

# CHEMISTRY OF METAL DINITROANTHRANILATES—PART I

## Dinitroanthranilates of copper and silver

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(Received 12 November 1973 ; revised 20 August 1974)

Copper and silver dinitroanthranilates have been prepared and the stoichiometry of the complexes have been determined by micro analysis, conductometric and potentiometric studies. The IR studies show the presence of  $-\text{H}_2\text{N} \rightarrow \text{M}$  bond, where M is silver or copper. Various explosive properties such as explosion delay, explosion temperature and activation energy, explosion pressure, impact sensitivity, friction sensitivity and ballistic mortar power of these dinitroanthranilates have also been studied.

Explosive nature of metal picrates have been studied by number of workers<sup>1,2</sup>. Recently Kenney<sup>3</sup> has reported new complexes of picric acid having different explosive properties. The chemistry and explosive properties of metal picramates have also been studied by several workers<sup>4,5,6</sup>. Interest in nitrobenzoic acid as explosive has chiefly centered around trinitrobenzoic acid. The chemistry and explosive characteristics of transition metal trinitrobenzoates have been studied by Excales<sup>7</sup>. A search through literature reveals that no work seems to have been carried out on its simple derivative dinitroanthranilic acid (2-amino-3, 5-dinitrobenzoic acid) having an amino group in place of nitro group in *ortho* position to the carboxyl group. It will be of great interest to study the explosive characteristics of transition metal dinitroanthranilates. Glowiak<sup>8,9</sup> reported that in the case of lead salts of certain polynitrophenols, the substitution of a  $\text{NO}_2$  group by  $\text{NH}_2$  group results in an increase of its sensitiveness to impact and flame which is very interesting combination of explosive properties. It may, therefore, be expected that the metal complexes of dinitroanthranilates may be better explosives.

The present study deals with the preparation and characterisation of silver and copper dinitroanthranilates with the help of micro analysis, potentiometric, conductometric and IR studies. Its explosive properties like explosion delay, explosion temperature, activation energy, explosion pressure, impact sensitivity, friction sensitivity and ballistic mortar power have also been determined.

The aim of these investigations is to study the explosive properties of silver and copper dinitroanthranilates with a view to explore the possibility of their use as primary explosives.

### MATERIALS AND METHODS

All the chemicals used were of B.D.H. (A.R.) quality. 3,5-dinitroanthranilic acid was prepared by the method of P. Cohn<sup>9</sup>.

#### *Preparation of Sodium Salt*

The sodium salt of 3,5-dinitroanthranilic acid was prepared by suspending a known weight of the acid in water and then treating it with an equivalent amount of sodium bicarbonate solution. The resulting product was digested on water bath to ensure complete reaction. On cooling, the product was filtered. The filtrate on evaporation gave yellow crystals of sodium 3,5-dinitroanthranilate.

The electrical conductance of the solution was measured on Systronic's conductivity bridge at  $30^\circ \pm 1^\circ\text{C}$ . The monovariation method was employed to determine the composition of the complex.

The pH measurements were carried out with a Systronic pH meter.

The IR spectra of these complexes were recorded in  $\text{KBr}$  on a Perkin Elmer infrared spectrophotometer model 337.

#### *Isolation of the Compound*

Copper sulphate and silver nitrate solutions were added to the aqueous solution of sodium dinitroanthranilate. The products were filtered and washed with water and finally with alcohol. Metal dinitroanthranilates were dried in desiccator and then analysed for their constituents. Results of microanalysis are given in Table 1.

TABLE I.  
ANALYTICAL DATA OF METAL DINITROANTHRANILATE

Complex	Metal (%)		N (%)		H <sub>2</sub> O (%)	
	Found	Calculated	Found	Calculated	Found	Calculated
(C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub> )	32.33	32.35	12.23	12.59		
(C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>2</sub> Cu·2H <sub>2</sub> O	11.49	11.51	14.96	15.23	6.78	6.52

RESULTS AND DISCUSSION

Conductometric Studies

Fig. 1 represents the plot of specific conductance against the volume of sodium dinitroanthranilate solution added to metal solution and Fig. 2 shows the plot of specific conductance against the volume of metal solution added to ligand solution. Curve A represents the titration for silver and B for copper in both the figures. In Fig. 1 initial concentration of metal salt solution 0.04 M, initial concentration of ligand 0.04 M, in case of A and initial concentration of metal salt solution 0.02 M, initial concentration of ligand 0.02 M in case of B; Total volume 50 ml. and in Fig. 2 initial concentration of metal salt solution is 0.04 M, initial concentration of ligand is 0.04 M in case of A and in case of B initial concentration of ligand is 0.02 M, initial concentration of metal salt solution is 0.02 M; Total volume 50 ml.

From Fig. 1 it is clear that in the beginning the conductance remains almost constant but after the addition of one equivalent of sodium dinitroanthranilate to the solution of silver nitrate, and two equivalents to the copper sulphate the conductance increases. These observations clearly show the formation of 1 : 1 complex in case of silver and 1 : 2 complex in case of copper. Similar results were obtained in case where metal solution is added to ligand solution.

Potentiometric Studies

The results of potentiometric studies are given in Fig. 3 and 4.

In Fig. 3 curves A, B, C, D represent the potentiometric titration of silver nitrate and sodium dinitroanthranilate in the molar ratio of 1 : 0, 1 : 1, 1 : 2 and 1 : 3 respectively with sodiumhydroxide (0.1 M). The examination of the curve A shows only one inflexion at one equivalent of alkali. This shows that one mole of alkali is needed for the formation of one mole of silver hydroxide. In curve B the sharp rise in pH shows that all the metal has been bound to the ligand. Similar nature of the curve C and D is also obtained in the case of 1 : 2 and 1 : 3 metal ligand ratio which is a bit higher in pH than the curve B due to excess of sodiumdinitroanthranilate. This also supports the formation of 1 : 1 complex.

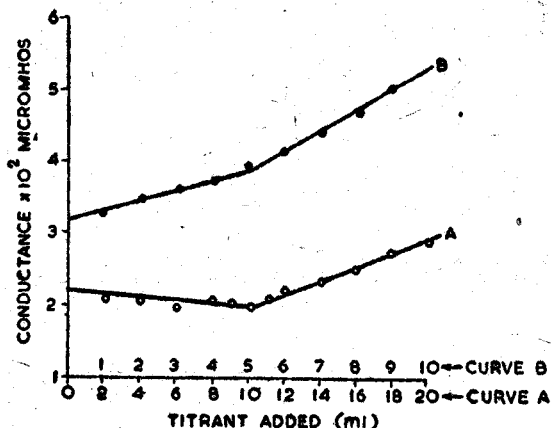


Fig. 1.—Conductometric titration curves : (A) Silver nitrate-sodium-dinitroanthranilate; (B) Copper sulphate-sodium-dinitroanthranilate.

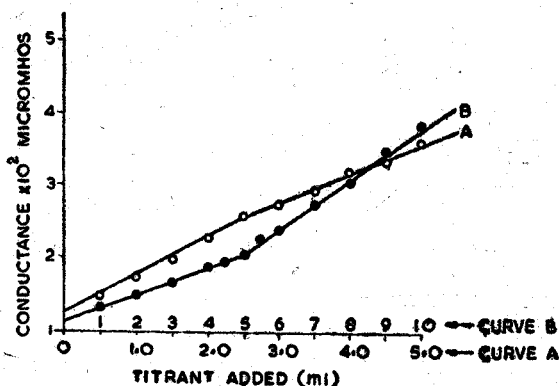


Fig 2.—Conductometric titration curves : (A) Silver nitrate-sodium-dinitroanthranilate; (B) Copper-sodium-dinitroanthranilate.

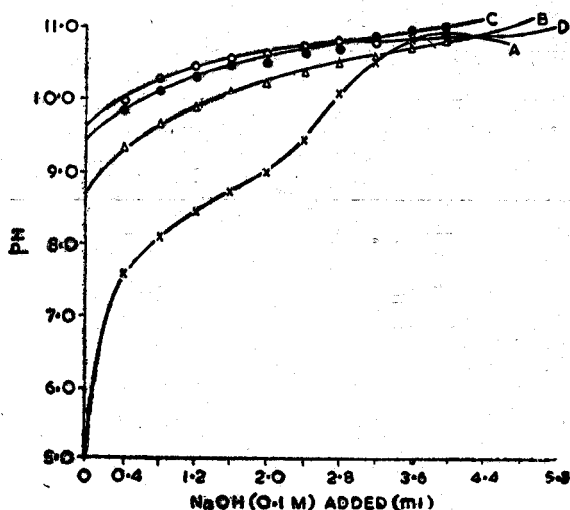


Fig. 3—Electrometric titration of: (A) Silver nitrate 5 ml (0.05M) + 45 ml  $H_2O$ ; (B) Silver nitrate (0.05M) 5ml + 5ml sodium-dinitroanthranilate + 40  $H_2O$ ; (C) Silver nitrate (0.05M) 5ml + 10 ml sodium-dinitroanthranilate + 35  $H_2O$ ; (D) Silver nitrate (0.05M) 5 ml + 15 ml sodium dinitroanthranilate + 30  $H_2O$ .

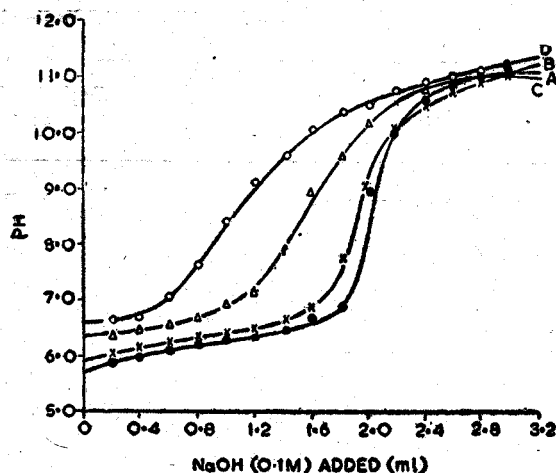


Fig. 4—Electrometric titration of: (A) Copper sulphate 5 ml (0.02M) + 45 ml  $H_2O$ ; (B) Copper sulphate 5 ml (0.02M) + 5 ml sodium-dinitroanthranilate (0.02M) + 40 ml  $H_2O$ ; (C) Copper sulphate 5 ml (0.02M) + 10 ml sodium-dinitroanthranilate (0.02 M) + 35 ml  $H_2O$ ; (D) Copper sulphate 5 ml (0.02M) + 15 ml sodium-dinitroanthranilate (0.02M) + 30 ml  $H_2O$ .

In Fig. 4 curves A, B, C & D show the potentiometric titration of copper sulphate and ligand in the molar ratio of 1 : 0, 1 : 1, 1 : 2 and 1 : 3 with sodium hydroxide. In curve A only one inflexion is obtained at two equivalents of alkali. This shows that for the formation of copper hydroxide, two moles of alkali are needed. In curve B, only one inflexion is obtained when one equivalent of alkali has been added. This shows that half of the  $Cu^{++}$  ion present in the solution has been bonded with the ligand and only half of the  $Cu^{++}$  ion is free to react with one equivalent of alkali. The sharp rise in pH with addition of alkali as seen in curve C shows the absence of metal ion in solution as whole of  $Cu^{++}$  is bonded to the ligand. The curve D is similar to that of C but higher in pH, due to excess of sodium salt of ligand. This shows the formation of 1 : 2 complex.

#### Infrared Spectroscopy

The absorption associated with the  $-NH$  degenerate deformation mode<sup>10</sup> is expected to appear in the region  $1600\text{ cm}^{-1}$  but it is greatly masked by the strong absorption due to  $-NO_2$  group in the same region. The  $-NH$  asymmetric stretching frequency observed at  $3500\text{ cm}^{-1}$  in the spectra of sodium dinitroanthranilate, is lowered to  $3300\text{ cm}^{-1}$  after complex formation. Similar type of lowering was also noted by a number of workers<sup>11-13</sup> in anthranilic acid and amino acid complexes. The  $-NH$  rocking and twisting modes<sup>10</sup> which appear at  $900\text{ cm}^{-1}$  in sodium-dinitroanthranilate are shifted to  $940$  and  $935\text{ cm}^{-1}$  in copper and silver complexes. Curran & co-workers<sup>10,12,13</sup> have also observed similar type of shift. The above observation clearly indicates the presence of  $N \rightarrow M$  bond.

The characteristic  $C=O$  frequency at  $1670\text{ cm}^{-1}$  is greatly masked by  $-NO_2$  group in the same region. Only the peak associated with carboxylate ion appeared at  $1525\text{ cm}^{-1}$  in sodium salt. A shift in the peak from  $1525\text{ cm}^{-1}$  to  $1550\text{ cm}^{-1}$  and  $1545\text{ cm}^{-1}$  is observed after chelation in the case of copper and silver dinitroanthranilate respectively. The small shift indicates the presence of electrostatic  $COO^- \rightarrow M^+$  bond. This is in quite agreement with the results obtained by Sandhu & co-workers<sup>11</sup> and Curran *et al*<sup>12,13</sup>.

#### DETERMINATION OF EXPLOSIVE PROBLEMS

The complexes used for the measurement of explosive properties were dried at  $100^\circ C$  for two or three hours. Explosion delay, explosion temperature, activation energy, explosion pressure, impact sensitivity, friction sensitivity and ballistic mortar power are recorded in Tables (2—4).

TABLE 2

VALUES OF EXPLOSION DELAY, EXPLOSION TEMPERATURE AND ACTIVATION ENERGY

Complex	Explosion delay at 340° ± 0.2 (Sec)	Explosion temperature for explosion delay of 10 Sec (°C)	Activation energy (K cal/mole)
Copper dinitroanthranilate	60.7 ± 0.2	394 ± 0.2	24.45
Silver dinitroanthranilate	32.5 ± 0.2	371 ± 0.2	11.13

### Explosion Delay

Explosion delay was measured by using the method of Copp *et al.*<sup>14</sup>. Approximately 10 mg dry sample was taken in a pyrex tube which was suddenly plunged into potassium hydrogen sulphate bath maintained at a temperature of 340° ± 0.2°C. The interval between time of insertion and explosion was noted with the help of stop watch. This gives explosion delay of complex, in every case mean of three readings were taken (Table 2).

### Explosion Temperature

Explosion temperature is a temperature necessary to cause explosion in 10 seconds when few mg of the sample are inserted in the potassium hydrogen sulphate bath. Explosion temperature was determined with the help of Weber's method<sup>15</sup>. A chromel-alumel thermocouple was used to measure the temperature of bath and readings were recorded at 10° intervals. Readings are recorded in the Table 2.

### Thermal Sensitivity

The explosion delay ( $D_B$ ) for the build up of an explosion decreases with an increase in temperature. Values of explosion delay ( $D_B$ ) at various temperatures are given in Table 2. The variation of  $\log(D_B)$  with  $(1/T)$  (where T is absolute temperature) of bath are plotted in Fig. 5. The activation energies ( $E^{\ddagger}$ ) of the reaction have been determined by using the method of Singh and co-workers<sup>16,17</sup> and are given in Table 2.

It would be seen from Table 2 that thermal stability decreases from copper to silver. Thermal stability decreases with the increase of atomic number and atomic radii, which is supported by explosion delay, explosion temperature and activation energy data.

On the basis of the bond dissociation energies<sup>18,19</sup> and considering the different linkages present in the metal dinitroanthranilate, may be presumed that in the beginning of the explosion the breaking of the N-O linkages<sup>20,21</sup> takes place. This helps the oxygen which is linked to nitrogen to be consumed for the complete oxidation of carbon and hydrogen obtained by the rupture of the ring and thus produce a large amount of heat.

### Explosion Pressure

Pressure of gases developed by an explosive on explosion is a very important factor, because on this depends the capacity of an explosive to do work, although the character of the work is determined by the rate at which the pressure is built up. Explosion pressures were measured by using the method of Yoffe<sup>22</sup>. Explosion was carried out in molten potassium hydrogen sulphate bath. The results obtained are shown in Table 3.

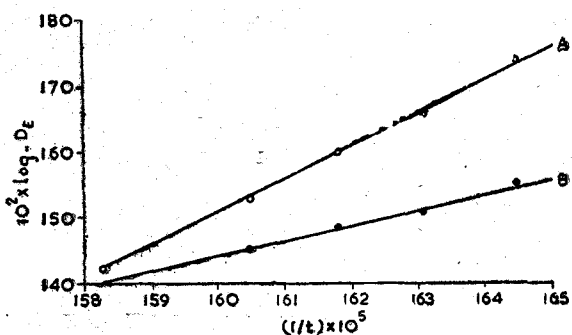


Fig. 5—Variation of  $\log t$  with reciprocal of absolute temperature: (A) Copper dinitroanthranilate; (B) Silver dinitroanthranilate.

TABLE 3  
EXPLOSION PRESSURE FOR COPPER AND SILVER DINITROANTHRANILATE

Compound	Height (H) (cm)	Explosion pressure (Dynes/cm <sup>2</sup> × 10 <sup>4</sup> )
Copper dinitroanthranilate	2.55	3.3944
Silver dinitroanthranilate	2.05	2.7288

Density of Mercury (d)=13.595 gm/c.c. ; Gravitational Acceleration (g)=979.15 cm/Sec<sup>2</sup>

From the table it is clear that pressure exerted during the explosion of copper dinitroanthranilate is more than that of silver dinitroanthranilate.

### SHOCK SENSITIVITY

All explosives are generally brought to detonation by a mechanical shock. The investigation of the degree of sensitiveness is important because it determines the applications to which explosives can be put, and also the precautions necessary to ensure safe manufacture, handling and transportation.

#### *Impact Sensitivity*

Impact sensitivity of copper and silver dinitroanthranilates were measured by using the method of Taylor and Weale<sup>23</sup>. Approximately 10 mg dry sample was placed in between two stainless steel Hoffman rollers. These rollers were kept in position by steel collar. A hammer of definite weight was dropped from a known height on to the sample. Five consecutive tests were carried out at each height and number of ignitions were recorded.

These results show that copper and silver dinitroanthranilates do not ignite with 10 kg weight when dropped from a height of 200 cms. This clearly indicates that the copper and silver dinitroanthranilates are mild explosives and are safe for handling and transportation.

#### *Friction Sensitivity*

The sensitiveness of explosives to a glancing blow is usually taken as a measure of their comparative sensitiveness to friction. It was measured by Torpedo Friction test which was modified in design<sup>24</sup>.

The method consists of allowing a torpedo shaped striker of known weight (1 kg) made up of mild steel to slide down a V groove set at a selected angle (70°) on to a weighed quantity (10 mg) of an explosive mounted on a mild steel anvil. Usually 5 consecutive tests were carried out at each height.

The results obtained in friction sensitivity clearly show that copper and silver dinitroanthranilates do not ignite with 1 kg. weight slid from a height of 170 cms. This also indicates that the copper and silver dinitroanthranilates are mild explosives.

#### *Ballistic Mortar Power*

Ballistic mortar and trauzal block<sup>25</sup> are satisfactory methods for the determination of available energy. However in U.S.A. the ballistic mortar<sup>26</sup> is preferred to trauzal block.

Ballistic power was measured by using the method of Taylor and Morris<sup>27</sup>. Apparatus consists of two parts, one the mortar, in which charge is fired and other the pendulum which receives the impact and stemming. The 4 gm of the explosives is wrapped in a tin foil, and fired with copper detonator in a steel chamber, attached to a pendulum bar, suspended on knife edges. The explosive ejects the projectile on to a rubber matting and the corresponding recoil of mortar is shown on the scale.

Duplicate shots for explosive and also for the same amount of special gelatine (80%) were fired. Ballistic mortar power results are given in Table 4.

TABLE 4

BALLISTIC MORTAR 'POWER' FOR COPPER AND SILVER DINITROANTHRANILATES

Compound	Angle of recoil	Power
Copper dinitroanthranilate	4°54'	18.39 (Partially decomposed)
Silver dinitroanthranilate	3°52'	10.42 (Partially decomposed)

## ACKNOWLEDGEMENTS

The authors are thankful to Dr. S.K. Srivastava of this department for useful suggestions and keen interest throughout the work. Their thanks are also due to Dr. R.S. Kapil, C.D.R.I., Lucknow for recording Infrared Spectra and Dr. G.M. Chopra, Research Manager, Indian Explosives Limited, Gomia for providing experimental facilities for the determination of impact sensitivity, friction sensitivity and ballistic mortar power.

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