L.S COLLEGE MUZAFFARPUR

Dept. of chemistry

what is Dimethylglyoxime?

Dimethylglyoxime is a white powder with the **molecular formula $C_4H_8N_2O_2$.**

Dimethylglyoxime is soluble in methanol or in sodium hydroxide solution. It is one of the first selective organic reagents applied in analytical chemistry. It is an extraordinary sensitive and specific reagent for nickel. Many derivatives of Dimethylglyoxime has been synthesized and proposed. Although commonly used as a reagent specific to nickel, Dimethylglyoxime actually allows the detection of other metal ions.

Other name – *2,3-Butanedione, Biacetyl dioxime, dioxime, N-(3-hydroxyiminobutan-2-ylidene)hydroxylamine*

$C_4H_8N_2O_2$	Dimethylglyoxime
Density	1.37 g/cm^3
Molecular Weight/ Molar Mass	116.12 g/mol
Boiling Point	Not determined
Melting Point	240 to 241 °C
Chemical Formula	$CH_3C(NOH)C(NOH)CH_3$

Physical Properties of Dimethylglyoxime – $C_4H_8N_2O_2$

Odour	Odorless
Appearance	Off White Powder
Complexity	112
Dipole moment	0
Hydrogen Bond Donor	2
Solubility	Insoluble in water, soluble in alcohol

Chemical Properties of Dimethylglyoxime – $C_4H_8N_2O_2$

- Nickel cation reacts with dimethylglyoxime forms an insoluble red precipitate of nickel dimethylglyoxime.

$Ni^{2+} + 2C_4H_8N_2O_2 \rightarrow Ni(C_4H_7N_2O_2)_2\downarrow$(red precipitate) $+ 2H^+$

- Dimethylglyoxime reacts with ferrous sulphate and ammonium hydroxide forms a complex compound of iron and ammonium sulphate and water is formed.

$FeSO_4 + 2NH_4OH + 2C_4H_8N_2O_2 \rightarrow Fe(C_4H_7N_2O_2)_2 + (NH_4)_2SO_4 + 2H_2O$

Uses of Dimethylglyoxime – $C_4H_8N_2O_2$

- Widely used in analytical chemistry as a selective precipitating reagent, detecting reagent and photometric reagent for nickel, palladium, platinum and some other metal ions.
- Used as a test for nickel release and used for jewellery and for other objects that come in direct contact with the skin. In many countries the dimethylglyoxime test is now commercially available in pharmacies or chemist shops.
- Used as a specific precipitant for nickel and palladium. Nickel precipitates as a bright red voluminous compound from ammoniacal solution, white palladium come down as a yellow compound from dilute hydrochloric acid solutions. These are dried and weighed as stoichiometric compounds.

Frequently Asked Questions

What is Dimethylglyoxime used for?

Dimethylglyoxime is used for the identification and quantification of nickel into the bright red compound of nickel bis(dimethylglyoximate)

Why is Dimethylglyoxime insoluble in water?

Ni(DMG)2 is a neutral complex the abbreviation is dmgH2 for neutral form, and dmgH for anionic form, where H stands for hydrogen that is usually insoluble since there are no charges on the compound to bind and solve the ion by polar water molecules.

What type of ligand is DMG?

Dimethylgloxine (dmg) is a bidentate ligand chelating large amounts of metals. Only two dmg molecules per metal center are needed, because Ni(dmg)22 + has a square-planar geometry. To the aqueous array, add 1 per cent dmg.

What is the role of DMG in analytical chemistry?

Dimethylglyoxime (DMG) is an analytical reagent used from its aqueous solution to precipitate Ni. The method is very effective in terms of selectivity and completeness for Ni recovery but is hardly industrially adopted. The cause is attributed on calcination to the failure of the reagent.

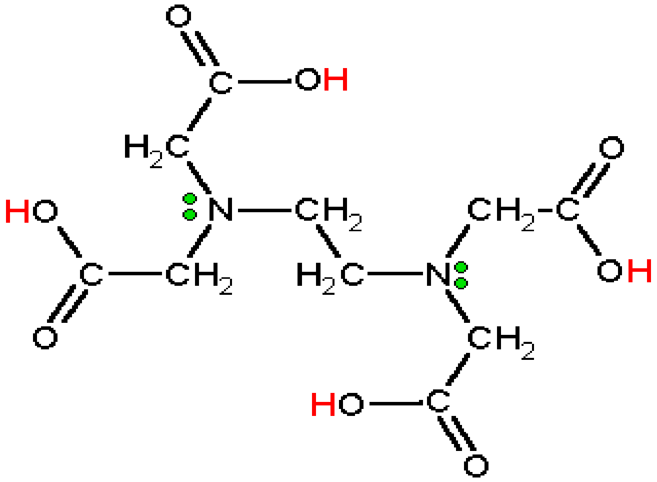
Is DMG Bidentate?

Dimethylgloxine (dmg) is a bidentate ligand chelating large amounts of metals. Only two dmg molecules per metal center are needed, because Ni(dmg)22 + has a square-.

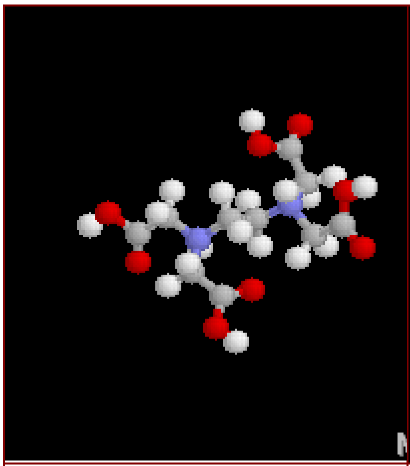
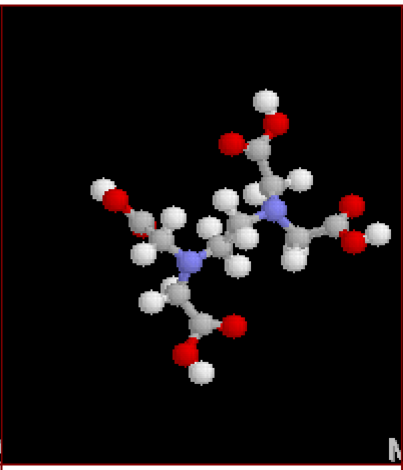
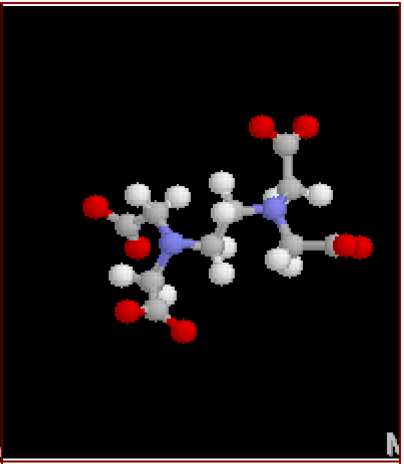
Related Chemical Compounds	
Potassium carbonate (K_2CO_3)	Hydrogen sulfate (HSO_4^-)
Zinc carbonate ($ZnCO_3$)	Dinitrogen trioxide (N_2O_3)
Oxalate ($C_2O_4^{2-}$)	Methylene blue ($C_{16}H_{18}ClN_3S$

The EDTA Molecule

EDTA or ethylenediaminetetraacetic acid is a novel molecule for complexing metal ions. It is a polyprotic acid containing four carboxylic acid groups (acidic hydrogens are red) and two amine groups with lone pair electrons (green dots). The classic structural formula is given below. EDTA is synthesized on an industrial scale from ethylenediamine, formaldehyde, and a source of cyanide (HCN or NaCN). On a worldwide basis over 100,000 metric tons are produced annually.



Besides the four carboxylic group hydrogens, EDTA can add two more hydrogens onto the amine groups. The structures of the fully protonated form (left), the typical form found in many textbook (center, matching the 2D structure above), and the fully deprotonated (all acidic H's removed) form (right) are given below.

		
forms at very low pH or very acidic condition (fully protonated) H_6Y^{+2}	classic form H_4Y	forms at very high pH or alkaline conditions (fully deprotonated) Y^{-4}

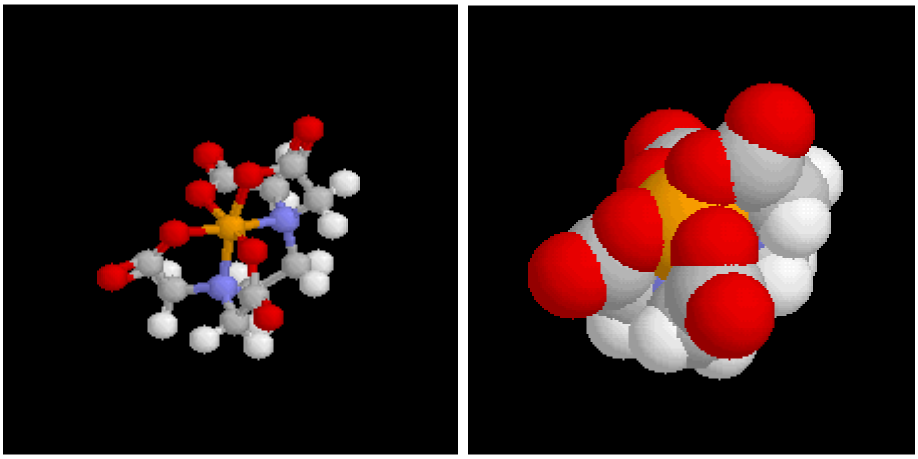
Complexing Metals

The unusual property of EDTA is its ability to chelate or complex metal ions in 1:1 metal-to-EDTA complexes. The fully deprotonated form (all acidic hydrogens removed) of EDTA binds to the metal ion. The equilibrium or formation constants for most metals, especially the transition metals, are very large, hence the reactions are shifted to the complex. Many of the reactions are pH dependent, especially the weaker forming complexes with Ca^{+2} or Mg^{+2}.

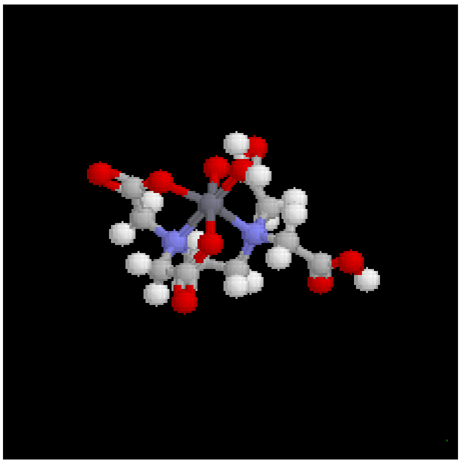
$$M^{+n} \quad + \quad Y^{-4} \quad \rightarrow \quad MY^{n-4} \qquad K_f = (MY^{n-4})/(M^{+n})(Y^{-4})$$

Metal analysis can be done by titration with EDTA and the use of a metal ion indicator. The pioneering work with EDTA was done by Gerold Schwarzenbach in the 1940's. The common reagent for making EDTA solutions is $Na_2H_2Y \cdot 2H_2O$. The values of K_f increase with the charge on the metal ion and as ionic radius decreases with constant charge. Water hardness, mostly from dissolved Ca^{+2} and Mg^{+2}, is determined by EDTA titration at pH = 10

The structure of a classical complex of Fe^{+3} with EDTA is shown below. This is EDTA acting as a hexadentate ligand or all six sites on the ETDA bind to the metal ion. How would you describe the geometry of the octahedral Fe^{+3} in the complex?

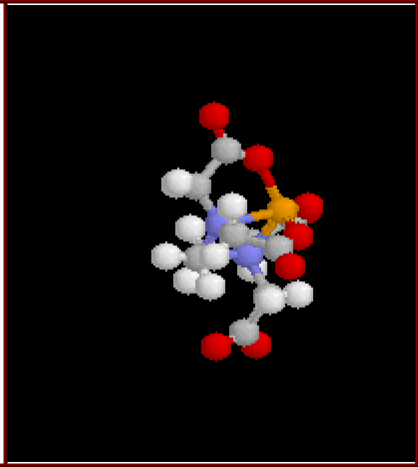
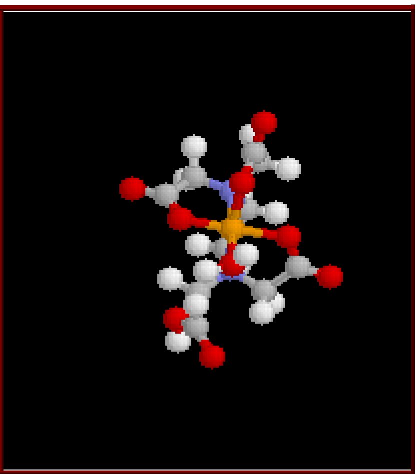


The octahedral coordination of the Fe-EDTA (left) and many other such complexes are very strained. The space-fill version of the structure (right) shows how crowded the structure appears. Consider the structure of Cr^{+3} with EDTA shown below. What is different for the Cr-EDTA complex compared to the Fe-EDTA complex?



A number of metal-EDTA complexes have been reported to have the EDTA acting as a pentadentate ligand (only five sites on EDTA bind, one carboxylic group does NOT). A water molecule or another ligand is in the sixth site, so the complexes are still octahedral in geometry.

So let's examine the formation of the complex. The animation below was produced in Spartan '04 by placing an Fe^{+3} (green) next to the EDTA with acidic H's removed (fully deprotonated as Y^{-4}) and then minimizing the energy. Note that EDTA forms only five bonds to the Fe^{+3}, as the complex forms (center image is complex at end of animation). The image to the right has a molecule of water added, plus the EDTA has picked up a hydrogen ion on the carboxylic acid group not bound to the iron, and energy minimized to form the six coordinate complex.

		
Animation of Y^{-4} complexing Fe^{+3} This is an avi file, so you'll need to have Real Player or Windows Media Player configured accordingly in order to see it.	complex with EDTA as a pentadentate ligand	octehedral complex with EDTA and water

Uses of EDTA

Because of its strong complexing ability for most metal ions, it is used in the food industry as a sequestering agent. The complexing of the metal ion may prevent further reactions, such as binding metals that are cofactors for enzymes, or just remove a metallic taste, such as metal contamination added during processing. See the Dow Chemical site on the use of their commercial product - Versene. Some typical examples are given below.

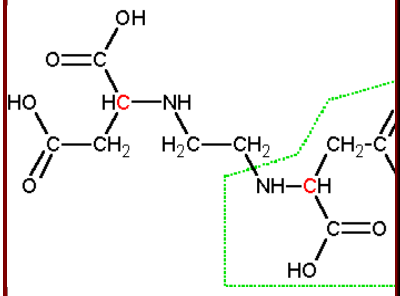
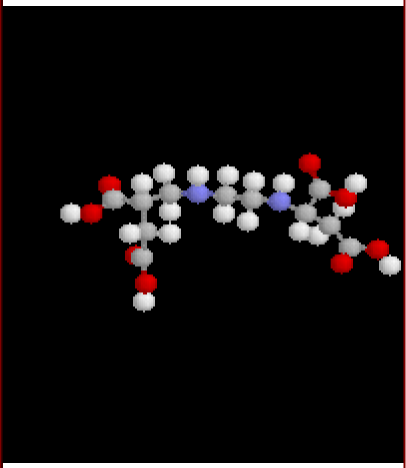
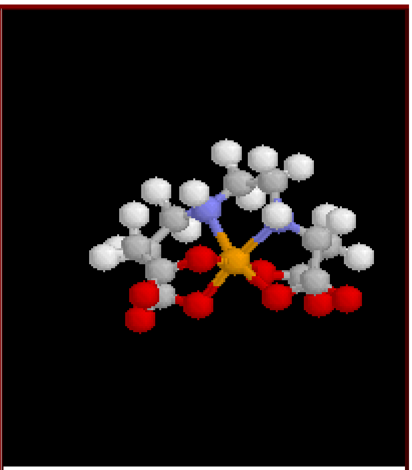
Recent studies have shown that NaFeEDTA and Na_2EDTA added to typical iron fortification compounds in cereals increased the absorption of iron in adult humans.

This same property allows EDTA use for incidents of lead poisoning by the medical profession. The formation constant for Pb-EDTA complex is 10^{18}. Intravenous injection of $Na_2CaEDTA$ solution is given at 25 mg/kg body mass/day over 6 hours for 5 days when blood lead levels go over 45 μg/dL. The Pb^{+2} ion replaces the Ca^{+2} ion in the complex because the formation constant for the lead complex is greater than the calcium complex.

$$Pb^{+2} + CaY^{-2} \rightarrow PbY^{-2} + Ca^{+2} \qquad K \sim 10^{8}$$

The five day limit is there to prevent Zn^{+2} depletion, since the Zn^{+2} ion replaces the Ca^{+2} ion in the complex too. EDTA is added to stored blood in blood banks as an anticoagulant to bind Ca^{+2} ion. Other reported uses of EDTA in medicine do not have a proven clinical basis.

Another major use of EDTA has been in detergents to act as a builder (chelates metals) especially as a replacement for phosphates, a major nutrient in wastewater. However, a problem with EDTA is its inability to biodegrade in the environment. EDTA is found in many natural waters and occurs at higher levels in wastewater effluents. Western European countries have banned the use of EDTA in detergents. For a complete discussion of the chelating agents in the environment - click here. EDDS (S, S'-ethylenediaminedisuccinic acid), a structural isomer of EDTA, has been used as a biodegradable substitute. EDDS is a good complexing agent and is broken down during wastewater treatment processes. This is a contribution to green chemistry by making a minor structural change.

		 >
EDDS structure showing chiral carbons in red - both must be S. l-Aspartic acid	biodegradable S, S'-EDDS molecule	octahedral $FeEDDS^{-}$ complex

EDTA is added to many commercial beers to stabilize foaming, taking advantage of the surfactant properties of EDTA, and used to remove scale by complexing calcium from calcium carbonate that forms on the processing equipment.

The blue color of the Cu-EDTA complex is used in many shampoos.