

Some Reactions of Tin Oxide Chloride and Titanium Oxide Chloride

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Some reactions of tin oxide chloride with pyridine and with tetrahydrothiophen are reported, and it is suggested that products are normally of the form SnO_2 and $\text{SnCl}_4 \cdot \text{L}_2$. Reaction of tin oxide chloride or titanium oxide chloride with acetylacetone appears to lead to the known compounds $\text{MCl}_2(\text{acac})_2$ (where Hacac = acetylacetone, M = Sn or Ti). Several preparations of " $\text{TiO}(\text{acac})_2$ " did not (with the present authors) lead to a monomeric species. The nature of the cation TiOCl_4^{2-} is discussed as is the characterisation of "metal-oxygen double bonds" using vibrational spectroscopy.

AN examination of the occurrence of multiple bonding suggests the existence of definite regularities related to the position of the elements in the Periodic Table. At normal temperatures for pure compounds we know of no exceptions to the rule: ‡ "double bonds involving a σ -bond plus a p_π - p_π bond are found only between first-row elements or between first-row elements and the non-transition elements of Group VI." The reasons for this behaviour (which involves both a kinetic and a thermodynamic problem) could be attributed to (i) small inner-shell ($1s^2$) repulsions of first-row elements (leading to extensive p_π - p_π overlap),¹ (ii) smaller sizes of first-row elements leading to low co-ordination numbers, and (iii) more efficient filling of orbitals in the polymer than in the monomer.² From the behaviour of the elements of Group VI it appears that electronegativity differences may also be important, and it is interesting that SO_2 is monomeric while the isoelectronic PO_2^- is only known as a polymeric species. In inorganic chemistry the importance of the above "rule" is that it allows a large number of observations on the chemistry of the non-transition elements to be rationalised. In the case of multiple bonds involving d_π - p_π bonding the situation is much less clear and reasons for polymerisation of " $\text{M}=\text{O}$ " are not well understood.

We were interested in the compound tin oxide

chloride⁴ as a possible route to compounds containing a formal tin-oxygen double bond, *i.e.*, $\text{Sn}=\text{O}$ with no necessary charge distribution. The addition of pyridine to tin oxide chloride had already been reported.⁴ Thus, co-ordination of a bidentate ligand could lead to a monomeric five-co-ordinate species, analogous to the known⁵ SnCl_5^- ion. Similarly, reactions of tin oxide chloride with acetylacetone might be a convenient preparation for the (unknown) $\text{SnO}(\text{acac})_2$ (where Hacac = acetylacetone). The related compound $\text{TiO}(\text{acac})_2$ had already been reported by several investigators.⁶

Solutions of tin oxide chloride in ethyl acetate to which pyridine was added gave a precipitate which had formula, given by analysis, $\text{SnOCl}_2 \cdot \text{py}$ (py = pyridine). However, the i.r. spectrum of the precipitated solid (4000 — 250 cm^{-1}) was identical with that of the known⁷ compound $\text{SnCl}_4 \cdot \text{py}_2$ except for the presence of a weak broad band centred around 600 cm^{-1} , similar to that found in tin dioxide. This strongly suggested decomposition of the tin oxide chloride to tin dioxide, with simultaneous formation of the adduct $\text{SnCl}_4 \cdot \text{py}_2$. As we know of no suitable inert solvent for either of these compounds, separation appeared to be impossible. The adduct $\text{SnCl}_4 \cdot 2$ tetrahydrothiophen⁸ is soluble in organic solvents, and we therefore added tetrahydrothiophen to a solution of tin oxide chloride in ethyl acetate. This led to a precipitate of tin oxide together

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‡ Species such as POCl_2^+ and VO_2^+ are mentioned in the literature, but the evidence for them is not conclusive.³

¹ K. S. Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140.

² I. R. Beattie and T. Gilson, *Nature*, 1962, **193**, 1041.

³ See, however, K. Dehnicke and J. Weidlein, *Angew. Chem.*, 1966, **5**, 1041.

⁴ K. Dehnicke, *Z. anorg. Chem.*, 1961, **308**, 72.

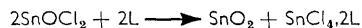
⁵ R. F. Bryan, *J. Amer. Chem. Soc.*, 1964, **86**, 734.

⁶ (a) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552; see also M. Cox, J. Lewis, and R. S. Nyholm, *ibid.*, 1965, 2840; (b) A. N. Nesmeyanov, O. V. Nogina, and V. A. Dubovitskii, *Bull. Acad. Sci., U.S.S.R.*, 1961, 403; (c) A. Yamamoto and S. Kambara, *J. Amer. Chem. Soc.*, 1957, **79**, 4345; A. Yamamoto and S. Kambara, *J. Chem. Soc. Japan*, 1959, **80**, 1239.

⁷ I. R. Beattie, G. P. McQuillan, and M. Webster, *J. Chem. Soc.*, 1963, 1514.

⁸ I. R. Beattie and L. Rule, *J. Chem. Soc.*, 1964, 3267.

with a supernatant ligand which, when evaporated to dryness, left a residue of the 1:2 adduct of tin tetrachloride with tetrahydrothiophen. It thus appeared that addition of ligands to tin oxide chloride was likely to result in reactions of the type:



Similarly, although tin oxide chloride appears to be completely soluble in acetylacetone, from the resultant solution we could only isolate the known⁹ $\text{SnCl}_2(\text{acac})_2$. In view of these unsatisfactory results we decided to investigate reactions of titanium oxide chloride¹⁰ with acetylacetone, as the compound $\text{TiO}(\text{acac})_2$ appeared to be well characterised.

As with the corresponding tin compound, reaction of titanium oxide chloride with acetylacetone led to the formation¹¹ of bisacetylacetonatodichlorotitanium(IV). In view of the fact that evolution of hydrogen chloride during this reaction could lead to conversion of any $\text{TiO}(\text{acac})_2$ into $\text{Ti}(\text{acac})_2\text{Cl}_2$, we prepared the compound $\text{TiO}(\text{acac})_2$ by the literature method¹² involving aerial oxidation of a solution of trisacetylacetonatotitanium(III). We find it to be dimeric in benzene (by osmometry) and showing no band in the region of 1087 cm^{-1} . It was reported^{6a} that $\text{TiO}(\text{acac})_2$ prepared as described above was monomeric in benzene (by cryoscopy) with a titanium-oxygen stretching frequency of 1087 cm^{-1} . However, Selbin¹³ suggested that a band at 1085 cm^{-1} was given erroneously in the earlier Paper and refers to a private communication from one of the original workers. In a further Paper^{6a} both monomer, with a band at 1087 cm^{-1} , and dimer, with a broad band at 830 cm^{-1} , are discussed. It is interesting that $\text{TiO}(\text{acac})_2$ prepared from the reaction between acetylacetone and dipropoxytitanium oxide^{6b} has been reported to be monomeric in dilute solution. (*M* by cryoscopy in benzene; *m. p.* $235\text{--}236^\circ$.) By contrast, the product obtained from the hydrolysis of bis(acetylacetonato)dibutoxytitanium was formulated as a dimer.^{6c} (*M* by cryoscopy in benzene; *m. p.* 235° , decomp.)

In view of the conflicting nature of these and previous results independent experiments were carried out and the molecular weight in benzene found by cryoscopy. The compound was again found to be dimeric and showed no 1087 cm^{-1} band. Selbin¹³ suggests that a band at $1020\text{--}1035\text{ cm}^{-1}$ may be a Ti-O stretching vibration. We find a band in this region for a range of acetylacetonates and there is no obvious additional band in $\text{TiO}(\text{acac})_2$.

Over a period of about 2 years we have prepared $\text{TiO}(\text{acac})_2$ from $\text{Ti}(\text{acac})_3$ using a variety of conditions. In all cases the molecular weight has indicated a dimeric formulation. On several occasions the compound $\text{Al}(\text{acac})_3$ was obtained as an impurity. This misled us for some time as the material which crystallised from solution had a homogeneous red colour [presumably

due to solid solution of small amounts of the expected impurity $\text{Fe}(\text{acac})_3$]. Figure 1 shows the i.r. spectra of our " $\text{TiO}(\text{acac})_2$ " obtained as a crystalline solvate, but with the benzene removed before spectroscopic examination. For this compound in the range $700\text{--}1100\text{ cm}^{-1}$ there is no obvious band which can be attributed to a Ti-O-Ti vibration. We frequently obtained material with a broad band in the 800 cm^{-1} region but this appeared to occur only in samples which had not been purified by crystallisation. In Figure 1 we include the spectrum of "monomeric $\text{TiO}(\text{acac})_2$." Appreciable variations in the 800 cm^{-1} region were observed during our preparations. Samples of material showing a broad band in the 800 cm^{-1} region frequently showed

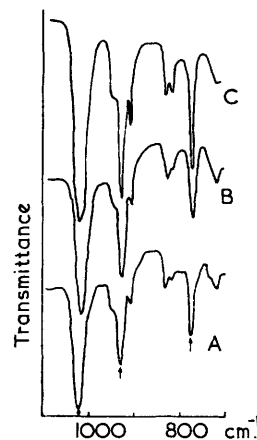


FIGURE 1 Infrared spectra of " $\text{TiO}(\text{acac})_2$." (A) Sample kindly supplied by Dr. Cox. (B) Our sample from the vacuum experiment between $\text{Ti}(\text{acac})_3$ and oxygen, after standing in the air. (C) Sample obtained from oxidation of benzene solutions of $\text{Ti}(\text{acac})_3$.

evidence of OH absorptions in the 3500 cm^{-1} region. We believe that the compound under examination is binuclear and contains two acetylacetonate residues per titanium. It is also probably oxygen-bridged rather than acetylacetonate-bridged. However, we note that the effective monohydrate $[\text{TiOH}(\text{acac})_2]_2\text{O}$ would not easily be detected analytically or by molecular weight studies. In an attempt to break the oxygen bridges, we dissolved $\text{TiO}(\text{acac})_2$ in pyridine and precipitated with light petroleum. The precipitated material was unsolvated, but contained appreciable hydroxy-groups, in contrast to the related $\text{VO}(\text{acac})_2$ which will readily co-ordinate one additional ligand.

Passage of hydrogen chloride gas into a solution of " $\text{TiO}(\text{acac})_2$ " in benzene led to the known monomer $\text{TiCl}_2(\text{acac})_2$. We therefore attempted to make titanium oxide chloride react with sodium acetylacetonate. Although a yellow compound was obtained, showing similarities in i.r. spectrum to that of $\text{TiO}(\text{acac})_2$, it contained a broad band in the region of 830 cm^{-1} . We also studied the reaction of trisacetylacetonatotitanium-

⁹ G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1924, **125**, 375.

¹⁰ K. Dehnicke, *Z. anorg. Chem.*, 1961, **309**, 266.

¹¹ W. Diltthey, *Ber.*, 1904, **37**, 588.

¹² M. Cox, Ph.D. Thesis, London University, 1961.

¹³ J. O. L. Selbin, *J. Chem. Educ.*, 1964, **41**, 86.

(III) with dry oxygen in a vacuum system. The quantity of oxygen consumed corresponded to the reaction



but the product was a red-brown resinous mixture.

When we had nearly completed this work Feltz reported the preparation of a tetraethylammonium salt of the monomeric anion $[\text{TiOCl}_4]^{2-}$. The corresponding rubidium salt gave evidence of polymeric Ti-O-Ti linkages, showing a broad band in the i.r. spectrum centred at about 850 cm^{-1} . We have repeated the preparation of $(\text{Et}_4\text{N})_2\text{TiOCl}_4$ ¹⁴ and $(\text{Me}_4\text{N})_2\text{TiOCl}_4$,¹⁵ and confirm the experimental observations. The assignment of a monomeric anion is based on the absence of a broad band around 850 and the presence of a strong narrow band at 975 cm^{-1} . Since we can find no strong band in the "Ti-O stretching region" in " $\text{TiO}(\text{acac})_2$ " it is possible that absence of a broad strong band at around 800 cm^{-1} does not necessarily imply the absence of bridging oxygens so that this assignment is based primarily on the strong band at 975 cm^{-1} . However, even here, caution must be exercised because this vibration is very close to a strong (degenerate) band of the Et_4N^+ or Me_4N^+ cation, and in the crystal, partial resolution of the degeneracy could lead to a band near

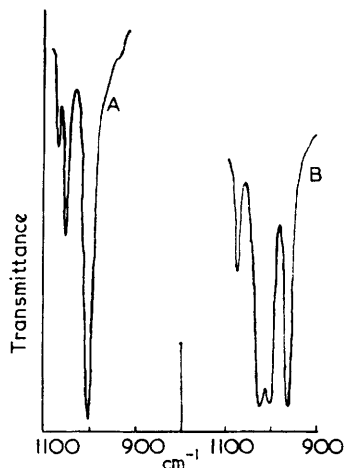


FIGURE 2 Infrared spectrum of (A) Et_4NCl , (B) $(\text{Et}_4\text{N})_2\text{TiOCl}_4$

975 cm^{-1} . Thus, in Figure 2 we show the infrared spectrum of tetraethylammonium chloride and of $(\text{Et}_4\text{N})_2\text{TiOCl}_4$ in the region of 1000 cm^{-1} .

Finally, we wish to comment on assignments of terminal M=O vibrations from i.r. spectroscopy. It is known that the compound $\text{VO}(\text{acac})_2$ is a stable monomer with^{6a} a "metal-oxygen stretching frequency" at 995 cm^{-1} and that chains of Ti-O-Ti- can lead to broad bands in the region of 800 cm^{-1} . However, at present there is insufficient evidence for us to understand under what conditions broad or narrow bands may arise; e.g., the broad bands could be due to crystal imperfections. Another important point is the M-O-M angle.

If we consider a terminal oxygen M-O and then form a (linear) oxygen-bridged dimer, where the mass of M is large relative to oxygen the "antisymmetric" M-O-M stretching frequency will occur at the same position (using a SVFF calculation) as the terminal M-O frequency (making the reasonable assumption that the force constant of a terminal M-O link is twice that of a bridging M-O). Decreasing the angle will clearly lower the bridging frequency. In practice it appears that¹⁶ $[\text{GePcO}]_n$ (Pc = phthalocyanine) shows a "Ge-O stretching frequency" at about 870 cm^{-1} . We should perhaps note here that titanium is lighter than germanium. An even more interesting example is the compound¹⁷ $(\text{pyPcMn})_2\text{O}$ which has been reported as showing¹⁸ a "metal-oxygen stretching frequency" at 1096 cm^{-1} . It is pointless to argue that because the M-O-M bond is linear, then there must be a higher force constant in the bridge due to $d_{\pi}-p_{\pi}$ bonding. Such comments are merely extensions of the basic problem.

EXPERIMENTAL

Preparation of Solvents and Reagents.—Solvents were normally dried over calcium hydride before vacuum-distillation into ampoules. Pyridine was dried with silicon tetrachloride, followed by vacuum-distillation. Ethyl acetate and acetylacetone were dried with molecular sieve, followed by vacuum-distillation. Tin oxide chloride and titanium oxide chloride were prepared using literature methods^{4,10} (analysis by hydrolysis and potentiometric titration of chloride. Found: Cl, 34.3. Calc. for Cl_2OSn : Cl, 34.5%. Found: Cl, 52.3. Calc. for Cl_2OTi : Cl, 52.6%). Tetraethyl- and tetramethyl-ammonium chloride were recrystallised from chloroform, then dissolved in chloroform and precipitated with light petroleum, and dried at 140° *in vacuo*.

$\text{SnOCl}_2, \text{py}$.—Tin oxide chloride was dissolved in ethyl acetate and pyridine added. The precipitate was removed by centrifuge. The compound was also made by direct addition of pyridine to solid tin oxide chloride. (Analysis by hydrolysis and potentiometric titration. Found: Cl, 24.8. Calc. for $\text{C}_5\text{H}_5\text{Cl}_2\text{NOSn}$: Cl, 24.9%). The i.r. spectrum of the product closely resembled that of the adduct $\text{SnCl}_4, \text{py}_2$ but contained a weak broad band centred at about 600 cm^{-1} .

$\text{SnOCl}_2, \text{C}_4\text{H}_8\text{S}$.—Addition of tetrahydrothiophen to an ethyl acetate solution of tin oxide chloride led to a white precipitate which was insoluble in benzene or excess tetrahydrothiophen. A chloride test on the solid proved negative. The supernatant liquid was evaporated to dryness *in vacuo* and yielded a compound having a spectrum closely similar to that of the adduct $\text{SnCl}_4, 2\text{C}_4\text{H}_8\text{S}$. (Quantitative experiment. Initial weight of $\text{SnOCl}_2 = 13.61\text{ mg}$. Weight of precipitate = 5.0 mg . (Calc. 5.0 mg). Weight of residue from supernatant liquid = 14.4 mg . (Calc. 14.4 mg). Repeat: Initial weight of $\text{SnOCl}_2 = 53.4\text{ mg}$. Weight of precipitate = 21.0 mg . (Calc. 19.6 mg). Weight of residue from supernatant liquid = 51.4 mg . (Calc. 56.7 mg). The calculated are derived from the equation



¹⁴ A. Feltz, *Z. anorg. Chem.*, 1965, **334**, 242.

¹⁵ A. Feltz, *Z. anorg. Chem.*, 1965, **338**, 155.

¹⁶ R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, 1962, **1**, 717.

¹⁷ L. H. Vogt and D. H. Templeton, *Science*, 1966, **151**, 569.

¹⁸ Quoted in J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 1959, 195.

$\text{SnOCl}_2 \cdot \text{Hacac}$.—Acetylacetone was added directly to solid tin oxide chloride and the whole warmed to about 80° , when solution appeared to be complete. On cooling, a white solid was precipitated. (Analysis by hydrolysis and potentiometric titration. Found: Cl, 18.1. Calc. for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Sn}$: Cl, 18.3%.) The i.r. spectrum closely resembled that of a sample of $\text{SnCl}_2(\text{acac})_2$.*

$\text{TiOCl}_2 \cdot \text{Hacac}$.—The reaction was carried out in a manner similar to that described for the tin compound. A bright red solution resulted which was evaporated *in vacuo* to yield a red solid. It was very difficult to remove final traces of solvent. (Analysis by combustion. Found: C, 39.4; H, 4.8. Calc. for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Ti}$: C, 37.8; H, 4.4%.) The i.r. spectrum closely resembled that of a sample of $\text{Ti}(\text{acac})_2\text{Cl}_2$.

$\text{Ti}(\text{acac})_3$.—This was prepared by the method used by Cox¹² using commercial "titanous sulphate" or "titanous chloride" solutions. On one or two occasions titanium(IV) solutions in hydrochloric acid were reduced by elemental tin to obtain the titanium(III) solutions. The blue $\text{Ti}(\text{acac})_3$ was extracted into benzene and either allowed to oxidise directly to " $\text{TiO}(\text{acac})_2$ " or obtained as a solid by removal of the solvent under vacuum. In the latter case the solid was purified by vacuum-sublimation.

" $\text{TiO}(\text{acac})_2$ ".—This compound was prepared by allowing solutions of $\text{Ti}(\text{acac})_3$ in benzene to oxidise in the open laboratory. The solid product was obtained by (a) pumping to dryness, (b) allowing to crystallise slowly (when a benzene solvate was obtained), or (c) precipitation by light petroleum or crystallisation from a light petroleum—

* The i.r. spectrum suggests one strong Sn—Cl stretching frequency at 334 cm^{-1} , which could be taken to indicate *trans*-stereochemistry. However, there is an accidental degeneracy here as the main Raman band is at 338 cm^{-1} .

benzene mixture (when again a solvate was apparently formed). During some of these experiments crystals of trisacetylacetonatoaluminium(III) were obtained and identified by X-ray diffraction, analysis, and molecular weight. [Analytical data on a variety of " $\text{TiO}(\text{acac})_2$ " samples. Found: C, 44.8, 44.55, 43.5, 43.65; H, 5.65, 5.15, 5.0, 4.9; Ti, 18.3, 17.55. Calc. for $\text{C}_{10}\text{H}_{14}\text{O}_5\text{Ti}$: C, 45.8; H, 5.4; Ti, 18.3%]. Molecular weight data similarly refer to a variety of samples of $\text{TiO}(\text{acac})_2$, some of these containing broad bands in the region of 800 cm^{-1} . By cryoscopy: 548, 623, and 532. By vapour phase osmometer: 531, 524, 621, 587, and 567.

$\text{Ti}(\text{acac})_3 + \text{O}_2$ (*Vacuum Experiment*).— $\text{Ti}(\text{acac})_3$ (1.334 g.) was dissolved in benzene and allowed to react with dry oxygen in an all-glass vacuum system with no taps or joints; oxygen uptake 0.024 g. The product was a brown-red resinous material.

$\text{TiO}(\text{acac})_2 + \text{HCl}$.—A sample of $\text{TiO}(\text{acac})_2$ was dissolved in benzene to yield a yellow solution. Passage of dry hydrogen chloride gas into this solution changed the colour to deep red. Removal of volatiles left a red solid (Found: C, 41.2; H, 4.9; Cl, 20.2. Calc. for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Ti}$: C, 37.8; H, 4.4; Cl, 22.4%).

Salts of the TiOCl_4^{2-} Anion.—Tetraethyl- or tetramethylammonium chloride was allowed to react with a suspension of titanium oxide chloride in acetonitrile. The mixture was warmed to increase solubility, and then cooled to room temperature. The i.r. spectra of the products appeared to be closely similar to those reported in the literature.

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