

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Bis(cyclopentadienyl)titanium(IV) Pseudohalide Complexes

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The nature of the titanium–thiocyanate bonding mode in bis(cyclopentadienyl)titanium(IV) thiocyanate has recently<sup>1,2</sup> been the subject of some unresolved conjecture. Giddings<sup>1</sup> has pointed out the potential use of the complex, if the thiocyanates are N bonded, as a monomer for the preparation of polythioureas or thiocarbamates containing bis(cyclopentadienyl)titanium groups in the backbone. However, he tentatively concluded that the thiocyanate groups are S bonded, on the basis of the color of the complex, its lack of reaction with butylamine, and its infrared spectrum, which was only partially analyzed. Alternatively, the pronounced difference<sup>2</sup> between the two rates with which the two thiocyanate groups are exchanged with chloride may be interpreted as resulting from different bonding modes. As part of our general study<sup>3</sup> of the coordination chemistry of ambidentate ligands, we wish to report the results of a more detailed analysis of the infrared spectrum of the complex and the synthesis and partial characterization of its selenocyanate and cyanate analogs, the latter representing the first example of an O-bonded cyanate complex.

### Experimental Section

**Preparation of Compounds.** Bis(cyclopentadienyl)titanium(IV) pseudohalides— $(C_5H_5)_2Ti(NCS)_2$  was prepared according to the method of Giddings.<sup>1</sup> The new selenocyanate and cyanate complexes,  $(C_5H_5)_2Ti(NCSe)_2$  and  $(C_5H_5)_2Ti(OCN)_2$ , were prepared in an analogous manner, using acetone solutions of the same<sup>1</sup> concentrations, containing  $(C_5H_5)_2TiCl_2$ , prepared by the method of Wilkinson and Birmingham,<sup>4</sup> and  $KXCN$  ( $X = Se, O$ ) in a 1:2.2 mole ratio. They were refluxed for periods of 4 and 5 hr, respectively. Both were recrystallized from acetone, giving greenish black crystals of the selenocyanate and reddish orange crystals of the cyanate, in, respectively, 69 and 66% yields.

*Anal.* Calcd for  $C_{12}H_{10}N_2Se_2Ti$ : C, 37.14; H, 2.60; N, 7.22. Found: C, 37.25; H, 2.71; N, 7.05. Calcd for  $C_{12}H_{10}N_2O_2Ti$ : C, 54.98; H, 3.85; N, 10.68. Found: C, 54.98; H, 4.01; N, 10.56.

**$[(C_5H_5)_4N]_2[M(NCO)_4]$  Complexes.**—These isocyanates [ $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)$ ] were prepared according to the method of Forster and Goodgame.<sup>5</sup>

**Physical Measurements.**—Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany. Molar conductances, at 25°, of  $10^{-3}$  M solutions of the complexes in nitrobenzene and *N,N*-dimethylformamide were measured with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. The values obtained for the titanocene complexes are shown in Table

TABLE I

MOLAR CONDUCTANCES OF TITANOCENE COMPLEXES

Complex	Solvent	$\Lambda_M, \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
$[(C_5H_5)_2Ti(NCS)_2]$	Nitrobenzene	0.00, 9.18 <sup>a</sup>
	DMF	17.7, 84.2 <sup>b</sup>
$[(C_5H_5)_2Ti(NCSe)_2]$	Nitrobenzene	0.00, 8.00 <sup>a</sup>
	DMF	68.5, 100 <sup>b</sup>
$[(C_5H_5)_2Ti(OCN)_2]$	Nitrobenzene	0.00, 2.24 <sup>a</sup>
	DMF	16.7, 5.11 <sup>b</sup>
$[(C_5H_5)_2TiCl_2]$	Nitrobenzene	0.00, 9.86 <sup>a</sup>
	DMF	12.8, 68.4 <sup>b</sup>

<sup>a</sup> Four days later. <sup>b</sup> Six days later.

I. Infrared spectra, in the 4000–400- $\text{cm}^{-1}$  range, of complexes held in Nujol suspension between KBr plates were measured on a Perkin-Elmer Model 337 recording spectrophotometer. The spectra of the titanocene complexes in the C–X stretching and NCX bending ranges ( $X = S, Se, O$ ) are shown in Figure 1. A Perkin-Elmer Model 421 spectrophotometer was used to record high-resolution spectra of solutions of the complexes in the C–N stretching range (2200–2000  $\text{cm}^{-1}$ ). Matched 0.1-mm sodium chloride cells were employed. The integrated absorption intensities,  $A$  ( $M^{-1} \text{cm}^{-2}$ ), of the C–N stretching bands were determined by Ramsay's method of direct integration.<sup>8</sup> The infrared data for the titanocene and  $[(C_5H_5)_4N]_2[M(NCO)_4]$  complexes are shown in Table II. Visible-ultraviolet spectra of acetone solutions of the complexes were measured on a Cary 14 spectrophotometer, using 1-cm matched quartz cells. The data obtained for the titanocene complexes are shown in Table III.

### Discussion

All of the titanocene complexes prepared in this study function as nonelectrolytes in nitrobenzene solution (Table I). Except for the cyanate complex, all undergo extensive solvation in DMF, although none of the molar conductances reaches the values cited<sup>7</sup> for 2:1 electrolytes. The decrease, with time, of the molar conductance of the cyanate complex may be attributed to the formation of polymeric species *via* cyanate bridging groups.

The behavior of the infrared absorption bands of the thiocyanate and selenocyanate ions upon coordination has been extensively catalogued.<sup>8</sup> Contrary to Giddings' conclusion,<sup>1</sup> the C–N stretching band is quite useful in determining the bonding mode of these ambidentate ligands. Although the position of the band does not permit an unequivocal conclusion, except, perhaps, in a homologous series of complexes of the same metal,<sup>9,10</sup> the integrated absorption *intensity* of the band invariably increases when the ions are N bonded and decreases when they are S or Se bonded,<sup>8</sup> relative to the free-ion values ( $SCN^-$ ,  $4.4 \times 10^4 M^{-1} \text{cm}^{-2}$ ;  $SeCN^-$ ,  $3.1 \times 10^4 M^{-1} \text{cm}^{-2}$ ; both in butanone solution<sup>11</sup>). Solvent effects are negligible, if the solvent is nonhydrogen bonding.<sup>11</sup> The C–S and C–Se stretching frequencies are equally diagnostic, increasing when the ions are N bonded and decreasing when they are S or Se bonded,<sup>8</sup> relative to the free-ion values ( $SCN^-$ ,

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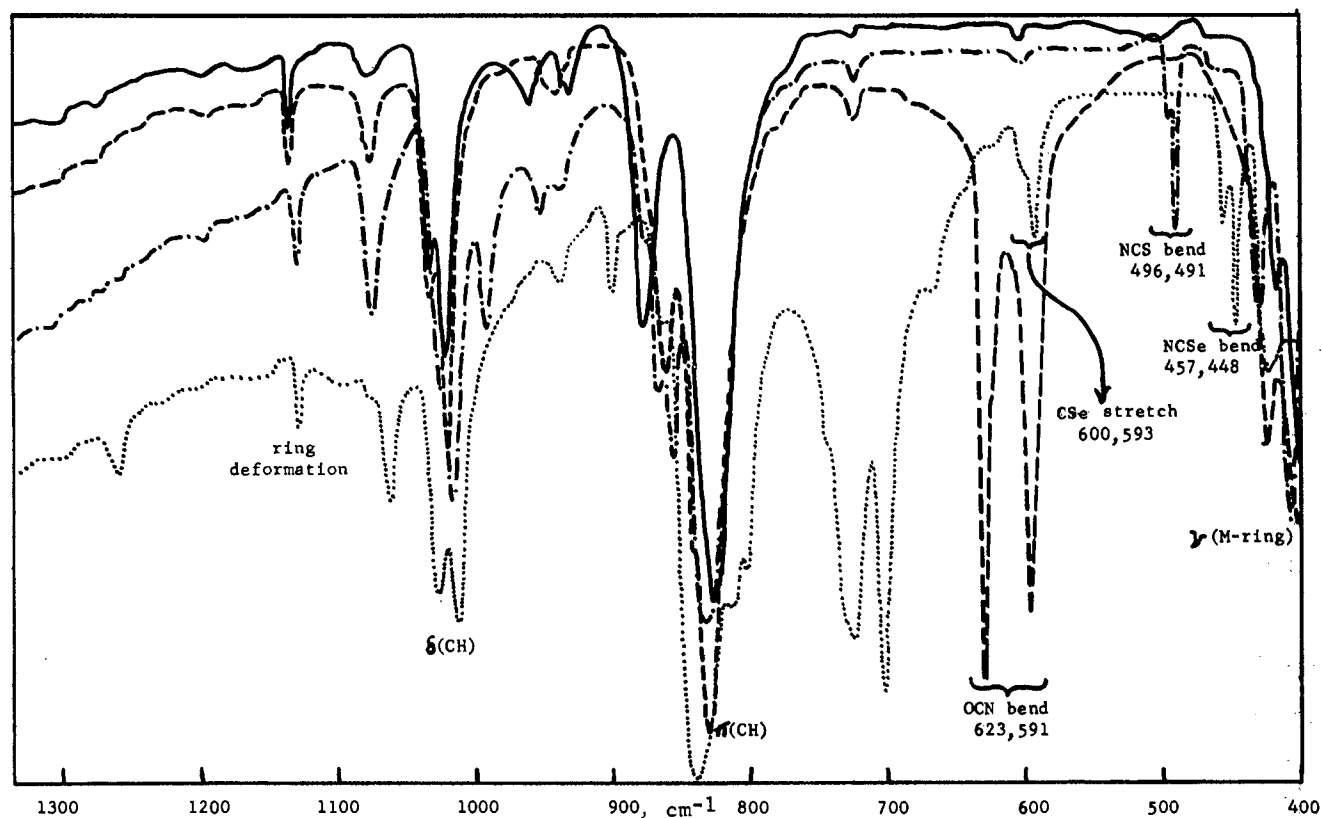


Figure 1.—Infrared spectra of  $\text{Ti}(\text{C}_5\text{H}_5)_2\text{X}_2$  complexes (Nujol mulls): —,  $\text{X} = \text{Cl}$ ; ---,  $\text{X} = \text{OCN}$ ; - · - ·,  $\text{X} = \text{NCS}$ ; · · · ·,  $\text{X} = \text{NCSe}$ .

TABLE II  
INFRARED DATA FOR THE COMPLEXES<sup>b</sup>

Complex	C-X str, <sup>a</sup> $\nu_1(\text{XCN})$ , $\text{cm}^{-1}$	XCN bend, <sup>a</sup> $\nu_2(\text{XCN})$ , $\text{cm}^{-1}$	C-N str, $\nu_3(\text{XCN})$	
			Freq, $\text{cm}^{-1}$	$10^{-4}A$ , <sup>b</sup> $M^{-1}$ $\text{cm}^{-2}$
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{NCS})_2$	<i>c</i>	496, 491	2064 <sup>d</sup> 2026 <sup>d</sup>	12 <sup>d</sup> 17 <sup>d</sup>
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{NCSe})_2$	600, 593	457, 448	2050 <sup>e</sup> 2015 <sup>e</sup>	12 <sup>e</sup> 10 <sup>e</sup>
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{OCN})_2$	<i>c</i>	623, 591	2235 <sup>d</sup> 2199 <sup>d</sup>	9.7 <sup>d</sup> 11 <sup>d</sup>
KOCN [( $\text{C}_2\text{H}_5$ ) <sub>4</sub> N] <sub>2</sub> [M(NCO) <sub>4</sub> ]	1300, 1205 <sup>f,g</sup>	636, 626 <sup>f</sup>	2170 <sup>a,f</sup>	<i>h</i>
M = Mn(II)	1328 m <sup>i</sup>	626 m <sup>i</sup>	2198 <sup>d</sup>	15 <sup>d</sup>
Co(II)	1329 m <sup>i</sup>	620 m <sup>i</sup>	2208 <sup>d</sup>	16 <sup>d</sup>
Ni(II)	1330 m <sup>i</sup>	621 m <sup>i</sup>	2205 <sup>d</sup>	13 <sup>d</sup>
Cu(II)	1324 m <sup>i</sup>	618 m <sup>i</sup>	2225, 2201 sh <sup>d</sup>	12 <sup>d</sup>
Zn(II)	1333 m <sup>i</sup>	624 m, 615 m <sup>i</sup>	2212 <sup>d</sup>	13 <sup>d</sup>
Cd(II)	1328 w <sup>i</sup>	622 s <sup>i</sup>	2193 <sup>d</sup>	14 <sup>d</sup>

<sup>a</sup> Nujol mull. <sup>b</sup> Integrated absorption intensity, calculated per mole of coordinated  $\text{XCN}^-$ . <sup>c</sup> Obscured by cyclopentadienyl absorption. <sup>d</sup> In  $5.0 \times 10^{-3} M$  nitromethane solution. <sup>e</sup> In  $2.5 \times 10^{-3} M$  acetone solution. <sup>f</sup> Data taken from T. C. Waddington, *J. Chem. Soc.*, 2499 (1959). <sup>g</sup> Doublet due to Fermi resonance between the overtone of the bending and the fundamental C-O stretching frequencies. The unperturbed C-O stretching vibration should have a value of  $1254 \text{ cm}^{-1}$ : A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959). <sup>h</sup> Solubility in organic solvents insufficient to permit measurement. <sup>i</sup> Data taken from A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965). <sup>j</sup> Data taken from ref 5. <sup>k</sup> Abbreviations: m, medium; w, weak; s, strong; sh, shoulder.

$749 \text{ cm}^{-1}$ ,<sup>12</sup>  $\text{SeCN}^-$ ,  $558 \text{ cm}^{-1}$ <sup>13</sup>). The NCS and NCSe bending frequencies increase or remain about the same when the groups are N bonded, but at least one band of the multiplet is found at a decidedly lower frequency when S or Se bonded,<sup>3</sup> relative to the free-ion values ( $\text{SCN}^-$ ,  $486, 471 \text{ cm}^{-1}$ ,<sup>12</sup>  $\text{SeCN}^-$ ,  $424, 416 \text{ cm}^{-1}$ <sup>13</sup>). Seen in this context, the infrared spectra

and data for the thiocyanate and selenocyanate complexes shown in Figure 1 and Table II unequivocally indicate that the  $\text{NCS}^-$  and  $\text{NCSe}^-$  ions are N bonded, both in solution and in the solid state.

Parenthetically, it is of interest to note that the C-N stretching frequencies exhibited by the thiocyanate and selenocyanate complexes are among the lowest yet recorded for such complexes. This effect appears to be characteristic of isothiocyanate com-

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TABLE III

Complex	Absorption maxima, kK <sup>a</sup>	
	sh	br
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(NCS) <sub>2</sub>	30.4 (9150), 29.2 (9470), 22.8 (9930), 18.2 (247)	
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(NCSe) <sub>2</sub>	30.9 (8230), 23.2 (6480), 20.9 (7260)	
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(OCN) <sub>2</sub>	30.8 (3850), 26.5 (3910), 20.3 (282)	
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	30.9 (3750), 25.7 (2240), 19.2 (430)	

<sup>a</sup> Molar absorptivity shown in parentheses.

plexes of metals having high formal oxidation states, e.g.: Nb(NCS)<sub>6</sub><sup>2-</sup>, 2035 cm<sup>-1</sup>; Nb(NCS)<sub>6</sub><sup>-</sup>, 1954, 1911 cm<sup>-1</sup>.<sup>14</sup>

All of the cyanate complexes previously reported<sup>5,15-20</sup> have been found to be N bonded, the frequency shifts of their infrared bands, relative to those of the free ion, following the patterns exhibited by isothiocyanates and isoselenocyanates. Although the data shown in Table II for the titanocene-cyanate complex (also see Figure 1) are not as conclusive as those shown for its higher homologs, the absence of a C-O stretching band in the N-bonded range, the lower frequency NCO bending vibration, and the pronounced increase in the C-N stretching frequency all serve to indicate that the cyanate groups are O bonded. The similarity of the integrated absorption intensity of the C-N stretching band to the values exhibited by known isocyanate complexes (Table II) may be due to the small difference in mass between the nitrogen and oxygen atoms.

Coutts and Wailes<sup>19</sup> have recently reported the preparation of the corresponding titanium(III) complex, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiNCO. They concluded, on the basis of mass spectral data and the C-N stretching frequency of the complex (2175 cm<sup>-1</sup>), that the cyanate group is N bonded. This represents, when compared with the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(OCN)<sub>2</sub> complex prepared in this study, a second example of the sensitivity of the bonding mode of an ambidentate ligand to the oxidation state of the metal to which it is coordinated. Both this example and the Cu<sup>I</sup>-SCN and Cu<sup>II</sup>-NCS N-heterocyclic amine complexes previously reported<sup>21</sup> exhibit a trend which is opposite to that predicted by Jørgensen,<sup>22</sup> namely, that the class b<sup>23</sup> or soft-acid<sup>24</sup> character of a metal should increase as its oxidation state increases, owing to increasing covalency in the bonds. The Ti-NCS, Ti-NCSe, and Ti-OCN bonding pattern exhibited by the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti<sup>2+</sup> moiety is precisely that which would be expected for a hard acid and follows that previously elucidated by Rivest<sup>25</sup> for TiCl<sub>4</sub>; i.e., Ti(NH<sub>2</sub>CSNH<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub> contains N-bonded thiourea ligands, but, in Ti(OC(NH<sub>2</sub>)<sub>2</sub>)Cl<sub>4</sub>, the urea groups are O bonded.

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Extensions of this work to other ambidentate ligands and cyclopentadienyl complexes are in progress.

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## Hydrogen Bonding in Dimethylboric Acid

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Dimethylboric acid, (CH<sub>3</sub>)<sub>2</sub>BOH, was first prepared by Schlesinger and Walker.<sup>1</sup> The Trouton constant was later found to be 29.7, indicating some degree of association in the liquid phase.<sup>2</sup> The present study was undertaken to determine whether the association is of a monomer-dimer type or involves higher polymers, and, further, whether association takes place through hydrogen bonding or by boron-oxygen coordination.

### Experimental Section

A high-vacuum apparatus of conventional design was used. Vapor pressure measurements were carried out in a tensimeter<sup>3</sup> attached to the vacuum system. Infrared spectra were measured using a Perkin-Elmer Model 421 grating spectrometer. For the solution spectrum, a 5-10% solution in carbon tetrachloride was prepared in the vacuum system and transferred by syringe to a standard 0.1-mm solution cell. The gas-phase spectrum was obtained using dimethylboric acid at 10 mm of pressure in a 5-cm cell with potassium bromide windows. A Varian A-60 spectrometer operating at 36° was used in the nmr studies; the variable-temperature investigation was carried out using a Varian HA-100 instrument. Nmr sample tubes were flamed lightly under vacuum and were sealed off after the components of solution had been distilled into them from the vacuum system.

Spectral grade solvents, dried over molecular sieves, were used in the infrared and nmr studies. Phillips pure grade *n*-butane was used in the tensimetric work; it was freed from water by slow distillation through a -78° trap.

Dimethylboric acid was prepared by hydrolyzing purified dimethylboric anhydride (vapor pressure 148 mm at 0°)<sup>4</sup> with the stoichiometric quantity of water at room temperature. Distillation involving traps at -46, -78, and -196° yielded the pure product (vapor pressure 36 mm at 0°; lit.<sup>2</sup> 36 mm at 0.4°) in the -78° trap.

### Results

The vapor pressure lowering in *n*-butane solutions of dimethylboric acid was investigated over a range of temperature and concentration. The results summarized in Table I establish that the system is complex,

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