INTRODUCTION

Metal carbonyls and their derivatives occupy a position of peculiar interest in the chemistry of transition metals. Currently many compounds with unusual structure, reactions and physical and chemical properties have been discovered. Moreover, their variegated patterns of molecular structure these compounds are themselves the test subject in many phases of modern chemical scientific research and development.

Metal carbonyls are coordination complexes of transition metals with carbon monoxide. These complexes may be homoletic, i.e. contain only CO ligands, such as nickel carbonyl (Ni(CO)₄), but more commonly metal carbonyls contain a mixture of ligands, such as Re(CO)₅(2,2'-bipyridine)Cl. Carbon monoxide is an important building block for the synthesis of many compounds, e.g. hydroformylation, and metal carbonyl catalysts are central to its utilization. Metal carbonyls are toxic, in part because of their ability to carbonylate hemoglobin to give carboxyhemoglobin, which will not bind O₂.

Binary metal carbonyls are those compounds which are formed between carbon monoxide and zerovalent transition metals. Binary metal carbonyls have come into existence ever since Ludwig Mond [1] discovered nickel tetracarbonyl in 1890 which eventually led to the synthesis of many analyses, led primarily by Walter Hieber who prepared the first metal hydride H₂Fe(CO)₄. Since then the binary carbonyls of all the transition metals of G-5 to G-8 (except Niobium & Tantalum) have been prepared.

A series of complexes [M(CO)₅(Hdpf - κP)], where M=Cr(1), Mo(2) and W(3), Hdpf is 1′-(diphenylphosphanyl)ferrocene carboxylic acid, was obtained by thermally -induced (2) or photochemically-assisted (1,3) displacement of carbon monoxide with Hdpf from the corresponding hexacarbonyl complexes. The complexes were characterized by NMR, UV-VIS and IR spectroscopies and further studied by cyclic voltammetry. The solid-state structure of complex one has been determined by single-crystal X-ray diffraction.

Objective of the proposed work

Survey of literature showed that the metal mixed carbonyl complexes of G-6 metal carbonyls have remained most unexplored. It is thought to be worthwhile the study of above mentioned topic for well establishment the generality of the reactions and would be given a possible mechanism, since long live such reactions have played an important role in organometallic chemistry mainly in the synthesis of novel compounds having antimicrobials, antifungal, antibacterial, anticancerous, antileucaemal and antineoplastic and catalytic behaviour. These studies will thought to be more beneficial for man kind, scientific societies & country.

Literature Survey

Ligands in which nitrogen & oxygen act as donor atoms cannot engage themselves in synergic σ - π bonding because, they both lack the necessary vacant
orbitals for accepting the electron density from filled metal d-orbitals. Exceptions are
the compounds like 1, 10-phen, 2,2’ – bipy and 2, 2’, 2” terpyridine in which the
nitrogen atom is a part of the heterocyclic systems. For aliphatic amines,
hydrogenated heterocyclic systems, alcohols, ethers, hydrogenated furans, etc., there
can be only a pure σ-donor function and complete replacement of CO by these
ligands in metal carbonyls cannot occur. With these donors, the CO stretching
frequencies can drop well below the so called ‘bridging CO region’ without the
presence of any bridging CO group.

Some metal carbonyls are found in living organisms (Porphyrins), some are
employed in chemical processes for biomass exploitation (furan derivatives), and
others are used as precursors of new electrical conductors (polypyrroles,
polythiophenes). A large number of compounds are now known where E may be a
main group or a transition element of heterocyclopentadiene, or heteroles,
containing an element other than oxygen, sulphur, or nitrogen. The chemistry of
phospholes has been most extensively developed[2]. Displacement of carbonyl
ligands from Cr(CO)₆ leads exclusively to the complexation of the arene in C-
phenylated siloles. This type of complexation was also found in attempts to co-
dordinate the silaflourence-1 with chromium.

Group-6 ligands containing sulphur as donor atom has been investigated in
the CO displacement reactions of octahedral metal carbonyls. The bidentate ligands
(o-methylthio) benzene, 1, 8-bis-(methylthio) naphthalene and 3, 5-dithiahexane
have also been reported to react with molybdenum hexacarbonyl or (diene)
disubstituted derivatives of G-6 metal carbonyls, LM (CO)₅ and L₂M(CO)₄ have been
synthesized by the action of ligands like PH₃ on halopentacarbonyl metallate anions,
[M(CO)₅X] in octahydrotriborotetracarbonyl metallate anions [M(CO)₄B₂H₆] in
tetrahydrofuran [5]. The long time U.V. irradiation of a mixture of the metal carbonyl
and one of the ligands as PMe₃, Me₂P(OMe), MeP(OMe)₂, P(OMe)₃, (MeO)₂PF or
MeOPF₂ in an organic solvent has been studied [6] to achieve the higher substitution
products.

Recently, by the carbonylation of (C₅H₅N)₂CrCl₃ in pyridine at 85°C and ~ 60
atm. pressure, an electrochemical synthesis of chromium hexacarbonyl (85%) has
also been reported.

All the three G-6 metal hexacarbonyls are monomeric, diamagnetic and of
octahedral geometry (I).

An unstable pentacarbonyl of tungsten has been isolated by the low
temperature irradiation of tungsten hexacarbonyl. The existence of neutral
pentacarbonyls of G-6 as reaction intermediates have been previously postulated
[3].

Reductive carbonylation of transition metal halides metal carboxylates or
other complexes under different experimental conditions are generally employed for
the preparation of metal carbonyls. For example the carbonylation of chromolls or
chromic acetylacetonate or certain organic salts (e.g. acetate), in presence of
powdered zinc or magnesium with pyridine as solvent, gave 80-90% yield or
chromium hexacarbonyl. The carbonylation of chromic chloride takes place in the
presence of aluminium chloride, powdered aluminium or a mixture of both [Al+AlCl₃]
triethyl aluminium [5] and lithium aluminium hydride, to produce chromium hexachlorides in good yields. All the G-6 metal hexacarbonyls have been obtained in high yields by reductive carbonylation of chromium (III), molybdenum (V) and tungsten (VI) chloride, respectively, in diethyleneglycoldimethyl ether in the presence of metallic sodium [6].

Many metal carbonyl anion have also been reported in addition to these neutral carbonyls in this group. The ions \([\text{M(CO)}_6]^{2-}\) (M = Cr, Mo or W) are produced as sodium salts by the action of metallic sodium on the hexacarbonyls in liquid ammonia [7]. Recently a facile synthetic route for their preparation has been reported, which involves the alkali metal reduction of \(\text{M (CO)}_6\) \([\text{M(CO)}_5\text{(halide)}]\) or \([\text{M}_2(\text{CO})_{10}]^{2-}\) in hexamethyolphosphoramide (HMPA).

The profile of the spectra are very similar and the shifts of approximately 100 cm\(^{-1}\) for each absorbance maximum in going from neutral carbonyl to the anionic species is as expected for the improved metal to carbon \(\pi-\) bonding in presence of an excess of negative charge.

Although the formation of trinuclear species \([\text{M}_3(\text{CO})_{14}]^{2-}\) has been known since long, physical data or structural information are not available. It is possible that two metal-metal bonds are present to give a linear structure, \([\text{(CO)}_5\text{M-M(CO)}_5]^{2-}\) in which each metal atom is essentially in an octahedral environment.

The anions \([\text{M}_2(\text{CO})_{10}]^{2-}\) (M = Cr, Mo or W) [16] were obtained by the reduction of the hexacarbonyls with sodium borohydride in liquid ammonia. The structure of these ions is likely to be the same as that of the neutral \(\text{M}_2(\text{CO})_{10}\) carbonyls of G-7, with which they are isoelectronic. This is supported by the very close similarities of the infra-red spectra in the carbonyl stretching region.

The IR spectra of \([\text{Cr(CO)}_5]^{2-}\) species in tetrahydrofuran shows bands at 1819s and 1768s, broad cm\(^{-1}\) while in HMPA the band positions are considerably in the lower region (\(\nu\text{ CO}: 1760s\) and 1722s cm\(^{-1}\)). The difference in the two spectra may be attributed to the distortion of \([\text{Cr(CO)}_5]^{2-}\) from \(D_{3h}\) symmetry (II) to \(C_{4V}\) (III) in the two media.

Two strong infra-red active bands below 1800 cm\(^{-1}\) as expected for trigonal bipyramidal \([\text{M(CO)}_5]^{2-}\) species have been observed for \([\text{M(CO)}_5]^{2-}\) in HMPA. Thus no co-ordination of \([\text{M(CO)}_5]^{2-}\) with HMPA takes place. In contrast ion-pair formation has been suspected when tetrahydrofuran was used as a solvent.

As the number of complexes with ferrocene ligands possessing other donor group(s) besides the phosphane moiety is still rather limited, we decided to study a series of complexes \([\text{M(CO)}_5\text{L}]\) (M=Cr, Mo and W) with \(1^{-}\)(diphenylphosphanyl)ferrocenecarboxylic acid (Hdpf) as a potential multifunctional hybrid donor in this paper. We report the preparation and spectral and cyclovoltammetric study of a series of complexes \(\text{M(CO)}_5(\text{Hdpf - }_1\text{P})\), where M=Cr, M and W.
Bonding in Metal Carbonyls

Carbon monoxide bonds to transition metals using "synergic" pi back-bonding.

The bonding has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of nonbonding electron pair on carbon with a blend of d, s, and p-orbitals on the metal. A pair of π bonds arises from overlap of filled d-orbitals on the metal with a pair of π-antibonding orbitals projecting from the carbon of the CO. The latter kind of binding requires that the metal should have d-electrons, and that the metal is in a relatively low oxidation state (<+2).

The π-bonding has the effect of weakening the carbon-oxygen bond compared with free carbon monoxide. Because of the multiple bond character of the M-CO linkage, the distance between the metal and carbon is relatively short, often < 1.8 'Å'.

In the formation of metal carbonyls the qualitative features of bonding mechanisms have been described in numerous reviews [8], a semiquantitative approach of bonding has also been reported recently [9]. The accepted bonding mechanism may be exemplified on the consideration of the following points:

(a) Structure of carbon monoxide,
(b) Nucleophillic attack on carbon of carbon monoxide,
(c) Effect of carbon monoxide on the metal d- orbitals.

The various workers [10,11] have studied the structure of carbon monoxide. The qualitative features of the ultraviolet spectrum of CO has been explained successfully in terms of the configuration \( (\sigma^* \pi)^2 (\sigma^* \pi)^2 (\pi, \sigma^*)^4 \), which is consistent with presence of lone pair of electrons on each of the atom of the molecule and a triple bond between carbon and oxygen.

The results of molecular orbital calculations given by Sahni [11] have been supported by qualitative molecular orbital description of Jaffe and Orchin [10], who have shown that in the case of carbon monoxide, since the atomic orbitals of the two atoms which form the sigma bond are not equivalent, their relative energies must also be considered, as it is well known that two atomic orbitals can form a strong bond only if their energies are fairly close.

The \( p_z \) and s orbitals of each of the carbon and oxygen atoms (the z axis are taken as bond axis) belonging to the same symmetry species can accordingly be
hybridized in the cylindrical field of the molecule. The hybridization leads to an energy level scheme in which each atom has two $\pi$–orbitals and two $\sigma$–orbitals.

Thus, the hybridization of the s and p orbitals results in two new levels, one ($\sigma_2$) below the p level of the isolated atom and one ($\sigma_1$) above the s level of the isolated atom. Owing to the large energy difference between s & p orbitals of the isolated carbon and oxygen atoms, the $\sigma_1$ of carbon contains only one and $\sigma_1$ of oxygen contains two electrons. Then the criterion of hybridization of similar energies in CO can only be met if $\sigma_1$ of carbon interacts with $\sigma_2$ of oxygen to form the sigma bond. As a result,

$$:C\equiv O:$$

The lone pair on the carbon atom in above molecule will be in a $\sigma_2$ orbital and has largely pz character and the lone pair on oxygen atom will be in the $\sigma_1$ orbital, and has largely s character. The ionization potential of the carbon lone pair is thus quite low, making it relatively a basic loan pair. This relatively high energy level of the lone pair and the fact that it is largely p in character and thus strongly directional should be responsible for the many reactions in which carbon monoxide acts as a nucleophile.

Thus CO molecule is likely to be attached to the electrophilic groups facilitating the attachment of the other molecule or vacant orbitals of transition metals resulting a primary step in the formation of metal carbonyls.

The primary step of bonding involves a co-ordinate $\sigma$–bond formation by the interaction of lone pair of electrons on the carbon atom of CO with the vacant metal orbitals. Based upon the fact that the electrostatic potential of a transition metal is modified by the potential of the surrounding carbonyl groups, the calculations of Craig and Doggett [12] suggest that the penetration of the $\sigma$ lone pair of CO into the electron cloud of the metal causes an expansion of $d_e$ orbitals, i.e. the effect of CO attack on the metal d-orbitals results in an expansion of the metal $d_e$ orbitals and thus increases the overlap with CO p$\pi$ orbitals, facilitating the electron withdrawal.

The $d_e$ orbitals of the metals are expanded more and more as the number of carbonyl groups with p-character of the carbon lone pair electrons increases. The secondary step of interaction of filled metal $d_e$ orbitals with CO, p-orbitals results in ($d\pi - p\pi$) back bonding and which strengthen the metal-carbon bond.

The above two modes of bonding are thus mutually reinforcing, "Synergic" charge removal from the metal through TC "back bonding" leads to more extensive $\sigma$ bond formation, while the charge thus donated to the metal facilitates further back bonding.
Substitution Reactions:

A wide variety of ligands can displace CO from G-6 metal hexacarbonyls. Only in few isolated cases a complete displacement of all the CO molecules have been observed. In all the cases, the presence of other ligands may stabilize the metal-carbon bond and degree of substitution may be determined by this stabilization, together with the affinity of the metal for the entering ligand as well as the nature of group attached to the donor atom of the ligand.

Three types of ligands have been mainly employed for the substitution of carbon monoxide in metal carbonyls:

(1) Ligands with one or more free electron pairs having vacant orbital or orbitals that can be vacated to receive $\pi$-electrons from the metal, e.g. substituted phosphines, arsines, stibines, sulphides, selenides, organic phosphites, arsenites, nitriles; heterocyclic or aromatic ring systems, which possess both $\sigma$ donor and $\pi$-acceptor properties.

(2) Ligands with one or more free electron pairs lacking in suitable empty orbitals to receive electron density from the metal orbitals, e.g. amines, amides, ketones, ethers & alcohols, which bond through the first row atoms i.e. which act as $\sigma$-donors only.

(3) Ligands without a free electron pairs, but with $\pi$-bonding electrons, e.g. amines, dienes, polyenes, cyclic polyenes, aromatic compounds and certain ions as $\text{C}_7\text{H}_7^+$, which act as $\pi$ donors.

The inductive and mesomeric effects of substituents upon the donor atoms influence both its donor & acceptor properties [13]. Despite the differences in reactivity & stability of their derivatives, the donor atoms as sulphur, phosphorus and arsenic (in sulphides, phosphines & arsines) appear to possess essentially the same double bonding capability [14]. Antimony & Bismuth donors resemble arsenic and phosphorus in this respect [15].

Since this work deals mainly with the class 1 & 2 ligands, a detailed description of the reactions of the ligands of only this class is given here.

Ligands of class A include P, As, Sb & Bi of G-5A (in (III) oxidation state) and S, Se & Te of G-6A (in (II) oxidation state) atoms as donor atom. Substitution reaction of metal carbonyls occurs fairly readily with this class of ligands because they possess vacant d-orbitals available for $d\pi - p\pi$-back bonding in order to decrease the electron density on metal atom, yet it is extremely difficult to displace all the carbon monoxide molecules by other ligands.

One of the possible explanations may involve $\pi$-bonding concept which is in qualitative agreement with the drop in CO stretching frequency with increased substitution. Since the M-C $\pi$-bonding & presumably the bond strength, increase with substitution, it follows that each step in the replacement of CO from a metal carbonyl is of higher frequency than the preceding step. Substitution by the poorer $\pi$-bonding ligands than the CO will then decrease the lability of each successive
CO ligand making them harder to displace from the metal carbonyl. However, since the extent of \( \pi \)-back bonding varies widely for these ligands and appear to be, to a marked degree, a function of the electronegativities of the substituents on the donor atom, so with few ligands complete substitution of the CO have been observed.

The effect of steric hinderance also play an important role in differentiating the \( \sigma \)- and \( \pi \)-bonding capabilities of a number of ligands like PPh\(_3\), AsPh\(_3\) & SbPh\(_3\) in substituted metal carbonyls. It has been suggested [16] that PPh\(_3\) is a better donor and acceptor than AsPh\(_3\) which in turn is a better donor-acceptor than SbPh\(_3\).

The long time ultraviolet irradiation of a mixture of the metal carbonyl and one of the ligands such as PMe\(_3\), Me\(_2\)P(OMe), MeP(OMe)\(_2\), P(OMe)\(_3\), (MeO)\(_2\)PF or MeOPF\(_2\) in an organic solvent has been studied [17] to achieve the higher substitution products. This method is efficient for obtaining penta or hexa substituted derivatives [17].

Ligand behaviour of several P(III) derivatives like phosphine, primary, secondary & tertiary, unsaturated tertiary phosphines, organometalophosphines, substituted aminophosphines, tertiary phosphites, dialkyl or phenylalkylphosphonites, cyanophosphines, halo or halophenylphosphines has been extensively investigated in the substitution reactions of chromium, molybdenum or tungsten hexacarbonyl.

Substitution reactions of primary & secondary phosphines with chromium, molybdenum & tungsten hexacarbonyls have not been extensively investigated [18-20].

Simple substitution products are generally prepared by direct displacement of carbon monoxide from the metal carbonyl by a donating group. This may be accomplished by refluxing the metal carbonyl and the ligand in an appropriate common organic solvent or by heating the reactants in an evacuated sealed tube or autoclave or by strong ultraviolet irradiation from a mercury arc lamp.

However the preparation of di- and trisubstituted derivatives by displacement of olefine like 2,5- norbornadiene [21], cycloocta- 1,5 - diene, bicyclohepta 2,5 – diene [22], cycloheptatriene [14] or arenes [14] from the corresponding metal tetra or tricarbonyl complex is often convenient.

Mono- and disubstituted derivatives of G-6 metal carbonyls, LM(CO)\(_5\) and L\(_2\)M(CO)\(_4\) have also been synthesised by the action of ligands like PH\(_3\) on halopentacarbonyl metallates, [M(CO)\(_5\)X]\(^-\) or octahydrotriborotetraacarbonyl metallate anions, [M(CO)\(_4\)B\(_3\)H\(_8\)]\(^-\) in tetrahydrofuran [23].

Reductive carbonylation of trans- WCl\(_4\) (PR\(_3\))\(_2\) by sodium amalgam in tetrahydrofuran solution at 20°C under carbon monoxide in presence of PR\(_3\) has been reported [24] to give di and trisubstituted products.
A few derivatives of silicon, titanium or zirconium containing phosphorus ligands have been synthesised by two different routes & the structure of the complexes obtained have been established on the basis of IR and NMR spectral data [19-20].

Tertiary phasphine (t- Phosphine) derivatives like triphenylphosphine, tri(m-toly) phosphine and tri(p-toly) phosphine react with metal hexacarbonyl to give simple substitution products under mild conditions. Under drastic conditions the reactions of such ligands with chromium hexacarbonyl yield two series of complexes, [Cr(CO)3L] and [Cr(CO)2L]2[41].

Thermal reactions between [M(CO)6] and pentamethyl cyclopenta arson yielded [M(CO)4(AsMe)5]2, which are bridged arsinido derivatives containing chains of arsenic atoms linking two metal atoms. The NMR and mass spectral data for pentamethylcyclopenta arson indicate that it exists in the form of a five-membered ring system with a puckered conformation and with one As atom displaced from the plane of the other four. A rapid rotation of the puckering in the As ring was identified. The cyclo-arsine appeared sufficiently flexible to act as a mono-, bi-, or tridentate ligand.

Compared to nitrogen donor ligands, a few oxygen donors have been studied. Acetone, methanol and ether [26] displace 1 CO molecule from [M(CO)6] (M = Mo, W) to form [M(CO)5L] derivatives. These derivatives have not been isolated & have been studied in solution. Tetrahydrofuran, diglyme and dimethylformamide [27] displace upto three CO molecules from [M(CO)6]. These trisubstituted derivatives having M-O bond open a new route for the formation of trisubstituted molecules with other ligands, which are not so reactive as to give the trisubstituted derivatives directly.

A number of triaryl phosphine oxides [28] and substituted arylphosphine oxides [29], which possess oxygen donors, yield the mono-, di- and trisubstituted derivatives from [M(CO)6]. These reactions have been studied both by UV and reflux methods. In the di- and trisubstituted derivatives, the phosphine oxides are in the cis positions. Configurational studies have also been made using IR & NMR spectra.

Ligands in which nitrogen & oxygen act as donor atoms cannot engage themselves in synergetic $\sigma - \pi$ bonding because they both lack the necessary vacant orbitals for accepting the electron density from filled metal d-orbitals. Exceptions are the compounds like 1,10-phen; 2,2'- bipy and 2,2',2" terpyridine in which the nitrogen atom is a part of the heterocyclic $\pi$ systems. For aliphatic amines, hydrogenated heterocyclic systems, alcohols, ethers, hydrogenated furans, etc., there can be only a pure $\sigma$ - donor function and complete replacement of CO by these ligands in metal carbonyl's cannot occur. With these donors, the CO stretching frequencies can drop well below the so called 'bridging C-O region' without the presence of any bridging C-O group.

A number of aliphatic and alicyclic amines [30] have been studied in the ligand exchange reactions of metal hexacarboxyns. Both reflux and UV irradiation methods have been employed. The replacement of CO molecule upto the
disubstituted stage has been achieved by the UV irradiation methods, while the reflux method yielded derivatives upto the trisubstituted stage. Ligands like Picoline, 3, 4- lutidine and 3- chloropyridine displaced one CO from [M(CO)\textsubscript{5}L](L=pyridine, \(\gamma\) – picoline) to form cis- disubstituted derivatives [31]. Ligands like transition metal ion Schiff's bases [32] and azide ion [33] have also been investigated. Apart from these, a number of ligands possessing nitrogen and a second donor atom like P, As or S have been investigated in such reactions [34].

Direct reaction of 2- pyridinocarboxaldehyde-2-pyridyl-hydrazone (Paphy) [35] with [Mo(CO)\textsubscript{5}] in diglyme at 120°C gave orange red compound, stable in air, while the reaction of tetraethylammonium chloropentacarbonylmolybdenum with paphy in diglyme at room temperature gave.

The information concerning the structure of an organic molecule which may be gained from an ultra violet visible spectrum is more limited than in the case of I.R., N.M.R. and mass spectra, invariably it is necessary to cross-relate such information with that obtained from the results of different spectra, in order to provide a sound basis on which to proceed towards the characterization of functional groups and the final identification of the compounds.

The principal features which may be detected from electronic spectra are multiple bonded systems, conjugated systems and aromatic (and hetero aromatic) nuclei. The electronic transitions in these systems which give rise to absorption in the 200-700 nm region are \(\eta \rightarrow \pi^*\) and these are of diagnostic value. The \(\eta \rightarrow \sigma^*\) electronic transition which arises in saturated compounds containing the heteroatoms sulphur, nitrogen, bromine and iodine is of less importance since it leads to absorption just below 200 nm. Gussian analysis of the [Cr(CO)\textsubscript{6}] spectrum at lower temperature yielded a weak band at 30950 cm\(^{-1}\) corresponding to the 30700 and 30600 cm\(^{-1}\) band in [Mo(CO)\textsubscript{6}] and [W(CO)\textsubscript{6}] respectively which also might be a part of the vibrational structure associated with \(^1A_{1g} \rightarrow ^1T_{1g}\) transition.

Several ligand field parameters have also been calculated by the measurement of electronic spectra. The value of \(\Delta\), B and C (ligand field parameters) derived from the electronic spectra of these complexes. The \(\Delta CO\) value in the series actually shows a very slight difference (decrease) because the interelectronic interaction effects should decrease in the order 3d > 4d > 5d. Indeed evidence from ionizat\(ion\) potential and charge transfer spectral data indicates that the \(^2T_{2g}\) level remains stationary down a series, such as [M(CO)\textsubscript{6}] (M = Cr, Mo, W).

Thus, it is inferred from these and thermochemical [36] data that the d-\(\sigma\) bonding actually decreases and it is the increased \(\pi\) bonding in carbonyl complexes that holds (4d) and (5d) at values comparable to the (3d) values. IR spectra of metal complexes has been used, as a guide in the identification of the bonding atoms, and useful information on the nature of metal-ligand bond, and the stability of complex can be had, since on co-ordination of a metal to a ligand, bands are shifted to lower or higher frequencies with possible variation in intensity, while the far infra-red spectra of metal chelates can be most useful, for differentiating various stereochemistries [37]. It is generally accepted, that (Ni-X) stretching frequencies of tetrahedral complexes, fall in the region of 300 cm\(^{-1}\) (X = Br). At the same time the
corresponding bands occur around 200 cm\(^{-1}\) and 160 cm\(^{-1}\), (X = Cl or Br), respectively [38, 39].

Various aspects from infra-red spectral studies are generally concluded and enlisted into two sections:

**Section (1)** Characteristic frequencies above 700 cm\(^{-1}\) (700-4000 cm\(^{-1}\))

I. They involve mainly stretching vibrations, except for the vibrations involving Hydrogen,
II. The mass of one atom is usually small.
III. The force constant between the atoms is usually larger.
IV. They are often localised characteristic frequencies, and may not be affected too much neighbouring groups.

**Section (2)** Characteristic frequencies below 700 cm\(^{-1}\) (200-700 cm\(^{-1}\)) Far IR spectra.

I. They involve mainly skeletal bonding vibrations for light atoms, and stretching vibrations for heavy atoms.
II. The mass is usually large, but not always.
III. The force constant is usually small.
IV. The vibrations are often associated with three or more atoms.
V. They are influenced more by neighbouring groups, and may occur over a wide range of frequencies.

From far infra red spectra of various metal complexes derived from substituted thioureas, \(\nu\) (M-Thiourea-N), \(\nu\) (M-thioketo-S) and \(\nu\) (M-Cl) are reported in medium & weak intensity bands in the region 525-500 cm\(^{-1}\), 475-430 cm\(^{-1}\) and 240-230 cm\(^{-1}\) respectively. The far IR spectra, (400-100 cm\(^{-1}\)) show various important bands, such as \(\nu\) (M-Cl), \(\nu\) (M-CNS), bridging reported at nearly 230+10 cm\(^{-1}\), 180+5 cm\(^{-1}\), 270+10 cm\(^{-1}\) respectively.


Toxicity depends on the dosage: Carbon monoxide (CO) is known as a toxic gas, responsible for the deadly effect of auto exhaust in closed garages, for example. Paradoxically, the human body itself produces 3-6 cm\(^3\) of CO daily. Certain diseases cause this quantity to increase, which can be detected on the patient’s breath. British researchers working with Brian E. Mann at the University of Sheffield and Roberto Motterlini at the Northwick Park Institute for Medical Research in Harrow have now developed a family of CO-releasing complexes that could turn out to be a new class of medicines.
CO has been demonstrated to play a crucial role as a signal carrier in certain physiological processes, particularly in the cardiovascular system, and is important in various areas of medicine. It thus helps to suppress rejections after organ transplants, and reduces the damage caused by disruption of the blood supply to an organ or tissue (ischemia).

Using CO as a drug thus seems obvious. Mann and Motterlini don't want to use CO as a gas however; they were searching for a "solid" form, a compound that would release CO inside the body. They chose to use metal carbonyl complexes, which consist of several CO molecules and various other ligands grouped around a central metal atom. A number of ruthenium and iron complexes proved to be particularly promising. The ruthenium complexes very quickly release CO in the presence of myoglobin, a protein involved in oxygen transport in muscles. In trials, they demonstrated a vasodilatory effect and a significant increase in life expectancy in animals after heart transplants. Also noteworthy is a special iron complex that does not transfer CO to myoglobin, yet still acts as a vasodilator. In this case, the CO seems to be released directly into cells, which may make it possible to bring CO directly into tissues.

Given the well-known toxicity of CO, it seems improbable that it could be medically useful as a gas. However CO-releasing molecules such as our carbonyl complexes could lead to the development of new drugs for the treatment of cardiovascular diseases as well as neurodegenerative and inflammatory diseases, Mann says optimistically. After all, an equally toxic gas, nitrogen monoxide (NO), has also gained great importance in the form of NO-releasing drugs. Northwick Park Hospital and the University of Sheffield have formed a company, hemoCORM, to develop new pharmaceuticals based on this discovery.

Siloles with unsaturated groups at silicon give monosubstituted complexes with the vinyl group bonded to the transition metal. Obviously, the unsaturated \( \eta^2 \) ligand is always in the endo position, With such ligands the reactivity of molybdenum & tungsten is very similar.

**Magnetic Studies:**

Magneto chemistry is one of the means, by which inorganic and coordination compounds are investigated and its success is mainly determined by the circumstances that the theory of Para magnetism developed by Van-Vleck based on Boltzmann distribution of electrons, in the stationary energy states of polyatomic systems, which define the form of temperature dependence of magnetic susceptibility [46].

Coordination complexes of dibasic tridentate ligand are of considerable research interest, because of the possibility of dimetallation leading to bimetallic compounds, with unusual magnetic properties [47]. Further, it is evident that on severe heat treatment of the chelates, there is a transition from a low spin to a high spin state. It is also reported that the presence of an absorbed component of air, reduces the value of effective magnetic moment (\( \mu_{\text{eff}} \)) for almost all chelates, derived from substituted phenyl rings.
This behavior was concluded due to temperature equilibrium of spin states (TESS). Magnetic moments of manganese, iron, cobalt, nickel, copper complexes have been reported [48] as 5.67, 5.25, 4.6, 3.3, 2.62 B.M. respectively and are within the range required for spin free d5, d6, d7, d8, d9, systems respectively. In case of cobalt values suggest octahedral stereochemistry of the complexes and the metal ions are well separated having no spin-interaction.

The study of the complexing behaviour of these ligands, with trace metal ions will provide valuable information for a better understanding of the true nature of the diseases. It requires a considerable knowledge of co-ordination chemistry in the search of a better metal based drug and successful drug designing.

An advancing form of the coordination chemistry of metal chealates, which is the central theme of inorganic chemistry in gaining ground specially with the advent of Ligand Field Theory, Advanced spectroscopic analysis and calculation of various Ligand field parameters and their sterochemical relations.

Gao, Basolo et al. described the use of pyridine N-oxide to facilitate CO release from Fe(CO)\textsubscript{5}. It has been established well the generality of the reaction and suggested a possible mechanism. Since that time such reactions have played an important role in organometallic chemistry, particularly in the synthesis of metal carbonyl datives.

The effect of steric hinderance also play an important role in differentiating the $\sigma$ - and $\pi$ It – bonding capabilities of a number of ligands like PPh\textsubscript{3}, AsPh\textsubscript{3} & SbPh\textsubscript{3} in substituted metal carbonyls. It has been suggested that PPh\textsubscript{3} is a better donor and acceptor than AsPh\textsubscript{3} which in tum is a better donor – acceptor than SbPh\textsubscript{3}.

Metal carbonyls and their derivatives display sharp intense CO stretching vibrations in the 1700-2200 cm\textsuperscript{-1} region, the number and relative intensities of which are functions of the molecular symmetry. The frequencies (energies) of CO absorption in the infrared are often diagnostic of the type of bond that the CO forms with the metal center.

The two most important units are the terminal (M-C-O) and bridging (MC(O)-M) groups whose CO frequencies in natural molecules usually, but not always, fall in the 1990-2125 and 1700-1850 cm\textsuperscript{-1} regions respectively.

**Planning of proposed work**

In the present synopsis, efforts have been made in the direction of seeking a correlation of the thermal, spectral and magnetic properties of metal complexes, derived from their various derivatives of present working plan on the proposed work has been restricted to the following aspects :

1. The preparation & characterization of various derivatives of undertaken ligands with different aldehydes having Nitrogen ,Oxygen ,Sulphur ,Phosphorus as biologically active donor atoms to obtain required complexes viz anisaldehyde, benzaldehyde, salicyaldehyde, vanilline, furfuraldehyde etc. to obtain required ligands for complexation with Chromiumr, Molybdenum and Tungsten carbonyl compounds.
2. The preparation and characterization of G-6 metal mixed carbonyl derivatives synthesized with suitable ligands as Tetra alkyl diphosphine disulphides (TDD), 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (DTTT), 2-hydroxy-1-napthaldehyde ethanesulfonylhydrazone (Nafesh). Their characterization is well planned using chemical, physical methods, molecular weight determination, magnetic measurements & spectral (electronic and infra red) studies.

**Fourier Transform Infrared Spectral Studies:**

Recording & interpretation of the FT-IR spectra of the synthesized organic compounds and their isolated complexes are employed in measuring the coordination sites of the proposed and selected specific ligands.

**Electronic Spectral investigations:**

Recording & interpretation of the electronic (reflectance) spectra of the isolated complexes and computation of relevant and field parameters were carried out, which provide a deeper understanding of the micro symmetry about the central metal ion.

**Magnetic behaviour:**

The magnetic studies, in powder form of the isolated complexes at the room temperature have been very useful in revealing an accurate description of many phisico-chemical properties of the complexes, e.g. oxidation state, steric effects, magnetic behaviour of the central metal ions and micro-symmetry of the complexes.

**Nuclear Magnetic Resonance Spectral studies:**

Recording & interpretation of the Nuclear Magnetic Resonance (NMR) spectra of the synthesized complexes would be utilized to find out the specific organic groups which present in the complexes.

**Work Done**

The preliminary investigation of the undertaken work has been well accomplished. Different usable suitable ligands have been prepared and some ligands are bought from Ranbaxy Fine chemical Ltd., Sisco Chem Pvt. Ltd., and Thomas Baker chemical Ltd. And have well characterized till date. The job of literature survey has been well accomplished. For FT-IR, Elemental Analysis, the isolated complexes, $C_7H_8 Mo (CO)_4$, $M(CO)_4L$, where $M=Cr$, Mo, W and $L= R_2P(S)P(S)R_2$ and $R= Et$, n-Pr, n-Bu have been already send at Choksi Labs. Ltd., Panchkula (HR) for their further studies.

**Future Scope of the proposed Work**

As we know that there is no end of any success and thrust for better understanding of each nook and corner. Efforts for further investigations must not be quenched our present studies proposed in this synopsis still chemical
chemotherapeutical, biochemical and analytical investigations and in order to get a deep insight for structural and stereo-chemical behaviour of metal ligand bonding. Pharmacological studies of various prepared complexes for study which has been undertaken thought to be strong coordination sites, thus detailed evaluation of anti-viral, anti-leukemic activity and anti-bacterialial property of proposed ligands along with their isolated G-6 metal mixed carbonyl compounds may provide a new era for pharmacological investigation. Further work might be done in getting the activities of these ligands against different human diseases like small pox, blood disorder, tumor, influenza and ailments caused by protozoa, cardiovascular, antialergic, antineoplastic, anticancerous etc.

**Analytical and Industrial investigations:**

Somewhat much deeper investigation of undertaken ligands along with their G-6 metal mixed carbonyl complexes may be carried out in conversion and solar energy, different analytical areas e.g. polarographic, gravimetric, spectrophotometric studies, pesticidal characteristic having agricultural utility, antioxidant activity etc.

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