XIV.—*The Metallic Picrates.*

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THE present investigation was rendered necessary by the numerous discrepancies between the statements of previous workers as to the composition and properties of the metallic picrates. In many instances the older data have had to be corrected.*

The metallic salts were, in general, prepared by bringing together picric acid and the carbonate of the metal in question, and evaporating the solution until the crystals appeared on cooling. The chief difficulty encountered is due to the rapidity with which the crystals alter in the air.

Lithium Picrate.

Beamer and Clark obtained the anhydrous salt from alcoholic solution. No hydrated salts appear to have been prepared.

Tetrahydrate, $C_6H_2(NO_2)_3 \cdot OLi, 4H_2O$.—This is obtained by mixing

* In order to avoid repetition, the references used throughout the present paper are collected together in the following lists, and the authors are referred to only by name in dealing with their work on the various salts:

Welter, *Ann. Chim. Phys.*, 1795, [i], **29**, 301; *Scher. Jour.*, 1800, **3**, 715; Chevreul, *Ann. Chim. Phys.*, 1809, [i], **72**, 113; Hatchett, *Gehl. Ann.*, 1803, **1**, 369; Fourcroy and Vauquelin, *Gehl. Ann.*, 1804, **2**, 231; Liebig, *Schweig. Jour.*, 1827, **49**, 373; *Pogg. Ann.* 1828, **13**, 191; *Ann. Chim. Phys.*, 1827, [ii], **35**, 72; 1828, **37**, 286; Miller, *Pogg. Ann.*, 1835, **36**, 478; Rose, *Pogg. Ann.*, 1840, **49**, 186; Dumas, *Ann. Chim. Phys.*, 1836, [ii], **63**, 265; 1841, **2**, 204; *J. pr. Chem.*, 1841, **24**, 218; *Annalen*, 1841, **39**, 353; Marchand, *J. pr. Chem.*, 1841, **23**, 363; 1844, **32**, 35; *Annalen*, 1843, **48**, 336; 1844, **52**, 345; Schunck, *Annalen*, 1841, **39**, 7; Laurent, *Ann. Chim. Phys.*, 1841, [iii], **3**, 221; *J. pr. Chem.*, 1842, **25**, 427; *Rev. Scient.*, **9**, 26; *Annalen*, 1842, **43**, 219; Kopp, *Ann. Chim. Phys.*, 1845, [iii], **13**, 233; Rieckher, *Arch. Pharm.*, 1845, [ii], **44**, 158; Stenhouse, *Annalen*, 1846, **57**, 88; *J. pr. Chem.*, 1846, **39**, 221; *Journ. Chem. Soc.*, 1868, **21**, 150; Cahours, *Ann. Chim. Phys.*, 1849, [iii], **25**, 26; *J. pr. Chem.*, 1849, **46**, 337; Schabus, *Jahresber.*, 1850, 392; Moretti, compare Gmelin's *Handbuch de Chemie*, 1852, Bd. v, 685; Carey Lea, *Silliman's Journ.*, 1858, **26**, 379; 1860, **30**, 402; 1861, **31**, 78; *Chem. Gaz.*, 1859, 1; *Rep. Chim. pure.*, 1859, **1**, 227; von Rath, *Pogg. Ann.*, 1860, **110**, 114; Kuhlmann, *Annalen*, 1863, **126**, 78; *Bull. Soc. chim.*, 1864, [ii], **1**, 330; *Jahresber.*, 1864, 254; Böttger, *Jahresber. Phys. Vereins. Frankfurt*, 1865, **66**, 56; *Jahresber.*, 1866, 860; Müller, *Zeitsch. für Chem.*, 1865, 189; *Pogg. Ann.*, 1865, **124**, 103; Müller and Stenhouse, *Jahresber.*, 1866, 580; *Quart. Journ. Chem. Soc.*, 1866, **4**, 235; Frisch, *J. pr. Chem.*, 1867, **100**, 229; *Jahresber.*, 1867, 622; Lossen, *Annalen*, 1868, *Suppl.*, **6**, 233; Post and Mehrrens, *Ber.*, 1875, **8**, 1552; Beamer and Clarke, *Ber.*, 1879, **12**, 1068; Reyehler, *Ber.*, 1884, **17**, 2264; Tschelzoff, *Ann. Chim. Phys.*, 1886, [vi], **8**, 233; v. Rothenberg, *Ber.*, 1894, **27**, 690; Varet, *Ann. Chim. Phys.*, 1896, [vii], **8**, 130; Hantzsch and Auld, *Ber.*, 1906, **39**, 1105; Cook, *J. Amer. Chem. Soc.*, 1906, **28**, 613.

equivalent quantities of lithium carbonate and picric acid and allowing the aqueous solution to evaporate slowly at the ordinary temperature. It crystallises in yellow, prismatic needles, which gradually pass into the monohydrate with separation of water even when kept in atmosphere saturated with moisture :

Found, $N = 13.77$.

$C_6H_2O_7N_3Li \cdot 4H_2O$ requires $N = 13.71$ per cent.

The *monohydrate*, $C_6H_2(NO_2)_3 \cdot OLi, H_2O$, is obtained when the tetrahydrate is allowed to stand (preparation I) or, more rapidly when heated to 80° (preparation II). It is also formed when a hot concentrated solution of the salt in water is allowed to cool rapidly (preparation III), and when the anhydrous salt is exposed to air under ordinary conditions (preparation IV) or in an atmosphere 75 per cent. saturated with moisture at 25° (preparation V) :

Found, $N = (I) 16.90$; $(II) 16.55$; $(III) 16.46$. $H_2O = (I) 6.84$; $(II) 6.85$.

$C_6H_2O_7N_3Li, H_2O$ requires $N = 16.64$; $H_2O = 7.12$ per cent.

Loss of weight on exposing tetrahydrate to a temperature of 80° :

Found, (a) 17.91 ; (b) 18.07 .

$C_6H_2O_7N_3Li, 4H_2O$ requires (for a loss of $3H_2O$) 17.60 per cent.

Increase in weight on exposing anhydrous salt to air :

Found, (IV) 7.52 ; (V) 7.57 .

$C_6H_2O_7N_3Li$ requires for $1H_2O$ an increase of 7.66 per cent.

The monohydrate is obtained in dark orange-yellow, rhombic crystals by rapidly cooling a saturated solution, or by allowing the tetrahydrate to stand. When prepared by the other methods, it is a dark yellow powder.

The *anhydrous* salt, $C_6H_2(NO_2)_3 \cdot OLi$, is obtained by exposing either of the foregoing salts to a temperature of 150° :

Found, $N = 16.46$.

$C_6H_2O_7N_3Li$ requires $N = 16.64$ per cent.

The salt is a pale yellow powder which rapidly re-absorbs one molecule of water. It explodes with moderate violence at $318-323^\circ$.*

Sodium Picrate.

Previous workers—Liebig, Marchand, Schunck, Rieckher, Cahours.

This salt has generally been thought to be anhydrous ; the present

* The ignition points of these salts were determined by dropping a small quantity of the anhydrous compound into a tube heated in a metallic bath ; the ignition point given is the temperature at which ignition occurs within two seconds of the time of introducing the salt into the tube.

work has shown, however, that it crystallises with one molecule of water.

The *monohydrate*, $C_6H_2(NO_2)_3 \cdot ONa, H_2O$, crystallises from a hot aqueous solution in small, yellow needles (preparation I).

It is also produced as a yellow powder when the anhydrous salt is exposed to an atmosphere saturated with moisture to the extent of 75 per cent. at 25° (preparation II) :

Found, $N = (I) 15.76$; $(Ia) 15.50$; $(Ib) 15.52$. $H_2O = (I) 6.10$; $(Ia) 6.62$; $(Ib) 6.51$.

$C_6H_2O_7N_3Na, H_2O$ requires $N = 15.65$; $H_2O = 6.69$ per cent.

Increase of weight on exposing anhydrous salt to a moist atmosphere (preparation II) = 7.38 :

$C_6H_2O_7N_3Na$ requires for $1H_2O$ an increase of 7.17 per cent.

The *anhydrous* salt, $C_6H_2(NO_2)_3 \cdot ONa$, is obtained by exposing the monohydrate to a temperature of 150° :

Found, $N = 16.80$.

$C_6H_2O_7N_3Na$ requires $N = 16.77$ per cent.

The salt is a pale yellow powder, which explodes feebly at $310-315^\circ$.

Potassium Picrate, $C_6H_2(NO_2)_3 \cdot OK$.

Previous workers—Welter, Chevreul, Fourcroy and Vauquelin, Liebig, Müller, Dumas, Marchand, Schunck, Laurent, Kopp, Rieckher, Stenhouse, Cahours, Schabus, Frisch, Post and Mehrstens.

The analytical data given by these authors agree, in general, in showing the salt to be anhydrous. This is confirmed by the present work :

Found, $N = 15.47$.

$C_6H_2O_7N_3K$ requires $N = 15.76$ per cent.

The salt crystallises from an aqueous solution in yellow, iridescent, prismatic needles. It explodes with moderate violence at $311-316^\circ$.

Rubidium Picrate, $C_6H_2(NO_2)_3 \cdot ORb$.

This salt has apparently not previously been prepared. It crystallises from water in anhydrous yellow needles :

Found, $N = 13.67$.

$C_6H_2O_7N_3Rb$ requires $N = 13.43$ per cent.

It explodes with moderate violence at $300-315^\circ$.

Cæsium Picrate, $C_6H_2(NO_2)_3 \cdot OCs$.

This salt also has apparently not been previously prepared. It crystallises from water in anhydrous, yellow needles :

Found, N = 11.89.

$C_6H_2O_7N_3Cs$ requires N = 11.67 per cent.

It explodes with moderate violence at 272—277°.

Ammonium Picrate, $C_6H_2(NO_2)_3 \cdot ONH_4$.

Previous workers—Chevreul, Hatchett, Liebig, Rose, Dumas, Marchand, Schunck, Laurent, Kopp, Cahours, Reychler.

All these authors agree as to the absence of water of crystallisation. Liebig and Cahours both recognise the existence of a yellow and red variety of the salt. These observations have been confirmed in the present work. The salts were obtained by the action of ammonia or ammonium carbonate on picric acid, the latter method being more liable to give rise to the red variety :

Found, N = (red variety) 22.71 ; (yellow variety) 22.70.

$C_6H_6O_7N_4$ requires N = 22.81 per cent.

On heating, both modifications volatilise without detonation.

Hydrazine Monopicrate, $C_6H_2(NO_2)_3 \cdot OH, N_2H_4$.

Previous worker—Rothenberg.

This author's analysis agrees with the above formula, which has been confirmed in the present work :

Found, N = 26.70 ; 26.80.

$C_6H_7O_7N_5$ requires N = 26.87 per cent.

The salt crystallises in orange needles, which, on heating, volatilise without explosion.

Silver Picrate, $C_6H_2(NO_2)_3 \cdot OAg$.

Previous workers—Chevreul, Liebig, Dumas, Marchand, Schunck, Laurent, Rieckher, Stenhouse, Cahours, Carey Lea, Müller and Stenhouse, Post, and Mehrstens.

The analytical data given points in most cases to the absence of water of crystallisation ; in other cases, however (Marchand, Laurent, Post and Mehrstens), the presence of one molecule of water is indicated.

For the present work, silver picrate was obtained by dissolving silver oxide in a hot saturated solution of picric acid. The salt separated on cooling in yellow needles, which contained no water of crystallisation :

Found, N = 12.45.

$C_6H_2O_7N_3Ag$ requires N = 12.53 per cent.

The compound exploded feebly at 336—341°.

Cupric Picrate.

Previous workers—Liebig, Marchand, Müller, Tschelzoff, Carey Lea.

Marchand obtained a mixture of the normal salt with a basic salt, and removed the latter by extraction with alcohol. His analysis of the normal salt corresponded with a pentahydrate which lost four molecules of water at 110° . Müller obtained analytical data which corresponded approximately with $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cu}, 10\frac{1}{2}\text{H}_2\text{O}$.

Tschelzoff described an octahydrate. The present work has not confirmed any of the data.

Undecahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cu}, 11\text{H}_2\text{O}$.—This salt is deposited, on cooling, from a hot concentrated solution in large, green prisms:

Found, $\text{N} = 11.85$. $\text{H}_2\text{O} = 27.84$; 27.76 .

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Cu}, 11\text{H}_2\text{O}$ requires $\text{N} = 11.73$; $\text{H}_2\text{O} = 27.60$ per cent.

The *tetrahate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cu}, 4\text{H}_2\text{O}$, is obtained as a greenish-yellow powder when the anhydrous salt is exposed to an atmosphere saturated with moisture to the extent of 75 per cent. at 25° .

The anhydrous salt absorbed $\text{H}_2\text{O} = 13.55$:

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Cu}$ requires increase of $4\text{H}_2\text{O} = 13.86$ per cent.

The *anhydrous* salt, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cu}$, is obtained by heating either of the foregoing salts to a temperature of 80° :

Found, $\text{N} = 15.95$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Cu}$ requires $\text{N} = 16.20$ per cent.

The salt is a greenish-yellow powder, which absorbs water from the atmosphere. It explodes violently at 282 — 287° .

Magnesium Picrate.

Previous workers—Liebig, Marchand, Tschelzoff.

Marchand's data led him to regard the salt as a pentahydrate, whilst Tschelzoff considered it an octahydrate.

The present work does not confirm these data.

Nonahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Mg}, 9\text{H}_2\text{O}$.—This salt crystallises from a hot concentrated solution in silky, yellow needles:

Found, $\text{N} = 13.32$; 13.39 .

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{Mg}, 9\text{H}_2\text{O}$ requires $\text{N} = 13.11$ per cent.

Hexahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Mg}, 6\text{H}_2\text{O}$.—This was obtained by exposing the anhydrous salt to the air (preparation I), or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation II). The increase in weight corresponds with the addition of $6\text{H}_2\text{O}$.

Increase in weight on exposing anhydrous salt to air = (I) 22.39 .

Increase in weight on exposing anhydrous salt to an atmosphere 75 per cent. saturated with moisture at $25^{\circ} = 22.40$:

$C_{12}H_4O_{14}N_6Mg$ requires increase of $6H_2O = 22.49$ per cent.

The *dihydrate*, $[C_6H_2(NO_2)_3 \cdot O]_2Mg, 2H_2O$, is obtained when the nonahydrate is heated to a temperature of 80° :

Found, N = (I) 16.35 ; (II) 16.42. $H_2O =$ (I) 7.09.

$C_{12}H_4O_{14}N_6Mg, 2H_2O$ requires N = 16.30 ; $H_2O = 6.97$ per cent.

Loss of weight on exposing nonahydrate to a temperature of $80^{\circ} = 19.33$:

$C_{12}H_4O_{14}N_6Mg, 9H_2O$ requires $7H_2O = 19.62$ per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Mg$, is obtained when any of the above hydrates are heated to a temperature of 150° :

Found, N = 17.32.

$C_{12}H_4O_{14}N_6Mg$ requires N = 17.53 per cent.

This salt explodes very feebly at $367-372^{\circ}$.

Calcium Picrate.

Previous workers.—Chevreul, Liebig, Marchand, Tschelzoff.

According to Marchand, the crystalline salt is a pentahydrate ; Tschelzoff gives a formula containing $6H_2O$. The present work shows that the crystals consist of a decahydrate.

Decahydrate, $[C_6H_2(NO_2)_3 \cdot O]_2Ca, 10H_2O$, crystallises from a hot concentrated solution, on cooling, in yellow plates :

Found, N = (I) 12.59 ; (II) 12.37. $H_2O =$ (I) 26.95 ; (II) 26.03.

$C_{12}H_4O_{14}N_6Ca, 10H_2O$ requires N = 12.45 ; $H_2O = 26.63$ per cent.

Pentahydrate?, $[C_6H_2(NO_2)_3 \cdot O]_2Ca, 5H_2O$, appears to be formed when the anhydrous salt is exposed to the air (preparation I) or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation II).

Increase in weight of anhydrous salt : (I) 17.50, 17.07 ; (II) 17.00 :

$[C_6H_2(NO_2)_3 \cdot O]_2Ca$ requires for $5H_2O$ an increase of 18.15 per cent.

The *anhydrous* salt is produced when the decahydrate is heated to 80° :

Found, N = 16.56 ; 16.57.

$C_{12}H_4O_{14}N_6Ca$ requires N = 16.97 per cent.

It is a yellow powder, which explodes violently at $323-328^{\circ}$.

Strontium Picrate.

Previous workers.—Chevreul, Marchand, Rieckher, Cahours, von Rath, Tschelzoff.

Marchand and von Rath found the salt to contain $5H_2O$; the

former showed that one molecule of water remained on heating to 150° . Tschelzoff found $6\text{H}_2\text{O}$, and Rieckher gives data which would correspond with $6\text{H}_2\text{O}$ if the salt be assumed to lose all its water at 130° . The present work confirms Marchand's results.

Pentahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Sr}, 5\text{H}_2\text{O}$, crystallises in yellow needles from a hot concentrated solution (preparation I); it is also formed when the monohydrate is exposed to the air (preparation II), or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation III):

Found, N = (I) 13.29; 13.48.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Sr}, 5\text{H}_2\text{O}$ requires N = 13.29 per cent.

Increase in weight on exposing monohydrate to air = (II) 13.00; (III) 13.18:

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Sr}, \text{H}_2\text{O}$ requires for an addition of $4\text{H}_2\text{O}$ an increase of 12.82 per cent.

The *monohydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Sr}, \text{H}_2\text{O}$, is obtained when the pentahydrate is exposed to a temperature of 80° :

Found, N = 14.70; 14.70.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Sr}, \text{H}_2\text{O}$ requires N = 14.99 per cent.

Loss of weight on heating pentahydrate = 11.79; 11.75.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Sr}, 5\text{H}_2\text{O}$ requires (for a loss of $4\text{H}_2\text{O}$) 11.37 per cent.

The salt is a yellow powder, which explodes fairly violently at $340\text{--}345^{\circ}$.

The *anhydrous* salt, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Sr}$, is obtained when either of the foregoing salts is heated to 200° , but even at this temperature the water is expelled with difficulty:

Found, N = 15.40; 15.40.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Sr}$ requires N = 15.49 per cent.

Barium Picrate.

Previous workers—Chevreul, Liebig, Dumas, Marchand, Schunck, Laurent, Rieckher, Cahours, Carey Lea, Post and Mehrstens, Tschelzoff, Cook.

The analytical data show considerable discrepancies; those of Liebig correspond with $2\frac{1}{2}\text{--}4\frac{1}{2}\text{H}_2\text{O}$. Post and Mehrstens found $4\text{H}_2\text{O}$; Marchand and Rieckher, $5\text{H}_2\text{O}$; Laurent and Tschelzoff, $6\text{H}_2\text{O}$; Cook, $3\text{H}_2\text{O}$ and $5\text{H}_2\text{O}$, and Marchand and Tschelzoff also obtained evidence of the formation of a monohydrate on heating. The present work confirms the existence of only one definite hydrate.

The *pentahydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Ba}, 5\text{H}_2\text{O}$, crystallises from a concentrated aqueous solution in yellow, prismatic needles:

Found, $N = 12.14$. $H_2O = 13.23$.

$C_{12}H_4O_{14}N_6Ba, 5H_2O$ requires $N = 12.29$; $H_2O = 13.17$ per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Ba$, is obtained when the pentahydrate is exposed to a temperature of 80° :

Found, $N = 14.09$.

$C_{12}H_4O_{14}N_6Ba$ requires $N = 14.19$ per cent.

The salt is a yellow powder, which explodes with moderate violence at $333-337^\circ$. On being exposed to the air or to an atmosphere 75 per cent. saturated with moisture at 25° , an intermediate hydrate appears to be formed; thus the increase of weight corresponded with the addition of:

In the air of the laboratory, (I) $4.5H_2O$; (II) $4.65H_2O$.

In moist atmosphere (75 per cent. saturated at 25°), $4.6H_2O$.

Zinc Picrate.

Previous workers—Marchand, Carey Lea, Müller, Tschelzoff.

Marchand believed he obtained salts containing $8H_2O$, $5H_2O$, $2H_2O$, and H_2O , but the analytical data show great discrepancies.

Tschelzoff's zinc determination points to the presence of $9H_2O$, but the loss of weight corresponds more nearly with $8H_2O$. Müller investigated the double picrate of zinc and sodium. The present work has shown the existence of salts containing $9H_2O$, $6H_2O$, and $2H_2O$.

Nonahydrate, $[C_6H_2(NO_2)_3 \cdot O]_2Zn, 9H_2O$.—This separates from the concentrated solution in yellow, prismatic needles:

Found, $N = 12.41$; 12.40 .

$C_{12}H_4O_{14}N_6Zn, 9H_2O$ requires $N = 12.32$ per cent.

Hexahydrate, $[C_6H_2(NO_2)_3 \cdot O]_2Zn, 6H_2O$.—This was formed by exposing the anhydride to an atmosphere 75 per cent. saturated with moisture.

Increase in weight of anhydrous salt = 20.50 :

$C_{12}H_4O_{14}N_6Zn$ requires the addition of $6H_2O = 20.72$ per cent.

In the air of the laboratory, the amount of moisture absorbed was rather less (5.4 and 5.6 molecules).

The *dihydrate*, $[C_6H_2(NO_2)_3 \cdot O]_2Zn, 2H_2O$, is formed when the nonahydrate is heated to 80° :

Found, $N =$ (I) 15.11 ; (II) 15.04 .

$C_{12}H_4O_{14}N_6Zn, 2H_2O$ requires $N = 15.1$.

Loss of weight on exposing nonahydrate to a temperature of $80^\circ = 18.54$:

$C_{12}H_4O_{14}N_6Zn, 9H_2O$ requires (for a loss of $7H_2O$) 18.44 per cent.

The *anhydrous* salt, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Zn}$, is produced when any of the hydrates are heated to 150° :

Found, $N = 15.93$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Zn}$ requires $N = 16.15$ per cent.

It is a brownish-yellow powder, which explodes violently at $350\text{--}355^\circ$.

Cadmium Picrate.

Previous workers—Müller, Carey Lea.

The analysis given by Müller corresponds with a heptahydrate. This has been confirmed in the present work.

Heptahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cd}\cdot 7\text{H}_2\text{O}$.—This salt was obtained from hot concentrated solution in the form of yellow, hexagonal plates:

Found, $N = (\text{I}) 12.13$; $(\text{II}) 11.97$. $\text{H}_2\text{O} = (\text{I}) 18.29$; $(\text{II}) 17.93$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Cd}\cdot 7\text{H}_2\text{O}$ requires $N = 12.12$; $\text{H}_2\text{O} = 18.15$ per cent.

The *pentahydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cd}\cdot 5\text{H}_2\text{O}$, is formed when the anhydrous salt is exposed to an atmosphere 75 per cent. saturated with moisture at 25° .

Increase in weight $= 16.14$:

$[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cd}$ requires for $5\text{H}_2\text{O}$ an increase $= 15.84$ per cent.

The same result was not obtained when the anhydrous salt was exposed to the air of the laboratory, approximately 4 molecules only of water being absorbed.

The *anhydrous* salt, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cd}$, is formed when the heptahydrate is exposed to 80° :

Found, $N = 14.61$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Cd}$ requires $N = 14.81$ per cent.

It is a yellow powder, which explodes violently at $336\text{--}341^\circ$.

Mercuric Picrate.

Liebig and Moretti described a mercurous picrate; Chevreul, Varet, Carey Lea, and Hantzsch and Auld have described mercuric salts. Varet and Hantzsch and Auld give directions for the preparation of a tetrahydrated normal mercuric salt by digesting freshly-precipitated mercuric oxide with an aqueous solution of picric acid at 80° .

In the present investigation, all attempts to prepare this substance by repeating this work gave rise to the basic compound described below.

Hexahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Hg}\cdot\text{Hg}(\text{OH})_2\cdot 6\text{H}_2\text{O}$.—This compound was obtained by three slightly different methods:

(1) By keeping a well-stirred mixture of picric acid, in excess (46 grams in two litres of water), and freshly-precipitated mercuric oxide

(21 grams) at a temperature of 80° for forty-eight hours. On cooling, the salt separated as beautiful orange-yellow needles.

(2) By warming a similar mixture for a few hours only. In this case, the salt, which was precisely similar in appearance, was much contaminated with free picric acid, which was, however, readily removed by crystallisation from hot water.

(3) By boiling a similar mixture for seven hours after maintaining it at 80° for forty-eight hours. On analysis:

Found, N = (I) 8.46; (II) 8.44; (III) 8.50. H_2O = (I) 10.25.

$C_{12}H_{18}O_{22}N_6Hg_2$ requires N = 8.44; H_2O = 10.82 per cent.

The compound forms beautiful orange needles, which change to a pale yellow colour on losing the water of crystallisation. On warming with water, a residue of mercuric oxide is obtained, and on concentrating the solution the hydrated basic salt again separates, picric acid being left in solution.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Hg, Hg(OH)_2$, is obtained by exposing the finely-powdered hexahydrate over sulphuric acid in a vacuum:

Found, N = 9.46. H_2O = 44.82.

$C_{12}H_6O_{16}N_6Hg_2$ requires N = 9.46; H_2O = 44.93 per cent.

The salt is a pale yellow powder, which volatilises without explosion on heating.

Aluminium Picrate.

Previous workers—Carey Lea, Müller, Moretti.

Müller gives analyses which correspond with a basic salt,

whilst Lea gives no analytical data.

Hexadecahydrate, $[C_6H_2(NO_2)_3 \cdot O]_3Al, 16H_2O$.—This was prepared by digesting freshly-precipitated aluminium hydroxide with an aqueous solution of picric acid for several days, and concentrating the filtrate; on cooling, the salt was deposited in pale yellow needles (preparation I). It may also be obtained by exposing the tetrahydrate to an atmosphere 75 per cent. saturated with moisture at 25° (preparation II):

Found, (I) N = 12.81.

$C_{18}H_6O_{21}N_9Al, 16H_2O$ requires N = 12.64 per cent.

Increase of weight on exposing the tetrahydrate to moist air = (II) 27.84:

$C_{18}H_6O_{21}N_9Al, 4H_2O$ requires increase of $12H_2O$ = 27.59 per cent.

A similar result is not obtained on exposing the tetrahydrate to the air of the laboratory, only approximately 10.7 molecules of water being absorbed.

The *tetrahydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_3\text{Al}, 4\text{H}_2\text{O}$, is obtained from the hexadecahydrate by heating to 80° :

Found, $\text{N} = 16\cdot01$; $16\cdot07$.

$\text{C}_{18}\text{H}_6\text{O}_{21}\text{N}_9\text{Al}, 4\text{H}_2\text{O}$ requires $\text{N} = 16\cdot13$ per cent.

Loss of weight on exposing the hexadecahydrate to a temperature of $80^\circ = 22\cdot33$; $22\cdot56$:

$\text{C}_{18}\text{H}_6\text{O}_{21}\text{N}_9\text{Al}, 16\text{H}_2\text{O}$ requires loss (of $12\text{H}_2\text{O}$) = $21\cdot92$ per cent.

The tetrahydrate thus obtained is a yellow powder, which on heating decomposes without explosion.

Thallium Picrate, $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OTl}$.

Previous workers—Kuhlmann, Böttger.

No analytical data are given by these authors. In the present work, thallium carbonate was dissolved in aqueous picric acid, and the filtrate concentrated. The anhydrous salt crystallised in silky, yellow needles. No loss of weight occurred on heating:

Found, $\text{N} = 9\cdot68$.

$\text{C}_6\text{H}_2\text{O}_7\text{N}_3\text{Tl}$ requires $\text{N} = 9\cdot75$ per cent.

The salt explodes feebly at 273 — 275° .

Zirconium Picrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_4\text{Zr}$.

This salt has apparently not been previously prepared. It was obtained from zirconium carbonate and picric acid, and crystallises in anhydrous, silky, yellow needles:

Found, $\text{N} = 16\cdot67$.

$\text{C}_{24}\text{H}_8\text{O}_{28}\text{N}_{12}\text{Zr}$ requires $\text{N} = 16\cdot80$ per cent.

The salt suffered practically no loss in weight on heating; it exploded freely at 317 — 322° .

Cerium Picrate.

This salt has apparently not been previously prepared. In the present work, it was obtained from cerium carbonate and picric acid.

Undecahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_3\text{Ce}, 11\text{H}_2\text{O}$, crystallises from a concentrated aqueous solution (preparation I), and can also be obtained by exposing the anhydrous salt to air (preparation II) or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation (III)):

Found, $\text{N} = 12\cdot32$.

$\text{C}_{18}\text{H}_6\text{O}_{21}\text{N}_9\text{Ce}, 11\text{H}_2\text{O}$ requires $\text{N} = 12\cdot35$ per cent.

Increase in weight on exposing anhydrous salt to air = (II) $24\cdot32$; (III) $24\cdot60$:

$\text{C}_{18}\text{H}_6\text{O}_{21}\text{N}_9\text{Ce}$ requires for $11\text{H}_2\text{O}$ an increase of $24\cdot03$ per cent.

The salt separates from a concentrated aqueous solution in amber-coloured, flat, prismatic crystals. By either of the other methods, it is obtained as a brown powder.

The *trihydrate*, $[C_6H_2(NO_2)_3 \cdot O]_3Ce, 3H_2O$, is obtained by heating the undecahydrate to 80° :

Found, N = (I) 14.30 ; (II) 14.23. H_2O = (I) 6.69 ; (II) 6.92.

$C_{18}H_6O_{21}N_9Ce, 3H_2O$ requires N = 14.38 ; H_2O = 6.22 per cent.

Loss of weight on heating undecahydrate to 80° = 14.04 ; 14.11 :

$C_{18}H_6O_{21}N_9Ce, 11H_2O$ requires loss (of $8H_2O$) = 14.09 per cent.

It is a brown powder, which absorbs moisture from the air.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_3Ce$, is obtained when either the undecahydrate or trihydrate is heated to 150° :

Found, N = 15.22.

$C_{18}H_6O_{21}N_9Ce$ requires N = 15.29 per cent.

The salt is a brown powder, which explodes violently at $306-313^\circ$.

Lead Picrate.

Previous workers—Chevreul, Liebig, Marchand, Laurent, Kopp, Rieckher, Post and Mehrtens, Tschelzoff.

The analytical data vary very considerably ; they correspond with 1 to 5 molecules of water of crystallisation. Various basic salts are also described.

Tetrahydrate, $[C_6H_2(NO_2)_3 \cdot O]_2Pb, 4H_2O$.—Picric acid was treated with lead carbonate, and the salt obtained in the form of silky, yellow needles :

Found, N = 11.46.

$C_{18}H_4O_{14}N_6Pb, 4H_2O$ requires N = 11.46 per cent.

The *monohydrate*, $[C_6H_2(NO_2)_3 \cdot O]_2Pb, H_2O$, results when the tetrahydrate is retained at 80° for some time (preparation I), and also when the anhydrous salt is exposed to air (preparation II) :

Found, N = (I) 12.56. H_2O = 2.77 ; 2.71.

$C_{12}H_4O_{14}N_6Pb, H_2O$ requires N = 12.37 ; H_2O = 2.65 per cent.

Increase in weight on exposing anhydrous salt to air (II) = 2.73 ; 2.71 :

$C_{12}H_4O_{14}N_6Pb$ requires for $1H_2O$ an increase of 2.72 per cent.

In an atmosphere 75 per cent. saturated with moisture, 1.3 molecules of water were absorbed.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Pb$, is obtained when the tetrahydrate or monohydrate is heated to 150° .

It is a yellow powder, which explodes violently at $270-275^\circ$, and differs from all other picrates in being extremely sensitive to shock or friction.

Chromium Picrate.

Carey Lea describes a chromium-ammonium compound, but chromium picrate has apparently not been prepared.

A basic chromium salt, corresponding approximately with the composition $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_3\text{Cr}, 2\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}\cdot\text{CrO}, 27\text{H}_2\text{O}$, is obtained by mixing equivalent quantities of barium picrate and chromium sulphate and evaporating the filtrate in a vacuum over sulphuric acid.

The salt separates in green crystals:

Found, Cr = (I) 8.30; (II) 8.61. N = (I) 11.38.

$\text{C}_{30}\text{H}_{10}\text{O}_{36}\text{N}_{15}\text{Cr}, 27\text{H}_2\text{O}$ requires Cr = 8.61; N = 11.60 per cent.

A salt of the composition

is produced when the salt just described is heated to 80° .

Loss of weight on heating to 80° = (I) 18.21; (II) 18.11:

$\text{C}_{30}\text{H}_{10}\text{O}_{36}\text{N}_{15}\text{Cr}, 27\text{H}_2\text{O}$ requires for loss (of $18\text{H}_2\text{O}$) = 17.86 per cent.

The *anhydrous* salt, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_3\text{Cr}, 2\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}\cdot\text{CrO}$, is produced when the foregoing salt is heated to 150° .

Loss of weight on heating to 150° = (I) 10.16; (II) = 10.49.

$\text{C}_{30}\text{H}_{10}\text{O}_{36}\text{N}_{15}\text{Cr}, 9\text{H}_2\text{O}$ requires loss (of $9\text{H}_2\text{O}$) = 10.88 per cent.

Manganese Picrate.

Previous workers—Marchand, Müller, Carey Lea.

Marchand obtained an octahydrate which readily lost three molecules of water; Müller found only a pentahydrate. The present work shows the existence of the octahydrate and a trihydrate, but renders the formation of a pentahydrate highly improbable.

The *octahydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Mn}, 8\text{H}_2\text{O}$, separates in yellow prisms from a hot concentrated solution (preparation I).

It is also obtained when the anhydrous salt is exposed to the air (preparation II) or to an atmosphere 75 per cent. saturated at 25° (preparation III):

Found, N = (I) 12.90; 13.02.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Mn}, 8\text{H}_2\text{O}$ requires N = 12.85 per cent.

Increase in weight on exposing anhydrous salt in air = (II) 27.96; (III) 27.52:

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Mn}$ requires for $8\text{H}_2\text{O}$ an increase of 28.18 per cent.

The *trihydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Mn}, 3\text{H}_2\text{O}$, is produced when the octahydrate is heated to 80° :

Found, N = 15.11. $\text{H}_2\text{O} = 9.44$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6, 3\text{H}_2\text{O}$ requires N = 14.90; $\text{H}_2\text{O} = 9.56$ per cent.

Loss of weight on heating octahydrate to $80^{\circ}=13.77$; 13.80 ; 14.02 :

$C_{12}H_4O_{14}N_6Mn, 8H_2O$ requires loss (of $5H_2O$) = 13.74 per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Mn$, is produced when either the octa- or tri-hydrate is heated to 150° .

It is a yellow powder, which explodes with violence at $325-330^{\circ}$.

Ferrous Picrate.

Previous workers—Müller, Carey Lea.

The analysis given by Müller corresponds approximately with a pentahydrate. The present work has not confirmed this, but an octahydrate has been obtained.

Octahydrate, $[C_6H_2(NO_2)_3 \cdot O]_2Fe, 8H_2O$.—Hot concentrated solutions of ferrous sulphate and barium picrate are mixed and filtered. The ferrous picrate separates from the filtrate, on cooling, in yellow, hexagonal prisms:

Found, $N = 12.81$. $H_2O = 21.72$; 21.64 ; 21.91 .

$C_{12}H_4O_{14}N_6Fe, 8H_2O$ requires $N = 12.84$; $H_2O = 21.96$ per cent.

The crystallised salt is bright yellow, but becomes dark green directly it begins to lose water.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Fe$, is obtained when the octahydrate is exposed in a vacuum desiccator over concentrated sulphuric acid:

Found, $N = 16.18$.

$C_{12}H_4O_{14}N_6Fe$ requires $N = 16.45$ per cent.

The *anhydrous* salt is a dark green powder, which explodes feebly at $315-320^{\circ}$. On exposure to the air, it absorbs from 3 to 4 molecules of water.

Attempts to prepare ferric picrate were without result; no precipitate was found under the conditions described by Moretti.

Cobalt Picrate.

Previous workers—Marchand, Müller, Carey Lea.

Marchand obtained analytical data corresponding with a pentahydrate. This is not confirmed by the present work. The hydrates obtained contain $9\frac{1}{2}$, 6, and 2 molecules of water, and are strictly analogous to the nickel salts.

Hydrate, $[C_6H_2(NO_2)_3 \cdot O]_2Co, 9\frac{1}{2}H_2O$.—This is deposited on allowing a hot solution containing 10 grams of the anhydrous salt in 20 c.c. of water to cool:

Found, $N = 12.53$.

$C_{12}H_4O_{14}N_6Co, 9\frac{1}{2}H_2O$ requires $N = 12.27$ per cent.

The salt crystallises in brown needles.

Hexahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Co}, 6\text{H}_2\text{O}$.—This crystallises on cooling from a hot solution containing 10 grams of the anhydrous salt in 15 c.c. of water (preparation I).

It is also produced when the anhydrous salt is exposed to air (preparation II) or to an atmosphere 75 per cent. saturated at 25° (preparation III).

Increase in weight on exposing anhydrous salt to air = (II) 21.07 ; (III) 21.03.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Co}$ requires for $6\text{H}_2\text{O}$ an increase = 20.98 per cent.

When obtained as in preparation (I), the salt crystallises in brown laminae ; by either of the other methods, it is a brown powder.

The *dihydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Co}, 2\text{H}_2\text{O}$, is formed when either of the above hydrates are heated to 80° .

Dihydrate from $9\frac{1}{2}$ hydrate : Found, $\text{N} = 15.32$. $\text{H}_2\text{O} = 6.10$.

Dihydrate from hexahydrate : Found, $\text{N} = 15.20$. $\text{H}_2\text{O} = 6.00$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Co}, 2\text{H}_2\text{O}$ requires $\text{N} = 15.28$; $\text{H}_2\text{O} = 6.54$ per cent.

Loss in weight on heating $9\frac{1}{2}$ hydrate to $80^\circ = 19.43$; 19.39 ; 19.38 :

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Co}, 9\frac{1}{2}\text{H}_2\text{O}$ requires a loss (of $7\frac{1}{2}\text{H}_2\text{O}$) = 19.68 per cent.

Loss of weight on heating hexahydrate to $80^\circ = 11.84$; 11.62 :

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Co}, 6\text{H}_2\text{O}$ requires a loss (of $4\text{H}_2\text{O}$) = 11.59 per cent.

Obtained by either method the salt is a brown powder.

The *anhydrous* salt, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Co}$, is obtained when any of the above hydrates are heated to 150° .

It is a brown powder, which explodes with moderate violence at $320-325^\circ$.

Nickel Picrate.

Previous workers—Marchand, Müller, Carey Lea.

Marchand describes an octahydrate, a pentahydrate, and a monohydrate. The present work has not confirmed the existence of any of these salts.

Hydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Ni}, 9\frac{1}{2}\text{H}_2\text{O}$.—This crystallises in green needles when a hot solution containing 10 grams of the anhydrous salt in 20 c.c. of water is allowed to cool :

Found, $\text{N} = 12.47$.

$\text{C}_{12}\text{H}_4\text{O}_{14}\text{N}_6\text{Ni}, 9\frac{1}{2}\text{H}_2\text{O}$ requires $\text{N} = 12.28$ per cent.

Hexahydrate, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Ni}, 6\text{H}_2\text{O}$.—This crystallises in green laminae when a hot solution containing 10 grams of anhydrous salt in 15 c.c. of water is allowed to cool (preparation I).

It is also produced when the anhydrous salt is exposed to air (pre-

paration II) or to an atmosphere 75 per cent. saturated at 25° (preparation III).

Increase in weight on exposing anhydrous salt to air = (I) 20·24 ; 20·90 ; (II) 20·24.

$C_{12}H_4O_{14}N_6$ requires for $6H_2O$ an increase of 20·99 per cent.

Obtained by preparation I, the salt crystallises in the form of green laminæ ; by either of the other methods, it is a green powder.

The *dihydrate*, $[C_6H_2(NO_2)_3 \cdot O]_2Ni \cdot 2H_2O$, is obtained from either of the above hydrates on heating to 80°.

Dihydrate from $9\frac{1}{2}$ hydrate : Found, N = 15·26.

Dihydrate from hexahydrate : Found, N = 15·21. $H_2O = 6\cdot70$:

$C_{12}H_4O_{14}N_6Ni \cdot 2H_2O$ requires N = 15·29 ; $H_2O = 6\cdot54$ per cent.

Loss in weight on heating $9\frac{1}{2}$ hydrate to 80° = 19·90 ; 20·09 :

$C_{12}H_4O_{14}N_6Ni \cdot 9\frac{1}{2}H_2O$ requires a loss (of $7\frac{1}{2}H_2O$) = 19·69 per cent.

Obtained by either method, the salt is a green powder.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Ni$, is obtained when any of the above hydrates are heated to 150°. It is a green powder, which explodes with moderate violence at 335—340°.

Our thanks are due to the Director of Artillery, the Ordnance Research Board, and the Explosives Committee for permission to publish these results, and also to Messrs. C. S. Roy, H. J. Merriman, and F. W. Myers for assistance in the work.

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