

## Dithiocarbamates of Titanium(III)

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DITHIOCARBAMATES of titanium(III), previously unknown, have now been prepared from bis-(cyclopentadienyl)titanium chloride ( $\pi\text{-C}_5\text{H}_5$ )<sub>2</sub>TiCl and the sodium salt of the dithiocarbamate in air-free aqueous solution under an atmosphere of argon. The products, which precipitated as green air-sensitive solids, are substantially pure as isolated,

absorption in the i.r. spectrum no definite conclusions can be drawn regarding the co-ordination number of the metal, but all other properties support a bidentate dithiocarbamate-ligand and a four-coordinate metal. The frequencies of the "thioureide" band (C-N stretch), common to most dithiocarbamates, are shown in the Table and indicate

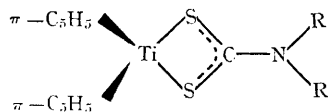
Characterisation of ( $\pi\text{-C}_5\text{H}_5$ )<sub>2</sub>TiS<sub>2</sub>CNR<sub>2</sub>

R	Colour	M.p.	C-N stretch (cm. <sup>-1</sup> )
NH <sub>2</sub> .. .. .	Pale green	160° (decomp.)	1390
NMe <sub>2</sub> .. .. .	Blue green	174 (decomp.)	1495
NEt <sub>2</sub> .. .. .	Deep green	100—102	1488
NPr <sup>n</sup> <sub>2</sub> .. .. .	Deep green	56—59	{ 1480
			{ 1490
NBu <sup>n</sup> <sub>2</sub> .. .. .	Deep green	43—44	1480
N(n-C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> .. .. .	Deep green	oil	1475
NBz <sub>2</sub> .. .. .	Grey green	138 (decomp.)	1470
N[CH <sub>2</sub> ] <sub>5</sub> .. .. .	Deep green	162—164 (decomp.)	1480

but can be sublimed or distilled with some decomposition. Molecular-weight measurements of the compounds, R = Et, Pr<sup>n</sup>, and Bu<sup>n</sup>, in boiling tetrahydrofuran, indicated that these are essentially monomeric in this solvent. The first two of the series, R = H and Me, were too insoluble for ebulliometric measurements.

The magnetic susceptibilities of the first three compounds, R = H, Me, and Et, measured at room temperature by the Gouy method, clearly indicate one unpaired electron per titanium atom. Because of interference from the cyclopentadienyl

partial double-bond character for C-N. A shift to lower wave-number with increase in alkyl-chain lengths is also evident.



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