CHAPTER-I

Introduction
TRANSITION METAL IONS

The modern IUPAC definition states that transition metals (68 in number including the heaviest element un-un-bium with atomic number 112 and mass number 227) or their ions have an incomplete or partially filled \((n-1)d\) or \((n-2)f\) subshell. They display all the properties common to metals, such as low ionization potentials, high conductivity, malleability and ductility. They exhibit variable oxidation states and thus, form compounds with characteristic hue and intensity. Both the colours (due to the absorption in the visible region) and the magnetic properties (unpaired electrons) of transition metal compounds are striking in contrast to those of non-metal compounds. Also, the flexible bonding characteristics of transition metals and their ability to form stronger bonds with ligands, than non-transition metal ion of similar charge and atomic number does, has led to the formation of a large number of coordinate compounds with commonly observed stereochemistry (tetrahedral, square planar or squashed planar, squashed tetrahedral, trigonal bipyramidal or square pyramidal, octahedral, trigonal psismatic or tetragonal bipyramidal). In addition to the difference in kind, there is also a difference in degree in the properties of transition and non-transition elements which is due to the weak shielding of the nucleus by electrons in d and f orbitals as compared to the strong shielding provided by s and p electrons. Observations of colour and reactions related colour changes of coordination complexes have been important. An insight into this shows that only small changes in the coordination sphere apparently can lead to large changes in colour.

Because the d orbitals project well out to the periphery of atoms or ions, the electrons present in these orbitals are strongly influenced by, and in turn affect the environment of the ion. Consequently many properties (magnetic susceptibility, electronic spectra, electron paramagnetic resonance spectra etc.) of the ion (with partially filled d sub-shells), which depend upon the number and arrangement of the electrons present in the outermost d sub-shell, are determined by the environment of the ion. Therefore, with the help of above-mentioned physical properties, one can establish the structure of the complex (stereochemistry, oxidation state, presence of metal-metal bond etc.) in the d-block transition metal complexes.
The magnetic moment and its temperature dependence are found to be useful in getting an idea about the number of unpaired electrons, oxidation state, spin state of metal ion, stereochemistry, existence of exchange interaction etc. in the complex. Generally, three types of magnetic behaviour are shown by transition metal complexes: (i) paramagnetism, (ii) antiferromagnetism and (iii) ferromagnetism.

Such compounds where there is no secondary magnetic interaction between the neighboring paramagnetic centres are called magnetically dilute. Paramagnetic centres are present in these compounds, separated from one another by a number of diamagnetic atoms. For magnetically dilute copper(II) complexes, the value of magnetic moment at room temperature lies in the range 1.78 to 2.2 B.M\(^2\) which is sufficiently higher than the spin-only value for one unpaired electron. The magnetic moment is calculated from the corrected magnetic susceptibility by the relation:

\[
\mu_{\text{eff}}(\text{at TK}) = 2.828 \left( \chi_m \times T \right)^{1/2}
\]  

There are also certain compounds where distance between paramagnetic ions is small and the intervening atoms are capable of transmitting the magnetic interaction. Such compounds are called magnetically concentrated compounds. These interactions either lead to (a) decrease or (b) increase in magnetic moment. If the magnetic moment decreases then the compound is called antiferromagnetic and if it increases then the compound is called ferromagnetic. Ferromagnetism occurs due to the sublattice magnetic ordering.

The transition temperature \(T_B\) of a magnetic material is an important factor as it governs the classification of a material as ferro-, ferri- or superparamagnetic. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization verses temperature (M vs. T) measurements are commonly used to determine \(T_B\), also known the blocking temperature, of magnetic materials. The blocking temperature \(T_B\) is a measure of the thermal energy required to overcome the superexchange transition and is defined as the temperature at which the nanoparticles do not relax during the time of measurement; they are blocked.
Introduction

Magnetization versus applied field curves (hysteresis loop/curve measurements) are time dependent measurements of the magnetic moment of a sample with the variation of the magnetic field in a hysteresis fashion. Hysteresis curves provide information such as saturation magnetization ($M_s$), coercivity ($H_c$), remanence magnetization ($M_r$) and squareness ratio ($M_r/M_s$) for a given sample. These values are specific to the temperature at which the hysteresis loop experiment is performed, as the magnetic moment of a sample depends upon the temperature. Saturation magnetization is determined by observing the magnetic moment of the material at the largest applied magnetic field. For nano samples where saturation magnetization has not been attained at the maximum field applied, the saturation magnetization is determined by extrapolating the magnetization ($M$) versus inverse of field ($1/H$) curve to $1/H = 0$. Remanence magnetization is determined by locating the point on y-axis, where there is a magnetization in zero applied magnetic field. Coercivity is determined by locating the point on the x-axis, where the magnetization is zero in an applied magnetic field.

Transition metal complexes absorb energy in the ultra violet and visible regions of electromagnetic radiation spectrum and occasionally in the near infrared region. The absorption of energy in the visible region by transition metal complexes gives colour to these complexes. This absorption of energy is due to rearrangement of electrons in the outermost partially filled $d$ sub-shell. Different arrangements of electrons in $d$ sub-shell have different energies and such arrangements correspond to states which are designated by group theory symbols. All states have different energies due to interelectronic and electron-ligand interactions in different stereochemistries. The most stable arrangement lies lowest and forms the ground state. On absorption of energy of appropriate value, electronic transition takes place from ground state to excited state of the metal complex. In case of transition metal complexes, these transitions occur between levels which have a large contribution from the metal orbitals and, therefore, they are referred to as $d$-$d$ transitions. Generally bands arising from such transitions are symmetry forbidden but become allowed by higher state mixing (as in tetrahedral case $d$-$p$ mixing), vibronic coupling, spin-orbit coupling or distortion of symmetry. The intensities of
these bands are, therefore, also dependent upon the stereochemistry of the complex. From energies of \(d-d\) transitions and their intensities, information about the stereochemistry and oxidation state of the complex can be known.

A very intense band, usually in the ultraviolet region for most of the transition metal complexes is observed because of the charge transfer transitions, and this transfer of charge is usually from the ligand to metal. More accurately the transitions occur between molecular orbitals which have different contributions of ligand and metal d orbitals. Sometimes these absorptions are quite useful in assigning a structure to the complex.

Transition metal – oxygen, nitrogen and sulfur donor complexes with tunable coordination environments result into versatile physico-chemical properties and offer scope for applications in biochemistry, agriculture, catalysis and industry. Hence the participation of transition metal compounds in nearly every phase of life involves bond formation and cleavage, exchange of functional groups, blocking of functional groups, influence upon stereochemical configuration, oxidation-reduction reactions, storage, transfer and transmission of energy. Variable coordination number and oxidation states of transition metal ions are the virtues enabling them to exhibit these properties. Zeigler-Natta catalysts of TiR\(_4\) type are used in polymerization of ethylene. The compound ClRh(PPh\(_3\))\(_3\) acts as a hydrogenation catalyst and HCo(CO)\(_4\) catalyses the 'oxo' processes in the conversion of olefins into aldehydes. Some areas of current research interest include solid state chemistry, relationship between structure and reactivity, variable oxidation states, heteropoly complexes, macrocyclic and stereochemically non rigid ligands and nitrogen-and-oxygen-containing complexes.

Ferromagnetic compounds, which are very few (a small number of metals and alloys, a fair range of oxides, and a few transition metal halides) have great industrial importance ranging from permanent electromagmets to cores for inductances and magnetic recording tape and such sophisticated uses as the modulation of laser beams for speech transmission and 'bubble domain' devices for the next generation of computer stores. Magnetic materials made of manganese complexes of porphyrin derivatives have been made which have promising use in a variety of devices of our everyday life.
Copper is an essential element present in all organisms both land and marine. Cu(II) is fairly stable and has a well defined aqueous chemistry. In recent years, a great deal of studies on Cu(II) complexes have been driven for modeling biological molecules containing Cu(II). Copper plays two important roles in haemoglobin synthesis; one as part of an enzyme responsible for a step in the formation of the porphyrin system, and the other by releasing the required iron from various storage sites in the body. Probably the earliest commercial use of copper as fungicide was in the form of copper sulphate solution, employed as a seed dressing to destroy cereal diseases such as blight. Later on the use of copper sulphate was restricted because it caused damage to the leaves. In 1982, the discovery of Bordeaux mixture (basic copper hydroxide formed by adding slaked lime to copper sulphate solution) has overcome this problem and at the same time improved the adherence of the fungicides to the foliage. Paris green, an insecticide made by boiling white arsenic with basic copper acetate and a little acetic acid, is some times mixed with the fungicide prior to spraying on crops to check insect pest at the same time. Copper compounds, (often the sulphates), are recommended for destroying slugs, water snails carrying bilharzia to humans and liver fluke to sheep, mosquito larvae in malaria prevention, and for treating wood and cotton articles against fungi and insects.

In plants zinc is a constituent of the enzyme carbonic anhydrase, a catalyst involved in the conversion of carbon dioxide into carbonic acid. Zinc is also a constituent of the pyridine nucleotide enzyme, horse-liver alcohol dehydrogenase, and it seems likely that the metal atom is involved in linking the enzyme to the coenzyme NADH (NAD\(^+\) = nicotinamide adenine dinucleotide). This may be via the nitrogen atoms or the pyrophosphate residue of NADH. Another zinc-containing enzyme is carboxypeptidase A, with a molecular weight of about 34,000; it catalyses the hydrolysis of esters and peptides. Zinc is also thought to participate in some twenty other enzyme systems associated particularly with protein and carbohydrate metabolism. It forms complexes with proteins such as sperm whale myoglobin (in which two strongly-held zinc ions are attached to each molecule). The original isolator of crystalline Insulin found that it contained about...
0.5% of zinc; which certainly seems necessary for the production of crystalline insulin.\(^{21}\)

Iron-sulfur proteins having iron-sulfur clusters containing sulfide-linked di-, tri-, and tetrairon centers in variable oxidation states are found in a variety of metalloproteins, such as the ferredoxins, as well as NADH dehydrogenase, hydrogenases, coenzyme Q - cytochrome c reductase. succinate - coenzyme Q reductase and nitrogenase. Iron-sulfur clusters are best known for their role in the oxidation-reduction reactions of mitochondrial electron transport. Both complex I and Complex II of oxidative phosphorylation have multiple Fe-S clusters. They have many other functions including catalysis through aconitase, generation of radicals by SAM-dependent enzymes, and as sulfur donors in the biosynthesis of lipoic acid and biotin. Additionally some Fe-S proteins regulate gene expression. Fe-S proteins are vulnerable to attack by biogenic nitric oxide.\(^{22}\)

**CARBAMATE COMPOUNDS**

Carbamate compounds which involve only oxygen or oxygen and nitrogen both as donar atoms are the ligands analogous to dithiocarbamates and belong to the 1,1-dioxo chelating class of compounds. Thus these compounds containing the\(^{\text{O}}\text{O}\text{CNR}_2\) group are named considering that they are formally derivatives of carbamic acid \(\text{H}_2\text{NCO}_2\text{H}\). These share with carbonic acid \(\text{HO}_2\text{CO}_2\text{H}\) the important property to be reluctant to oxidation, whereas the corresponding anions \(\text{H}_2\text{NCO}_2^-\) (A) and \(\text{HO}_2\text{CO}_2^-\) (B) are well established.\(^{23}\)

![Chemical structures](attachment:image.jpg)

\(\text{(A)}\)

\(\text{(B)}\)
Though carbamate complexes of $\text{O}_2\text{CNR}_2$ are not as extensive or as useful as their sulphur analogous, the dithiocarbamates, yet since the earliest studies (Fukuto et al. 1954)$^{24}$ some thousands of carbamates have probably been screened for insecticidal potential, but probably less than thirty are currently marketed in commercially significant amounts.

The simplest form of the synthesis of carbamates is given by the following equation (2):

\[ 2 \text{NH}_2\text{H} + \text{CO}_2 \xrightarrow{\text{H}_2\text{O}} \text{NH}_2\text{NH}CO\text{NH}_4 \]  

(2)

The ammonium salt of carbamic acid

The backbone of carbamate structures is carbamic acid Figure I-1, the monoamide of carbon dioxide. The acid does not exist in a free form, since it spontaneously decomposes into carbon dioxide and ammonia. On the other hand, salts of carbamic acids, called carbamates, are much more stable. One such salt, namely ammonium carbamate Figure I-2 has been used as a commercial insecticide and rodenticide$^{25}$ after mixing it with aluminium phosphide. The acid salts are readily soluble in water, but hydrolyse at higher temperatures.

\[ \text{NH}_2\text{NO}^+\text{C}^-\text{NH}_2 \]  

Figure I-2
One of the main goals in carbon dioxide chemistry is its incorporation into organic substrates. This process may involve the formation of C-CO$_2$, O-CO$_2$, N-CO$_2$ bonds. Prior coordination of carbon dioxide to a metal cation as the dialkylcarbamato group, [M(O$_2$CNR$_2$)$_n$]$_m$ may accomplish the two-fold objectives of stabilizing carbon dioxide as an O donor and promote its reactivity towards electrophiles. The preparation of transition-metal carbamates has been given in literature and this bonding situation may lead to electrophilic attack by acyl chlorides at the carbamate oxygen, with formation of the otherwise difficult to synthesize mixed carboxylato-anhydrides. The transition metal carbamato complexes formulated as [M(O$_2$CNR$_2$)$_n$]$_m$ n and m being the oxidation number of the central metal atom M and the nuclearity of the system, respectively were found to be synthesized by the synthetic procedure based on the exchange reaction between a metal halide and the dialkylcarbamate obtained by the in situ interaction of a secondary amine and carbon dioxide, shown by reactions (3) and (4).

$$2NHR_2 + CO_2 \rightleftharpoons [NH_2R_2]^+ [R_2NCO_2]^-$ (3)

$$MX_n + n[NH_2R_2]^+ [R_2NCO_2]^-$ $\rightarrow$ [M(O$_2$CNR$_2$)$_n$] + nNH$_2$R$_2$X (4)

Alkali-metal carbamates were found to be N-alkylated and the reaction of alkali - metal carbamates M(O$_2$CNEt$_2$) with Mel can be shown by the following equation (5).

$$M(O_2CNEt_2) + 2Mel \rightarrow [NMe_2Et_2] + MI + CO_2 (5)$$

Synthetic methodologies of carbamate complexes have been known. Reactions of cationic metal complexes containing labile ligands with anions and CO$_2$ commonly resulted in the formation of carbamate complexes. In the reactions, free amines have been shown to promote the reaction in most cases, implicating a pathway involving ligand exchange with pre-formed carbamic acid HO$_2$CNR$_2$, derived from free amine and CO$_2$. However, synthesis of carbamate complexes via direct insertion of CO$_2$ into M-NR$_2$ bond is scarce.
Thermodynamically stable carbon dioxide is reactive towards nucleophilic reagents, as shown by the well established syntheses of carboxylic acids from Grignard reagents, the synthesis of salicylic acid from sodium phenoxide, the formation of \( \text{HCO}_3^- \) in alkaline solution, the synthesis of urea and of the \( \text{R}_2\text{NCO}_2^- \) anion from ammonia (\( \text{R} = \text{H} \)) or from secondary amine, and the \( \text{C} \)-co-ordination of carbon dioxide to electron-rich transition metals. In contrast \( \text{O} \)-co-ordination of \( \text{CO}_2 \) to transition or non-transition metal complexes or reactions of \( \text{CO}_2 \) with electrophiles are unprecedented in literature. The reactivity of carbon dioxide differs from that of the \( \text{CO}_2 \) fragment within the carbamato ligand. As a matter of fact, metal carbamates do not generally react with nucleophiles, as exemplified by the \( \text{N,N-dialkylcarbamato derivatives of magnesium(II)} \) which are inert toward organic (as in \( \text{LiMe} \) and \( \text{MgBrPh} \)) or organometallic (as in \( \text{NaMn(CO)}_5 \) and \( \text{NaFeCp(CO)}_2 \)) nucleophiles. Consistently, metal carbamates are readily reactive with electrophillic reagents such as water, proton containing substances, alkyl and aryl halids. This is in agreement with valence-bond arguments suggesting that the oxygen atom of the \( \text{CO}_2 \) moiety in dialkylcarbamato metal derivatives acquire a partial negative charge, the coordinated ligand thus being the potential site of attack by electrophile (Figure I-3). Attack by electrophiles at nitrogen atom includes elimination of \( \text{CO}_2 \) while attack at oxygen atom may allow the \( \text{CO}_2 \) moiety to be retained in the products.

Inorganic carbamate centres are implicated as intermediates in metal catalyzed pathways for the generation of organic carbamates and polyurethanes. However, any consideration of the role that carbamate ligands play in synthetic chemistry must account for their unique \( \text{C-N} \) bond lability when compared to carboxylato ligands as illustrated in Scheme I-1. Carbamate ligand (A) undergo
acid-dependent hydrolysis to liberate CO\textsubscript{2} and this suggested to proceed via the Zwitterionic species HA\textsuperscript{+}. Carbamate complexes also undergo acid independent C-N metathesis reactions. Exchange of the carboxyl group with free CO\textsubscript{2} and CS\textsubscript{2} is commonly observed in metal carbamate complexes and these reactions appear related to CO\textsubscript{2} exchange in low-valent metal carbamates and in sixteen and eighteen electron metal formato complexes that have been studied by the Darenbourg group. C-N bond metathesis by exchange of the amino moiety with free amine has also been reported.

\[
\begin{align*}
R'\text{N}-H+C=O & \rightarrow R'\text{N}-H-C=O \quad (a) \\
& \rightarrow R'\text{N}-H-C=O \quad (b) \\
& \rightarrow R'\text{N}-H-C=O \quad (c)
\end{align*}
\]

Scheme 1-1

The general formula of carbamates - N-substituted esters of carbamic acid is:

\[
R'\text{NH-C-OR}^2
\]

where R\textsuperscript{2} is an aromatic or aliphatic moiety. Three main classes of carbamate pesticides are known:

(a) Carbamate insecticides; R\textsuperscript{1} is a methyl group;
(b) Carbamate herbicides; R\textsuperscript{1} is an aromatic moiety; and
(c) Carbamate fungicides; R\textsuperscript{1} is a benzimidazole moiety.
Carbamic acids can also be stabilized by the formation of simple alkyl esters, such as ethyl carbamate, which is commonly called urethane Figure I-4.

\[
\begin{align*}
\text{O} & \\
H_2C\text{O} - C - \text{NH}_2 &
\end{align*}
\]

Figure I-4

This compound has found a variety of uses including applications as a veterinary anaesthetic, topical bactericide and solubilizer or co-solvent for pesticides, fumigants and cosmetics.\(^\text{85}\) Unfortunately, certain analogues of urethane are carcinogenic to lungs and a few other tissues.\(^\text{86,87}\) Consequently, considerable concern has been shown with regard to use of carbamate chemicals as insecticides.

In addition to alkyl esters, aryl esters of carbamic acids have also been investigated. A typical example is phenyl carbamate Figure I-5. If one of the protons attached to the nitrogen atom is replaced by methyl group, the resulting compound, phenyl-N-methyl carbamate, is mildly toxic to a few insect species.

\[
\begin{align*}
\text{O} & \\
O - C - \text{NH}_3 &
\end{align*}
\]

Figure I-5

In a search for new effective insecticides of this series, a large number of methylcarbamates have been synthesized (TABLE I-1). The most commonly employed method for synthesizing these compounds involves the reaction of methyl isocyanates with appropriate phenols (alkyl, dialkyl, haloalkyl, alkoxy, naphthols, dihydronaphthols, dihydrobenzofuran-7-ol etc.) equation (6). Tertiary amines are usually used as catalysts.
### TABLE I-1

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Structural Formula</th>
<th>Trade or Common name</th>
<th>Chemical Name</th>
<th>Specific Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><img src="image1" alt="CPMC" /></td>
<td>CPMC</td>
<td>2-chlorophenyl-N-methylcarbamate</td>
<td>Soil insecticide</td>
</tr>
<tr>
<td>2.</td>
<td><img src="image2" alt="MTMC" /></td>
<td>MTMC, MIMC, Moohal</td>
<td>3-Methylphenyl-N-methylcarbamate</td>
<td>Pests of rice</td>
</tr>
<tr>
<td>3.</td>
<td><img src="image3" alt="MPCM" /></td>
<td>Banol (carbanolate)</td>
<td>6-chloro-3,4-xylencyl-N-methylcarbamate</td>
<td>Agricultural and animal parasites</td>
</tr>
<tr>
<td>4.</td>
<td><img src="image4" alt="Banol" /></td>
<td>Maqbarl</td>
<td>3,5-Xylyl-N-methylcarbamate</td>
<td>Soil insecticide</td>
</tr>
<tr>
<td>5.</td>
<td><img src="image5" alt="H-28" /></td>
<td>H-28</td>
<td>3-sec-butylyphenyl-N-methylcarbamate</td>
<td>Pests of rice</td>
</tr>
<tr>
<td>6.</td>
<td><img src="image6" alt="H-22" /></td>
<td>H-22</td>
<td>3-tert-butylyphenyl-N-methylcarbamate</td>
<td>Insecticide</td>
</tr>
<tr>
<td>7.</td>
<td><img src="image7" alt="Aminocarb" /></td>
<td>Aminocarb (Matacil)</td>
<td>4-dimethylamino-3-tolyl-N-methylcarbamate</td>
<td>Insecticide and molluscide</td>
</tr>
<tr>
<td>8.</td>
<td><img src="image8" alt="Carbofuran, Furadan" /></td>
<td>Carbofuran, Furadan</td>
<td>2,2-dimethyl-2,3-dihydrobenzofuranyl-7-N-methylcarbamate</td>
<td>Systemic soil insecticide</td>
</tr>
<tr>
<td>9.</td>
<td><img src="image9" alt="Mobam" /></td>
<td>Mobam</td>
<td>4-benzothiényl-N-methylcarbamate</td>
<td>Contact insecticide</td>
</tr>
<tr>
<td>10.</td>
<td><img src="image10" alt="Sevin (carbaryl)" /></td>
<td>Sevin (carbaryl)</td>
<td>1-Naphthyl-N-methylcarbamate</td>
<td>Systematic insecticide</td>
</tr>
<tr>
<td>11.</td>
<td><img src="image11" alt="Propoxur (beygon)" /></td>
<td>Propoxur (beygon)</td>
<td>2-Isopropoxy phenyl-N-methylcarbamate</td>
<td>Systematic insecticide</td>
</tr>
<tr>
<td>12.</td>
<td><img src="image12" alt="UC-10854" /></td>
<td>UC-10854</td>
<td>3-Isopropylphenyl-N-methylcarbamate</td>
<td>Systematic insecticide</td>
</tr>
<tr>
<td>13.</td>
<td><img src="image13" alt="Mesurol" /></td>
<td>Mesurol</td>
<td>4-Methylmercapto-3,5-dimethylphenyl-N-methylcarbamate</td>
<td>Insecticide and acaricide</td>
</tr>
<tr>
<td>14.</td>
<td><img src="image14" alt="Thiophanate-methyl (Topsin-M)" /></td>
<td>Thiophanate-methyl (Topsin-M)</td>
<td>Dimethyl[1,2-phenylene bis[methylcarbonothioyl] bis(carbamate)]</td>
<td>Systemic fungicide</td>
</tr>
<tr>
<td>15.</td>
<td><img src="image15" alt="Thiophanate-methyl (Topsin-M)" /></td>
<td>Thiophanate-methyl (Topsin-M)</td>
<td>Dimethyl[1,2-phenylene bis[methylcarbonothioyl] bis(carbamate)]</td>
<td>Systemic fungicide</td>
</tr>
</tbody>
</table>
Another method for the above synthetic purpose is the reaction of the phenols with methylcarbamoyl chloride equation (7).

\[
\text{ArOH} + \text{CH}_3\text{NHCOCI} \rightarrow \text{ArOCONHCH}_3 + \text{HCl}
\] (7)

Though the yield of the product obtained is good, but degree of purity is less. The reaction of methylamine with diarylcarbonates is, however, suitable for the preparation of halo-substituted methylcarbamates equation (8). The above diarylcarbonates in turn is prepared by reacting appropriate phenol/phenolates with phosgene in the presence of tertiary amine. Separation of the carbamates from the phenol can be accomplished by extraction of the phenol with aqueous solutions of alkalies. This process using phosgene and isocyanate is highly toxic and hence unsafe. Another incentive to eliminate phosgene is the economic penalty incurred because the chlorine content of phosgene is wasted and converted into NaCl. Caustic soda is consumed in the conversion and the disposal of waste salt solutions presents ecological problem itself (equations 9,10).

\[
\text{ArOH} + (\text{C}_2\text{H}_5)_3\text{N} \rightarrow \text{ArOCOCI} + (\text{C}_2\text{H}_5)_3\text{NHCl}
\] (9)

\[
\text{ArOCOCI} + \text{ArONa} \rightarrow (\text{ArO})_2\text{CO} + \text{NaCl}
\] (10)

Production of carbamates by reductive carbonylation and oxidative carbonylation routes are economically not viable because only one third of the CO could be utilized effectively. As such are hazardous in nature because it involves handling of CO+O\text{2} mixtures at harsh conditions (50-400 bar;443 k). Ecofriendly routes of the preparation of carbamates are highly desirable.

In general, simple esters or N-substituted derivatives of carbamic acid are unstable compounds, especially under alkaline conditions, undergo decomposition...
into parent alcohol, phenol, ammonia, amine and carbon dioxide. The salts and esters of substituted carbamic acid are more stable than carbamic acid. This enhanced stability is the basis for the synthesis of many derivatives that are biologically active pesticides.\(^9\) Carbamate ester derivatives are crystalline solids of low vapour pressure with variable, but usually low, water solubility. They are moderately soluble in solvents such as benzene, toluene, xylene, chloroform, dichloromethane and 1,2-dichloroethane. In general they are poorly soluble in non-polar organic solvents such as petroleum hydrocarbons but highly soluble in polar organic solvents such as methanol, ethanol, acetone, dimethylformamide etc.\(^9\)

However, only a limited number of these compounds find use as insecticides in agriculture.

Among carbamates category, carbaryl (Figure I-6, 1-naphthyl-N-methylcarbamate), carbofuran (Figure I-7, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methylcarbamate) and propoxur (Figure I-8, 2-isopropoxyphenyl-N-methylcarbamate), carbendazim (Figure I-9 MBC, Methyl-2-benzimidazolecarbamate), thiophanate-methyl \{Figure I-10 Dimethyl[1,2-phenylenebis(iminocarbonothioyl)]bis[carbamate]\} and benomyl \{Figure I-11 Methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate\} are the most commonly used pesticides till date and are undergoing commercial developments since their introduction in 60's.
The carbamate compounds undergo alkaline hydrolysis forming phenolic compounds with the simultaneous liberation of methylamine, equation (11). This hydrolysis reaction proceeds smoothly and quantitatively at room temperature.

\[
\text{VI} + 2\text{KOH} \rightarrow \text{OH} + \text{K}_2\text{CO}_3 + \text{CH}_3\text{NH}_3 \quad (11)
\]

Complexes of \(\text{R}_2\text{NCO}_2^-\) are not as extensive or as useful as their sulphur analogues the dithiocarbamates. Carbamates are often obtained in insertion reactions of \(\text{CO}_2\), equation (12).

\[
\text{Ti(NMe}_2)_4 + 4\text{CO}_2 \rightarrow \text{Ti(O}_2\text{CNMe}_2)_4 \quad (12)
\]

Such insertions may be carried out \textit{in situ} as in reactions of cobalt or lanthanide halides with \(\text{R}_3\text{NH}\) and \(\text{CO}_2\) in hexane to give, for example, \(\text{Co}_6(\text{O}_2\text{CNEt}_2)_{12}\) or \([\text{Yb}(\text{O}_2\text{CN - Pr}_2)]_4\) (equation 13).

\[
\text{MCl}_n + 2n\text{NHR}_2 + n\text{CO}_2 \rightarrow \text{M(O}_2\text{CNR}_2)_n + n\text{NH}_2\text{R}_2\text{Cl} \quad (13)
\]

Except in certain cases (e.g. \(\text{NO}_2^-\), 2,2\(^\prime\)-bipyridyl, pyridine, \(\text{CN}^-\) and \(\text{CO}\) complexes where \(\text{M-O}\) or \(\text{M-N}\) \(d-\pi - p-\pi\) interaction can take place), oxygen and nitrogen have no \(\pi\)-orbitals available to accept the electrons from the suitably placed \(d\) orbitals on the metal atoms. On the other hand sulfur and phosphorus
have vacant $d$ orbitals which can be used for $d$-$\pi$ bonding. Such $\pi$ bonding is possible only with transition metals in their normal oxidation state. Thus, for these metal ion complexes the stability increases in the order:

$$\text{Sb} > \text{As} > \text{P} > \text{N} \quad \text{or} \quad \text{Te} > \text{Se} > \text{S} > \text{O} \quad \text{or} \quad \text{I} > \text{Br} > \text{Cl} > \text{F}$$

Though sulfur and oxygen resemble each other in having two unshared pairs of electrons in the bivalent state yet their donor properties are quite different. The difference is because of two reasons: Firstly lower electronegativity of sulfur as compared to oxygen results in lesser ionic character and hence alters the relative stabilities of various kinds of bonds. This drastically reduces the importance of hydrogen bonding in sulfur compounds, although there is existence of weak S$...$H$-$S bonds. Secondly sulfur has the ability to make frequent use of $d$- $\pi$ orbitals to form multiple bonds which imparts it some special properties.

Although carbamates are mostly chelate, they can be unidentate and have bridging modes similar to $\text{CO}_3^{2-}$ and $\text{RCO}_2^-$. Different bonding arrangements encountered until now for $\text{N,N}$-dialkylcarbamato complexes of transition elements are given in Figure I-12.\textsuperscript{90,91}

![Figure I-12](attachment:image.png)
APPLICATIONS OF CARBAMATE COMPOUNDS

Carbamate compounds have attained special importance as synthetic organic insecticides. Carbamate pesticides have been divided into three classes: (i) the carbamate ester derivatives, used as insecticides, are generally stable and have a low vapour pressure and low water solubility, (ii) the carbamate herbicides having the general structure R¹NHC(O)OR², in which R¹ and R² are aromatic and/or aliphatic moieties and (iii) carbamate fungicides containing a benzimidazole group.⁸⁹

Carbaryl, carbofuran and propoxur (baygon), thiophanate methyl, carbendazim etc. are the most widely used carbamate based pesticides. The applications of carbamate compounds can be classified under following categories:

Insecticidal value:

‘Physostigmine’⁹² is a naturally-occurring carbamate possessing anticholinesterase activity. Carbamate compounds possess the powerful anticholinesterase activity, so, these are cholinesterase (from the family of serine esterase) inhibitors and hence widely used as pesticides or insecticides. Poisoning by such compounds can result in an acute but usually manageable medical crisis and may damage the CNS and PNS, as well as cardiac and skeletal muscle tissues.⁹³ Hence, the carbamates are widely used as insecticides.

Carbaryl (1-naphthyl-N-methylcarbamate), propoxur (2-isopropoxyphenyl-N-methylcarbamate), carbofuran (2-isopropoxyphenyl-N-methylcarbamate), methiocarb (3,5-dimethyl-4-methylthiophenyl-N-methylcarbamate), aldicarb and oxamyl are the examples of the carbamate compounds, which are used as insecticides. Carbaryl is the most widely used insecticide. In Britain⁹⁴, it is recommended for use against caterpillars of the winter moth, as well as earwigs and capsid bugs. In U.S.A. it is used 90 crops, but some 40% of its total American usage is on cotton. It is used to control the pests of cotton and fruit crops. Propoxur (Baygon) has a relatively long residual action- it can persist for as long as six weeks and is an example of ‘heavier armory’ of insecticides. It is used against refractory
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pests such as cockroaches, ants, earwigs, crickets and millipedes. It is much more toxic than carbaryl to higher animals, but is considered to be safe because of its low mammalian toxicity. Carbofuran is used against pests, viz. corn root worm, rice water weevil, wire worm, sugar cane borer, bud worm, flea beetle, pea aphids, horn worms, broad mite and potato tuber moth etc.

Methiocarb has been introduced as an insecticide in 1965 but has since been found additionally be a valuable molluscicide. It is used on cotton, vegetables and hops for the control of fruit flies, codling moth, leafhoppers and mites. It has also been used in the form of seed dressing to act as a bird repellant. Aldicarb and oxamyl are used against the various pests and these also possess the nematocidal properties.

Fungicidal value:

Carbamates are also used as fungicides. They are all systemic fungicides. They come under the group benzimidazole fungicides which includes carbendazim (Methyl-2-benzimidazolecarbamate), benomyl [Methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate] and thiophanate methyl [Dimethyl[1,2-phenylenebis(iminocarbonothioyl)]bis[carbamate]].

Benzimidazole (Figure I-13) in the parent substance of a family of systemic fungicides, including thiophanate methyl, benomyl, carbendazim and thiaendazole. The thiabendazole is non carbamate member of the group. If one of the hydrogen atoms of the anionic group of carbamic acid is replaced by the benzimidazole radical, benzimidazole carbamate is formed. Benomyl is a wide-spectrum systemic fungicide introduced in 1967. It has been used for foliar

\[ \text{Figure I-13} \]
application, for seed and soil treatment, as a root and bulb dip and for post harvest protection of produce. It is also effective against mites, primarily as an ovicide. Its systemic properties can be enhanced by surfactants. Benomy is rapidly hydrolysed within plants, the butylcarbamoyl side chain being removed to give carbendazim, the methyl ester of benzimidazole carbamate (MBC) carbendazim is fungitoxic and is indeed marketed as a systemic fungicide which is used as a spray on European cereals, especially to control eye spot (Pseudocercosporella). Injection of solutions of salts especially the hydrochloride, hypophosphite and phosphate into the tanks have given some control of Dutch elm disease. Thiophanate methyl, another fungicide come under group benzimidazole is a systemic fungicide with a wide biological spectrum and is used to control scab in apples and also used as paints for pruning cuts etc. Like benomyl it also decomposes into carbendazim in plants.

**Herbicidal value:**

Role of carbamates as herbicides has been classified into three categories:

1. **Translocated carbamates:**

   Barban I-14 (a) and asulam I-14 (b) are the examples of translocated carbamates.

   ![Chemical structures of Barban and Asulam](image1)

   (a) Barban   (b) Asulam

   **Figure I-14**

   Barban attacks such troublesome grasses as black-grass and reed canary-grass but it is marketed primarily for the control of wild oat growing amongst wheat or amongst some varieties of barely. Asulam provides a means of controlling bracken
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(pteridium aquilinum) on hill and grazing lands, and in non-cropped land, at a price, which is economically acceptable.

2. **Soil acting phenyl carbamates:** Soil-acting carbamates include:

   (a) Phenyl-NH-COO-R  
       (e.g. propanil)  
       R-esters of  
       phenyl carbamic acid.

   (b) Alkyl-NH-COO-Aryl  
       (e.g. carbaryl)  
       Aryl esters of  
       alkyl carbamic acid

   (c) Phenyl-NH-CO-R  
       (e.g. propanil)  
       Non esters;  
       phenyl substituted amides

   The phenylcarbamates used as soil acting herbicides are solids with moderately low vapour pressure, although appreciable amounts may volatilise when application is made to a solid surface. These herbicides kill the plants (weeds) generally by interfering with the process operating in the plant such as, photosynthesis, mitosis and oxidative phosphorylation etc. These include; chlorpropham, propanil, chlorbufam, carbaryl, carbatamide, propanil, swep etc. Figure I-15

![Chemical structures](http://example.com/structure.png)

**Figure I-15**

Chlorpropham  
Chlorbufam  
Carbitamide
Contact herbicides/ contact carbamates:

Phenmedipham Figure I-16 is a carbamate herbicide which is marketed principally to control seedlings of broad leafed weeds in fodder beet, sugar beet and red beet. Its mode of action is common with that of other herbicidal carbamates, i.e. probably on the light reaction of photosynthesis, where it inhibits electron transport and non-cyclic photophosphorylation.

\[
\text{Phenmedipham}
\]

Figure I-16

3. Medical value:

In medical field many carbamate compounds, viz. carbaryl wettable powder (WP) have been advocated for the control of water snails, which is the alternate host of the pathogenic organism causing a disease bilharzia. Carbaryl is employed against the vectors of diseases, viz. brancroftian filariasis, malaria and dengue.96

Some carbamate compounds having cholinesterase inhibitor activity have been useful for the treatment of glaucoma and myasthenia gravis and others are in clinical trials as therapy for Alzheimer's dementia.93

Urethane (ethyl carbamate) has found variety of uses including applications as a veterinary anaesthetic, topical bactericide and solubilizer or co-solvent for pesticides, fumigants and cosmetics.95 Moreover, carbamates are often found in biological systems, and these bound to bivalent cations have been suggested to be involved in important processes related to carbon dioxide biochemistry, such as the biotin-mediated carboxylation,97-99 the bacterial synthesis of methane from CO₂100 and the fixation of CO₂ in the photosynthetic Calvin cycle.101-103 The β² Mn²⁺ ion is present in some biotin-containing enzymes,104 and can replace alkaline-earth metal ion in ribulose bis(phosphate) carboxylase.101-103
Also, alpha - zinc - vinyl carbamates are used as anionic - Friedel - crafts equivalents.\textsuperscript{105}

4. **Other Applications**

Carbamates can also be used in practical organic chemistry to obtain isocyanates.\textsuperscript{106-107} This method is advantageous when any difficulties occur in a classical isocyanate synthesis based on a reaction between amines and phosgene. This is especially the case when a required carbamate compound can be obtained from a reaction of alcohol, amine and urea, this process, employing TiCl\textsubscript{4}, BiCl\textsubscript{3}, NiCl\textsubscript{2}, Zn(CN)\textsubscript{2}, potassium and copper acetates and sometimes also other compounds, could be utilized for the commercial manufacture of carbamates.\textsuperscript{108,109}

Carbamates can also be applied in the manufacture of increased abrasion resistance polyurethane compositions and as compounds adjusting viscosity values of oils and greases\textsuperscript{110-113} There also are reports on these compounds being employed in modern reprography due to their light and heat sensitivity.\textsuperscript{114}

Carbamates are widely used as protecting groups for amines in amino-acids, peptide and oligonucleotide chemistry.\textsuperscript{115} Carbamates are also useful because of their chemical stability towards acids, bases and hydrenation.\textsuperscript{115}
**METAL CARBAMATES**

Metal compounds involving nitrogen or oxygen donor ligands have attained an increasingly interest in the past ten to fifteen years\textsuperscript{116,117} The chemistry of carbamato metal complexes is quite recent in the scientific literature. The first homoleptic derivative of this class, tetrakis(N,N-dimethylcarbamato)titanium(IV), of formula $\text{Ti(O}_2\text{CNMe}_2\text{)}_4$, was reported in 1965.\textsuperscript{118,119} and was synthesized by exhaustive carbonation of the dimethylamido precursor $\text{Ti(NMe}_2\text{)}_4$. The metal amido/CO\textsubscript{2} route to N,N-dimethylcarbamato complexes was further pursued in 1974, for early transition metals\textsuperscript{120-126}, which are known to form stable dialkylamido complexes. Shortly thereafter, the first N,N-dimethylcarbamato complexes of metal cations of group 5 and 6\textsuperscript{120-126}, and of uranium(IV), $[\text{U(O}_2\text{CNR}_2\text{)}_4]_n$\textsuperscript{127} were prepared by carbonation of the corresponding dialkylamido precursors (equation 14).

$$\text{M(NR}_2\text{)}_n + n\text{CO}_2 \rightarrow \text{M(O}_2\text{CNR}_2\text{)}_n$$  \hspace{1cm} (14)

An alternative synthetic route to N,N-dialkylcarbamato metal complexes from metal chloride in the presence of the secondary amine and carbon dioxide was also found to be viable. This route was first adopted for the synthesis of N,N-dialkylcarbamato derivatives of uranium(IV)\textsuperscript{128} and later extended to several halides of transition d and f metals, whose amido complexes are not easily available. This is essentially a ligand substitution reaction whereby the anionic chloride ligand of the starting material is substituted by the carbamato group, formed \textit{in situ} by the $\text{R}_2\text{NH}/\text{CO}_2$ system (equation 15).

$$\text{MCl}_n + n\text{CO}_2 + 2n\text{R}_2\text{NH} \rightarrow \text{M(O}_2\text{CNR}_2\text{)}_n + n[\text{R}_2\text{NH}_2]\text{Cl}$$  \hspace{1cm} (15)

Dell' Amico and Calderazzo etc.\textsuperscript{23} have been reported the detailed study on the compounds containing monoanionic N,N-dialkylcarbamato ligand, of formula $\text{O}_2\text{CNR}_2^-$, R being H, an alkyl or an aryl group. They have synthesized the N,N-dialkylcarbamato metal complexes (both of main group elements as well as transition elements). Among alkali and earth-alkali metal cations, lithium and magnesium carbamato complexes have been studied to some extent. The
diethylcarbamato derivatives of formula $M(O_2CNEt_2)_n$, $M = Li, Na, K$, have been prepared$^{129-131}$ by treating a suspension of the alkali metal in toluene at about 50 °C with the appropriate amine, in the presence of CO$_2$. Carbamato derivatives of magnesium(II), aluminium(III), silicon(IV), tin(IV), lead(IV) and antimony(III) have also been reported in literature using same synthetic route involving treatment of metal halide with secondary amine in presence of carbon dioxide.

N,N-dialkylcarbamato derivatives of early transition metals were the first to be prepared, as obtained through the $M(NR_2)_n/CO_2$ route. The first homoleptic derivative to be prepared was Ti($O_2CNMe_2$)$_4$$^{118}$ due to the availability of the corresponding homoleptic N,N-dialkylamido complexes as starting materials. Other compounds of the same class prepared by this route are Nb($O_2CNMe_2$)$_5$$^{121}$, Ta($O_2CNMe_2$)$_5$$^{122,123}$ and W($O_2CNMe_2$)$_6$$^{124}$.

However, a more general preparative method was necessary in order to overcome the initial restriction that N,N-dialkylamido metal complexes with aryl- or simple alkyl group are sometimes difficult to prepare and are not reported in the literature. The use of other more viable preparative methods initiated with the finding$^{128}$ that $[U(O_2CNMe_2)]_n$ can readily be produced by a $R_2NCO_2^-/Cl^-$ metathetical reaction. The formation of homoleptic dialkylcarbamato complex of uranium(IV) can thus be described as in equation (16):

$$UCl_4 + 4[R_2NH_2][O_2CNMe_2] \rightarrow \frac{1}{n}[U(O_2CNMe_2)]_n + 4[R_2NH_2]Cl \quad (16)$$

$R = (Me, Et)$

This methodology can be applied to several metal; halides. The TaCl$_2/Et_2NH/CO_2$ route gives the homoleptic compound of tantalum(V), Ta($O_2CNEt_2$)$_5$, which has been shown by X-ray crystallography to be mononuclear with the central metal atom surrounded by three bidentate and two monodentate diethylcarbamato groups in a slightly distorted square-antiprismatic geometry. On the other hand, the Ta(NMe$_2$)$_5/CO_2$ route$^{125}$ affords the product of partial substitution Ta(NMe$_2$)$_2(O_2CNMe_2)_3$. The preparation of N,N-Di-iso-propylcarbamato derivatives of titanium(III), niobium(II) have also been reported in literature.$^{132-135}$

The carbamato derivative of chromium(II)$^{136,137}$ was prepared both by carbonation...
of the amido derivative Cr(NEt₂)₄ and via the metal chloride/amine route from anhydrous chromium(II) chloride in the presence of NHEt₂. Dinuclear structure with four bridging carbamate groups have been reported for this compound. The ethyl derivative of manganese(II) of formula Mn₆(O₂CNEt₂)₁₂ and hexanuclear cobalt derivatives Co₆(O₂CNR₂)₁₂ were prepared by reacting anhydrous metal [Mn(II) and Co(II)] chloride with the appropriate amine under carbon dioxide.

The first N,N-dialkylcarbamato derivatives of lanthanides(Ln) were synthesized by reacting the anhydrous chlorides of ytterbium(III) and erbium(III) with the NHR₂/CO₂ system in a hydrocarbon medium.

In addition to homoleptic compounds, non-homoleptic compounds (of main group as well as transition elements) formed by incomplete removal of the anionic ligands by R₂NCO₂⁻ in reactions using a metal containing precursor or partial carbonation of the amido precursor by carbon dioxide have also been reported in literature. The non-homoleptic carbamate derivative of magnesium of formula [Mg(O₂CNEt₂)Br(THF)]₂, characterized by X-ray diffraction methods, was prepared (equation 17) by reacting the methyl-bromide Grignard reagent with CO₂ and Et₂NH in THF.

\[
\begin{align*}
\text{Et₂NH/THF} & \quad \text{MgMeBr} & \quad \rightarrow & \quad [\text{Mg(O₂CNEt₂)Br(THF)}]₂ \quad (17) \\
& \quad \text{CO₂} & \quad & 
\end{align*}
\]

The carbamate groups are in bridging position, while the bromides are terminal. The N-alkyl- or N,N-dialkylcarbamato derivatives of boron, B(O₂CNR₂)₂X (X = Ph, o-C₆H₄O₂, R₂ = Et₂; H, Et; iBu)¹⁴⁴, aluminium, Al(O₂CNEt₂)Et₂ and thallium(III) Ti(O₂CNMe₂)Me₂ have been obtained from B(NR₂)₂X, Al₂(Net₂)Et₄ and Ti(NMe₂)Me₂, respectively upon reaction with CO₂. Non-homoleptic carbamate complexes of silicon of formula Si(O₂CNHR)Me₃ (R = Me, Bu, allyl, Ph), tin(IV), Sn[(O₂CNMe(SnMe₃))]Me₃ and germanium of formula (Et₃Ge)(O₂CNHCO₂)(GeEt₃) have also been reported in literature. The carbamate complex of germanium is not stable and decomposes to isocyanate derivative of germanium(IV), GeEt₃(NCO), and to triethylgermanium oxide.¹⁴⁸ Non-homoleptic carbamate
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complexes of transition elements are also studied and reported in literature. With
the amido complexes of titanium(IV) and tantalum(V), only the use of carbon
dioxide in sub-stoichiometric amounts allows the isolation of partly carbonated
compounds such as Ti(O₂CNMe₂)₂(NMe₂)₂, Ti(O₂CNMe₂)₃(NMe₂)₂ and
Ta(O₂CNMe₂)₃(NMe₂)₂. The former compound is mononuclear, contains
hexacoordinated titanium(IV) with bidentate carbamate ligands, while the
tantalum(V) compound is heptacoordinated with one mono and two bidentate
O₂CNMe₂ ligands. An amido bridged non-homoletic carbamate complex of
chromium(III), Cr₂(O₂CNEt₂)₄(μ-NEt₂)₂ and dimethylcarbamato bridged
compound of molybdenum with terminal amido groups, i.e. Mo(O₂CNEt₂)₄(NEt₂)₂
have also been mentioned in the literature. The rhenium(V) compound of 5d²
electronic configuration ReO₂l(PPh₃)₂ was reacted with phenyl isocyanate, and
the formation of the carbamate-nitrene-amino derivative of formula
Re(O₂CNHPh)(NPh)₂(NH₂Ph)(PPh₃) was observed, showing monodentate
coordination of the N-phenylcarbamato group.

Chloro-carbamato complexes of platinum(IV) of formula Pt((O₂CNHR)₂
Cl₂(NH₃)₂)₂ have been isolated from the reaction of a bis-hydroxy derivative of
platinum(IV) with the appropriate alkyl isocyanate.

Organometallic derivatives containing carbamato ligands are still relatively
uncommon. Some cyclopentadienyl compounds have been obtained through the
metal-chloride or the metal-amido routes as reported in literature.

Arpitha Thakkalapally and Vladimir Benin reported the preparation and
characterization of several N-2-(trimethylsilyl)ethyl-N-nitrosocarbamates, designed
as precursors to thermally unstable secondary N-nitrosocarbamate anions via
fluoride-assisted cleavage. X-ray structural study demonstrate that the cone N-
nitrosocarbamate moiety has a nearly planar geometry.
CARBAMATES OF COPPER AND ZINC:

There is paucity of literature on carbamate complexes of copper. Carbamate complexes of copper have been found to exist mainly in the +1 and +2 oxidation states.

The carbon dioxide uptake by transition metal amide complexes to produce transition metal carbamato - complexes has been studied from the mechanistic and structural viewpoints. Little is known, however, about the reaction and stability of the carbamato ligand. The copper - promoted formation of the urethanes from carbon dioxide, amines, and alkyl halides involves an isolable copper(I) carbamato - complex as the key of intermediate, shown in reaction:

\[
\begin{align*}
\text{CuOBu}^1 + R^1R^2\text{NH} + \text{CO}_2 & \rightarrow R^1R^2\text{NCO}_2\text{Cu} \\
& \rightarrow \text{Bu}^1\text{OH} \\
& \rightarrow \text{Bu}^1\text{NC} \\
R^1R^2\text{NCO}_2\text{Me} & \leftarrow \text{Mel} \\
& \rightarrow R^1R^2\text{NCO}_2\text{Cu(CNBu)}^1_n
\end{align*}
\]

Boguslavskii et. al. have reported the structure of binuclear adducts of copper(II) carbamates and phosphates with bases from ESR data. For adducts of copper(II) carbamate and phosphate complexes in solutions a binuclear structure of the half - open lantern type is realized in which two Cu\(^{2+}\) ions are connected only by two bridge anions present in the cis position relative to one another. The ESR parameters of this low - symmetry correspond to the rhombic component of the fine structure and have been interpreted on the basis of a model of dipole – dipole interactions for nonpunctate magnetic dipoles. Further unstable mononuclear and polynuclear carbamate complexes of copper(II) have been reported from the reversible combination of CO\(_2\) with ephedrinate and amino complexes of copper(II). The conclusions regarding the structure of the mononuclear carbamate complexes have been drawn from the ESR data. Synthesis of carbamato derivatives of copper(II), a d\(^9\) system, Cu\(_2\)(O\(_2\)CNEt\(_2\))\(_4\)(NHEt\(_2\))\(_2\) have been reported in the literature by carbonation of
copper(II) chloride in the presence of the appropriate amine and a dinuclear structure
with four bridging carbamate groups. The mononuclear derivative of copper(II)
Cu(O_2CNMe_2)_2(NHMe_2)_2 has also been obtained from copper metal and
[NH_2Me_2][O_2CNMe_2] in the presence of dioxygen^158 in the reaction which may be given
as:

\[ 2Cu + O_2 + 4[NH_2Me_2][O_2CNMe_2] \rightarrow 2Cu(O_2CNMe_2)_2(NHMe_2)_2 + 2H_2O \] \hspace{1cm} (18)

In this compound the central copper atom is pseudo coordinated to two terminal
bidentate carbamate groups and to two trans amine groups.

Complexes of 4-cyano-2,2-dimethylbutyraldoxime-N-methylcarbamate
(DIBAM) Figure I-17 with copper, cobalt or zinc halides in 1:1 molar ratio have been
reported in literature. These complexes possess excellent storage stability and
have ability to control insects. The complexing agents, in most of the cases,
coupled to the DIBAM through both the CN group and the C=O group. These
complexes are extreamly stable and may be stored as such, even at elevated
temperatures over extended period of time.\textsuperscript{159}

Carbamate complexes of zinc have also not been extensively reported in
literature. From the possible routes of zinc carbamate complexes, which have
been reported in the past, the following three involve direct reactions with CO₂: (i) electrochemical oxidation of anodic zinc in the presence of a nitrogen base and CO₂, (ii) autoclave reaction between zinc powder and a secondary amine at high temperature and CO₂ pressures and (iii) reactions of ZnX₂ (X = halogen or alkyl) with a secondary amine and CO₂. Zinc is oxidized in the first two routes from Zn₀ to ZnⅡ, the third route already starts with a ZnⅡ compound. An example for the first route (which is relatively uncommon) is provided by the formation of the carbamate complex Figure I-18(1). Interestingly, the complex features a μ²-coordinated carbamato ligand while the other examples feature predominantly μ¹-coordinated carbamato ligands. CO₂, which can be formulated as a dimethylammonium carbamate salt [NH₂Me₂][O₂CNMe₂] in the electrolysis in acetonitrile, leads to [NH₂Me₂][O₂CNMe₂] with three bridging and two terminal carbamate units. An example for the second route is the autoclave reaction between zinc powder and HNEt₂ at 150°C and 50 atm of CO₂ in toluene. [Zn₄O(O₂CNEt₂)₆] Figure I-18(2) featuring a μ⁴-coordinated O atom in the centre is the characterized product of this reaction. It has been claimed that the oxygen atom stems from deoxygenation of the CO₂ (the redox reaction thus comprising reduction of the O atoms and oxidation of Zn). Complexes of the formula [Zn₄O(O₂CR)₆] [R = diethylamino, piperidino and pyrrolodine] are also accessible using standard Schlenk techniques, e.g. by addition of H₂O to a mixture of dialkylzinc and the secondary amine (in a twofold access) into which CO₂ had been introduced. [Zn₄O(O₂CNEt₂)₆] has been prepared (also by standard Schlenk techniques) by reaction between ZnO in acetonitrile and [NH₂Me₂][O₂CNMe₂] under CO₂ and [Zn₄O(O₂CNBu₂)₆] by reaction between ZnSO₄, [NH₂Bu₂][O₂CNBu₂] and H₂O. The third route leads to complexes in which carbamate ligands replace some of the X (halogen or alkyl) ligands of ZnX₂; for example the tetranuclear complex Zn₄Me₂(O₂CNEt₂)₆ was isolated as product of reaction between ZnMe₂, HNEt₂ and CO₂. Zn₄Me₂(O₂CNEt₂)₆ has been shown to react further with ZnMe₂ to give [MeZn(O₂CNEt₂)]₄. Other complexes
of the general formula \([\text{MeZn}(\text{O}_2\text{CNR}_2)]_4\) \((R = \text{iPr and tBu})\) were synthesized directly from \(\text{ZnMe}_2\), the corresponding secondary amine and \(\text{CO}_2\). From these complexes it can be concluded that slight modifications could lead to different products indicating that the carbamate ligands could easily be replaced by other ligands and that the complex sizes could vary.

Homoleptic derivatives of zinc(II) have been reported. The ionic carbamate derivative \([\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]\) dissolves in \(\text{MeCN}\) and reacts under an argon atmosphere with zinc powder evolving dihydrogen and and producing the homoleptic ionic zinc(II) derivative, \([\text{NH}_2\text{Me}_2][\text{Zn}_2\text{O}_2\text{CNMe}_2]\)\(_5\).\(\text{MeCN}\) (equation 19).

\[
2 \text{Zn} + 5 [\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2] + \text{MeCN} \longrightarrow [\text{NH}_2\text{Me}_2][\text{Zn}_2\text{O}_2\text{CNMe}_2]\)\(_5\).\(\text{MeCN} + 2\text{H}_2 + 4\text{NHMe}_2 \quad (19)
\]
The X-ray data confirm the presence of the \([Zn_2O_2CNMe_2]^-\) anion with three bidentate bridging carbamate groups and one terminal monodentate anionic ligand on each zinc atom. This is one of the few examples of structurally characterized anionic N,N-dialkylcarbamato derivatives reported in the literature.\(^\text{23}\)

The reaction of CO\(_2\) with alkylzinc alkylamide (RZnNE\(_2\)) gave an unusual tetrameric species \([(CH_3)_2Zn_4(O_2CN(C_2H_5)_2)_6]^+\)\(^\text{170}\) which reacts with dimethyl to give a distorted cubane \([(CH_3)_4Zn_4(O_2CN(C_2H_5)_2)_4]\).\(^\text{171}\) M. Azad Malik et. al.\(^\text{172}\) have synthesized and explained the X-ray structure of two more carbamates of zinc:

\[
\begin{align*}
(\text{I}) & \quad [(Me_2NCH_2)_2Zn(O_2CN(C_2H_5)_2)_2] \\
(\text{II}) & \quad [C_5H_5NZnMe(O_2CN(C_2H_5)_2)_3]
\end{align*}
\]

Both compounds are crystalline solids and are stable over a period of months. According to X-Ray structure of (I) the zinc atom is coordinated to four oxygens, two from each chelating carbamate group and two nitrogen atoms from the chelating N,N,N,N'-tetramethylethylenediamine (TMEDA) ligand.\(^\text{172}\) The coordination around zinc is distorted octahedron. The structure of the compound (II) consists of dimeric molecular units \([(Et_2NCO_2)_2MeZn_2NC_5H_5]\) in which each zinc atom is four coordinated. One of the zinc atom is coordinated to the nitrogen atom of pyridine and three oxygen atoms, one each from the three bridging carbamate groups, whereas the other zinc atom is linked to one methyl carbon and three oxygen atom, one each from the carbamate group.\(^\text{172}\) Alpha-zinc-o-vinyl carbamates have been studied as anionic Friedel-Crafts equivalents.\(^\text{173}\) To develop useful, single-molecule, precursors for materials such as ZnSe, large number of mixed alkyl, dialkylchalcogen carbamates\(^\text{180,181}\) have been prepared. The crystallographic studies of these complexes have shown that these are typically dimers with approximately tetrahedral coordination at the metal (ME\(_3\)O)\(^\text{174,175}\) (E= S or Se). One route to such species involves, in a formal sense, the insertion of CS\(_2\) or CSe\(_2\) into the appropriate mixed alkyl – alkylamide\(^\text{174-175}\). The insertion reaction of CO\(_2\) with RMNR\(_2\) (R = Me (Zn & Cd), R = Et (Zn) and R' = Et ) leads to the formation of tetrameric species with a unique structure.\(^\text{170}\) On the bases of X-ray
methods, the complex [Me₂Zn₄(O₂CNEt₂)₆] has the tetrameric molecular structure, where zinc atoms lie in a plane and the unit is centrosymmetric with two independent zinc atoms. Four carbamates bond along the edge of the Zn₄ parallelogram with normal Zn – O distances. Two further carbamates bridge across the diagonal of the parallelogram above and below the plane of the zinc atoms; oxygen atoms via monoatomic bridge to zinc atoms and the tetrahedral coordination at zinc atom is completed by methyl group. The other zinc atom is five coordinate with a weak monoatomic bridge from one of the edge – bridging carbamates Zn – O. In this complex, the coordination at zinc can be viewed either as a flattened tetrahedron consisting of the normal zinc – oxygen contacts with oxygen coordinating to the open – up face of the tetrahedron, or as a distorted trigonal bipyramid with weak axial ligation from oxygen. A large number of structures have been reported in which both an alkyl group and oxygen atoms coordinate to zinc. Coordinative saturation at zinc is often attained by some degree of association, and common structural units include dimers such as the fused tetrahedra in K₂[Et₂Zn(OBu')₂ZnEt₂] and [MeZn(S₂CNEt₂)]₂. Another common geometry is based on a tetrahedral arrangement of zinc atoms as in basic zinc acetate [Zn₄O(O₂CMe)₆] and the cubane structure found for neutral alkoxy species such as [(MeZn(OMe))₄]. The tetranuclear basic zinc carbamates Zn₄O(O₂CAm)₆ (Am = N-diethylamino, N-piperidyl, N-pyrrolidyl) were shown by transient FTIR spectroscopy to undergo C – N bond methathesis reaction that results in the exchange of the carboxyl group with bulk carbon dioxide and exchange of the amino group with bulk secondary amine (transamination) have been reported in literature.

The formal insertion of carbon dioxide into a series of methyl zinc dialkylamide complexes (MeZnNR₂) initially from solvent – free, tetrameric zinc carbamato complexes [Me₄Zn₄(O₂CNR₂)₄] [NR₂ = N(–Pr)₂ (1), N(–Bu)₂ (2), and piperidinyl (3)]. These compounds have been characterized by traditional techniques as well as single – crystal X – ray diffraction analyses. The tetrameric backbones seen in the solid state for 1 – 3 were structurally similar to each other. Addition of excess pyridine (py) to 1 – 3 breaks apart the tetramers and converts them into solvated dimeric species [Me₂Zn₂(O₂CNR₂)₂(py)₂] [(NR₂ = N(i-
Pr)\textsubscript{2} (4), N(\textit{i}-Bu)\textsubscript{2} (5), and piperidinyl (6). X-ray crystallographic analysis of 4 and 5 confirmed the dimeric structure in the solid state.\textsuperscript{168}

Despite the richness of different carbamate complexes which have been isolated, surprisingly little is known about their reactivity. Four examples are as follows: (i) complexes of the formula \([RZn(O_2CNR_2)]_4\) were treated with pyridine (py) leading to decomposition of the tetrameric complex to give dimeric complexes of the formula \([R(py)Zn(O_2CNR_2)]_2\).\textsuperscript{168} (ii) \([OZn_4(O_2CNR_2)]_6\) complexes are amenable to transamination,\textsuperscript{71} leading effectively to an exchange of the \(R\) groups. (iii) the CO\textsubscript{2} units in \([OZn_4(O_2CNR_2)]_6\) complexes can also be replaced, as shown by experiments with \textsuperscript{13}C-enriched CO\textsubscript{2};\textsuperscript{84} this reaction shows that the bonding situation in these carbamate complexes is reminiscent of the bonding situation in enzymes featuring carbamate units and also in other transition metal carbamate complexes. (iv) As already mentioned \([Zn_4Me_2(O_2CNEt_2)]_6\) has been shown to react with ZnMe\textsubscript{2} to give \([MeZn(O_2CNEt_2)]_4\)\textsuperscript{162} and with TMEDA to give the mononuclear bis(carbamate) complex \([((Et_2NC_02)Zn(TMEDA)]).\textsuperscript{172}

The reaction of \((N\text{-methyltetraphenylporphynato})\text{ethylzinc(II)}, Zn(NMTPP)\text{Et, with secondary amines in the presence of CO}_2\) has been used to prepare N,N-dialkylcarbamato derivatives\textsuperscript{183} (equation 20), the reaction being accelerated by visible light. Further, it has been reported that the zinc-carbon bond of Zn(NMTPP)\text{Et is activated via excitation of the porphyrin ring. The spectroscopic product identification showed a \textsuperscript{13}C NMR signal at 157 ppm typical of the carbamate function.}

\[
\text{Zn(NMTPP)Et} + \text{CO}_2 + \text{NHR}_2 \rightarrow \text{Zn(O_2CNR_2)(NMTPP)} + \text{EtH} \quad (20)
\]

\(R = \text{Et, Pr, 'Pr, 'Bu}\)