

CHEMISTRY OF METAL (BENZYLIDENE) PICRAMATE—PART III BENZYLIDENE PICRAMATES OF ZINC, CADMIUM AND MERCURY

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Benzylidene picramates of zinc, cadmium and mercury have been prepared by treating the corresponding aqueous sulphate and chloride solutions with sodium salt of 4'-dimethylaminobenzylidene-2-hydroxy-3, 5-dinitroaniline. A metal : ligand ratio of 1:2 has been established in all these cases. I.R. spectral studies of metal benzylidene picramates show $N \rightarrow M$ coordination (where M is zinc, cadmium or mercury). Explosive properties of these benzylidene picramates have also been studied and it was found that the thermal stability increases as the atomic radius decreases or ionization potential increases.

A number of explosive properties of metal picrates and picramates have been studied by various workers¹⁻⁶. Little work, however, seems to have been carried out on benzylidene picramates of metals. The present communication deals with the chemistry and explosive properties of zinc, cadmium and mercury benzylidene picramates.

EXPERIMENTAL

All the chemicals used were of AnalaR grade (BDH). 4'-Dimethylaminobenzylidene-2-hydroxy-3, 5-dinitroaniline was prepared by refluxing picramic acid and *p*-dimethylamino-benzaldehyde at 100° C in ethanol for 3-4 hours in 1 : 1 molar ratio. Sodium benzylidene picramate was prepared by suspending a known weight of 4'-dimethylaminobenzylidene-2-hydroxy-3, 5-dinitroaniline in water and then treating it with an equivalent amount of sodium bicarbonate. The resulting mixture was digested on water bath to ensure complete reaction. After cooling, the product was filtered and washed with ice-cool water. Red crystals of sodium benzylidene picramate were obtained.

The general method employed for the preparation of metal benzylidene picramate is similar to that employed for metal picramates. The benzylidene picramate in question is simply prepared by adding a solution of an appropriate salt of the metal to a solution of sodium benzylidene picramate. For example, the benzylidene picramates of zinc, cadmium and mercury was precipitated from zinc sulphate, cadmium chloride and mercury chloride respectively. After keeping the reaction mixture overnight, the precipitate was separated by filtration, washed with water and ethanol and dried in a vacuum desiccator to constant weight and analysed for its constituents. This simple procedure was employed in the preparation of all these compounds. Results of microanalyses are listed in Table 1.

Spectrophotometric (visible) measurements were carried out with the help of a Unicam SP 8000 recording Spectrophotometer and a Unicam Spectrophotometer number 23704. (Job's continuous variation method⁷). The pH measurements were carried out with a Leeds and Northrup Co. (Philadelphia, U.S.A.) pH meter. The electrical conductances of the solutions were measured with a Toshniwal's conductivity bridge (type CL01/02). Job's monovariation method⁷ was employed to determine the composition of these complexes. I.R. spectra of the complexes were recorded with the help of a Perkin-Elmer Infrared Spectrophotometer model 337 using KBr pellet technique in the range of 400-4000 cm^{-1} . T.G. was carried out on a thermogravimetric analyser supplied by Planning and Development Division, Fertilizer Corporation of India, Sindri Bihar. The magnetic susceptibility measurements were carried out with the help of Gouy's method using a semimicro balance and a field of 1000 gauss at room temperature (303°K).

EXPLOSIVE PROPERTIES

The compounds used for the measurements of explosive properties were dried at 373-383°K for 2-3 hours to constant weight.

The explosive properties like explosion delay, explosion temperature, activation energy and explosion pressure were measured in a manner similar to that reported in an earlier communication⁶.

For measuring explosion delay (D_E), approximately 20 milligrams of the prepared compound was taken in a small pyrex tube (diameter 0.96 cm and thickness 0.14 cm) at the room temperature. The tube was then suddenly plunged into a paraffin liquid bath maintained at 595° K. The interval between the time of insertion and the moment of explosion was noted with the help of a stop watch. A mean of three reading was taken as the final reading in each case. Values of D_E are given in Table 2.

To measure explosion temperature (T_E), the above experiment was carried out at various temperatures in potassium hydrogen sulphate bath (instead of liquid paraffin) and D_E was plotted against the temperature of the bath. Explosion temperature was read off from this plot as the temperature necessary to cause explosion in exactly 10 seconds. Results are recorded in Table 2.

Thermal sensitivity of an explosive is related to the activation energy controlling⁸ D_E

$$\log D_E = \frac{E}{4.57 T} + B$$

(T is the absolute temperature of the bath in which the experiment is carried out). Curves obtained by plotting D_E against $1/T$ are given in Fig. 1.

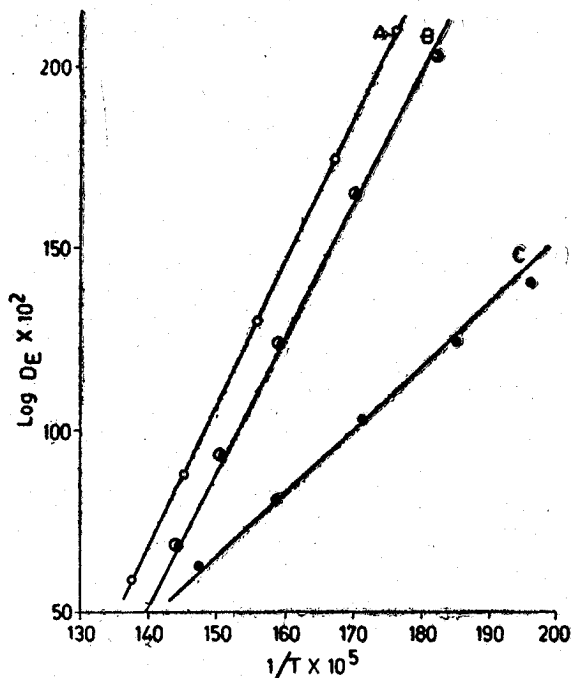


Fig. 1—Variation of $\log D_E$ with reciprocal of absolute temperature. A=Zinc benzylidene picramate, B=cadmium benzylidene picramate and C=mercury benzylidene picramate.

Explosion pressure was measured in a manner similar to that employed by Yoffe⁹ for studying thermal decomposition of azides. Instead of silicone oil potassium hydrogen sulphate was used in the bath in which explosion was carried out. The results obtained are listed in Table 4.

RESULTS AND DISCUSSION

Result are recorded in Tables 1—5 : Plots of D_E against $1/T$ are given in Fig. 1 (values of E obtained by these straight line curves are given in Table 3).

TABLE 1
ANALYTICAL DATA FOR METAL BENZYLIDENE PICRAMATES

Complex*	M (%)	N (%)	H ₂ O (%)
Zn[C ₁₃ H ₇ (NO ₂) ₂ NO.N(CH ₃) ₂ (H ₂ O)] ₂	9.0 (8.6)	15.0 (14.7)	4.9 (4.7)
Cd[C ₁₃ H ₇ (NO ₂) ₂ NO.N(CH ₃) ₂ (H ₂ O)] ₂	13.7 (13.9)	13.7 (13.9)	4.3 (4.5)
Hg[C ₁₃ H ₇ (NO ₂) ₂ NO.N(CH ₃) ₂ (H ₂ O)] ₂	22.2 (22.4)	12.7 (12.5)	4.4 (4.0)

*Satisfactory C,H analyses were obtained for all complexes. Calculated values are given in parentheses.

TABLE 2
EXPLOSION DELAY AND EXPLOSION TEMPERATURE FOR THE METAL BENZYLIDENE PICRAMATES

Complex	Explosion delay at 593°K (sec.)	Explosion temp. for explosion delay of 10 sec (K)
Zinc benzylidene picramate	60.3	694±2
Cadmium benzylidene picramate	35.4	645±2
Mercury benzylidene picramate	9.1	582±2

TABLE 3
VALUES OF E FOR DIFFERENT COMPOUNDS

Complex	Activation energy (KJ/mole)
Zinc benzylidene picramate	78.50
Cadmium benzylidene picramate	62.22
Mercury benzylidene picramate	51.70

TABLE 4
EXPLOSION PRESSURE FOR DIFFERENT COMPOUNDS DENSITY OF MERCURY=13.595 g/ml; GRAVITATIONAL ACCELERATION (g)=980.665 cm Sec²

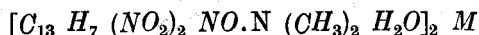
Complex	Height (m)	Explosion pressure* (bath temp. 623±2°K) (nm ⁻² × 10 ⁸)
Zinc benzylidene picramate	0.1050	14.00
Cadmium benzylidene picramate	0.0890	11.87
Mercury benzylidene picramate	0.0830	11.06

*The Explosion pressure was obtained by taking 10 mg of the explosive material.

TABLE 5
SOME CHARACTERISTIC ABSORPTION FREQUENCIES IN SCHIFF BASE AND ITS METAL DERIVATIVES

Compound	Characteristic absorption frequencies (cm ⁻¹)		
	Metal-Nitrogen	Coordinated water	-N=C
<i>p</i> -Dimethylamino benzylidene picramic acid	—	—	1630
Zn-(II) <i>p</i> -dimethylamino benzylidene picramate	495	700	1618
Cd-(II) <i>p</i> -dimethylamino benzylidene picramate	478	730	1615
Hg-(II) <i>p</i> -dimethylamino benzylidene picramate	490	680	1605

In all the cases, the spectrophotometric (visible), potentiometric and conductometric studies and micro-analysis point to the formation of complex in the metal : ligand ratio of 1:2. The general formula may be expressed as



where M stands for zinc (II), Cadmium (II) or mercury (II). Table 5 give some characteristic absorption frequencies in the Schiff base and its metal derivatives in the IR region. Absorption associated with $-N=C$ deformation mode is expected to appear near 1640 cm^{-1} .¹⁰⁻¹² In Schiff base a band appears at 1630 cm^{-1} while in the metal complexes it is found in the region $1620-1600\text{ cm}^{-1}$. The lowering in the $-N=C$ frequency in the complexes is due to the coordination of $-N=C$ with the metals^{11,13}. Other bands appear in the region $1600-1300\text{ cm}^{-1}$ and are due to ring deformation modes. Coordinated water gives bands in the range $880-650\text{ cm}^{-1}$.^{14,15}

In the Schiff base a band is present near 3475 cm^{-1} . This could be assigned to the phenolic group which normally absorbs in the region $3600-3500\text{ cm}^{-1}$. The shift in the absorption peak is due to the intramolecular hydrogen bond present between the hydrogen of the phenolic group and the oxygen of the nitro group ortho to each other^{12,16,17}. However, a band in the region $3600-3400\text{ cm}^{-1}$ could also be due to the presence of water molecules¹⁸ and is not influenced by coordination. But, hydrogen-bonding in the complexes is expected to disappear completely due to ionization of the labile hydrogen and coordination of the negative oxygen with the metal concerned. Thus, benzylidene picramic acid has two centres of coordination, viz. the nitrogen of the $-N=C$ group and the oxygen of the phenolic group.

In addition to these frequencies a frequency is observed between $500-300\text{ cm}^{-1}$. This may be assigned to the metal-nitrogen stretching modes similar to the metal-nitrogen stretching modes in metal glycine complexes assigned by Nakamura¹⁹. The metal-oxygen stretching frequency has been reported at $360-260\text{ cm}^{-1}$.^{20,21} However, Lane *et. al.*²² assumed that metal-oxygen vibration appears below 200 cm^{-1} because metal-oxygen band is highly ionic.

The magnetic susceptibility measurements carried out by us show that these benzylidene picramates are diamagnetic. This is also what we would expect for d^{10} ions¹⁴.

A gravimetric estimation of coordinated water molecules show that two molecules are present in each of these complexes. The fact that a bidentate ligand is involved and two water molecules are coordinated to it points to an octahedral geometry for these complexes which can be represented as shown in Fig. 2.

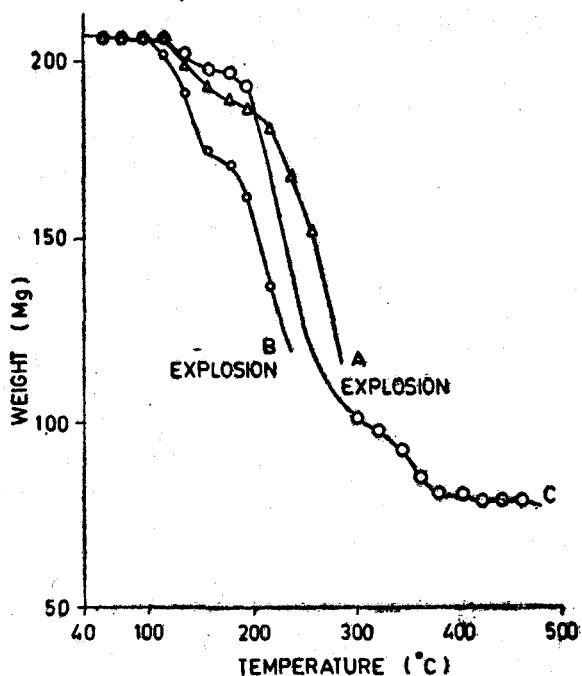
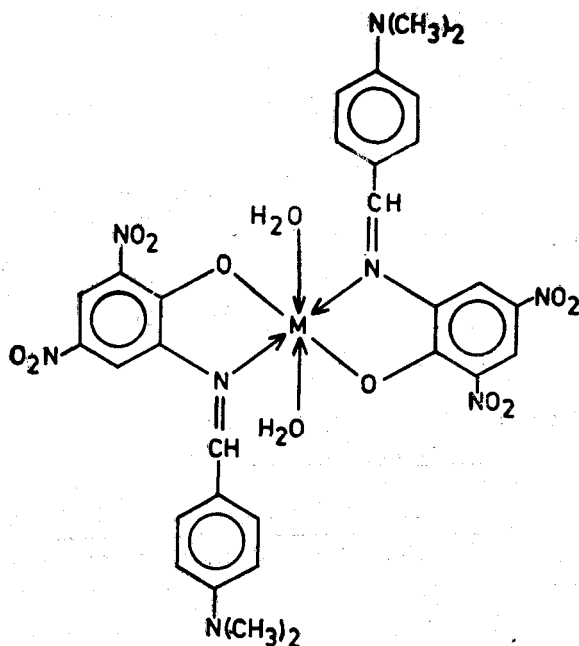


Fig. 2—Structural formula of metal (benzylidene) picramates [m stands for Zn (II), Cd (II) or Hg (II)].

Fig. 3—Thermogravimetric analysis of metal-benzylidene picramates (A=Zinc benzylidene picramate, B=Cadmium benzylidene picramate & C=Mercury benzylidene picramate).

From the T.G. study (Fig. 3) it has been observed that the zinc and cadmium benzylidene picramates explode at 553°K and 513°K respectively while mercury benzylidene picramate does not explode even up to 673°K. As obvious from the T.G. curve in the case of mercury complex, the loss in weight is accompanied by elimination of water molecules. A change in curve between 473-513°K clearly indicates that the complex is decomposed into mercury oxide. After 513°K a nearly constant weight is obtained which indicates that the complex is completely decomposed into mercury oxide between 473-513°K.

On the basis of the above discussion it may be concluded that the zinc benzylidene picramate is thermally more stable than the analogous complexes formed by cadmium and mercury. These conclusions are further supported by the data on explosive properties viz. explosion delay, explosion temperature and activation energy. For example, the explosion temperature, (T_E) follows the order: T_E (Zn complex) T_E (Cd complex) T_E (Hg complex), which is the same as that observed in T.G. Studies. It may be concluded that the thermal stability increases as the ionic radius decreases or ionization potential increases. This has also been established by various other workers²³⁻²⁵.

On the basis of the value of bond dissociation energies^{26,27} of different linkages present in the metal benzylidene picramates, it may be suggested that the initial stage in the explosion reaction is the breaking of the N-O linkage^{28,29} of the $-NO_2$ group directly linked to the benzene nucleus. This then enables the oxygen which was linked wholly to nitrogen to be consumed for the complete oxidation of carbon and hydrogen obtained from the ring rupture and thus produces a huge amount of heat.

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