

## References

1. CLEARE, M. J. & GRIFFITH, W. P., *J. chem. Soc.*, A (1970), 1117.
2. GRIFFITH, W. P., *Coordination chem. Rev.*, 8 (4) (1972), 379.
3. JOHNSON, N. P., *J. chem. Soc.*, (1969), 1843.
4. CHATT, J., GARFORTH, J. D., JOHNSON, N. P. & ROWE, G. A., *J. chem. Soc.*, (1964), 1012.
5. SAHA, H. K. & BANERJEE, A. K., *J. inorg. nucl. Chem.*, 34 (1972), 697.
6. PAUL, R. C., MADAN, HAMEET & CHADHA, S. L., *Indian J. Chem.*, 13 (1975), 1188.
7. JOHNSON, N. P., LOCK, C. J. L. & WILKINSON, G., *J. chem. Soc.*, (1964), 1054.

### Preparation & Characterization of Dimethylformamidyl Substituted Titanium(IV) Compounds

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Received 5 February 1977; accepted 11 March 1977

Dimethylformamidyl substituted titanium(IV) chlorides;  $TiCl_3[CON(CH_3)_2]_2 \cdot 2DMF$ ,  $TiCl_2[CON(CH_3)_2]_2 \cdot DMF$ ,  $TiCl_2[CON(CH_3)_2]_2$ ,  $TiCl[CON(CH_3)_2]_3$  and  $Ti[CON(CH_3)_2]_4$  have been prepared by the reaction of titanium(IV) chloride and dimethylformamidyl sodium. These compounds have been characterized by their elemental analyses, infrared, molar conductance and thermal studies.

IN continuation of our studies on the preparation of dimethylformamidyl substituted metal halides<sup>1</sup>, we now report the results of our investigations on the reactions between titanium(IV) chloride and dimethylformamidyl sodium. Solvolytic reactions of metal halides in dimethylformamide are completely lacking. Only in case of formamide a few partially solvolyzed products involving titanium(IV) chloride<sup>2</sup>, tin(IV) chloride and iron(III) chloride<sup>3</sup> have been reported.

Dimethylformamide (J. T. Baker analysed) was purified as reported in literature<sup>4</sup>. Dimethylformamidyl sodium was prepared as reported earlier<sup>5</sup>. Titanium(IV) chloride (Riedel) was used after distillation in dry nitrogen atmosphere.

*Preparation of compounds* — Titanium(IV) chloride when stirred with the suspension of dimethylformamidyl sodium,  $NaCON(CH_3)_2$  in carbon tetrachloride in different molar ratios (Table 1) for a period ranging between 4 to 24 hr gave yellow voluminous precipitates at 0°. The compounds were filtered and washed with carbon tetrachloride to remove unreacted titanium(IV) chloride. Sodium chloride and any unused dimethylformamidyl sodium were removed by treating the yellow mass with pure DMF. The DMF solution on evacuation yielded solid compounds. The last traces of dissolved sodium chloride were removed by successive treatments with fresh DMF till their solutions gave negative test for chloride ions. Generally three to four such treatments yielded pure products. Finally, the compounds were obtained by repeated washings with carbon tetrachloride and dried by keeping under vacuum ( $10^{-2}$  torr) for several hours.

The completely substituted product,  $Ti[CON(CH_3)_2]_4$  was obtained in small yields by refluxing the mixture in mole ratio 1:6 in methylene chloride for 3-4 days. The mixture was filtered and the filtrate was evacuated to get a white solid. It was purified by recrystallization from carbon tetrachloride-pet. ether. It was then sublimed at 40° at  $10^{-4}$  torr to get colourless crystals.

Complexes of some of these compounds with quinaline (Q) and ethylenediamine (en) were prepared by stirring their suspension in carbon tetrachloride with excess of base at 0°. The compounds were filtered under dry conditions, washed with petroleum ether and dried *in vacuo*.

Titanium was estimated gravimetrically as  $TiO_2$ . Chloride was determined as AgCl after fusing the compounds with  $Na_2CO_3$  and KOH. Carbon, hydrogen

TABLE 1 — ANALYTICAL DATA OF COMPOUNDS

Product	Molar conductance in DMF	Found (%) Calc.**				
		Ti	Cl	C	H	N
$TiCl_3[CON(CH_3)_2]_2 \cdot 2DMF$ (1)*	49.7	13.1 (12.9)	28.2 28.6	28.6 29.0	5.1 5.4	11.5 11.3
$TiCl_3[CON(CH_3)_2]_2 \cdot DMF \cdot Q$ (2)	48.2	11.4 (11.2)	24.3 24.9	42.2 42.0	4.6 4.7	9.5 9.8
$TiCl_3[CON(CH_3)_2]_2 \cdot 3en$ (3)	—	11.3 (11.8)	26.0 26.2	26.1 26.6	7.2 7.4	24.0 24.1
$TiCl_2[CON(CH_3)_2]_2 \cdot DMF$ (4)†	35.7	14.0 (14.3)	21.3 21.1	31.7 32.1	5.4 5.7	12.7 12.5
$TiCl_2[CON(CH_3)_2]_2$ (5)	32.1	18.5 (18.2)	26.8 27.0	27.3 27.4	4.6 4.6	10.2 10.6
$TiCl[CON(CH_3)_2]_3$ (6)‡	24.5	15.7 (16.0)	11.5 11.9	35.7 36.1	6.0 6.0	14.3 14.0
$Ti[CON(CH_3)_2]_4$ (7)‡	0.2§	13.5 (13.9)	—	44.0 42.9	7.3 7.1	17.3 16.6

\*Reactants in the molar ratio 1:1.5 ( $TiCl_4$ -sodium dimethylformamidyl).

†Reactants in the molar ratio 1:3.

‡Reactants in the molar ratio 1:6.

§In nitrobenzene.

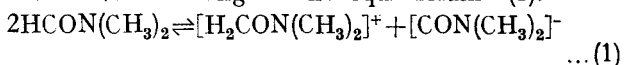
\*\*Calculated values are given in the parentheses.

and nitrogen were estimated microanalytically. The analytical results are given in Table 1.

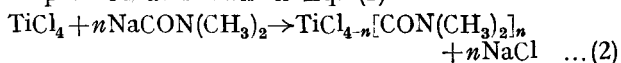
Infrared spectra of the compounds were recorded on Perkin-Elmer 621 grating spectrophotometer using KBr pellets. Thermal analysis was carried out by means of a MOM Budapest derivatograph (type Paulik, Paulik and Erdey) at a rate of  $10^\circ/\text{min}$  and working temperature range between  $20^\circ$  and  $1000^\circ$ .

All these compounds are extremely sensitive to moisture.

Dimethylformamide is known to undergo autoionization according to the equilibrium<sup>4</sup> (1).



Therefore, the solvolytic reactions of metal halides in dimethylformamide are likely to yield the corresponding metal dimethylformamidyls. But owing to the very poor acceptor nature of dimethylformamide, solvolytic reactions are slow and products of definite compositions are difficult to obtain. Instead alkali metal dimethylformamidyls have been found to be very specific in substitution reactions. These reactions of titanium(IV) chloride with dimethylformamidyl sodium may be visualized to proceed as shown in Eq. (2).



In the compounds  $\text{TiCl}_{4-n}[\text{CON}(\text{CH}_3)_2]_n$ , the value of  $n$  varies between 1 and 4 (Table 1).

Compound (1) combines with quinoline (Q) and ethylenediamine (en) to give compounds (2) and (3) respectively. However, compounds (4) and (6) do not form any addition compounds with quinoline even on warming. Molar conductances of their millimolar solutions in DMF or nitrobenzene exclude any appreciable ionic dissociation<sup>6</sup>. The insolubility of these compounds, except that of  $\text{Ti}[\text{CON}(\text{CH}_3)_2]_4$ , in common organic solvents suggests that these compounds may be polymeric in nature. Presumably both the oxygen and nitrogen atoms are taking part in intramolecular and in termolecular association. Compound (4) on heating at  $110^\circ/10^{-2}$  torr gave the desolvated product (5). Dimethylformamide was also distilled over by heating (1) at  $100^\circ/10^{-2}$  torr, but the residue did not correspond to any definite composition. It is significant to note that compounds (1 and 4) on heating do not lose CO unlike the alkali metal dimethylformamidyls which readily lose CO on heating at  $40-50^\circ$  (ref. 5). This has been confirmed by analysing the residue and also by their infrared spectra which always showed a strong absorption band at  $1640\text{ cm}^{-1}$  generally attributed to  $\nu\text{C}=\text{O}$  absorption. This further suggests that the oxygen atom in formamidyl anion is not free and is tied up by being bonded to titanium atom.

Further evidence on the nature of these compounds have been obtained by studying other physical measurements. The infrared spectra of these compounds are quite complex. All these compounds show a very intense and broad absorption at  $1640-1645\text{ cm}^{-1}$  arising due to  $\nu\text{C}=\text{O}$  band of the formamidyl group. The low value of this band from that in pure DMF suggests coordination through

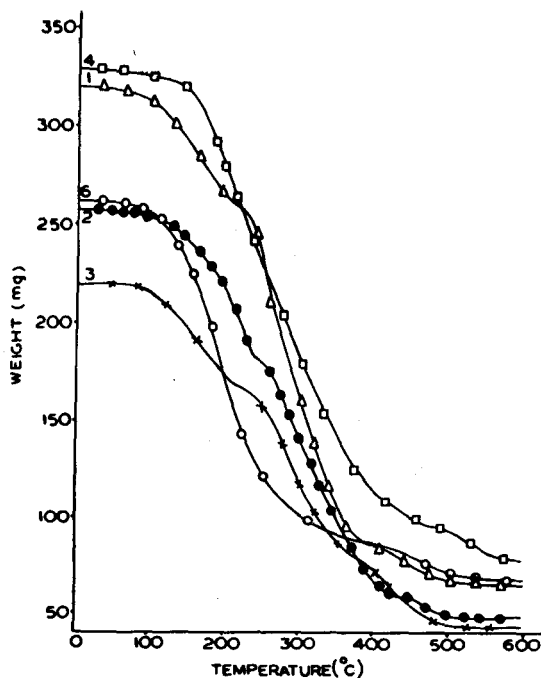


Fig. 1 — TG curves of dimethylformamidyl titanium(IV) compounds

the carbonyl oxygen. The broad nature of this band may arise as a result of the polymeric nature of these compounds. In the far IR region bands around  $550-510$ ,  $430-420$  and  $360-340\text{ cm}^{-1}$  are observed. The absorption around  $430-420\text{ cm}^{-1}$  is neither present in  $\text{NaCON}(\text{CH}_3)_2$  nor in the fully substituted product. Therefore, we assign this band to the  $\nu\text{Ti-Cl}$  absorption.

The thermal decomposition (TG and DTG curves) of these compounds when heated in air is a process consisting of several steps (Fig. 1). By projecting the DTG minima on the TG curves, we could easily find out the various inflexion points. All these compounds are thermally unstable above  $50^\circ$ . However, their main decomposition begins only above  $100-110^\circ$ . Compound (1) loses a molecule of DMF between  $50^\circ$  and  $240^\circ$ . On heating beyond  $240^\circ$  the entire organic mass is lost and an intermediate corresponding to the formation of  $\text{OTi}(\text{OH})_2$  is formed at  $420^\circ$ . Above this temperature, a molecule of water is lost and  $\text{TiO}_2$  is obtained as the final residue at  $520^\circ$ . Compound (2) loses a molecule of quinoline as a first step between  $75^\circ$  and  $240^\circ$  and above this temperature the entire volatile component is lost with the formation of  $\text{OTi}(\text{OH})_2$ . The final residue again corresponds to the formation of  $\text{TiO}_2$ . Compound (3) undergoes decomposition in three distinct steps. The first step between  $80^\circ$  and  $225^\circ$  corresponds to the loss of 1.5 molecules of ethylenediamine. The last but one step between  $225$  and  $380^\circ$  cannot be interpreted in spite of the fact that it is reproducible. It is, however, clear that  $\text{OTi}(\text{OH})_2$  is not formed as one of the intermediates. Compounds (4) and (6) lose weight in two steps corresponding to the formation of  $\text{OTi}(\text{OH})_2$  and  $\text{TiO}_2$ .

#### References

1. PAUL, R. C., ANAND, B. N. & KAPOOR, R., *Indian J. Chem.*, **15A** (1977), 52.

2. ARCHAMBAULT, J. & RIVEST, R., *Can. J. Chem.*, **36** (1958), 1461.
3. PAUL, R. C., MALHOTRA, K. C. & VAIDYA, O. C., *Indian J. Chem.*, **4** (1966), 198.
4. PAUL, R. C., GURAYA, P. S. & SREENATHAN, B. R., *Indian J. Chem.*, **1** (1963), 335.
5. PAUL, R. C., ANAND, B. N. & KAPOOR, R., *Indian J. Chem.*, **13** (1975), 1338.
6. GEARY, W. J., *Coord. chem. Rev.*, **7** (1971), 81.

**Insertion Reactions of Nickel Alkoxides with Phenyl & Naphthyl Isocyanates**

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Received 11 November 1976; accepted 24 February 1977

Nickel alkoxides, Ni(OR)<sub>2</sub> (R = Me and Pr<sup>i</sup>) add readily to isocyanates, R'NCO (R' = Ph and α-Naph) giving the addition products of the general formula, (OR)<sub>2-n</sub>Ni[N(R')COOR]<sub>n</sub>. These products on hydrolysis give urethanes. Reaction of the addition products with parent alcohols yield the alkoxides and urethanes.

INSERTION of a number of ligands like isocyanates, isothiocyanates, carbodiimides, ketenes, sulphur dioxide, carbon disulphide, etc. into M-O bond in the alkoxides of the non-transition elements has been reported<sup>1</sup>. However, such reactions are scarcely known in the case of transition elements except with the alkoxides of titanium<sup>2</sup>, zirconium<sup>3</sup> and niobium<sup>4</sup>. Because of the utility of these alkoxides as catalysts in the formation of urethanes<sup>5</sup>, the reaction of nickel methoxide<sup>6</sup> and isopropoxide<sup>7</sup> with isocyanates has now been studied.

Nickel alkoxides, Ni(OR)<sub>2</sub> (R = Me and Pr<sup>i</sup>) react exothermally with isocyanates, R'NCO (R' = Ph and α-Naph) in benzene to give the addition products (OR)<sub>2-n</sub>Ni[N(R')COOR]<sub>n</sub> (n = 1 or 2). These reactions are completed (monitored by IR, absence of NCO band at 2250 cm<sup>-1</sup> in the products and appearance of νCO at 1700 cm<sup>-1</sup> in the products) after refluxing the reactants in benzene for ~2 hr. Coloured products obtained were analysed after drying. The experimental conditions and the products obtained are listed in Table 1. In the case of bi-insertion products, Ni[N(R')COOR]<sub>2</sub> the band around 600-400 cm<sup>-1</sup> due to νNi-O was also absent.

These products are highly sensitive towards moisture. These addition products on treatment

with water in dioxane give urethanes HN(R')COOR (R = Me and Pr<sup>i</sup>; R' = Ph and α-Naph) and nickel hydroxide which was filtered off. The results are presented in Table 2.

Further these insertion products on treatment with parent alcohols yield the nickel alkoxides and urethanes (Eq. 1).

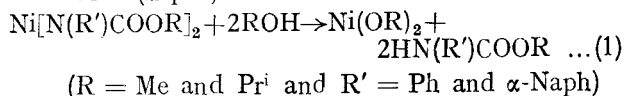


TABLE 1 — INSERTION PRODUCTS OF NICKEL ALKOXIDES WITH PHENYL AND α-NAPHTHYL ISOCYANATES IN DIFFERENT MOLAR RATIOS

Product	Ni (%)		N (%)	
	Found	Calc.	Found	Calc.
Ni(OMe) <sub>2</sub> : PhNCO (1:1) Light green solid (OMe)Ni[N(Ph)COOMe]	24.6	24.5	5.83	5.84
Molar ratio 1:2 Light green solid Ni[N(Ph)COOMe] <sub>2</sub>	16.5	16.4	7.76	7.80
Ni(OMe) <sub>2</sub> : NaphNCO (1:1) Light yellow solid (OMe)Ni[N(Naph)COOMe]	20.32	20.25	4.82	4.83
Molar ratio 1:2 Yellowish green solid Ni[N(Naph)COOMe] <sub>2</sub>	12.85	12.79	6.10	6.10
Ni(OPr <sup>i</sup> ) <sub>2</sub> : PhNCO (1:1) Brown solid (OPr <sup>i</sup> )Ni[N(Ph)COOPr <sup>i</sup> ]	19.96	19.84	4.66	4.73
Molar ratio 1:2 Reddish brown solid Ni[N(Ph)COOPr <sup>i</sup> ] <sub>2</sub>	14.20	14.14	6.68	6.75
Ni(OPr <sup>i</sup> ) <sub>2</sub> : NaphNCO (1:1) Brown solid (OPr <sup>i</sup> )Ni[N(Naph)COOPr <sup>i</sup> ]	17.06	16.97	3.97	4.05
Molar ratio 1:2 Brown solid Ni[N(Naph)COOPr <sup>i</sup> ] <sub>2</sub>	11.48	11.40	5.39	5.44

TABLE 2 — HYDROLYSIS OF Ni[N(R')COOR]<sub>2</sub>

Starting compound	Urethane product	m.p. °C	N (%)	
			Found	Reqd
Ni[N(Ph)COOMe] <sub>2</sub>	HN(Ph)COOMe	—	8.92	9.26
Ni[N(Ph)COOPr <sup>i</sup> ] <sub>2</sub>	HN(Ph)COOPr <sup>i</sup>	88	7.70	7.81
Ni[N(Naph)COOMe] <sub>2</sub>	HN(Naph)COOMe	122	6.90	6.96
Ni[N(Naph)COOPr <sup>i</sup> ] <sub>2</sub>	HN(Naph)COOPr <sup>i</sup>	106	6.08	6.10

TABLE 3 — REACTION OF Ni[N(R')COOR]<sub>2</sub> WITH PARENT ALCOHOLS

Reactants	Products	Found (%) (calc.) alkoxides		Found (%) (calc.) urethanes N
		Ni	Alkoxy	
Ni[N(Ph)COOMe] <sub>2</sub> + MeOH	Ni(OMe) <sub>2</sub> and HN(Ph)COOMe	48.2 (48.6)	51.9 (51.4)	— 9.3 (9.26)
Ni[N(Ph)COOPr <sup>i</sup> ] <sub>2</sub> + Pr <sup>i</sup> OH	Ni(OPr <sup>i</sup> ) <sub>2</sub> and HN(Ph)COOPr <sup>i</sup>	33.5 (33.2)	66.6 (66.8)	— 7.85 (7.81)
Ni[N(Naph)COOMe] <sub>2</sub> + MeOH	Ni(OMe) <sub>2</sub> and HN(Naph)COOMe	47.5 (48.6)	51.2 (51.4)	— 7.0 (6.96)
Ni[N(Naph)COOPr <sup>i</sup> ] <sub>2</sub> + Pr <sup>i</sup> OH	Ni(OPr <sup>i</sup> ) <sub>2</sub> and HN(Naph)COOPr <sup>i</sup>	32.8 (33.2)	66.5 (66.8)	— 6.08 (6.10)