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# Complexes of Titanium Halides with Acetone Azine and Its Isomer 3,5,5-Trimethyl-Pyrazoline

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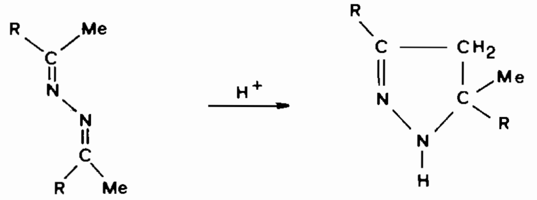
*Titanium(IV) chloride and bromide form complexes* $TiX_4(Me_2C{=}N{-}N{=}CMe_2)_2$ *in the presence of excess of acetone azine. When the halides are in excess, the products formed are* $(TiCl_4)_4(Me_2C{=}N{-}N{=}CMe_2)_3$ *and* $TiBr_4(Me_2C{=}N{-}N{=}CMe_2)$*. Titanium(III) chloride isomerises acetone azine to 3,5,5-trimethyl-2-pyrazoline catalytically at 100 °C; titanium(III) is oxidised to titanium(IV) under these conditions or upon long standing at room temperature and the complex* $[TiCl_3(Pz')Pz)_3]$ *can be isolated (Pz = 3,5,5-trimethyl-2-pyrazoline; Pz' = Pz – H).*

## Introduction

The cyclisation of methyl ketazines (I) to 3,5-dialkyl-5-methyl-2-pyrazolines(II) on treatment with various acids has long been established [1].



I II

More recently, the reaction has been shown to be acid catalysed [2] and is also catalysed by cobalt(II) and nickel(II) halides [3]. Complexes of tin(IV) [4, 5], titanium(IV) [6], copper(I) [7] and mercury(II) [8] halides with methyl ketazines have been reported and, although in some cases there is a deficiency of spectroscopic data available, these complexes appear to contain the uncyclised azine co-ordinated to the metal. The present work describes the results of an investigation into the reactions of titanium halides with acetone azine, which afford a range of complexes containing, as ligands, either unchanged acetone azine or its isomer, 3,5,5-trimethyl-2-pyrazoline.

## Results and Discussion

$TiCl_4$ and $TiBr_4$ in iso-octane solution react with excess acetone azine at room temperature affording complexes, $[TiX_4(Me_2C{=}N{-}N{=}CMe_2)_2]$ (X = Cl or Br). In the presence of excess metal halide, the products are $[TiCl_4(Me_2C{=}N{-}N{=}CMe_2)_{3/4}]$ and $[TiBr_4(Me_2C{=}N{-}N{=}CMe_2)]$ respectively (Table I). These are all extremely sensitive to moist air, diamagnetic, $d^0$ complexes; their i.r. spectra strongly suggest that unchanged acetone azine is present in the complexes and this is confirmed by base hydrolysis which liberates the free azine.

The four metal–halogen stretching vibrations in their far i.r. spectra (Table II) suggest that the complexes $[TiX_4(Me_2C{=}N{-}N{=}CMe_2)_2]$ are octahedral monomers, in which each acetone azine is co-ordinated to the metal *via* one of its 2 equivalent nitrogen atoms.

The unusual formulation of the complex $[TiCl_4(Me_2C{=}N{-}N{=}CMe_2)_{3/4}]$ is not unprecedented as azobenzene forms a similar complex with $TiCl_4$ [9]. We hoped to compare the X-ray powder photographs of the two compounds but, unfortunately, the acetone azine complex proved to be amorphous. Metal–halogen stretching frequencies could not be unambiguously assigned from the far i.r. spectra of either $[TiCl_4(Me_2C{=}N{-}N{=}CMe_2)_{3/4}]$ or $[TiBr_4(Me_2C{=}N{-}N{=}CMe_2)]$, and, as these complexes are insoluble in solvents with which they do not react, no structural information could be deduced.

Titanium(III) chloride does not react with acetone azine in the presence of a non-co-ordinating solvent, but reacts with the neat ligand at room temperature over 15 h to give a pale green compound, $[TiCl_3(Pz)_3]$ (Pz = 3,5,5-trimethyl-2-pyrazoline). This complex has a magnetic moment (Table II) and reflectance spectrum (Table III) typical of a $d^1$ octahedral complex. The i.r. spectrum clearly indicates the presence of pyrazoline in the complex and base hydrolysis confirmed the total absence of acetone azine in the liberated ligand (g.l.c. and n.m.r.)

TABLE I. Analytical Data for Complexes of Acetone Azine and 3,5,5-Trimethyl-2-pyrazoline.

| Complex | Elemental Analyses (%)[a] | | | | | M. pt. (°C) |
|---|---|---|---|---|---|---|
| | C | H | N | Cl or Br | Ti | |
| $[\mathrm{TiCl_4(Me_2C{=}N{-}N{=}CMe_2)_2}]$ | 35.0<br>(34.8) | 6.2<br>(5.8) | 13.6<br>(13.5) | 34.9<br>(34.3) | | 61 |
| $[\mathrm{TiBr_4(Me_2C{=}N{-}N{=}CMe_2)_2}]$ | 24.0<br>(24.3) | 4.2<br>(4.0) | 9.2<br>(9.5) | 53.6<br>(54.0) | | 61–2 (dec) |
| $[\mathrm{4TiCl_4 \cdot 3(Me_2C{=}N{-}N{=}CMe_2)}]$ | 19.5<br>(19.7) | 3.5<br>(3.3) | 7.6<br>(7.8) | 52.4<br>(51.8) | 17.5<br>(17.5) | 61 (dec) |
| $[\mathrm{TiBr_4(Me_2C{=}N{-}N{=}CMe_2)}]$ | 15.3<br>(15.0) | 2.9<br>(2.5) | 6.4<br>(5.8) | 66.1<br>(66.6) | | 47–50 |
| $[\mathrm{TiCl_3(Pz)_3}]$ | 44.0<br>(44.0) | 7.7<br>(7.4) | 16.9<br>(17.1) | 21.9<br>(21.7) | | 115 (dec) |
| $[\mathrm{TiCl_3(Pz')(Pz)_3}]$ | 47.3<br>(47.8) | 8.3<br>(8.0) | 18.2<br>(18.6) | 17.8<br>(17.6) | | |
| $[\mathrm{TiBr_3(Pz')(Pz)_3}]$ | 39.2<br>(39.2) | 6.7<br>(6.6) | 15.0<br>(15.2) | 31.9<br>(32.5) | | 93–4 |
| $[\mathrm{TiCl_3(Pz')(Pz)_2}]$ | 44.4<br>(44.0) | 7.6<br>(7.4) | 17.4<br>(17.1) | 21.3<br>(21.7) | | |

[a] Theoretical values in parentheses.

TABLE II. Physical Properties of Complexes of Acetone Azine and 3,5,5-Trimethyl-2-pyrazoline.

| Complex | Magnetic Moment (BM) | Molar Conductivity[a] (ohm$^{-1}$ mol$^{-1}$ cm$^{2}$) | Characteristic Infrared Vibrations (cm$^{-1}$)[b] | | |
|---|---|---|---|---|---|
| | | | ν(N–H) | ν(C=N) | ν(M–X)[c] |
| $[\mathrm{TiCl_4(Me_2C{=}N{-}N{=}CHMe_2)_2}]$ | diamag. | 36[d] | | 1664(m)<br>1643(m)<br>1628(s)<br>1605(br) | 439(m)<br>412(m)<br>350(vs)<br>329(vs) |
| $[\mathrm{TiBr_4(Me_2C{=}N{-}N{=}CMe_2)_2}]$ | diamag. | 43[d] | | 1639 (m, br) | 398 (m)<br>365(m)<br>310(m)<br>260(m) |
| $[\mathrm{4TiCl_4 \cdot 3(Me_2C{=}N{-}N{=}CMe_2)}]$ | diamag. | | | 1640(m, br) | not assignable |
| $[\mathrm{TiBr_4(Me_2C{=}N{-}N{=}CMe_2)}]$ | diamag. | 59[d] | | 1640(m, br) | not assignable |
| $[\mathrm{TiCl_3(Pz)_3}]$ | 1.67 | | 3308(w, sh)<br>3297(w, sh)<br>3289(w, sh) | 1640(m)<br>1617(m) | not assignable |
| $[\mathrm{TiCl_3(Pz')(Pz)_3}]$ | diamag. | 24 | 3298(m) | 1644(m)<br>1625(m)<br>1585(m) | not assignable |
| $[\mathrm{TiBr_3(Pz')(Pz)_3}]$ | diamag. | | 3298(w) | 1642(w, br) | not assignable |
| $[\mathrm{TiCl_3(Pz')(Pz)_2}]$ | diamag. | | 3300(w, sh) | 1642(m)<br>1623(m)<br>1588(m) | not assignable |

[a] In $NO_2Me$ solution (approx. $10^{-3}$ molar. [b] Nujol mull. [c] X = Cl or Br. [d] High values are probably due to partial hydrolysis: vs = very strong, m = medium, w = weak, sh = sharp, br = broad.

TABLE III. Diffuse Reflectance Spectra (cm$^{-1}$ × 10$^{-3}$) of Acetone Azine and 3,5,5-Trimethyl-2-pyrazoline Complexes.

| Complex | Charge Transfer | $^2B_{2g} \rightarrow {}^2A_{1g}$ | $^2B_{2g} \rightarrow {}^2B_{1g}$ |
|---|---|---|---|
| $[TiCl_4(Me_2C{=}N{-}N{=}CMe_2)_2]$ | 46.0, 43.0, 29.0, 21.0 | | |
| $[TiBr_4(Me_2C{=}N{-}N{=}CMe_2)_2]$ | 45.9, 37.2, 25.5, 21.5 | | |
| $[4TiCl_4 \cdot 3(Me_2C{=}N{-}N{=}CMe_2)]$ | 46.0, 36.7, 28.5, 20.8 | | |
| $[TiBr_4(Me_2C{=}N{-}N{=}CMe_2)]$ | 45.9, 37.2, 27.3, 17.8, 13.9 (sh) | | |
| $[TiCl_3(Pz)_3]$ | 47.0, 37.0, 32.2, 26.5(sh) | 16.2 | 15.0 (sh) |
| $[TiCl_3(Pz')(Pz)_3]$ | 46.4, 36.5, 22.2 | | |
| $[TiCl_3(Pz')(Pz)_2]$ | 45.8, 36.8, 20.7 | | |

sh = shoulder.

$[TiCl_3(Pz)_3]$ reacts further with acetone azine upon standing at room temperature for 1 week, giving a red-brown complex, $[TiCl_3Pz')(Pz)_3]$ (Pz' = Pz – H, 3,5,5-trimethyl-2-pyrazolinato-anion). The magnetic moment (Table II), reflectance spectrum (Table III) and general properties of this complex confirm that it contains titanium(IV). It is a non-conductor in nitromethane solution and liberates only pyrazoline on base hydrolysis. The complex is most probably six co-ordinate, containing pyrazoline of crystallisation but, as no change in composition occurs on evacuation at 70 °C for 12 h, a seven co-ordinate structure is possible. We have also prepared the bromo-analogue of this complex, which exhibits very similar properties.

In these reactions of titanium(III) halides with acetone azine at room temperature, cyclisation to 3,5,5-trimethyl-2-pyrazoline occurs at the metal centre, but the excess of acetone azine, used as the solvent may be recovered unchanged. However, when acetone azine is heated to 100 °C in the presence of trace amounts of $TiCl_3$, 90% conversion to pyrazoline is effected after 20 h; as expected, the $TiCl_3$ is converted to $[TiCl_3(Pz')(Pz)_3]$, which is presumably the active catalyst. To effect this cyclisation over 24 h using Co(II) or Ni(II) halides as catalysts, a temperature of *ca.* 200 °C is required [3].

Titanium(III) chloride reacts with 3,5,5-trimethyl 2-pyrazoline, but more slowly than with acetone azine and, after 1 week at room temperature, unreacted $TiCl_3$ is still present. However, the reaction goes to completion after 24 h at 100 °C and the Ti(IV) complex, $[TiCl_3(Pz')(Pz)_2]$, is isolated. (There is no evidence that $[TiCl_3(Pz)_3]$ is an intermediate). $[TiCl_3(Pz')(Pz)_2]$ undergoes no further reaction with the pyrazoline, possibly due to steric hindrance, but reacts with acetone azine at room temperature to give $[TiCl_3(Pz')(Pz)_3]$.

As all the reactions described were carried out in an atmosphere of pure, dry dinitrogen, it appears that the oxidation of Ti(III) to Ti(IV) is effected by the ligands, acetone azine and 3,5,5-trimethylpyrazoline. We have not been able to isolate the reduced forms of these ligands but, under different conditions, catalytic hydrogenation of acetone azine is reported to give both the hydrazine, $(Me_2CNHN)_2$ [10] and the primary amine $Me_2CHNH_2$ [11]. We have been unable to find any examples in the literature of pyrazolines acting as oxidising agents.

## Experimental

Infrared spectra were recorded in the range 4,000–200 cm$^{-1}$ on a Perkin–Elmer 577 spectrometer. Reflectance spectra were recorded on a Unicam SP 700C spectrophotometer. Magnetic susceptibilities were measured by the Gouy method at room temperature. Molar conductivities were measured using a Phillips PR9500 conductivity bridge. Carbon, hydrogen, nitrogen and titanium analyses were carried out by the Butterworth Microanalytical Consultancy, chloride was determined volumetrically and bromide gravimetrically.

### *Starting Materials*

Titanium(IV) bromide and titanium(III) bromide were prepared by the literature method [12] as were acetone azine [13] and 3,5,5-trimethyl-2-pyrazoline [2].

### *Preparation of Complexes*

All reactions and manipulations were carried out in an atmosphere of pure, dry dinitrogen or in vacuo using Schlenk-tube techniques. All solvents were dried by standard procedures. In general, complexes were dried at room temperature at 0.01 mm Hg for 6 h before analysing; the complexes of titanium(IV) obtained from $TiCl_3$–ligand reactions were dried however at 60 °C. Essentially quantitative yields were obtained from reactions using Ti(IV) halides.

### *Tetrachlorobis(acetone azine)titanium(IV)*

$TiCl_4$ (4 g) and iso-octane (150 cm$^3$) were distilled in vacuo into a 250 cm$^3$ flask cooled at –196 °C. The mixture was warmed to ensure thorough mixing of the two liquids, then re-frozen and acetone azine (10 cm$^3$, large excess) was distilled from barium oxide into the cooled mixture, which was then allowed to warm to room temperature, removed from the vacuum line and shaken, giving the *complex* as a homogeneous red powder.

### *Tetrabromobis(acetone azine)titanium(IV)*

Prepared similarly to I using $TiBr_4$ (3 g) and acetone azine (10 cm$^3$). *The complex* was obtained as a dark red precipitate.

### *Tris(acetone azine)tetrakis(tetrachlorotitanium(IV))*

$TiCl_4$ (5 g, large excess) and iso-octane (100 cm$^3$) were distilled in vacuo into a 250 cm$^3$ Schlenk flask, cooled at −196 °C. The mixture was warmed to room temperature and removed from the vacuum line. Acetone azine (1.3 cm$^3$) and iso-octane (20 cm$^3$) were distilled in vacuo into a second cooled flask. The solution was warmed to room temperature and added dropwise to the solution of $TiCl_4$, magnetically stirred at room temperature. The *complex* was precipitated as a red-brown solid.

### *Tetrabromo(acetone azine)titanium(IV)*

Prepared similarly to III using $TiBr_4$ (10 g) and acetone azine (2.5 cm$^3$). The *complex* was obtained as bright red precipitate which was filtered off and dried at 55 °C, 0.01 mm Hg for 7 h, during which time unreacted $TiBr_4$ sublimed from the *complex.*

### *Trichlorotris(3, 5, 5-trimethyl-2-pyrazoline)titanium(III)*

Acetone azine (15 cm$^3$) was distilled in vacuo from barium oxide into a flask containing $TiCl_3$ (2.0 g) cooled at −196 °C. The mixture was allowed to attain room temperature, removed from the vacuum line and then magnetically stirred for 15 h, during which time the suspended $TiCl_3$ reacted slowly to give the *complex* as a pale green precipitate in a red–brown solution; this was filtered off and washed with dry acetone azine (1 × 20 cm$^3$) (3.6 g, 56%).

### *Trichloro(3, 5, 5-trimethyl-2-pyrazolinato)tris(3, 5,5-trimethyl-2-pyrazoline)titanium(IV)*

Method 1: Prepared as above, using $TiCl_3$ (2.9 g) except that one reaction mixture was stirred for 1 week at room temperature. Excess acetone azine was then removed at 80 °C, 0.01 mm Hg, and benzene (150 cm$^3$) was distilled in vacuo onto the residual sticky red oil. The resultant, intensely coloured, solution was filtered to remove impurities, evaporated to dryness (room temperature, 0.01 mm Hg) and the product extracted with iso-octane (100 cm$^3$), giving the *complex* as a dark red powder (6.2 g, 55%).

Method 2: As method 1, but using $[TiCl_3(MeCN)_3]$ (2.0 g) in place of $TiCl_3$. Initially a green precipitate was formed, but this redissolved over 18 h to give a red–brown solution which afforded the *complex* (2.9 g, 67%).

### *Tribromo(3,5,5-trimethyl-2-pyrazolinato)tris(3,5,5-trimethyl-2-pyrazoline)titanium(IV)*

Prepared similarly to above using $TiBr_3$ (0.5 g) and acetone azine (5 cm$^3$). The reaction went to completion over 15 h and the intermediate, tribromotris(3,5,5-trimethyl-2-pyrazoline) was not isolated.

### *Trichloro(3,5,5-trimethyl-2-pyrazolinato)bis(3,5,5-trimethyl-2-pyrazoline)titanium(IV)*

3,5,5-trimethyl-2-pyrazoline (30 cm$^3$) was distilled in vacuo from barium oxide into a flask containing $TiCl_3$ (1.2 g) cooled at −196 °C. The mixture was allowed to attain room temperature, removed from the vacuum line and heated, with continuous magnetic stirring, at an oil bath temperature of 100 °C over 24 h. The resultant red–brown solution was evaporated to dryness at 100 °C, 0.01 mm Hg and the residual solid dissolved in benzene (100 cm$^3$). The solution was filtered to remove impurities and evaporated to dryness (room temperature, 0.01 mm Hg), giving the *complex* as a red–brown powder on extraction with iso-octane (100 cm$^3$) (2.0 g, 53%).

### *Catalytic Conversion of Acetone Azine to 3,5,5-trimethyl-2-Pyrazoline*

$TiCl_3$ (0.1 g) was added to dry acetone azine (40 g). The mixture was heated with continuous magnetic stirring at an oil bath temperature of 100 °C over 20 h, and then distilled *in vacuo* (no fractionation necessary) to give 3,5,5-trimethyl-2-pyrazoline (36 g, 90%). The purity of the product was confirmed by g.l.c. analysis.

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