



>>Entry Name: Titanium chloride (TiCl₃), 11Cl

Synonym(s): Titanium trichloride

CAS Registry Number: 7705-07-9

TiCl₃

Molecular Formula: Cl₃Ti

Molecular Weight: 154.238

Accurate Mass: 152.854503

Percentage Composition: Cl 68.96%; Ti 31.04%

of face-sharing octahedra. Milling the α -form causes rotation of Cl-Ti-Cl sheets through up to 60° and enhances catalytic activity

Source/Synthesis: The α -form results from H₂ reduction of TiCl₄ vapour above 500°. The β -form is synth. from TiCl₄ and R₃Al. Manuf. from ilmenite. Available commercially

Use/Importance: A very substantial interest is in alkene polym. catalysts. Powerful reducing agent, e.g. $\text{NO}_3^{(-)} \rightarrow \text{NH}_3$. Used, for example, with LiAlH₄, K, Zn/Cu couple, to generate low-valent Ti spp. which effect reductive coupling of carbonyls to vicinal diols and alkenes

Physical Description: α -form is a red-violet solid, β -form is a brown solid. The $\beta \rightarrow \alpha$ transformation occurs at 250-300° or at 40-80° in an inert solv. containing TiCl₄. Disproportionates to TiCl₂ and TiCl₄ above 475°. Readily oxidised in air

Melting Point: Mp 440 dec.°

Solubility: Sol. H₂O, alcohols; insol. Et₂O, CHCl₃, CCl₄, CS₂, C₆H₆

Other Data: Paramagnetic, $\mu_{\text{eff}} = 1.31\mu_{\text{B}}$ (300K), Néel temp. 165K

Hazard & Toxicity: Flammable, corrosive

Aldrich: 22097-3

Fluka: 89488

Sigma: T3279

>>Derivative: Trihydrate

Molecular Formula: Cl₃H₆O₃Ti

Molecular Weight: 208.284

Accurate Mass: 206.886198

Percentage Composition: Cl 51.06%; H 2.90%; O 23.04%; Ti 22.99%

Source/Synthesis: Synth. from wet Ph₄PCl + TiCl₃ in Me₂CO

Physical Description: Green cryst. + Ph₄PCl + 2 Me₂CO

Other Data: Octahedral Ti, three aqua ligands at *fac* positions

>>Derivative: Sesqui-DME complex

Molecular Formula: C₆H₁₅Cl₃O₃Ti

Molecular Weight: 289.421

Accurate Mass: 287.956623

Percentage Composition: C 24.90%; H 5.22%; Cl 36.75%; O 16.58%; Ti 16.54%

Source/Synthesis: Synth. from TiCl₃ and DME

Use/Importance: Used for the deoxygenative McMurry coupling of aldehydes and ketones to give alkenes

Physical Description: Air-sensitive fluffy, blue cryst.

References:

Inorg. Synth., 1960, **6**, 57, (*synth*)

Ger. Pat., 1971, 2 110 380; *CA*, **76**, 60312g, (*conversion $\beta \rightarrow \alpha$ -form*)

U.S. Pat., 1978, 4 098 868; *CA*, **90**, 107504c, (*manuf*)

Merck Index, 10th edn., 1983, No. 9313

Gerbasi, R. *et al.*, *Makromol. Chem.*, 1984, **185**, 221, (*cryst struct, α -form*)

McMurry, J.E. *et al.*, *J.O.C.*, 1989, **54**, 3748, (*DME complex, synth, use*)

Reetz, M.T., *Organometallics in Synthesis*, (Ed. Schlosser, M.), Wiley, 1994, 267, (*DME complex, synth, use*)

Encyclopaedia of Reagents for Organic Synthesis, (ed. Paquette, L.A.), Wiley, 1995, **7**, 4911; 4922; 4931, (*use*)

Chen, L. *et al.*, *Inorg. Chim. Acta*, 1998, **267**, 271-279, (*synth, cryst struct, trihydrate*)

Lewis, R.J., *Sax's Dangerous Properties of Industrial Materials*, 8th edn., Van Nostrand Reinhold, 1992, TGG250