each case but containing different amounts of the metal ion and the ligand...

(*ii*) Let the total volume of the complex prepared in each of the ten solutions is 10 mL and the proportions of the metal ion and the ligand in these solutions is varied as below :

Metal ion (vol)	0	1	2	3	4	5	6	7	8	9
Ligand (vol)	10	9	8	7	6	5	4	3	2	1

Thus, it is obvious that the sum of the concentrations of the ligand (C_L) and metal ion (C_M) is constant (10) in each case and only their ratios are changed.

i.e.,
$$C_L + C_M = C \quad \ldots(1)$$

(*iii*) The optical density (absorbance) of each of the solutions is measured by spectrophotometer. In this process, such a wavelength of light is chosen which is absorbed strongly by the complex only, and not by the metal ion and the ligand...

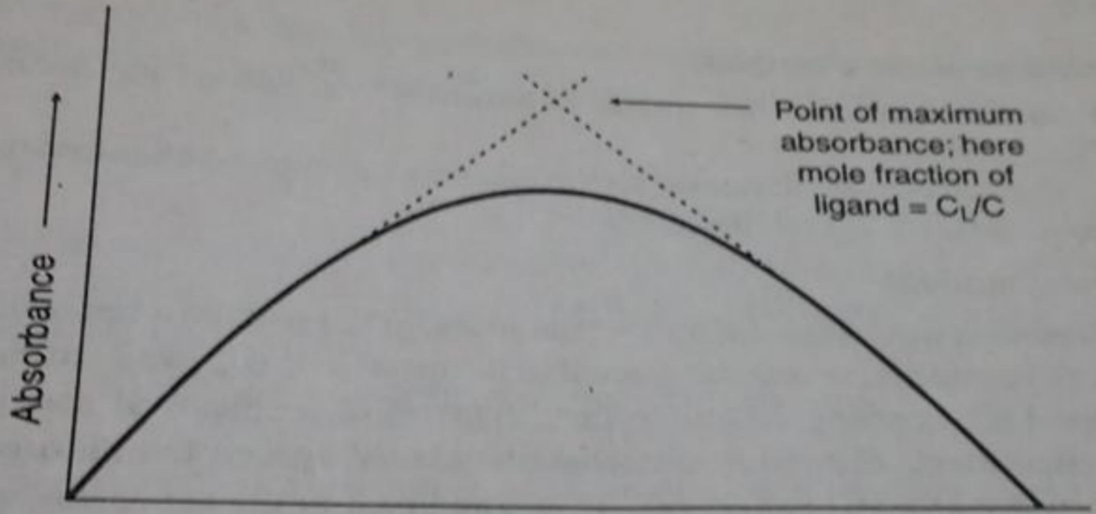


Fig. 1.7. Job's method for the determination of composition of a complex.

When the legs of the curve are extrapolated, they cross each other at a point at which absorbance is maximum.

Now if the formula of the complex is ML_n, then

$$n = \frac{C_L}{C_M} \qquad ...(2)$$

We also know that

$$x = \frac{C_L}{C} \qquad \ldots(4)$$

From eqs. (3) and (4)

$$x + \frac{C_M}{C} = 1$$

$$\therefore \qquad \frac{C_M}{C} = 1 - x \qquad \ldots(5)$$

Dividing equation (4) by (5), we get

$$\frac{C_L}{C} \times \frac{C}{C_M} = \frac{x}{1-x}$$

or

$$\frac{C_L}{C_M} = \frac{x}{1-x} \qquad \ldots(6)$$

From equations (2) and (6),

unreliable results.

2. The method is applicable only when there is no change in volume on mixing the solution of the metal ion and the ligand.

Mole-ratio method

This method was introduced by Yoe and Jones. In this method a series of solutions are prepared containing a constant amount of the metal ions (C_m) and varying amount of the ligand (C_l) keeping the total volume constant under identical conditions. The absorbance of these solutions is measured and plotted against the ratio of moles of ligands to moles of metal ion ($R = C_l/C_m$). The break in the curve will provide the composition of the complex.

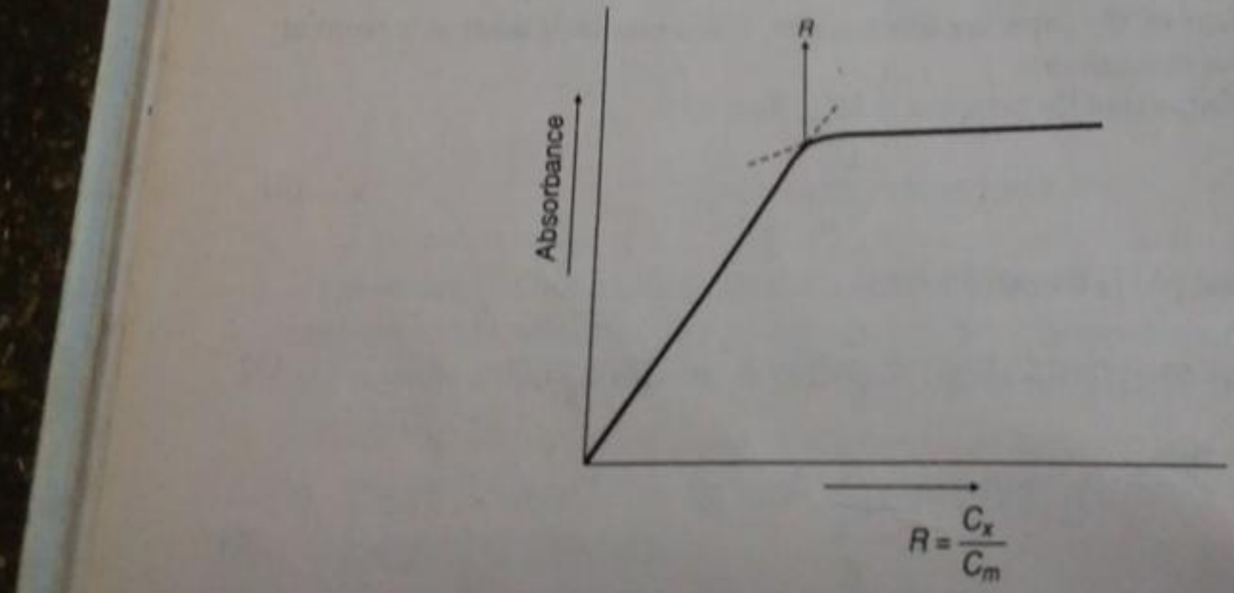


Fig. 1.8 Curve of mole-ratio method

analysis of inorganic anions; some of such uses are given below :

1. Separation of silver and mercury from each other

Silver ions are precipitated as white silver chloride precipitate which is soluble in ammonia due to the formation of silver ammonia complex.

$$Ag^{+} + Cl^{-} \longrightarrow AgCl\downarrow$$

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$$

The silver ammonia complex is soluble in water, owing to which it is separated from Hg_2Cl_2. It decomposes easily on treatment with dilute nitric acid in excess into silver chloride back.

$$[Ag(NH_3)_2]Cl + 2HNO_3 \longrightarrow AgCl\downarrow + 2NH_4NO_3$$

On the other hand, the white precipitate of Hg_2Cl_2 which is formed by the addition of HCl to mercury salt turns into black complex compound on treatment with

$\ldots_2O_3\downarrow + 2H_2O$
(Brown)

7. Separation of calcium and strontium

It is based on the fact that when excess of ammonium sulphate solution is added to Ca^{2+} and Sr^{2+} salts; the latter is precipitated as its sulphate, whereas the former remains in solution due to formation of a complex.

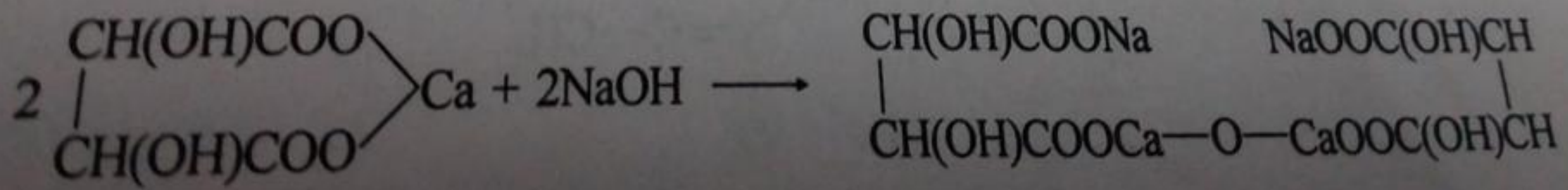
$$SrCrO_4 + (NH_4)_2SO_4 \longrightarrow \underset{\text{(white)}}{SrSO_4}\downarrow + (NH_4)_2CrO_4$$

$$CaCrO_4 + (NH_4)_2SO_4 \longrightarrow CaSO_4 + (NH_4)_2CrO_4$$

$$CaSO_4 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2[Ca(SO_4)_2]$$

8. Separation of tartarate from fluoride and oxalate

Fluoride, oxalate and tartarate are precipitated from the $CaCl_2$ solution as their calcium salts *viz.* calcium fluoride, calcium oxalate and calcium tartarate. All of these are insoluble in CH_3COOH. On addition of NaOH to their precipitate, calcium tartarate goes to solution in the form of complex whereas the other two remain unaffected.



9. Detection of cobalt (*cobalt nitrite test*)

Cobalt salts in neutral solution, acidified with acetic acid, give brilliant yellow precipitate with potassium nitrite solution. Firtsly, the cobaltonitrite complex is formed which is then oxidised to cobaltinitrite (HNO_2 functions as an oxidising agent : $2OHNO \rightarrow 2NO + H_2O + O$).

$$CoCl_2 + 6KNO_2 \longrightarrow K_4[Co(NO_2)_6] + 2KCl$$

$$2K_4[Co(NO_2)_6] + 2CH_3COOH + O \longrightarrow 2K_3[Co(NO_2)_6] + 2CH_3COOK + H_2O$$

Cobalt salts also form a complex with sodium bicarbonate. Whenever a cobalt salt is treated with an excess of sodium bicarbonate, a precipitate of cobalt carbonate is first formed which further forms a soluble complex sodiumcobaltocarbonate (nickel does not form the complex carbonate with sodium bicarbonate).

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

$$Na_2CO_3 + CoCl_2 \longrightarrow CoCO_3\downarrow + 2NaCl$$

$$CoCO_3 + 2Na_2CO_3 \longrightarrow Na_4[Co(CO_3)_3]$$

or

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4[Co(CO_3)_3] + 3H_2O + 3CO_2$$

$$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$$

$$CoCl_2 + 6NaHCO_3 \rightarrow Na_4[Co(CO_3)_3] + 2NaCl + 3H_2O + 3CO_2$$

The sodium cobaltocarbonate is oxidised in presence of an oxidising agent like bromine water to sodium cobalticarbonate.

$$2Na_4[Co(CO_3)_3] + 2NaHCO_3 + O \longrightarrow 2Na_3[Co(CO_3)_3] + 2Na_2CO_3 + H_2O$$

The cobalticarbonate complex is very stable and has an apple green colour which remains unchanged on heating. Cobalt ions are not precipitated from this complex by the usual reactions.

10. Complex of nickel

Nickel salts on treatment with an alkali solution give a precipitate of nickelous hydroxide. The precipitate is soluble in an excess of ammonia solution, and also in acids.

$$NiCl_2 + 2NaOH \longrightarrow Ni(OH)_2\downarrow + 2NaCl$$

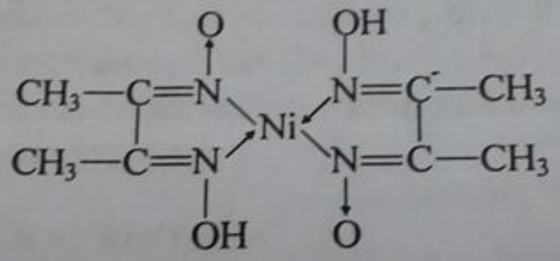
$$Ni(OH_2) + 2NH_4Cl + 4NH_4OH \longrightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

Owing to the formation of this complex, nickel is not precipitated as its hydroxid in presence of ammonium chloride in the III group.

11. Complexes is quantitative analysis

There are numerous reactions in quantitative analysis where complexes are formed. To mention a few are

(a) Estimation of nickel and other metals as dimethylglyoxime complex.



(b) Estimation of potassium as potassium tetraphenylborate.

(c) The most common application is the estimation of several cations (Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+} and Al^{3+}) using EDTA as titrant in presence of suitable indicator, *e.g.*, murexide solution.

(d) EDTA is used in the estimation of Ca^{2+} and Mg^{2+} ions in water (total hardness of water).

(e) EDTA is also used in softening hard water.

Complexation in Food Poisoning

Lead is a poison to the human system. It can cause encephalopathy (brain damage). This disease can produce convulsions, coma, blindness, mental retardation or even death. A person who has ingested lead is fed with $[Ca(EDTA)]^{2-}$. It reacts with the Pb^{2+} ions in the body to form $[Pb(EDTA)]^{2-}$.

$$Pb^{2+} + [Ca(EDTA)]^{2-} \rightarrow [Pb(EDTA)]^{2-} + Ca^{2+}$$

The complexed lead is excreted by the human body thus saving the victim from poisoning. The lead-EDTA complex is much more stable than the Ca-EDTA complex and therefore the Pb^{2+} ions in the body are readily trapped by EDTA. Victims who have ingested radioactive metals are treated with EDTA for detoxification. This chelant helps in quick elimination of the hazardous radioactive metals from the body.

Some of the enzymes in the human system have the cysteine unit, HOOC — CH(NH_2) — CH_2 — SH. The lead forms covalent bonds with the sulphydryl (SH) groups of cysteine and inhibits enzyme actions; this is the basis for lead poisoning. EDTA binds the lead atoms more strongly than cysteine does and consequently releases the enzyme for its normal physiological action.

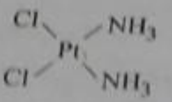
Q17. Write the use of coordination complexes in cancer therapy.

Ans :

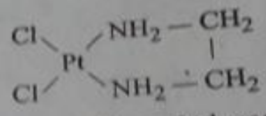
Metal Complexes in Therapy

Tumour Therapy

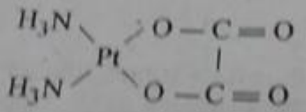
Some coordination compounds of platinum inhibit the growth of cancerous cells. Therefore, these compounds are used in cancer therapy. The structures of these antitumour complexes are represented below.



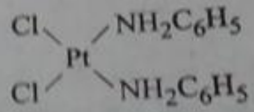
cis-Diamminedichloroplatinum(II)



cis-Dichloroethylenediamineplatinum(II)



Diammineoxalatoplatinum(II)



Dichlorodiphenylamineplatinum(II)

All these complexes have a common feature, namely, the cis arrangement of identical ligands. The trans isomers of these complexes do not have curative property. That chelation is involved in the mode of action of the antitumour agent with the cancer cells. The two cis groups in the drug molecule could probably get replaced by some other groups in the cancer cell, forming an association between the drug molecule and some species in the cancerous cells. Such an association may be the starting point for destroying cancerous cells. The replacement of the groups in the trans position by a chelating agent is not easy, and that is why the trans isomer of any of these complexes has no potency as a drug.

Q18. Write the use of Ziegler-Natta catalyst in polymerisation.

Ans :

Polymerisation of ethylene required high pressure, which is an expensive reaction condition. In addition, the product polythene was less crystalline and had a low melting point compared to the one formed with this catalyst. This catalyst is prepared from titanium tetrachloride ($TiCl_4$) and a trialkyl aluminimum (R_3A_1), say, Et_3A1.

$$nCH_2 = CH_2 \xrightarrow[\text{ambient temperature}]{\text{Ziegler-Natta catalyst, 1 atm pressure}} (C_2H_4)_n$$

Q19. How complexes useful in water softening.

Ans :

Complexes in Water Softening

The wastage of soap by its reaction with Ca^{2+} and Mg^{2+} in water is prevented by sequestering these ions with complexing agents, such as polyphosphates and polydentate amino acids.

Chelating agent : Chelators are used in chemical analysis as water softeners, commonly used synthetic chelator is EDTA estimation of hardness of water as Ca and Mg^{+2} ions form complexes with EDTA.

In general there are many applications where ability to easily determine water hardness is very important complexometric titration is one of the best way measuring total water hardness. At pH around 10 EDTA easily reacts with both calcium and magnesium in the same molar ratio (1 : 1) stability constant of calcium complex is a little bit higher. So calcium reacts first, magnesium later. Thus for the end point, we should use the same indicator that is Eriochrome Black-T.

Reactions : Reactions taking place during tetration are

$$Ca^{+2} + EDTA^{-4} \longrightarrow Ca\,EDTA^{-2}$$

$$Mg^{+2} + EDTA^{-4} \longrightarrow Mg\,EDTA^{-2}$$

Result : As water hardness is usually reported in terms of mg/L of calcium carbonate we will use for calculations slightly strange reaction equation.

$$CaCO_3 + EDTA \longrightarrow Ca\,EDTA + CO_3^{-2}$$

That allows direct calculation of calcium carbonate mass for known amount titrant used.

stability and hence, formation of complex ions depends on the following factors.

1. Nature of the central ion

(ionic potential of the central metal ion). In general, greater the ionic potential (charge/radius ratio) of a metal ion higher will be its tendency to attract electrons of the ligand and hence, more stable will be the complex. Thus, in other words, *the greater the charge and smaller the size of the central metal ion, greater will be the stability of the complex.* For example, complexes of the Fe^{3+} ion (having greater ionic potential) are more stable (stability constant 10^{31}) than that of Fe^{2+} ion (stability constant 10^{6}).

$$\phi_{Fe^{3+}} = \frac{3}{0.67} \quad \phi_{Fe^{2+}} = \frac{2}{0.76}$$

where ϕ stands for ionic potential.

The above view is supported by the following facts.

(*i*) The stability of complexes of somes of the cations having same charge but different ionic radii decreases with the increase in ionic radii

(*a*)	*Ion*	Cu^{2+}	>	Ni^{2+}	>	Co^{2+}	>	Fe^{2+}	>	Mn^{2+}
	Ionic radii (Å)	0.69		0.78		0.82		0.83		0.91
		Be^{2+}	>	Mg^{2+}	>	Ca^{2+}	>	Sr^{2+}	>	Ba^{2+}

(*ii*) Stability of complexes [illegible] radii decreases with decrease of the cationic charge, *e.g.*, the stability of complexes of La^{3+}, Sr^{2+} and K^{+} having nearly similar ionic radii decreases in the order.

$$La^{3+} > Sr^{2+} > K^{+}$$

2. Electronegativity of the central ion

The higher the electronegativity of the central ion, the greater is the stability of its complexes. This is because the bonding between a central ion and a ligand is due to donation of electron pairs by ligands, hence, naturally a strongly electronegative central ion will form stable complexes.

3. Electronic configuration of the central ion

In general, the most stable complexes are obtained from ions of transition elements because they have vacant $(n-1)\,d$ orbitals which can accommodate electrons donated by ligands.

4. Effective atomic number of the metal (*EAN rule*)

According to this rule a metal having effective atomic number equal to the atomic *metal ion is said to be more basic and hence, it will form more stable complex.* Thus, strong bases like CN^-, F^- and NH_3 are good ligands and form stable complexes with more electropositive metals like Na, Ca, Al, Ln, Ti and Fe.

In case of negative ligands, *the higher the charge and smaller the size, the more stable is the complex formed.* Thus, the stability of the complexes involving halide ions as ligands follows the order.

$$F^- > Cl^- > Br^- > I^-$$

In case of neutral ligands, *the larger the permanent dipole moment, the greater is the stability of the complex formed, e.g.*, the order of stability of the complexes formed by some neutral ligands is as follows :

Ammonia > Ethylamine > Diethylamine > Triethylamine

6. Environmental factors

Temperature and Pressure. The effect of temperature can be two fold. Firstly, the compounds containing volatile coordinating groups or ligands (*e.g.*, water, ammonia and ethylenediamine) are less stable at elevated temperature and commonly undergo decomposition on heating, *e.g.*, the hydrates loose water, the $[Co(NH_3)_6]Cl_3$ loses

ity of its
due to
central

...certain coordination compounds are changed from one form to other, e.g.,

$$\underset{\text{Red}}{AgHg[AgI_4]} \overset{45^\circ}{\rightleftharpoons} \underset{\text{Yellow}}{Ag_2[HgI_4]}$$

Similarly, reduction in pressure above a compound usually results in loss of volatile components.

7. Concentration factors

Certain complexes may exist in water solution only in presence of a high concentration of the coordinating particles, since, in such cases the water molecules apparently have greater coordinating tendencies than the molecules or ions originally present. For example, the yellow species of $[CuCl_4]^{2-}$ complex exists in the solid state but when dissolved in water, a pale blue hydrate of copper(II) ion is formed which on addition of excess of chloride ions (in the form of HCl, LiCl or other very soluble chloride) regenerates the yellow complex.

$$\underset{\text{Yellow}}{[CuCl_4]^{2-}} \underset{4Cl^-}{\overset{xH_2O}{\rightleftharpoons}} \underset{\text{Yellow}}{[Cu(H_2O)_x]^{2+}}$$

Similarly, the blue complexes of cobaltous ion of the type $[Co(CNS)_4]^{2-}$

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$$\underset{\text{Dark-reddish brown}}{[Fe(CNS)_6]^{2-}} \underset{6CNS^-}{\overset{6F^-}{\rightleftharpoons}} \underset{\text{Colourless}}{[FeF_6]^{3-}}$$

8. Nature of the ion outside the coordination sphere

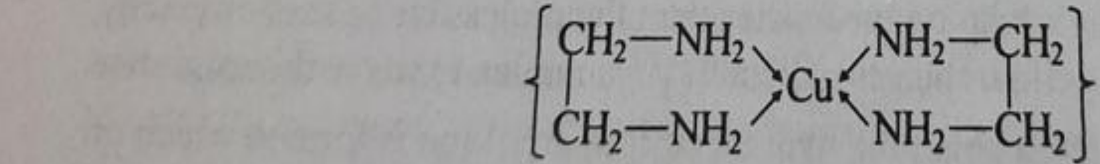
Whenever the ionisation sphere of a coordination compound has ions like CN^-, SCN^-, Cl^-, Br^-, $C_2O_4^{2-}$ and NO_2^- there is a great tendency of above types of ions to shift from ionisation to coordination sphere on thermal heating. On the other hand, the ions like NO_3^- and ClO_4^- show little or no such tendency and hence, complete absence of coordination reactions is usually assured in presence of perchlorate ions.

9. Ring formation (cyclization)

Ring formation is the most important factor in the formation of a coordinate compound, *a compound capable of cyclization will be relatively more stable* (owing to the reduced strain especially in case of five and six membered, including the ion metal)

polydentate ligands which are usually organic molecules, the most common being the **bidentate groups** or **bidentate ligands** *i.e.*, those which can occupy two positions, and the cyclic compounds so formed are known as chelates. The stabilising effect of coordination compounds produced by cyclisation may be illustrated by the example discussed in bidentate ligands.

A typical *bidentate group* is ethylenediamine, $NH_2CH_2 \cdot CH_2NH_2$, which contains a donor nitrogen atom at both ends of the molecules and thus, may attach itself in two coordination positions to a central metal ion to form five membered ring. The copper chelate of this group requires two molecules to form the following complex having two five membered rings.



The relatively high stability of the chelated complex over that of non-chelated complex can be easily judged by the high stability constants of zinc, cupric and nickel chelates of ethylenediamine than that of the corresponding stability constants of the simple amines.

Complex	Stability constant

	$[Zn(en)_2]^{2+}$	11.07
(2)	$[Cu(NH_3)_4]^{2+}$	12.67
	$[Cu(en)_2]^{2+}$	20.03
(3)	$[Ni(NH_3)_6]^{2+}$	6.74
	$[Ni(en)_3]^{2+}$	18.61

where $en = H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$

Similarly, the cobalt (III) and chromium (III) complexes with ethylamine are much less stable towards other reagent or towards heat than those formed by ethylenediamine.

Tridentate, tetradentate and other polydentate groups (ligands) are much less common than the bidentate groups, those studied are polyamines such as diethylenetriamine, $H_2N(CH_2)_2 \cdot NH(CH_2)_2NH_2$, triethylenetetramine, $NH_2(CH_2)_2NH \cdot (CH_2)_2 \cdot NH(CH_2)_2NH_2$, and ethylenediaminetetra-acetic acid (EDTA).