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Studies on Monocyclopentadienyl Titanium(IV) Dithiocarbamato Complexes

O. P. Pandey, S. K. Sengupta*, and S. C. Tripathi

Department of Chemistry, University of Gorakhpur, Gorakhpur-273001, India

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Titanium(IV) dithiocarbamato complexes of the types *Cp*Ti(S_2CNH*R*)Cl_2 and *Cp*Ti(S_2CNH*R*)$_2$Cl, where *R* = $C_8H_5N_2S$, $C_9H_5N_2SCl_2$ and $C_9H_7N_2S$, have been prepared by the reaction of monocyclopentadienyl titanium(IV) trichloride with the potassium salt of the appropriate dithiocarbamic acid in anhydrous dichloromethane. Conductance and infrared studies indicate that these complexes are non-electrolytes in which all dithiocarbamate ligands are bidentate. Therefore, 5 and 6 coordinate structures can be assigned to *Cp*Ti(S_2CNH*R*)Cl_2 and *Cp*Ti(S_2CNH*R*)$_2$Cl complexes, respectively. ^{1}H-NMR spectra indicate that there is rapid rotation of the cyclopentadienyl ring about the metal ring axis.

[Keywords: Cyclopentadienyl; Titanium(IV) complexes; Conductometric; IR; ^{1}H-*NMR]*

Untersuchungen von Monocyclopentadienyl-titan(IV)-dithiocarbamat-Komplexen

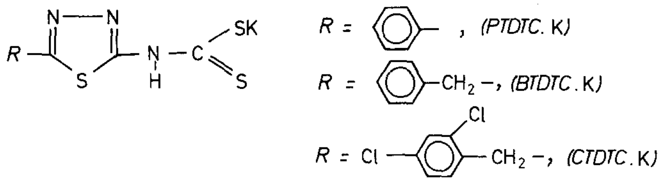
Es wurden Titan(IV)-dithiocarbamat-Komplexe vom Typ *Cp*Ti(S_2CNH*R*)Cl_2 und *Cp*Ti(S_2CNH*R*)$_2$Cl mit *R* = $C_8H_5N_2S$, $C_9H_5N_2SCl_2$ und $C_9H_7N_2S$ mittels der Reaktion von Monocyclopentadienyltitan(IV)trichlorid mit dem Kaliumsalz der entsprechenden Dithiocarbaminsäure in wasserfreiem Dichlormethan dargestellt. Leitfähigkeitsmessungen und IR-Untersuchungen zeigen, daß diese Komplexe Nichtelektrolyte sind, bei denen alle Dithiocarbamat-Liganden zweizähnig sind. Demnach können 5-, bzw. 6-koordinierte Strukturen für die Komplexe des Typs *Cp*Ti(S_2CNH*R*)Cl_2, bzw. *Cp*Ti(S_2CNH*R*)$_2$Cl angenommen werden. Die ^{1}H-NMR Spektren zeigen eine rasche Rotation des Cyclopentadienylrings um die Metall-Ring Achse an.

Introduction

There is extensive literature on metal dithiocarbamates[1,2]. The dithiocarbamato ligands by virtue of their low charge and small bites (~ 2.8–2.9 Å) are particularly well suited for stabilisation of higher coordination states of metals. Thus, dithiocarbamato derivatives of cyclopentadienyl titanium in various coordination states are known[3–6].

But in all these derivatives the dithiocarbamato group coordinates through two sulphur atoms resulting in the formation of four membered chelate rings.

In the present communication, we report the reactions of monocyclopentadienyl titanium(IV) trichloride with a new series of dithiocarbamate ligands in which one heterocyclic ring (thiadiazole) is attached to nitrogen. The most important result of this investigation is that these ligands form six membered chelate rings through N-coordination of the thiadiazole ring and one sulphur atom coordination of dithiocarbamato group. The structures of the ligands are given below:



Experimental

Reagents and General Techniques

Monocyclopentadienyl titanium(IV) trichloride was prepared[7] from Cp_2TiCl_2 and $TiCl_4$ in *p*-xylene. The ligands were prepared as reported in the literature[8]. Dichloromethane was dried by refluxing it for 30 h over calcium hydride. All experimental operations were carried out under strictly anhydrous conditions.

Titanium was determined gravimetrically as TiO_2 and chloride as AgCl. Sulphur was estimated as $BaSO_4$.

The details of the physical measurements are same as described earlier[9].

Preparation of the Complexes

All complexes were prepared by taking monocyclopentadienyl titanium(IV) trichloride and the proper ligand in 1 : 1 and 1 : 2 molar ratios separately and adding about 50 ml of anhydrous dichloromethane followed by a reflux time of 20–30 h. The solutions were then filtered and their volume reduced to 20 ml. Addition of dry hexane to these solutions and allowing them to stand overnight resulted in yellow-brown crystals of the products which were filtered and dried at 80 °C.

Through *Kumar* and *Kaushik* reported[10] the formation of derivatives of the type $Cp\mathrm{Ti}(DTC)_3$ with simple dithiocarbamate ligands, we did not isolate 1 : 3 derivatives with the ligands reported in this paper. This may be due to steric hindrance.

Experimental details are given in Table 1.

Results and Discussion

It is evident from analytical data (Table 2) that one mole of cyclopentadienyl titanium(IV) trichloride reacts with one mole or two

Table 1. *Reactions of* *Cp*TiCl$_3$ *with dithiocarbamates*

Reactants	taken (g)	Refluxing time (h)	Product, colour, yield (%)	Decomp. temp.	Conductance Mx $10^3 = 0.5$
*Cp*TiCl$_3$	Ligand				
1.0	*PTDTCK* = 1.4	22	*Cp*Ti(*PTDTC*)Cl$_2$, light yellow, 60	198	0.52
1.1	*PTDTCK* = 2.9	38	*Cp*Ti(*PTDTC*)$_2$Cl, yellow, 65	190	0.30
1.0	*BTDTCK* = 1.6	20	*Cp*Ti(*BTDTC*)Cl$_2$, brown, 60	239	0.48
1.0	*BTDTCK* = 3.1	40	*Cp*Ti(*BTDTC*)$_2$Cl, yellowish brown, 55	198	0.68
1.0	*CTDTCK* = 1.8	25	*Cp*Ti(*CTDTC*)Cl$_2$, brown, 60	210	0.50
1.2	*CTDTCK* = 3.8	40	*Cp*Ti(*CTDTC*)$_2$Cl, yellow, 68	230	0.45

Table 2. *Analytical data of the complexes*

Complex	Found (Calcd.) %				
	C	H	S	Ti	Cl
*Cp*Ti(*PTDTC*)Cl$_2$	38.2 (38.5)	2.4 (2.5)	21.8 (22.0)	10.8 (10.9)	16.2 (16.2)
*Cp*Ti(*PTDTC*)$_2$Cl	42.2 (42.3)	2.5 (2.6)	29.3 (29.4)	7.3 (7.3)	5.4 (5.4)
*Cp*Ti(*BTDTC*)Cl$_2$	40.1 (40.0)	2.8 (2.8)	21.3 (21.3)	10.5 (10.6)	15.7 (15.7)
*Cp*Ti(*BTDTC*)$_2$Cl	43.9 (44.0)	3.0 (3.0)	28.0 (28.2)	7.0 (7.0)	5.1 (5.2)
*Cp*Ti(*CTDTC*)Cl$_2$	34.6 (34.6)	2.1 (2.1)	18.3 (18.5)	9.0 (9.2)	27.3 (27.3)
*Cp*Ti(*CTDTC*)$_2$Cl	36.5 (36.6)	2.0 (2.0)	23.2 (23.4)	5.8 (5.8)	21.4 (21.6)

moles of potassium dithiocarbamate according to the following equations:

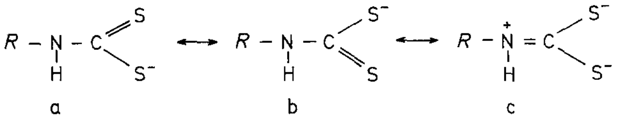
$$(C_5H_5)TiCl_3 + KS_2CNH\mathit{R} \xrightarrow{CH_2Cl_2} (C_5H_5)TiCl_2(S_2CNH\mathit{R}) + KCl$$

$$(C_5H_5)TiCl_3)TiCl_3 + 2\,K\cdot S_2CNH\mathit{R} \xrightarrow{CH_2Cl_2} (C_5H_5)TiCl(S_2CNH\mathit{R})_2 + 2KCl$$

The methods used for preparation and isolation of these compounds give materials of good purity as supported by their analyses and TLC. All these complexes are yellow to brown in colour. They are thermally stable but decompose above ~ 190 °C without melting. They are quite stable in air but solutions are hydrolysed. Conductance measurements in nitrobenzene indicate that they are essentially non-electrolytes. Magnetic susceptibility values at room temperature show they are all diamagnetic. The electronic spectra (visible) of all these complexes exhibit a single intense charge transfer band in the region 24 200–24 800 cm^{-1} in accordance with the electronic configuration (n − 1) d° nS°.

Infrared Spectra

The major interest in the preparation of these complexes is to study the effect of the attachment of the dithiocarbamate ligand to titanium metal in presence of the bulky thiadiazole ring. Due to some steric factors this might have some effect on the structure of the complexes. The structure of the dithiocomplexes can be represented by the following formalism:



The extent to which these resonance forms contribute to the structure and its effect on the physical and chemical properties has been extensively studied[11,12]. The monodentate and/or bidentate nature of the dithiocarbamato group in the ligand is reflected in the (C−S) stretching frequency. In case of bidentate behaviour a single strong band appears in the region 970–1 000 cm^{-1}, while a doublet is expected in the region 1 000 ± 70 cm^{-1} in the monodentate behaviour[13,14]. The complexes reported in this paper show two bands in the region 980–1 010 cm^{-1} indicating the presence of one complexed (C−S) group and one uncomplexed (C=S) group, i.e. monodentate bonding.

A strong band in the region 1 585–1 600 cm^{-1} in the ligands is characteristic[8] of the ν(C=N) group. However, in the complexes the νC=N band is found to split into two bands, with one band located almost at the original position at ~ 1 600 cm^{-1}, due to uncoordinated ν(C=N), and the other shifted to lower frequency (~ 20–25 cm^{-1}) arising from the coordinated C=N mode. The splitting of the ν(C=N) absorption band suggests that only one of the nitrogens is involved in coordination and the other is free and uncoordinated[9]. The ν(NH) band appears at ca. 3 200–3 150 cm^{-1} in the ligands. The persistence of this band at the same position in the complexes indicate the non-coordination of amino nitrogen. The ν(Ti−S) and ν(Ti−N) vibrations[9,10] appear at ca. 360–340 cm^{-1} and 330–400 cm^{-1}, respectively. An additional band near 440 cm^{-1} can be assigned[10] to ν(Ti−Cp) vibrations.

Absorption bands occurring at ~3 000 cm^{-1} ν(C−H), ~1 430 cm^{-1} ν(C−C) and 950 cm^{-1} δ(C−H) in the complexes are typical for the of cyclopentadienyl ring. All these bands are similar to those of mono(cyclopentadienyl) titanium(IV)[15]. *Davison* and *Rakita* have pointed[16] out that at 3 000 cm^{-1} η'-C_5H_5 should show four bands whereas η^5-C_5H_5 should show only one. In the complexes reported in this paper, only one band near 3 000 cm^{-1} indicate the pentahapto nature of cyclopentadienyl ring.

Thus, the infrared spectra suggest that the nitrogen of the thiadiazole ring and one of the sulphur atoms of the dithiocarbamate group are involved in chelation.

^{1}H-*NMR Spectra*

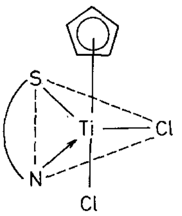
The ^{1}H-NMR spectra of these complexes have been recorded in $CDCl_3$ and dimethylformamide. Chemical shifts are given in Table 3. The resonance lines for the protons of the C_5H_5 ring always falls near δ 6.5 ppm. The appearance of a single, sharp signal for the protons of the cyclopentadienyl ring indicates the rapid rotation the ring about the metal-ring axis. A broad NH peak appears in all the complexes near 4.6 ppm. In bis-dithiocarbamato derivatives, *Cp*Ti(S_2CNH*R*)$_2$Cl, the dithiocarbamato groups are equivalent since only one signal has been observed for the phenyl or benzyl group. The integrated proton ratios correspond to the formula and supports an octahedral structure for *Cp*Ti(S_2CNH*R*)$_2$Cl and a trigonal bipyramidal structure for *Cp*Ti(S_2CNH*R*)Cl_2. However, the structure of the complexes are bound to be slightly distorted due to the presence of a cyclopentadienyl ring in the molecule. Comparing the lines observed for the free ligands with corresponding lines observed for their complexes, it has been found that

Table 3. ^{1}H-NMR *chemical shifts (δ/ppm) at 25 °C*

Compound	η^5-C_5H_5	NH	Aromatic ring	$-CH_2$
*Cp*Ti(*PTDTC*)Cl_2	6.55 s	4.60 s	7.30 s	–
*Cp*Ti(*PTDTC*)$_2$Cl	6.50 s	4.68 s	7.32 s	–
*Cp*Ti(*BTDTC*)Cl_2	6.58 s	4.62 s	7.40 t	4.20 m
*Cp*Ti(*BTDTC*)$_2$Cl	6.60 s	4.70 s	7.48 t	4.15 m
*Cp*Ti(*CTDTC*)Cl_2	6.50 s	4.60 s	7.32 t	4.12 m
*Cp*Ti(*CTDTC*)$_2$Cl	6.52 s	4.65 s	7.38 t	4.25 m

there is only little variation in the chemical shifts for the protons on the N – R groups. This variation can be attributed to the effect caused by the delocalisation of electrons between the N – CS_2 part of the ligand on coordination with the metal.

Thus, the following plausible structures may tentatively be suggested for the *Cp*Ti(S_2CNH*R*)Cl_2 (**1**) and *Cp*Ti(S_2CNH*R*)$_2$Cl (**2**) complexes.



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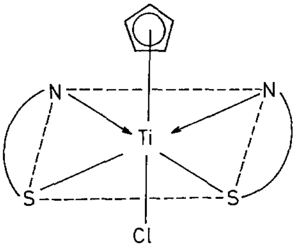

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Acknowledgement

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References

[1] *Campbell M. J. M.*, Coord. Chem. Rev. **15**, 279 (1975).
[2] *Coucouvanis D.*, Prog. Inorg. Chem. Vol. XI (*Lippard S. J.*, ed.), p. 233. New York: Interscience. 1970.
[3] *Coutts R. S. P., Wailes P. C., Kingston J. V.*, Aust. J. Chem. **23**, 469 (1970).
[4] *Coutts R. S. P., Wailes P. C., Kingston J. V.*, Aust. J. Chem. **23**, 463 (1970).
[5] *Coutts R. S. P., Wailes P. C.*, J. Organometal. Chem. **84**, 47 (1975).
[6] *Kaushik N. K., Bhusan B., Chhatwal G. R.*, Transition Met. Chem. **3**, 215 (1978).
[7] *Gorsich R. D.*, J. Amer. Chem. Soc. **82**, 4211 (1960).
[8] *Singh H., Yadava L. D. S., Mishra S. B. S.*, J. Inorg. Nucl. Chem. **43**, 1701 (1981).
[9] *Pandey O. P., Sengupta S. K., Tripathi S. C.*, Synth. React. Inorg. Met.-Org. Chem. **13**, 867 (1983).
[10] *Kumar S., Kaushik N. K.*, J. Inorg. Nucl. Chem. **43**, 2679 (1981).
[11] *Chatt J., Duncanson L. A., Venanzi L. M.*, Soumen Kemi **B 29**, 75 (1956).
[12] *Nakamoto K., Fujita J., Condrate R. A., Morimoto Y.*, J. Chem. Phys. **39**, 423 (1963).
[13] *Bonati F., Ugo R.*, J. Organometal. Chem. **10**, 257 (1967).
[14] *Manoussakis G. E., Tsipiz C. A., Hadjikostas C. C.*, Can. J. Chem. **53**, 1530 (1975).
[15] *Fritz H. P.*, Adv. Organometal. Chem. **1**, 262 (1964).
[16] *Davison A., Rakita P. E.*, Inorg. Chem. **9**, 289 (1970).