NOTES.

A Supposed Anomaly among the Plato-tetrammines. By H. D. K. DREW and G. H. WYATT.

A MIXED plato-tetrammine of the type $[Pta_2b_2]Cl_2$ should exist in only two forms, but in the single case of $[Pt(NH_3)_2dm_2]Cl_2$, where dm = dimethylamine, Jörgensen (*Z. anorg. Chem.*, 1906, **48**, 374) described two distinct β-forms, in addition to the usual α-form; one (A) was prepared by the addition of dimethylamine to β-$Pt(NH_3)_2Cl_2$, and the other (B) by the addition of ammonia to β-$Ptdm_2Cl_2$. Form A occurred in large, clear plates, and B only in crystalline aggregates. Aqueous solutions of A gave with potassium chloroplatinite a carmine-red plato-salt, crystallising with $1H_2O$; whereas freshly made aqueous solutions of B gave an anhydrous buff-coloured plato-salt. After being kept, solutions of B gave only the red plato-salt, which, however, changed into the other salt on standing under the mother-liquor. Both plato-salts gave the red form when recrystallised; and, moreover, both tetrammines gave the same mixed diamine dibromide, $Pt(NH_3)dmBr_2$, when degraded by means of hydrobromic acid.

We now find that there is only one form of the β-tetrammine, and that this gives either the hydrated or the anhydrous plato-salt according to experimental conditions, temperature and acidity being the determining factors. We suggest that failure to control these, together with the presence of a trace of impurity in Jörgensen's less well-defined tetrammine (B), account for his results, some of which we were unable to repeat.

EXPERIMENTAL.

(The red plato-salt is referred to as A′, and the buff salt as B′.)

β-$Ptdm_2Cl_2$, prep. from aq. $NHMe_2$ and K_2PtCl_4 at room temp. for 6 hr., forms yellow plates or needles when recryst. from H_2O (yield 75%) (Found: Pt, 54·8. Calc.: Pt, 54·8%); it gives practically no coloration with phenoxtellurine dibisulphate.

β-$[Pt(NH_3)_2dm_2]Cl_2$, prep. by dissolving β-$Pt(NH_3)_2Cl_2$ in $NHMe_2$ aq. at room temp. (10—14 days) (yield nearly quant.), forms a syrup on spontaneous evaporation; dried over P_2O_5 and recryst. from aq. EtOH, it forms colourless square prisms or hexagonal needles (Found: Pt, 49·7, 49·6, 49·8. Calc. for $C_4H_{20}N_4Cl_2Pt$: Pt, 50·0%). No difference could be detected between this specimen and that similarly obtained from the foregoing diammine; and neither showed any change when kept in aq. solution during 10 days. Both specimens behaved in the same manner towards K_2PtCl_4 whether they were freshly prep., recryst., or had been kept in the solid state or in solution. The plato-salt, β-$[Pt(NH_3)_2dm_2]PtCl_4$, thus obtained was B′ if the solution was strongly acid with HCl and A′ if it was neutral or faintly acid.

The red form (A′) occurs as bundles of slender needles (Found, in various samples: Pt, 57·5, 57·5, 57·4, 57·6, 57·5, 57·4, 57·8. Calc. for monohydrate: Pt, 57·7%), and the buff form (B′) as domed prisms with well-defined faces (Found: Pt, 58·7, 59·3, 59·5. Calc. for anhyd. salt: Pt, 59·5%). Both forms gave identical black colorations with phenoxtellurine dibisulphate. The following successive analyses relate to a sample of A′ as it gradually changed in air into B′: Pt, 57·0, 57·3, 58·6, 59·5%.

When kept in a desiccator, B′ is stable, but A′ slowly changes into it. Similarly, under the mother-liquor, A′ slowly changes into B′ in the more acid solutions, and the same change occurs under distilled water at room temp. but not at 0°. Recrystn. from moderately conc. acid yielded B′, but from H_2O gave A′.

Attempts to test whether a sat. solution of A′ would dissolve B′ were rendered indecisive by the transformation. For the same reason, regeneration of the tetrammino-chloride by heating each salt with 1 equiv. of $[Pt(NH_3)_4]Cl_2$ aq. afforded no information, but the mixed tetrammine so obtained from the A′ salt showed the same behaviour towards K_2PtCl_4 aq. as did the specimen prepared directly.

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The Nitration of p-*Dimethylaminoacetanilide by Nitrous Acid.* By H. H. HODGSON and J. H. CROOK.

p-DIMETHYLAMINOACETANILIDE [m. p. 132°; Auwers and Wehr, *Annalen*, 1904, **344**, 311, give m. p. 130°; *picrate*, light yellow micro-plates, m. p. 224° (Found: N, 17·4. $C_{16}H_{17}O_8N_5$ requires N, 17·2%)], when subjected to the procedure of Hodgson and Kershaw (J., 1930, 27), gave a trace of an Nnitroso-compound (m. p. 146°) and almost 100% of 3-*nitro*-p-*dimethylamino-acetanilide*, maroon parallelepipeds, m. p. 132° (Found: N, 18·9. $C_{10}H_{13}O_3N_3$ requires N, 18·8%); *hydrochloride*, colourless parallelepipeds, m. p. 180° (decomp.) (Found: N, 16·4; Cl, 13·5. $C_{10}H_{13}O_3N_3,HCl$ requires N, 16·2; Cl, 13·7%); *picrate*, orange plates, m. p. 172° (Found: N, 18·8. $C_{16}H_{16}O_{10}N_6$ requires N, 18·6%); *chloropicrate*, lemon-yellow rectangular plates, m. p. 149° (Found: Cl, 7·1. $C_{10}H_{15}O_{10}N_6Cl$ requires Cl, 7·3%). 3-Nitro-*p*-dimethylaminoacetanilide was synthesised by heating on the water-bath for 6 hr. a mixture of 4-chloro-3-nitroacetanilide (1·4 g.) and $NHMe_2$ (0·9 c.c. in 20 c.c. EtOH). Group inhibition of the displacement of an *N*-Me group by nitrous acid appears to be in the order NHAc$>$OMe$>$Me.

Although HNO_3 at equiv. dilution is inactive (*loc. cit.*), *p*-dimethylamino-acetanilide (1·8 g.), when dissolved in conc. H_2SO_4 (10 c.c.) and treated at 0° with HNO_3 (0·4 c.c.; *d* 1·5) in conc. H_2SO_4 (5 c.c.), yields 2-*nitro*-p-*dimethylaminoacetanilide*, deep red needles, m. p. 116° (Found: N, 19·0%); *picrate*, lemon-yellow hexagonal plates, m. p. 185° (Found: N, 18·9%); *chloropicrate*, long greenish-yellow parallelepipeds, m. p. 184° (Found: Cl, 7·2%). On hydrolysis, 3-*nitro*-4-*aminodimethylaniline* is obtained, deep red needles, m. p. 112° (Found: N, 23·4. $C_8H_{11}O_2N_3$ requires N, 23·2%); *picrate*, green-yellow micro-prisms, m. p. 205° (Found: N, 20·7. $C_{14}H_{14}O_9N_6$ requires N, 20·5%); *chloropicrate*, green-yellow needles, m. p. 204° (Found: Cl, 8·1. $C_{14}H_{13}O_9N_6Cl$ requires Cl, 8·0%). It is noteworthy that monopicrates and not dipicrates are formed.

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