Hydrazine. Part VIII. Some Salts of* 3 : 5 : 5-*Trimethyl*-Δ^2-*pyrazoline and of* 3 : 5 : 5-*Trimethyl*-1-iso*propylidene*-Δ^2-*pyrazolinium Ion.*

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(*With Notes on the Optical Properties of the Crystals.* By H. C. G. Vincent.)

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Salts of 3 : 5 : 5-trimethylpyrazoline are shown to condense with acetone, in acidic media, forming salts of a new ion which contain the *iso*propylidene radical attached to the pyrazoline ring. It is suggested that condensation occurs at the site of the positively charged nitrogen atom. Chloro-, bromo-, and iodo-stannates, -platinates, -antimonites, and -bismuthites of both 3 : 5 : 5-trimethylpyrazoline and 3 : 5 : 5-trimethyl-1-*iso*propylidene-pyrazolinium ion are described and characterised.

Parts I, II, IV, and VI of this series have described a variety of salts of some new bases, *viz.*, ketazines and hydrazones, obtained by crystallisation of mixed halides of certain metals and hydrazine from ketone–water mixtures. The chlorostannate, the first salt described, was originally reported as a hydrazinium salt containing acetone of crystallisation, but, for reasons set out in Part VI (*loc. cit.*), it was later re-formulated as the salt of dimethyl ketazine.

Parts I and II (*locc. cit.*) also described a chlorostannate of 3 : 5 : 5-trimethylpyrazoline containing 2 mols. of acetone of crystallisation, and now, in view of the revised formulation of the hydrazinium salt (above), it has become necessary to re-examine the mode of attachment of acetone in this and in many other similar salts containing 3 : 5 : 5-trimethylpyrazoline now described.

These salts are now also shown to contain a new type of cation, a product of condensation of acetone with the 3 : 5 : 5-trimethylpyrazolinium ion. The reasons for this revised view are : (1) The acetone in these, as in the ketazinium salts, though readily removable by hydrolysis in aqueous media, is not removable by heating (the dry salts can be heated *in vacuo* to 110° without loss in weight). (2) The acetone recoverable by hydrolysis is, in every salt so far made, exactly 1 mole per mole of 3 : 5 : 5-trimethylpyrazoline present (thus, salts containing univalent anions, *e.g.*, chloroantimonites, yield 1 mole of acetone, and salts containing bivalent anions, *e.g.*, chloroplatinates, yield 2 moles of acetone per " mole " of salt—this strict stoicheiometry would be most fortuitous if the acetone were not condensed, mole for mole). (3) The analytical results for the original salt (the chlorostannate) being somewhat inconclusive at the time because the authors were then uncertain of the reliability of carbon and hydrogen values obtainable for compounds containing volatile metal halides, have now been shown, by extended experience in the analysis of ketazinium and hydrazonium salts containing tin, antimony, and bismuth halides, to have been reliable enough to indicate the complete absence of oxygen. Moreover, the estimated percentages of metal and halogen in this and other similar salts described below agree better with a formulation which implies condensation with elimin-

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* Parts I, II, IV, VI, VII, *J.*, 1952, 4138; 1953, 354, 2491, 3445; 1954, 1385.

ation of water. (4) The infra-red spectrum of the chlorostannate shows no indication of a band characteristic of the acetone carbonyl group (personal communication from Dr. P. C. Carman).

These facts then suggest very strongly that acetone is not present in these compounds as an adduct, and, in considering the actual site of condensation, it is suggested that, by analogy with hydrazine which condenses to the ketazinium ion (Part VI), 3 : 5 : 5-trimethylpyrazoline reacts with acetone in acid solution to form the 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium ion. It is realised that this is not the only possible site, but a large body of experimental evidence will be presented in Part IX (following paper) to show that this is the position where condensation occurs in the compounds herein described.

The present paper describes some new salts of 3 : 5 : 5-trimethylpyrazoline (chloro-, bromo- and iodo-stannates, -platinates, -antimonites, and -bismuthites) and corresponding salts containing the condensed ion. The two series of salts are readily interconvertible; condensation of acetone and 3 : 5 : 5-trimethylpyrazoline salts occurs with the greatest facility in acid solution, and the salts of 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium ion crystallise from aqueous acetone or from methanol–acetone solution; on the other hand, these salts lose acetone on long standing in, or on evaporation with, acids, and yield salts of 3 : 5 : 5-trimethylpyrazoline. If the acid ion is stable (chloro- and bromo-platinates) the salts give clear solutions in water, but tin, antimony, and bismuth complex salts are decomposed on dilution with water, yielding insoluble hydrated oxide or basic halide. They are insoluble in light petroleum, benzene, carbon tetrachloride, chloroform, and ether but readily soluble in alcohol and in aqueous acetone. They crystallise well when solutions in acetone–water (approx. 8 : 1) are evaporated slowly in partly covered vessels.

EXPERIMENTAL

The methods of analysis used were those reported in Part VI (*loc. cit.*). As there indicated, combustion analysis of compounds of tin, antimony, and bismuth gives values for carbon and hydrogen which are less reliable than values obtained by standard methods for halogens and metals.

General Method of Preparation.—Except where otherwise stated, salts containing the 3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium ion were made by crystallisation, from aqueous acetone, of mixtures of metal halide and 3 : 5 : 5-trimethylpyrazolinium chloride, in the required molar ratios. Concentrated solutions of the mixed salts were usually made in the corresponding acid, the minimum of acid being used to counter the tendency of the metal salts to hydrolyse, and the clear solutions were then poured into 4 or 5 vols. of acetone. The mixtures usually became warm. They were then set aside to evaporate at room temperature, good crystals being obtained by slow evaporation in partly covered vessels.

The salts of 3 : 5 : 5-trimethylpyrazoline were, in some cases, obtained by evaporation of the above salts with the appropriate acid, followed by crystallisation, or by evaporation with alcohol (undried) followed by precipitation with ether; in both processes, acetone is removed by hydrolysis; in other cases, they were made by simple crystallisation of acidified solutions of the mixed halides of metal and 3 : 5 : 5-trimethylpyrazoline; but, being generally very soluble, these salts were more difficult to crystallise from aqueous solution.

Preparation of 3 : 5 : 5-*Trimethylpyrazolinium Chloride.*—This salt has hitherto been prepared from the free base, made from the hydrazine salt of maleic acid and from dimethyl ketazine (Curtius and Forsterling, *Ber.*, 1894, **27**, 771), from mesityl oxide (Curtius and Wirsing, *J. pr. Chem.*, 1894, **50**, 531), and from mesitylnitrimine (Harries, *Annalen*, 1901, **319**, 233). For the work described here it was conveniently made as follows: dry acetone (100 c.c.) was boiled under reflux with hydrazine dihydrochloride (50 g.) until the salt passed completely into solution (3—4 hr.). About 80% of the acetone was then distilled off and the concentrated liquor was seeded. The crude product was washed several times with dry acetone, yielding prisms (30 g.), m. p. 175—176° (lit., 176—177°). Yields were lower when undried acetone was used.

The corresponding bromide was made, for use in the preparation of some of the bromo-salts described, by repeated evaporation of the chloride with hydrobromic acid, but the use of the bromide was later found to be unnecessary, the bromo- and iodo-salts crystallising in the pure state from solutions containing the chloride if sufficient hydrobromic acid and hydriodic acid, respectively, were present.

Bis-(3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium*) *Hexachlorostannate*.—Acetone (50 c.c.) containing stannic chloride (5 c.c., 0·042 mol.) was boiled under reflux for several hours with hydrazine dihydrochloride (9 g., 0·086 mol.), whereupon the latter passed slowly into solution and the deep red liquor deposited yellowish crystals (20 g.). The crude product contained tin and chlorine in the atomic ratio 1 to 6·0, but it was contaminated with traces of bis(dimethyl ketazinium) hexachlorostannate, as shown by titration with iodate (Andrews's method). It was therefore boiled under reflux with fresh acetone (50 c.c.), whereupon the residue (16 g.; m. p. 215—218°) became colourless. It was identical in composition with a small crop (1 g.), m. p. 217—219° (decomp.), obtained by crystallisation of the acetone liquor [Found : C, 33·5; H, 5·4; N, 8·9; Cl, 33·2; Sn, 18·5; C_3H_6O, 18·3. $(C_9H_{17}N_2)_2SnCl_6$ requires C, 33·8; H, 5·3; N, 8·8; Cl, 33·4; Sn, 18·6; C_3H_6O, 18·2%]. The same salt, *bis*-(3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium*) *hexachlorostannate*, was also obtained by adding acetone to a solution of stannic chloride (0·3 c.c.) and 3 : 5 : 5-trimethylpyrazolinium chloride (0·7 g.) in ethanol (10 c.c.) acidified with hydrochloric acid, the m. p. of this sample being raised to 221° (decomp.) by recrystallisation from methanol–acetone.

The crystals are orthorhombic (or monoclinic elongated parallel to *b*), with an elongated needle habit, and sometimes a rectangular pinacoidal habit, resembling cubes; colourless in sections and without cleavage. $Bx^a(\gamma)$ is parallel to the elongation. Positive. $2V(\gamma) = 30$—$35°$. Dispersion faint, red > violet. $n_D : \alpha = 1{\cdot}55;\ \gamma = 1{\cdot}673$.

The salt is not deliquescent and is stable for long periods in air. It suffers no loss in weight when heated for several hours *in vacuo* at 110° [which is one reason for discarding the original formulation of the salt as a chlorostannate of 3 : 5 : 5-trimethylpyrazoline with acetone of crystallisation; Part I, *loc. cit.*)]. It is insoluble in light petroleum, benzene, carbon tetrachloride, chloroform, and ether; sparingly soluble in ethanol and acetone; and more soluble in mixtures of acetone with alcohol or water. It dissolves in about its own weight of water, but diluted solutions slowly become turbid. Aqueous solutions, and solutions in dilute acids, yield yellow precipitates with 2 : 4-dinitrophenylhydrazine only after several minutes, indicating that acetone is liberated slowly by hydrolysis. Hydrolysis is, however, accelerated by heat, and when the salt is evaporated with hydrochloric acid the resulting solution contains bis-(3 : 5 : 5-trimethylpyrazolinium) hexachlorostannate, described below. Aqueous alkalis also cause hydrolysis, liberating acetone and the free base, 3 : 5 : 5-trimethylpyrazoline, which was recovered by ether extraction and identified.

Bis-(3 : 5 : 5-*trimethylpyrazolinium*) *Hexachlorostannate*.—One method of preparing this salt has already been described (Part I, *loc. cit.*). It has also been made from a sample of bis-(3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium) hexachlorostannate, by evaporation on a water-bath with dilute hydrochloric acid and crystallisation of the concentrated liquid, but it was most readily obtained by crystallisation of mixtures of stannic chloride (1 mol.) and 3 : 5 : 5-trimethylpyrazolinium chloride (2 mols.) from hot dilute hydrochloric acid. It forms needles and prisms, m. p. 198° (decomp.) [Found : C, 25·3; H, 4·8; N, 10·0; Cl, 38·2; Sn, 21·1. Calc. for $(C_6H_{13}N_2)_2SnCl_6$: C, 25·8; H, 4·7; N, 10·0; Cl, 38·2; Sn, 21·3%].

The crystals are biaxial, probably monoclinic, with a pronounced flaky habit and cleavage parallel to (010), and colourless in mounts. Positive. $2V(D) = 31°$. Dispersion imperceptible. $n_D :\ \alpha = 1{\cdot}569,\ \gamma = 1{\cdot}605,\ (\gamma - \alpha) = 0{\cdot}036$.

Its solubilities resemble those of the preceding salt. Its solutions in alcohol or water, treated with acetone, yield bis-(3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium) hexachlorostannate.

Bis-(3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium*) *Hexabromostannate*.—Tin (2 g., 0·017 g.-atom) was added in small pieces to an excess of well-cooled bromine, and when the metal had dissolved completely the excess of bromine was removed in a current of hot air. Acetone (30 c.c.), hydrobromic acid (48%; 1 c.c.), and hydrazine monohydrobromide (3·8 g., 0·033 mol.) were then added and the solution was boiled under reflux. After 4 hr., the liquid had become reddish and yellow cubes began to separate, but boiling was continued for 10 hr., and there then seemed to be no further increase in yield. The crude product (13 g.) was crushed and heated under reflux with fresh acetone for another hour, the residue (10 g.) consisting of yellow cubes, m. p. 216—218°, identical with a small crop (1 g.), m. p. 217—218° (decomp.), obtained by crystallisation of the acetone extract [Found : C, 24·1; H, 4·0; N, 5·8; Br, 52·9; Sn, 13·0; C_3H_6O, 13·3. $(C_9H_{17}N_2)_2SnBr_6$ requires C, 23·9; H, 3·8; N, 6·2; Br, 53·0; Sn, 13·1; C_3H_6O, 12·8%]. A similar *salt*, m. p. 216—217° (decomp.), was obtained when a methanol solution of bis-(3 : 5 : 5-trimethylpyrazolinium) hexabromostannate, described below, was treated with an excess of acetone and the mixture set aside for a few hours. The hexabromostannate is similar to the hexachlorostannate in its behaviour towards organic solvents and aqueous acids and alkalis. It is also stable in air and non-deliquescent. The crystals are lemon-yellow cubes, colourless in microscopic mounts. Pseudo-cubic(?); $n_D = 1{\cdot}656$. The crystals are essentially isotropic, but show fine patchy anisotropic lamellæ and cross hatching parallel to the cube faces.

Bis-(3 : 5 : 5-*trimethylpyrazolinium*) *Hexabromostannate*.—A sample of bis-(3 : 5 : 5-trimethyl-1-*iso*propylidenepyrazolinium) hexabromostannate was boiled with a large volume of ethanol, and the resulting solution evaporated to small bulk, cooled, and treated with ether. Yellow crystals separated, m. p. 193° [Found: C, 17·6; H, 3·1; Br, 58·1; Sn, 14·3. $(C_6H_{13}N_2)_2SnBr_6$ requires C, 17·5; H, 3·2; Br, 58·2; Sn, 14·4%]. The *salt* was also made by adding ether to a solution of stannic bromide and 3 : 5 : 5-trimethylpyrazolinium bromide in ethanol. The crystals are biaxial, in anhedral grains without cleavage, and colourless in mounts. Positive. $2V(D) = 80$—$85°$ (estimated). Dispersion is very strong, red > violet, giving anomalous interference colours. n_D: $\alpha = 1{\cdot}651$, $\gamma = 1{\cdot}660$, $(\gamma - \alpha) = 0{\cdot}009$.

Bis-(3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium*) *Hexachloroplatinate*.—This *salt* was made by the general method (see above) from chloroplatinic acid hexahydrate (2·6 g.), 3 : 5 : 5-trimethylpyrazolinium chloride (1·5 g.), and acetone (10 c.c.). The orange-yellow cubes decompose, becoming black, at about 170°, and melt, with rapid decomposition, at about 185°. (Halogen in this, and in the bromoplatinate, described below, was determined by the author's method, *J. Appl. Chem.*, 1954, 47) [Found: C, 29·6; H, 4·6; Cl, 29·9; Pt, 27·3; C_3H_6O, 16·4. $(C_9H_{17}N_2)_2PtCl_6$ requires C, 30·1; H, 4·8; Cl, 29·8; Pt, 27·3; C_3H_6O, 16·2%]. The crystals are probably cubic, or pseudo-cubic, the cubes being often modified by small faces of the (110) and other forms. Symmetry appears to be cubic. Cleavage is absent, and the crystals are light yellowish-brown in mounts. They show distinct but low birefringence, in patches and irregular areas which cannot be resolved, giving rise to undulose extinction; they give no decipherable convergent light figure. $n_D = 1{\cdot}646$ (approx.).

Bis-(3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium*) *Hexabromoplatinate*.—Chloroplatinic acid hexahydrate (2·6 g.) and 3 : 5 : 5-trimethylpyrazolinium chloride (1·5 g.) were evaporated separately and repeatedly with hydrobromic acid and the resulting syrups were taken up in acetone and mixed. The dark liquid yielded dark red cubes which blacken at about 200° and melt at 219° with vigorous decomposition [Found: C, 21·7; H, 3·3; Br, 49·0; Pt, 19·9. $(C_9H_{17}N_2)_2PtBr_6$ requires C, 22·0; H, 3·5; Br, 48·9; Pt, 19·9%]. The crystals are probably cubic. They are isotropic, with a simple cubic habit. Cleavage is absent, and the crystals are brownish-red to yellow in mounts, and without pleochroism. $n_D = 1{\cdot}726$.

3 : 5 : 5-*Trimethyl*-1-iso*propylidenepyrazolinium Tetrachloroantimonite*.—The general method of preparation (see p. 2424) was used, and the crude product was recrystallised from acetone acidified with hydrochloric acid. The colourless needles or prisms contained acetone of crystallisation (Found: C, 27·3; H, 4·2; Cl, 32·5; Sb, 27·9; C_3H_6O, 17·4. $3C_9H_{17}N_2SbCl_4,C_3H_6O$ requires C, 27·5; H, 4·4; Cl, 32·6; Sb, 27·9; C_3H_6O, 17·7%). (The acetone determined is the total liberated on hydrolysis.) The *salt* has no sharp m. p., partial melting occurring at 60°, clearing at 80°. (Bubbles of vapour, probably acetone of crystallisation, are emitted within, and above, the melting range.) It loses all its acetone of crystallisation when heated to constant weight at 78°/20 mm. (Found: loss, 5·0. Required: loss, 4·5%), the product being pure 3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium tetrachloroantimonite*, m. p. 84—85° (Found: C, 26·2; H, 4·3; Cl, 34·2; Sb, 29·2. $C_9H_{17}N_2SbCl_4$ requires C, 25·9; H, 4·1; Cl, 34·2; Sb, 29·3%).

3 : 5 : 5-*Trimethylpyrazolinium Tetrachloroantimonite*.—Crystallisation of a solution containing antimony trioxide (3 g.) and 3 : 5 : 5-trimethylpyrazolinium chloride (3 g.) in the minimum of hot, 6N-hydrochloric acid (15 c.c.) yielded large rods or prisms, m. p. 55—56°, of the *hydrate* (Found: C, 17·8; H, 3·6; Cl, 36·1; Sb, 30·8. $C_6H_{13}N_2SbCl_4,H_2O$ requires C, 18·2; H, 3·8; Cl, 36·0; Sb, 30·8%). The crystals are probably monoclinic, being elongated, simply modified, pinacoidal rods, with distinct cleavage parallel to the rods. They are colourless. The extinction angle is about 15°. Positive. $2V(D) = 29°$. Dispersion perceptible, red > violet. n_D: $\alpha = 1{\cdot}595$, $\beta = 1{\cdot}601$, $\gamma = 1{\cdot}688$, $(\gamma - \alpha) = 0{\cdot}093$.

The hydrated salt loses water rapidly at 100° (Found: loss, 4·5. Required: loss, 4·6%) and, in air at 100°, there is a further small loss, probably of hydrogen chloride, by hydrolysis. A sample kept at 100° for 8 hr. in air lost 6·4% in weight, giving the impure anhydrous salt (Found: Cl, 37·2; Sb, 32·8. Calc. for $C_6H_{13}N_2SbCl_4$: Cl, 37·7; Sb, 32·4%).

3 : 5 : 5-*Trimethyl*-1-iso*propylidenepyrazolinium Tetrabromoantimonite*.—This solvated *salt* was made by the general method (see p. 2424) from antimony oxide, hydrobromic acid, 3 : 5 : 5-

trimethylpyrazolinium chloride, and acetone, and was recrystallisated from acetone containing 10% of hydrobromic acid. The yellow plates contained acetone of crystallisation (Found: C, 19·4; H, 3·1; Br, 52·1; Sb, 19·8; C_3H_6O, 12·8. $3C_9H_{17}N_2SbBr_4,C_3H_6O$ requires C, 19·5; H, 3·1; Br, 52·1; Sb, 19·8; C_3H_6O, 12·6%). The crystals are biaxial, poorly developed, equidimensional forms with some tendency to platy habit; they have no cleavage and are colourless in mounts. Orientation uncertain, the salt being unstable in available immersion liquids. Positive. $2V$ about 75°. Dispersion imperceptible. n_D: β, 1·72 (approx.). Birefringence very high.

The salt does not melt sharply; plastic flow occurs at 78°, vapour bubbles being emitted more rapidly as the temperature rises, and the melt clears at 87°. It loses its acetone of crystallisation when heated at 78°/20 mm. (Found: loss, 3·6. Required: loss, 3·1%), yielding 3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium tetrabromoantimonite*, m. p. 94—95° (Found: C, 18·2; H, 2·9; Br, 53·7; Sb, 20·6. $C_9H_{17}N_2SbBr_4$ requires C, 18·2; H, 2·9; Br, 53·7; Sb, 20·5%).

3 : 5 : 5-*Trimethylpyrazolinium Tetrabromoantimonite.*—This *salt* crystallises anhydrous from solutions containing antimony oxide and 3 : 5 : 5-trimethylpyrazolium chloride, in the required proportions, in excess of hydrobromic acid. It separates as large yellow prisms or rods, m. p. 66—67° (Found: C, 12·7; H, 2·6; Br, 57·6; Sb, 21·8. $C_6H_{13}N_2SbBr_4$ requires C, 13·0; H, 2·3; Br, 57·7; Sb, 22·0%). The crystals are probably monoclinic, being stout, simply modified, prismatic and pinacoidal forms, with some tendency to elongation, and without cleavage. Colourless in mounts. The optic axial plane is parallel to the elongation direction and is probably parallel to (010). Oblique extinction of about 10°. Positive. $2V(\gamma) = 46°$. Dispersion marked, red > violet. n_D: $\alpha = 1·750$, $\beta = 1·763$, $\gamma > 1·84$. Birefringence near 0·1.

3 : 5 : 5-*Trimethyl*-1-iso*propylidenepyrazolinium Tetraiodoantimonite.*—This *salt* is less soluble and crystallises more readily than the bromo- and chloro-analogues. It was obtained from a solution containing antimony iodide (1 g.), potassium iodide (0·3 g.), hydriodic acid (0·5 c.c.), 3 : 5 : 5-trimethylpyrazolinium chloride (0·3 g.), and acetone (10 c.c.) and was recrystallised from acetone–water (4 : 1) (Found: C, 14·2; H, 2·1; I, 65·0; Sb, 15·7. $C_9H_{17}N_2SbI_4$ requires C, 13·8; H, 2·2; I, 65·0; Sb, 15·6%). The crystals, m. p. 159°, are orange, orthorhombic (or monoclinic, elongated parallel to *b*), generally in irregular grains, but sometimes showing an elongated and platy habit. Cleavage is absent; reddish-yellow in mounts. $Bx^a(\gamma)$ is parallel to the elongation direction. Positive. $2V(D) = 60—65°$ (estimated). Dispersion faintly perceptible, red > violet. Pleochroism marked, maximum absorption γ (reddish-brown), α (yellow). n_D: $\alpha > 1·84$. Birefringence moderate.

3 : 5 : 5-*Trimethyl*-1-iso*propylidenepyrazolinium Tetrachlorobismuthite.*—Large, colourless, crystals of this *salt*, m. p. 156°, were obtained by the general method (Found: C, 21·2; H, 3·4; Cl, 28·2; Bi, 41·6; C_3H_6O, 11·0. $C_9H_{17}N_2BiCl_4$ requires C, 21·4; H, 3·4; Cl, 28·2; Bi, 41·5; C_3H_6O, 11·5%). The crystals are monoclinic, poorly developed, stout, pinacoidal forms with a tendency to elongation and with no pronounced cleavage. The optic axial plane is normal to (010). Positive. $2V(\gamma) = 22°$. Axial dispersion rather marked, red > violet, giving anomalous interference colours and incomplete extinction for Bx^a and optic axis sections. n_D: $\alpha = 1·644$, $\beta = 1·648$, $\gamma = 1·710$, $(\gamma - \alpha) = 0·066$.

3 : 5 : 5-*Trimethylpyrazolinium Tetrachlorobismuthite.*—This *salt* is exceedingly soluble and was obtained by slow evaporation, over sulphuric acid, of a solution containing bismuth oxychloride (5·2 g.) and 3 : 5 : 5-trimethylpyrazolinium chloride (3 g.) in concentrated hydrochloric acid (8 c.c.) (Found: C, 15·4; H, 2·8; Cl, 30·7; Bi, 45·1. $C_6H_{13}N_2BiCl_4$ requires C, 15·5; H, 2·8; Cl, 30·6; Bi, 45·0%). The crystals are orthorhombic or monoclinic (elongated parallel to *b*), with flaky, lath-shaped habit. Colourless in mounts. The optic axial plane is parallel to the elongation. Negative. $2V(\alpha)$ large, dispersion perceptible. Length positive. n_D (approx.): $\alpha = 1·650$, $\gamma = 1·775$, $(\gamma - \alpha) = 0·125$.

3 : 5 : 5-*Trimethylpyrazolinium Tetrabromobismuthite.*—Crystallisation, from hydrobromic acid solutions, of mixtures of bismuth bromide and 3 : 5 : 5-trimethylpyrazolinium chloride yielded stout, pinacoidal, yellow crystals of the *monohydrate* (Found: C, 11·0; H, 2·3; Br, 48·6; Bi, 31·6. $C_6H_{13}N_2BiBr_4,H_2O$ requires C, 10·9; H, 2·3; Br, 48·5; Bi, 31·7%). It loses the water of crystallisation slowly and completely at 105°, yielding the anhydrous *salt*, m. p. 170—171° (Found: C, 10·9; H, 2·0; Br, 50·1; Bi, 32·7. $C_5H_{13}N_2BiBr_4$ requires C, 11·2; H, 2·0; Br, 50·0; Bi, 32·6%). The crystals of the monohydrate are monoclinic, stout, modified elongated pinacoidal forms, pale yellow in mounts. Cleavage is distinct, parallel to the elongation. The optic axial plane is perpendicular to (010) and $Bx^a(\gamma)$ is inclined at about 25°

to the elongation direction. Positive. $2V(D) = 50—60°$ (estimated). Dispersion is very strong, red < violet, giving anomalous interference colours. n_D: β, slightly greater than 1·8 (the crystals are attacked by immersion liquids). Birefringence high.

3 : 5 : 5-*Trimethyl*-1-iso*propylidenepyrazolium Tetrabromobismuthite*.—Mixtures of bismuth bromide (2 mols.) and 3 : 5 : 5-trimethylpyrazolinium chloride or bromide (1 mol.) (see below), crystallised by the general method, yielded yellow crystals of the above *salt* (solvated) (Found: C, 17·3; H, 2·8; Br, 45·6; Bi, 29·7. $3C_9H_{17}N_2BiBr_4,C_3H_6O$ requires C, 17·1; H, 2·7; Br, 45·6; Bi, 29·8%). The crystals lose acetone slowly in air but rapidly at 78°/20 mm. (Found: loss, 2·7. Required: loss, 2·8%), and when heated in a m. p. tube, they emit bubbles of vapour at about 100°, melt partially at about 130° and finally at 149°. The crystals are biaxial, in anhedral grains, with no cleavage, and colourless in mounts. (The surface of the crystals undergoes decomposition to another substance—loss of acetone.) Positive. $2V(D) = 79°$. Dispersion very strong, red < violet, with anomalous interference colours. n_D: $\alpha = 1·721$, $\beta = 1·760$, γ not determined, because the crystals are attacked by immersion liquids.

The acetone-free *salt*, m. p. 149°, was obtained by heating the above salt at 78°/20 mm. (Found: C, 16·3; H, 2·5; Br, 47·0; Bi, 30·6. $C_9H_{17}N_2BiBr_4$ requires C, 15·8; H, 2·5; Br, 46·9; Bi, 30·6%).

When mixtures containing equimolar proportions of the salts were crystallised from aqueous acetone, the crystals had an entirely different composition. Many preparations were made and, though there were very small variations in composition, determinations of the optical properties of the samples showed them to be identical, the values for Br and Bi suggesting a double *salt* of the above acetone-free salt with 3 : 5 : 5-trimethylpyrazolinium bromide (Found: C, 21·0; H, 3·3; Br, 46·0; Bi, 25·8. $3C_9H_{17}N_2BiBr_4,2C_6H_{13}N_2Br$ requires C, 19·3; H, 3·2; Br, 46·1; Bi, 25·8%). The crystals are monoclinic, in laths and needles, or stout prismatic forms, with domes and pinacoids. They have a conchoidal fracture. Colourless in mounts. The optic axial plane is normal to (010), giving a maximum extinction angle of about 35° to the elongation direction. Negative. $2V(\alpha) = 86°$. Axial dispersion marked, red > violet. n_D: $\alpha = 1·715$, $\beta = 1·736$, $\gamma = 1·771$, $(\gamma - \alpha) = 0·056$.

3 : 5 : 5-*Trimethyl*-1-iso*propylidenepyrazolinium Tetraiodobismuthite*.—The various attempts to prepare this salt also indicate the existence of a double *salt* similar to the above bromo-salt. Mixtures, in equimolecular proportions, of bismuth iodide and 3 : 5 : 5-trimethylpyrazolinium chloride, dissolved in aqueous acetone, with the aid of hydriodic acid and potassium iodide, gave scarlet prisms, m. p. 186—188° (Found: C, 16·0; H, 2·4; I, 57·5; Bi, 20·4. $3C_9H_{17}N_2BiI_4,2C_6H_{13}N_2I$ requires C, 15·2; H, 2·5; I, 57·5; Bi, 20·3%). The crystals are monoclinic or triclinic, with poorly developed faces, occasionally with a platy, diamond-shaped habit. They are deep brownish-red to orange-red in mounts, and have no pronounced cleavage. The optic axial plane, which lies along the longer diagonal of the plates, is nearly perpendicular to their surface, which gives a near centred optic axis figure. Positive. $2V = 80°$ (approx.). Dispersion is weak, red < violet. Pleochroism imperceptible. n_D of α is much above 1·84. Birefringence low.

When an excess of bismuth iodide was used for the preparation (*e.g.*, 2 mols.) dark red crystals of 3 : 5 : 5-*trimethyl*-1-iso*propylidenepyrazolinium tetraiodobismuthite*, without acetone of crystallisation, were obtained, m. p. 171—172° (recrystallised from warm acetone) (Found: C, 12·4; H, 1·8; I, 58·7; Bi, 24·2. $C_9H_{17}N_2BiI_4$ requires C, 12·4; H, 1·9; I, 58·5; Bi, 24·0%). The crystals are monoclinic or triclinic, with a stout and somewhat elongated habit; they have no cleavage and are deep red in mounts. The orientation is uncertain. The optic axial plane is inclined to the elongation direction, giving a maximum extinction angle of 25° (approx.). Positive. $2V(D) = 65°$ (estimated). Dispersion not apparent. Pleochroism distinct; α, orange red; γ, deep red. n_D of α is much above 1·84. Birefringence moderate.

Combustion analyses were by Mr. R. von Holdt, and acetone determinations by Mr. M. C. B. Hotz.

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