The Preparation and the Molecular Structure of Bis(cyclopentadienyl)-titanium Trisulphur Tetranitride, an Eight-membered Titanium–Sulphur–Nitrogen Heterocycle

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The reaction of bis(cyclopentadienyl)titanium dicarbonyl with tetrasulphur tetranitride yields $cp_2TiS_3N_4$ (cp = cyclopentadienyl); *X*-ray crystallographic analysis of this compound reveals it to be based on an eight-membered TiS_3N_4 ring.

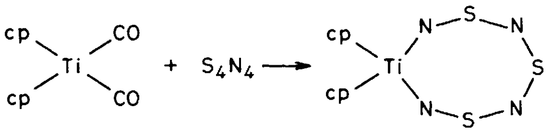
The structural diversity of titanocene sulphides cp_2TiS_x (cp = cyclopentadienyl)[1] and their ability to act as sulphur transfer agents in the synthesis of novel S_x rings[2] is well known. In order to explore the potential for similar reagents capable of stabilizing conjugated sulphur–nitrogen fragments we have undertaken a study of synthetic routes to molecules of the type $cp_2TiS_xN_y$. We report herein that the reaction of titanocene dicarbonyl with tetrasulphur tetranitride yields the novel eight-membered heterocycle $cp_2TiS_3N_4$ [equation (1)].

In a typical experiment a solution of $cp_2Ti(CO)_2$ [prepared by the carbonylation of cp_2TiCl_2 (10.0 mmol)][3] in 60 ml of tetrahydrofuran (THF) was added dropwise under nitrogen to

Table 1. Selected bond lengths (in Å) and valence angles (in degrees) in $cp_2TiS_3N_4$ (e.s.d's in parentheses).

	Molecule		
	1	2	3
d(Ti–N_a)	1.946(4), 1.962(4)	1.962(4), 1.951(4)	1.922(4), 1.962(4)
d(N_a–S_a)	1.490(4), 1.481(4)	1.487(4), 1.486(4)	1.499(4), 1.491(4)
d(S_a–N_b)	1.565(5), 1.565(5)	1.587(6), 1.565(5)	1.555(5), 1.585(5)
d(N_b–S_b)	1.600(5), 1.599(5)	1.582(6), 1.601(5)	1.605(5), 1.575(5)
Ti (*exo*)[a]	132.8	133.0	130.3
Ti (*endo*)	94.4(2)	94.8(2)	94.6(2)
N_a	150.5(2), 156.2(3)	149.7(3), 150.9(3)	154.2(3), 150.4(3)
S_a	124.3(2), 121.1(3)	123.2(3), 122.7(3)	121.9(3), 123.5(3)
N_b	144.4(3), 149.9(3)	147.0(3), 146.5(3)	147.5(3), 147.7(3)
S_b	121.8(2)	122.0(3)	122.2(2)

[a] Measured from the centre of the cyclopentadienide rings.



(1)

a solution of S_4N_4 (6.8 mmol) in 300 ml of THF. After 16 h the dark brown reaction mixture was filtered, concentrated *in vacuo* and passed down a 30 × 700 mm Bio Beads S-X8 column using toluene as eluant. The intense green fraction was separated and the solvent removed *in vacuo* to leave a dark green oil which, upon addition of 10 ml of acetonitrile and subsequent cooling to −30 °C, yielded green-black air stable needles of $cp_2TiS_3N_4$ (1.1 mmol), m.p. 105—107 °C, ^1H n.m.r. ($CDCl_3$), δ 5.84; u.v.–visible spectrum (CH_2Cl_2), λ_{max} (log ϵ), 584 (3.3), 458 (3.5), 324 nm (4.0).

Crystals of $cp_2TiS_3N_4$ suitable for *X*-ray work were obtained by recrystallization from methylene chloride–pentane. *Crystal data:* $C_{10}H_{10}TiS_3N_4$, $M = 330.3$, monoclinic, space group $P2_1/c$, $a = 7.802(2)$, $b = 20.012(4)$, $c = 25.099(4)$ Å, $\beta = 92.75(2)°$, $U = 3914(2)$ Å^3, $Z = 12$, $D_c = 1.693$ g cm^{-3}. A total of 3609 observed reflections was collected with an Enraf–Nonius CAD-4 diffractometer employing the θ–2θ technique ($2\theta_{max} = 50°$) with graphite-monochromated Mo-K_α radiation. There are three molecules in the asymmetric unit; distances and angles within these rings are given in Table 1. The values cited in the caption of Figure 1 represent average values. The final R value was 0.040 for a refinement using anisotropic thermal parameters for all non-hydrogen atoms.†

An ORTEP drawing of one of the three independent molecules is shown in Figure 1. In all three cases the seven-atom NSNSNSN sequence forms an approximately planar (to within 0.12 Å) unit, with the titanium atom lying 0.58 Å above this mean plane. In this conformation the eight-membered ring is less puckered than in the related $S_4N_4O_2$ molecule.[4] The geometry at titanium is similar to that observed in acyclic titanium(IV) nitrogen compounds [*i.e.* N–Ti–N 94.6(2)° *vs.* 94.7 and 93.9° in $cp_2Ti(NCO)_2$ and $cp_2Ti(NCS)_2$ respectively].[5,6] However, the variations in the S–N distances around the ring (see Figure 1) are significantly different from those in $S_4N_4O_2$ (mean distances N_a–S_a = 1.55, S_a–N_b = 1.50, N_b–S_b = 1.65 Å),[4] suggesting a somewhat different π-electronic structure.

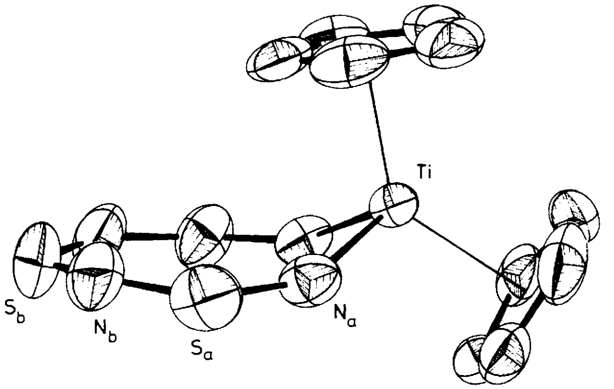


Figure 1. ORTEP drawing (50% probability ellipsoids) of one of the molecules of $cp_2TiS_3N_4$. Mean values of pertinent structural parameters are: d(Ti–N_a) 1.95(3), d(N_a–S_a) 1.49(1), d(S_a–N_b) 1.57(2), d(N_b–S_b) 1.59(2) Å, angles at Ti(*endo*) 94.6(2), N_c 152(4), S_a 123(1), N_b 147(3), S_b 122.0(2)° [numbers in parentheses represent ranges of six (or three) measurements].

Metal complexes containing binary sulphur–nitrogen ligands are generally restricted to the group 7 and 8 transition metals. The present compound represents the first of a potentially large number of cyclic metallothiazene derivatives based on the earlier transition metals.

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References

1 C. M. Bolinger, T. B. Rauchfuss, and S. R. Wilson, *J. Am. Chem. Soc.*, 1981, **103**, 5620; E. G. Muller, J. L. Petersen, and L. F. Dahl, *J. Organomet. Chem.*, 1976, **111**, 91; E. F. Epstein and I. Bernal, *ibid.*, 1971, **26**, 229; P. H. Bird, J. M. McCall, A. Shaver, and U. Siriwardane, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 384.

2 See R. Steudel, *Top. Curr. Chem.*, 1982, **102**, 149, and references therein.

3 B. Denerseman, G. Bouguet, and M. Bigorgne, *J. Organomet. Chem.*, 1975, **101**, C24.

4 H. W. Roesky, W. Schaper, O. Petersen, and T. Muller, *Chem. Ber.*, 1977, **110**, 2695.

5 S. J. Anderson, D. S. Brown, and A. H. Norbury, *J. Chem. Soc., Chem. Commun.*, 1974, 996.

6 A. C. Villa, A. G. Manfredotti, and C. Guastini, *Acta Crystallogr., Sect. B*, 1976, **32**, 909.

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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.