracil bridge with distances out of the plane of 0·109 Å for Ti(1) and 0·033 Å for Ti(2). The titanium–cyclopentadiene ring carbon distances [2·282(11)—2·538(12) Å] and the tilt angles of the rings are comparable to values observed for other dicyclopentadienyltitanium complexes.[8,9]

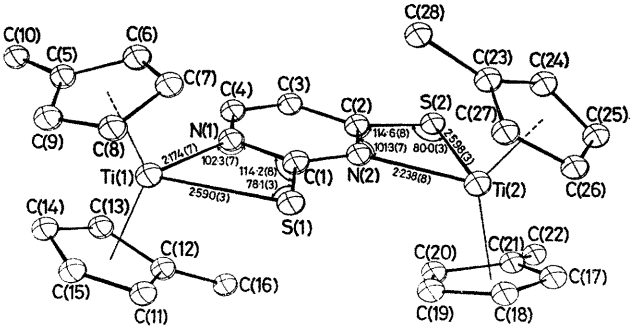


Figure. ORTEP plotting showing selected bond distances and angles in $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_2(\text{dtura})]$.

The dimensions in the Figure clearly show that the dtura^{2-} bridge is chelating the two titanium ions. A comparison of the bond distances and angles of the co-ordinated dtura^{2-} dianion with those[10] of the free pyrimidine $H_2\text{dtura}$ confirms that both the sulphur and nitrogen atoms of the pyrimidine are co-ordinated to the titanium ion. Convincing support for chelation by dtura^{2-} is the fact that the Ti(1)–N(1)–C(1) and S(1)–C(1)–N(1) angles and the corresponding angles found about the Ti(2) ion are all significantly less than the 120° expected for sp^2 hybridized atoms of the heterocyclic ring.

Both $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_2(\text{dtura})]$ and $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_3(\text{ttcyn})]$ exhibit unusual magnetic properties compared to the oxygen-containing analogues reported previously.[7] Thus, both $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_2(\text{ura})]$ and $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_3(\text{cyn})]$ were found to exhibit antiferromagnetic exchange interactions with exchange parameters of −2·2 and −0·93 cm^{-1}, respectively, while $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_2(\text{dtura})]$ and $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_3(\text{ttcyn})]$ exhibit ferromagnetic interactions with J = +2·0 and +3·1 cm^{-1}, respectively. The e.s.r. spectra in a toluene glass at liquid-nitrogen temperature of the two sulphur-containing species show zero-field splittings that are approximately four times those observed for the oxygen analogues. The magnetic field positions of the resonances in each spectrum were least-squares fit by a computer program[7] to give the spin Hamiltonian parameters g_x, g_y, g_z, D, and E. In the case of $[\{(\eta^5\text{-Me C}_5H_4)_2Ti\}_2(\text{dtura})]$, the axial zero-field splitting parameter, D, is 0·0530 cm^{-1}, compared to D = 0·0117 cm^{-1} for the ura^{2-} complex. The trinuclear ttcyn^{3-} complex gives D = 0·0324 cm^{-1} compared to D = 0·0095 cm^{-1} for the trinuclear cyn^{3-} complex. The large D values observed for the two sulphur-containing species are only explicable in terms of large pseudo-dipolar zero-field interactions. The Ti–Ti distance would not be very different in the ura^{2-} complex and the dtura^{2-} complex, and, consequently, the dipolar zero-field interactions would be expected to be approximately the same.

In marked contrast to the above findings, it was found that $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_2(\text{dhpyr})]$ and the analogous sulphur species $[\{(\eta^5\text{-MeC}_5H_4)_2Ti\}_2(\text{dtpyr})]$ both exhibit antiferromagnetic exchange interactions (J = − 1·4 and −1·6 cm^{-1}, respectively), and triplet-state e.s.r. spectra with only apparently dipolar zero-field splittings (D = 0·0077 and 0·0084 cm^{-1}, respectively).

We thank the N.S.F. and N.I.H. for grants to G.D.S. and D.N.H., respectively.

(*Received, 6th November* 1978; *Com.* 1185.)

---

† 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.

[1] D. J. Hodgson, *Prog. Inorg. Chem.*, 1977, **23**, 211.
[2] L. G. Marzilli, *Prog. Inorg. Chem.*, 1977, **23**, 255.
[3] D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Inorg. Chem.*, 1975, **14**, 2076, and references therein.
[4] T. J. Kistenmacher, T. Sorrell, and L. G. Marzilli, *Inorg. Chem.*, 1975, **14**, 2479.
[5] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 635.
[6] J. E. Bercaw, *J. Amer. Chem. Soc.*, 1974, **96**, 5087; J. E. McMurry, *Accounts Chem. Res.*, 1974, **7**, 281; P. C. Wailes, R. S. P. Coutts, and H. Weigold, 'Organometallic Chemistry of Titanium, Zirconium, and Hafnium,' Academic Press, New York, 1974.
[7] B. F. Fieselmann, D. N. Hendrickson, and G. D. Stucky, *Inorg. Chem.*, 1978, **17**, 1841.
[8] R. Jungst, D. Sekutowski, J. Davis, M. Luly, and G. Stucky, *Inorg. Chem.*, 1977, **16**, 1645.
[9] D. G. Sekutowski and G. D. Stucky, *J. Amer. Chem. Soc.*, 1976, **98**, 1376.
[10] E. Shefter and H. G. Mautner, *J. Amer. Chem. Soc.*, 1967, **89**, 1249.