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**Chandana Kumari**
Research Scholar, University Department of Chemistry, T.M.B.U Bhagalpur, Bihar, India

**Correspondence**
**Chandana Kumari**
Research Scholar, University Department of Chemistry, T.M.B.U Bhagalpur, Bihar, India

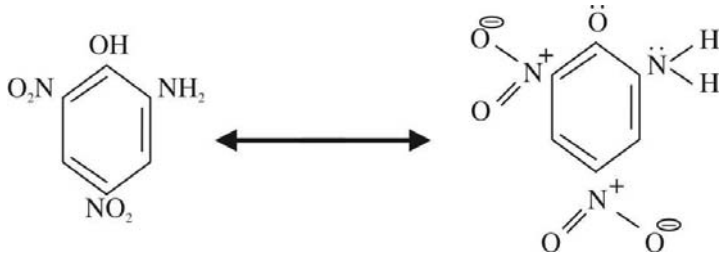
# Preparation of copper (II), mercury (II) and $UO_2^{2+}$ complexes with picramic Acid

## Chandana Kumari

**Abstract**
Complexes of metals with various ligands have been known from long time and synthesis and application of new ligands are always being tried to prepare varieties of complexes. In this direction, picramic acid which is 2-Amino -4, 6-dinitrophenol has been prepared in this laboratory and complexes with Copper (II), Mercury (II) and $UO_2^{2+}$ have been prepared. The characterization of theses complexes have been done in terms of elemental analysis, IR and UV Spectra and melting points.

**Keywords:** ligands, picramic acid, 2-amino-4, 6-dinitrophenol, copper (II), mercury (II), $UO_2^{2+}$

## Introduction
The complex ions and coordination compounds are the basis for some of the most exciting and active areas of chemical research today. Inorganic ions in the human body are present in coordination compounds as complex ions i.e. bio-inorganic chemistry; metal form many coordination compounds with organic compounds i.e. Organo-metallic chemistry and catalysts often function via coordination compounds or complex ions. Some coordination compounds are extremely stable whereas others are unstable; many have color that are quite different from the colors of their constituents. Some are readily soluble in water and others are soluble only in non-polar solvents some are volatile and others are not [1].
These metal complexes are formed with the help of or by the use of or due to the process of coordination. Complexes are generally made up of organic compounds with transition metals. During this process of coordination complexes, chelation, complexation and ligation have well defined role. It was also known that many metal salts in which normal valencies of metal atoms are fully satisfied combine with other molecule capable of independent existence to form what were considered to be molecular compounds [2]. Coordination compounds are also applicable for making dyes.
For complexation of metal designing of ligands becomes the most important part, with this purpose picramic acid has been selected because it contains one –OH group at one position and one $NH_2$ group at either at 2- position and the remaining 4 -position and 6-position or 2-position and 6position are occupied by -$NO_2$ groups, -$NH_2$ groups contains lone pair of electron and -OH group is acidic and can be deprotonated.




2-Amino-4,6-dinitrophenol (picramic acid)

Picramic acid is used in pyrotechnics and rocket fuel. Moreover, the acid and its salts are used in the preparation of dyes (Acid, Chrome), insecticide and are utilized as a colorometric reagent to determine albumin.

In many fields where picramic acid is used, like medicines, pharmacy, analytical, phamacology, domestic uses, alkaloids, drugs, etc. [3].

A method for the determination of sugar in normal urine [4].

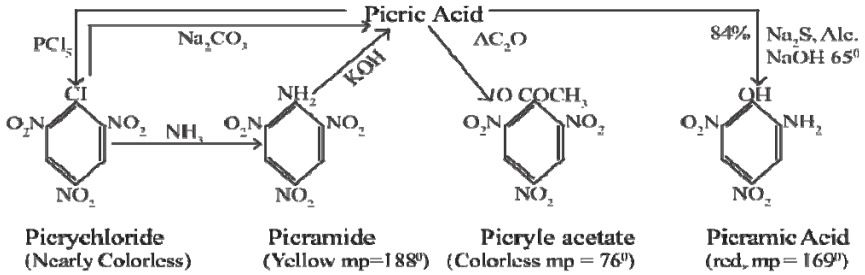
The importance of Picramic acid as a standard for benedict blood sugar determination.

Picric Acid is versatile organic compound used for variety of purpose like explosive, yellow dye for woollen fabrics etc. It can be used to prepare amino-derivatives like 2-amino-4,6 dinitro phonol; 2,4Diamino-6-nitrophenol and 2,4,6-Trinitrophenol etc. Picramic Acid is 2-Amino-4,6 dinitrophenol which has been used to prepare compounds. This is done very carefully and various methods are available in the literature by A. Girard [5], C, Lea [6] and also Grete Egerer [7].

A pure sample of picric acid required for the synthsis of Picramic Acid.

**Experimental**

Since an improved method of converting picric acid into picryl chloride is the action of ptoluene sulfonyl chloride (CH3 C6 H4 SO2 Cl) in the presence of dimethyl aniline in nitrobenzene solution (70% yield); the method is applicable also to 2, 4 - dinitrophenol (Ullmann, 1908) [8].




While going through literature we could identify one very important derivative of picric acid and this is Picramic Acid.

At first, picric acid is purified with water and removing the insoluble portion, if any by filtration, then on cooling, picric acid separates out in the form of fine yellow needles.

This purified picric acid can be used for preparing picramic acid. The reduction of only one - $NO_2$ group either at 2 or 6 position into -$NH_2$ group can be brought out by various methods like :-

1. By using Ammonium hydroxide and Zn-dust in neutral medium [9].
2. By using mixture of sodium sulphide and powdered sulphur i.e via sodium polysulphide [10].
3. By using $H_2S$ in Ammonium Hydroxide [11].
4. By using $Na_2S$ in 74% alcoholic NaOH at $600^0$C [12].

Preparation of picramic acid is not simple and involves selective reduction of one - $NO_2$ group present either at 2- or 6- position. This is done very carefully and various methods are available in literature.

We have also used method no. (i) and (ii) but no accurate melting point of Picramic Acid comes. So, we have followed the third method which was reported in literature may be effective. Hence this will be followed to prepare a sizeable quantity of picramic acid.

One method commonly used for the preparation of picramic acid is that of Girard [13], which states: If a cold saturated alcoholic solution of picric acid is neutralized with ammonium hydroxide and then saturated with hydrogen sulfide the liquid turns red and small red crystals are deposited. On distilling off the alcohol, sulfur and additional red crystals are deposited. They are the ammonium salt of picramic acid from which picramic acid can be obtained on addition of acetic acid to the hot aqueous solution.

We have prepared complex compounds of alcoholic solution of picramic acid with metals

like Mn (II), Ni (II), Fe (II), Al (III), Ag (I), Mg (II), Cu(II), Co(II) etc. But preparation of complexes with Picramic Acid is not very easy. It takes suitable time with suitable condition (like temperature, pressure and molar concentration).

Picramic acid is very hazardous for our health. Picramic acid is very risky for explosion by shock, friction, fire or other sources of ignition. It is toxic by inhalation and in contact with skin and also if swallowed too.

**Preparation of addition compounds of Picramic Acid**

**(A) Preparation of Addition compounds of $HgCl_2$ with Picramic Acid**

Taken one test tube Alcoholic solution of picramic acid in refluxing flask and also added about 2mg of $HgCl_2$ to it and reflux it for 10-15 hrs. A deep brown color residue is obtained. This complex compound is also vacuum dried and the melting point of this residue is observed at $158^0$C. Also the molecular weight of this addition product is 470.0gm.

**(B) Preparation of Addition compound of Picramic Acid with Anhydrous $CuCl_2$ compound**

Anhydrous $CuCl_2$ reacted with 1 test tube solution of picramic acid solution on condensing flask. The complex with copper were obtained by refluxing this compound. A brownish black compound was obtained. The melting point of this compound is found at $135^0$C. The total molecular weight of this complex compound is 333.5gm.

**(C) Preparation of complex Compound with Uranyl nitrate (anhydrous) $UO_2(NO_3)_2.6H_2O$**

Taken Uranyl nitrate is dried in conc. $H_2SO_4$ desiccator for one week. Then it was refluxing with alcoholic solution of picramic acid. After 10-15 hrs deep blue residue was obtained. The melting point is $162^0$c at the molecular weight of complex compound is 593.

**Summary & Conclusion**

All the used Chemicals and solvents were of Anal R grade. All of the Metal salts and Organic acids of analytical reagent grade were obtained from s,d-fine chemicals(Mumbai, India) and were used without further purification. Picric Acid was used as obtained from Merck (Germany and UK). The Major

solvent Ethenol was purified and dried by standard method. The molecular weights were determined by Rast Camphor Method.

Electronic spectra (MeOH) were recorded on Perkin-Elmer Lambda-2B-Spectrophotometer

FI-JR (in KBr) spectra were recorded at SAIF (Sophisticated Analytical Instrumentation Facility),

CDRI (Central Drug Research Institute) Lucknow. And the IR and UV Spectra of Picramic Acid and

Diamino Picramic Acid were recorded at Department of Chemistry Nagpur University Nagpur.

The Nature of the ligand field around the metal ion and the geometry of complexs have been deduced from the electronic spectra. The electronic absorption spectra of the complexes were recorded at room temperature using methanol and ethanol as solvent.

Solution of the complexes was made in methanol to check the reactivity and substitution behaviour against hydroxyl, aquo, amine, chloro acid thio-cynates ligand. The reaction were monitored by observing change in colour or precipitation [14-15].

Their preparation is not so easy, for this many researchers, and co-workers applied lots of methods for preparation of this dye. Some researchers said it is brown paste or brown dye, some of said red dye, and also for some of researchers, it is very difficult to investigate after making of picramic acid why this got Sulphur- smell. Picramic acid is prepared by Picric acid, and picric acid is already a yellow dye and explosive in nature too, it contains three - $NO_2$ group at 2,4,6 position and –OH group contain at 1-position. But the difficulty is to making the conversion of one $–NO_2$ group to $– NH_2$ group this conversion takes time with suitable conditions.

We have prepared complex compound of alcoholic picramic acid with metals like Mn(II),

Ni(II), Fe(II), Al(III), Ag(I), Co(II), Cu(II), $UO_2$(II) etc.

Some of them are well characterized with the help of their sharp melting point, IR, UV, Mass spectra, while some of them have not sharp melting points. Finally, there are great importance of picramic acid and also for its addition compound too. Now a days, many researchers, biologist, pharmacologists are doing progressive investigation for picramic acid.

Then all these functional groups help to prepare a new complex compounds with appropriate metals and form a good ligand. The tendency towards complex formation is most strongly displayed by elements in the middle of the long periods of the periodic table, especially by the elements of analytical group III, IV and V. It is precisely the cations of the metals of these groups that frequently play the role of complexing agents and give rise to a large variety of complex compounds. Organic substances that form stable soluble complexes with most of the cations have also found wide application. These substances are collectively known as complexes. Complexes are polybasic organic acids or their salts containing amino groups like amino acids.

All the ligands and complexes gave satisfactory analysis. The IR spectra of the ligands and their metal complexes were recorded in KBr disc in the region 4000-500cm-1 range in Perkin Elmer 783 FTIR spectrophotometer. The electronic spectra of complexes were recorded on Elico SL-164 double beam UV-Vis spectrophotometer in the range 200-500nm in DMF (10-3M) solution. Mass Spectra were recorded on JEOL SX 102/DA-6000 mass spectrophotometer from CDRI Lucknow and the mass spectra is shown at the region between 0-1000 m/z. The IR spectrum of all the eight complexes shows that

ν(C-H), ν (O-H) Phenolic, ν (-N-O), ν (C=C), ν (C=O), ν (C≡N), ν (N-H), ν(Free-OH) stretching

Vibrations were observed at (770 $cm^{-1}$-769.9$cm^{-1}$), (1217.3$cm^{-1}$ 1235.4$cm^{-1}$).

(1338.1$cm^{-1}$-1436.2$cm^{-1}$), (1552.4 $cm^{-1}$-1597.9$cm^{-1}$), (1627.4$cm^{-1}$-1724.5$cm^{-1}$), (2106.2$cm^{-1}$-2366.6$cm^{-1}$), (3359.3$cm^{-1}$-3475.7$cm^{-1}$) and (3630.8$cm^{-1}$-3698.8$cm^{-1}$) respectively [14-30].

These values are in agreement with those reported for similar compounds.

The electronic spectra of the ligands and all the complexes were recorded in DMF at room temperature. The aromatic band of the ligands at ~250nm is attributed to benzene π→π* transition.

The band around ~300 nm is due to the n→ π* transition of non-bonding electrons present on the nitrogen to azomethein group. The complexes of Co (II) and Cu (II) show less intense shoulders due to d-d transition of the metal ions. $UO_2$ (II) complexes the two bands observed at 1103.4$cm^{-1}$ and 655.3$cm^{-1}$ are assigned to ν3 vibrations of the coordinated -NO3 group. Which is resembles with correct vibration ν3=776.1$cm^{-1}$. Indicate the linear character of the $UO_2$ group.

Cu (II), the IR spectra observed at 532$cm^{-1}$ correct band is observed at ν3 (405$cm^{-1}$) for [M-$Cl_2$] linear.

As we have mention earlier, my calculated data like IR, UV, NMR & Mass Spectra for picramic acid and their complex compounds are good agreement with the observed value. Hence, ligation, chelation occurs in this process.

In the present work, we have tried to explore the preparation of another addition compound with picramic acid.

The present work on Picramic acid and its addition compound, the investigation will be very useful for researchers and their co-workers. A further pursuation our work will give an idea for making more and more additional compound in the field of dye chemistry because picramic acid is very interesting colour dye, explosive and toxic in nature. In addition, due to having three different types of functional groups like –OH, -$NO_2$ and -$NH_2$ group. Further work may be undertaken to prepare more and more complex compounds.

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