

XLV.—*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; Reychler, *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 Mehrrens.

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, Reyhler.

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 Mehrtens.

The analytical data given points in most cases to the absence of water of crystallisation ; in other cases, however (Marchand, Laurent, Post and Mehrtens), 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 *tetrahhydrate*, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Cu}, 4\text{H}_2\text{O}$, 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 Mehrtens, 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 Mehrtens 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.