Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms
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Lecture – 40
Classification of Ligands – Halogens

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. We are almost completing the classification of ligands. Now we are in the last series of ligand system, that is called halogens, group 17 elements. Of course, if you want to know more about the properties of halogens, always you can revisit my course on main group chemistry and look into the details about halogens.

And also, when I was discussing about oxygen donor atoms, I did not give more emphasis for sulfur, selenium or tellurium and they have some chemistry very similar to oxygen, but however, again visit chalcogen series or group 16 elements in my previous course on main group elements and then try to familiarize yourself about the donor and acceptor properties of chalcogens. With this, let me talk about the halogens.

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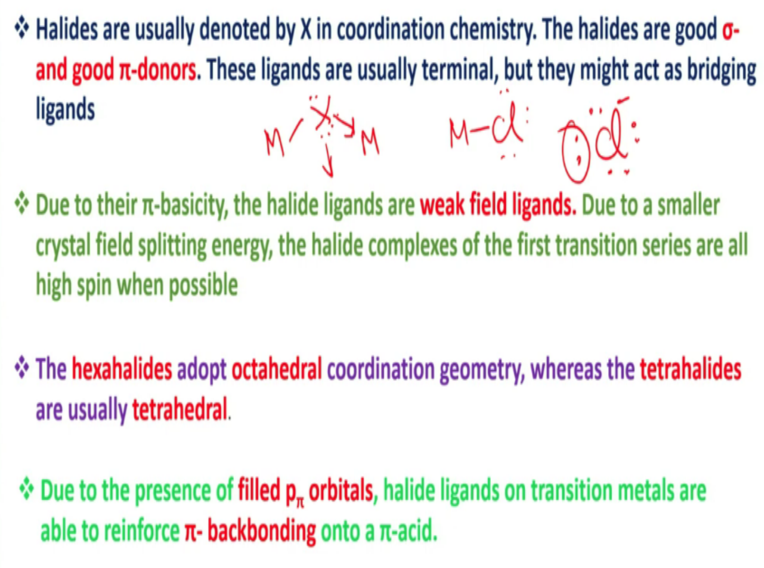

- Halides are usually denoted by X in coordination chemistry. The halides are good σ- and good π-donors. These ligands are usually terminal, but they might act as bridging ligands
- Due to their π-basicity, the halide ligands are weak field ligands. Due to a smaller crystal field splitting energy, the halide complexes of the first transition series are all high spin when possible
- The hexahalides adopt octahedral coordination geometry, whereas the tetrahalides are usually tetrahedral.
- Due to the presence of filled p_π orbitals, halide ligands on transition metals are able to reinforce π- backbonding onto a π-acid.

In my previous lecture, I just initiated discussion on halogens. I did mention about the nature of donor properties. It can establish, first as an anion, a covalent bond and then due to the presence of these pairs of electrons, it can establish another sigma bond and two more pi bonds. For example, I have shown here let us say this pair goes to establish a covalent bond and now among these three pairs one can form a sigma bond and other two can form pi bonds.

Due to the pi acidity and having low energy filled sigma orbitals and low energy filled pi orbitals, it can show up to 4 coordination number, that means it can act as an 8 electron donor or 4 pairs of electrons. We have examples in our own research, I shall show you all those things as we progress with this lecture. And of course, one can generate a series of homoleptic halogen series.

And when you consider coordination number 6 and having 6 hydrogen atoms or halides, they adopt preferably octahedral geometry and when we have 4, early metals prefer tetrahedral geometry, whereas late metals like palladium, platinum, they prefer square planar geometries.

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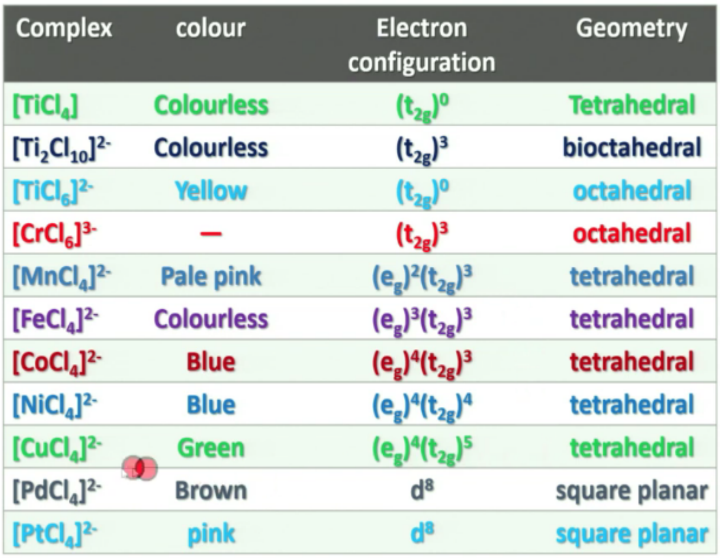

Complex	colour	Electron configuration	Geometry
$[TiCl_4]$	Colourless	$(t_{2g})^0$	Tetrahedral
$[Ti_2Cl_{10}]^{2-}$	Colourless	$(t_{2g})^3$	bioctahedral
$[TiCl_6]^{2-}$	Yellow	$(t_{2g})^0$	octahedral
$[CrCl_6]^{3-}$	—	$(t_{2g})^3$	octahedral
$[MnCl_4]^{2-}$	Pale pink	$(e_g)^2(t_{2g})^3$	tetrahedral
$[FeCl_4]^{2-}$	Colourless	$(e_g)^3(t_{2g})^3$	tetrahedral
$[CoCl_4]^{2-}$	Blue	$(e_g)^4(t_{2g})^3$	tetrahedral
$[NiCl_4]^{2-}$	Blue	$(e_g)^4(t_{2g})^4$	tetrahedral
$[CuCl_4]^{2-}$	Green	$(e_g)^4(t_{2g})^5$	tetrahedral
$[PdCl_4]^{2-}$	Brown	d^8	square planar
$[PtCl_4]^{2-}$	pink	d^8	square planar

And I have shown some homoleptic halide complexes here. And if you just look into titanium tetrachloride, colourless. Once when we say colourless, you should be able to correlate that one with the spectroscopic properties here. Of course, here, d-d transition is not possible because d^0 as a result it is colourless, of course 4 are there, it is tetrahedral. And then when you go to $[Ti_2Cl_{10}]^{2-}$, dianionic. It is also colourless, and it has 3 electrons, $[CrCl_6]^{3-}$, and this is octahedral. So then if you go for hexachlorotitanate, this is yellow in colour.

Again, it is t_{2g}^0, but here the yellow colour comes because of some charge transfer transition occurs. This is where the back bonding can be seen here. And in this case, it is octahedral hexachlorochromate, and we have this one with manganese, pale pink. Pale pink because here it splits into e and t_2 because it is tetrahedral. So, here, what happens we have 3 electrons in t and 2 electrons in e.

So, all are half-filled, spin forbidden, as a result it is pale pink. Of course, you will understand more when I go to spectroscopic properties of metal complexes, and $[FeCl_4]^{2-}$ again tetrahedral, colourless. And tetrachlorocobaltate, you can see blue in colour, it is tetrahedral. Nickel tetrachloro compound is blue in colour, we have tetrahedral geometry. $[CuCl_4]^{2-}$ is green, again tetrahedral.

Tetrachloropalladate or tetrachloroplatinate, they are respectively, brown and pink in colour, of course d^8 electronic configuration and they adopt square planar geometries. And also you know after going through crystal field theory and ligand field theory, why these molecules adopt square planar geometries.

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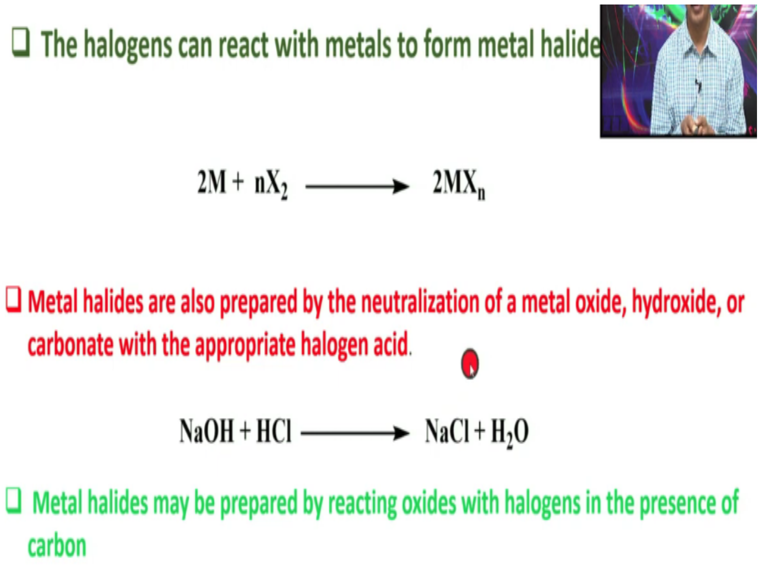

☐ The halogens can react with metals to form metal halide

$$2M + nX_2 \longrightarrow 2MX_n$$

☐ Metal halides are also prepared by the neutralization of a metal oxide, hydroxide, or carbonate with the appropriate halogen acid.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

☐ Metal halides may be prepared by reacting oxides with halogens in the presence of carbon

So, then what are the methods we have to prepare halogen complexes or halide complexes? So, you can directly interact; metals with halogens at higher temperature to generate homoleptic metal halides. And metal halides also can be prepared by the neutralization of a metal oxide or a metal hydroxide or carbonate with appropriate halogen acid, this is true only in case of alkali metals and alkaline earth metals, for example sodium chloride.

And of course, this reaction is not feasible when we talk about transition metals and metal halides may also be prepared by reacting metal oxides with halogen at high temperature using carbon.

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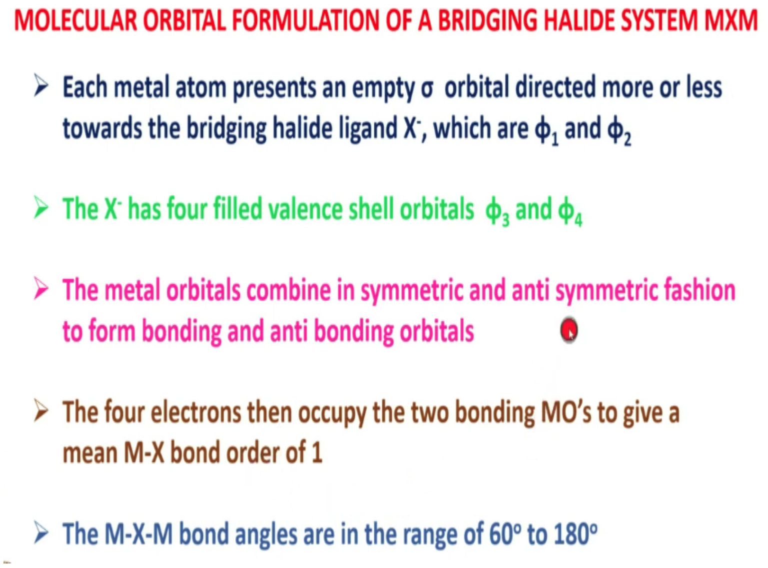

MOLECULAR ORBITAL FORMULATION OF A BRIDGING HALIDE SYSTEM MXM

- Each metal atom presents an empty σ orbital directed more or less towards the bridging halide ligand X^-, which are ϕ_1 and ϕ_2
- The X^- has four filled valence shell orbitals ϕ_3 and ϕ_4
- The metal orbitals combine in symmetric and anti symmetric fashion to form bonding and anti bonding orbitals
- The four electrons then occupy the two bonding MO's to give a mean M-X bond order of 1
- The M-X-M bond angles are in the range of 60° to 180°

And then when we look into the molecular orbital diagrams for explaining metal to halogen bond formation, whether the terminal bond or bridging bond, you can see here. Each metal atom presents an empty sigma orbital directed more or less towards the bridging halide ligand X^- generally denoted, the wave functions or phi1 and phi2. And halides have four filled valence shell orbitals. So, the metal orbitals combine in symmetric and antisymmetric fashion to form both bonding and antibonding orbitals.

And these four electrons then occupy two bonding metal orbitals to form one covalent bond and one coordinate board that results in a halogen bridging two metal centres and of course the angle can vary, it can be anywhere between 60 to 180° depending upon type of halogen under consideration and also to an extent what kind of metal we are considering. Here charge to size ratio or charge, everything matters, let me elaborate after a couple of slides.

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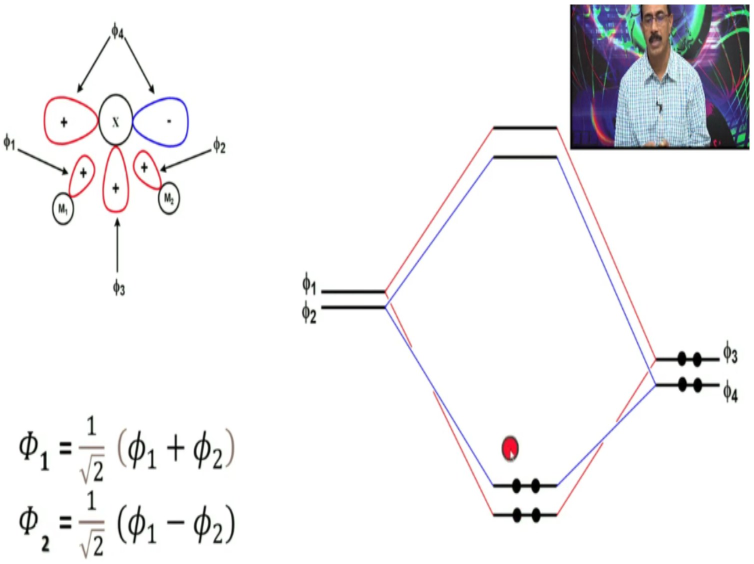

$$\Phi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$
$$\Phi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

So, here one can write a typical MO diagram to show the bridging nature of halogen, where it bridges two metals with one covalent bond and with one coordinate bond, both are sigma in nature.

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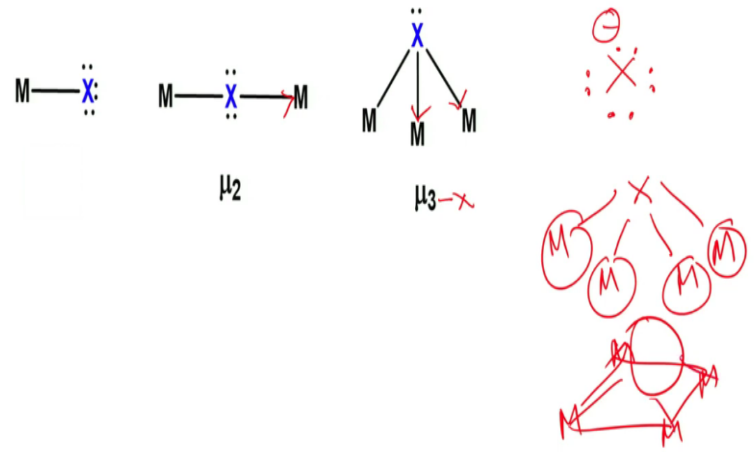
Binding Modes Of Halide Ligand



Let us look into the binding modes of halides. The simplest one is simple terminal, η^1 is more appropriate or κ^1. And now μ^2 means it is bridging. So, of course when it is bridging, this only symbolizes that the ligand is bridging, but it does not say in what way it is bridging, whether linear bridging is there are bent bridging is there or what is the angle, that information does not come, that information can only come from x-ray structure analysis.

And of course, when halogen bridges three metal centres we denote with μ^3-X, something like that, we can write and then of course if you take a typical X^-, octet is satisfied, you can see here also, one is gone and then here two are still there, one may be something like this. And now this is also something like this, usually represented as coordinate, but there is no need to write in terms of arrow, that is old fashion, nevertheless just stress upon the nature of bonds I have shown here.

Beside this one, what happens? A halide can also utilize all pair of electrons to bridge four metals. Very interesting, we have examples in our own laboratory, I will show you. Now the arrangement of this like square plane, it is something like this, we have metals here and the halogen sits here to establish bond utilizing all 4 valence electron pairs.

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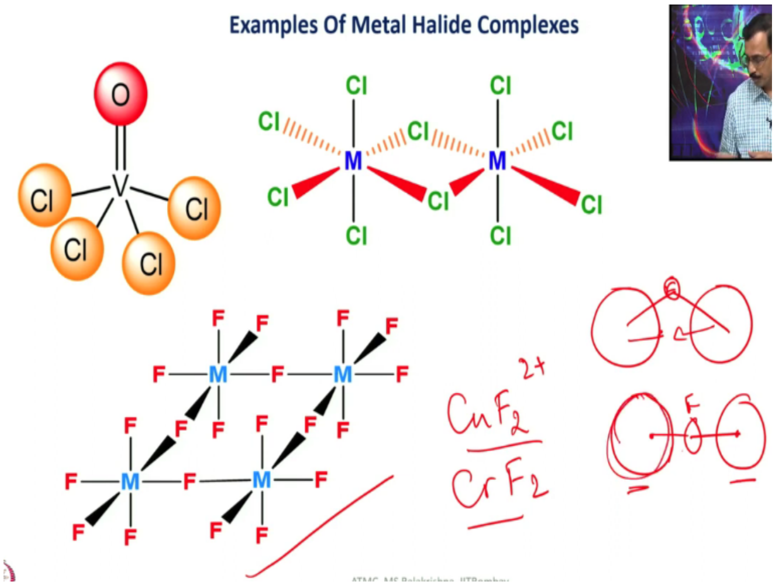

Examples Of Metal Halide Complexes

You can see some examples, I have shown here, metal halides. For example, oxyhalide is there VCl_4O, you can see here. And then we can see the bridging one here and many metals including even main group metals adopt this kind of geometry to have bent structure something like this, but when you go for fluorides, most of them have linear binding and hence they are tetrameric in nature.

Whereas in case of chlorides and to an extent with bromides and iodides, they are dimeric in nature, whereas with fluorides exclusively they prefer tetrameric geometry. The reason is very simple. When you look into the size, that is much smaller in size compared to chlorides, bromides and iodides. So in this case, for example if you bring two positively charged metals, something like this and if you have a bridging mode with fluoride, what would happen is something like this.

In order to stablish a bond since it is very small, they have to be brought very closer, when you bring them very closer it is almost like bringing two positively charged species very close to each other and they will repel, as a result what happens this is destabilized. The best way to bind in case of fluorides is to have a linear geometry, so something like this so that these charges are kept at farther distance to minimize the interaction between these two.

With this reason, what happens always whether you take main group elements or alkali metal and alkaline earth metals or any transition metals, usually in most of the occasions, we come across linear binding of fluorides when they are bridging two metal centres. And then in that case what happens, with great difficulty you can have trimeric structure, there will be some ring strain, as a result they adopt tetrameric structure, something like this shown here.

And this is what happens in case of CuF_2 and also CrF_2. So when we talk about CuF_2 or CrF_2, we should not think that there are only two ligands and they are linear know, they have octahedral arrangement, that means in the lattice they will be having something like this, but at the end if you look into the composition each copper has or each chromium has two fluorine atoms, whereas when you look into the lattice, the arrangement is like this, all of them have octahedral geometry.

And of course, here in this case it is a d^9 system, you can see tetragonal elongation will be there. And as I mentioned here, this is the most preferred one and the angle can vary from 160 or 150 to 180 depending upon other metals and their size and also their charge.

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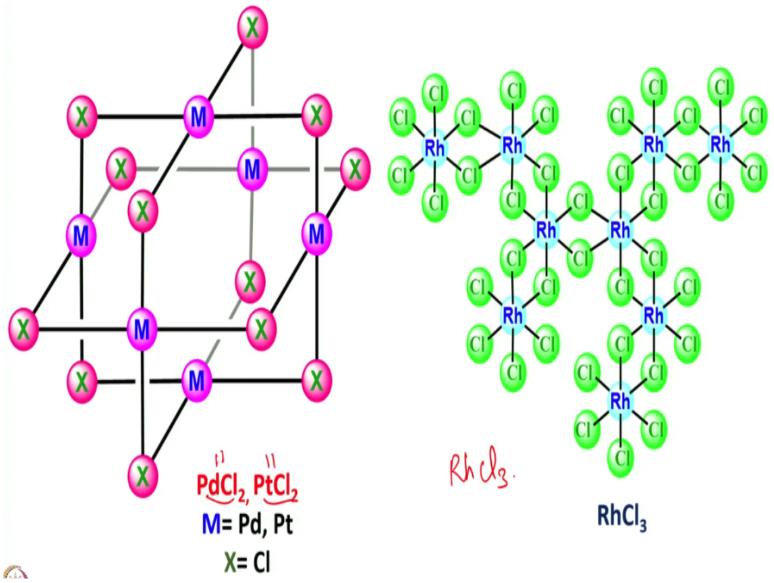

$PdCl_2$, $PtCl_2$

M= Pd, Pt

X= Cl

$RhCl_3$.

$RhCl_3$

This is the structure of palladium chloride and platinum chloride with chlorine as X. And in case of rhodium trichloride, this is the structure adapted by rhodium. You can see rhodium is octahedral, is surrounded by 6 chlorine atoms. Of course, composition does not change that is the reason whenever you write, always we write $RhCl_3$, same thing is true in case of palladium and platinum also, the ratio metal to halogen remains 1 is to 2 so that +2 can be explained oxidation state.

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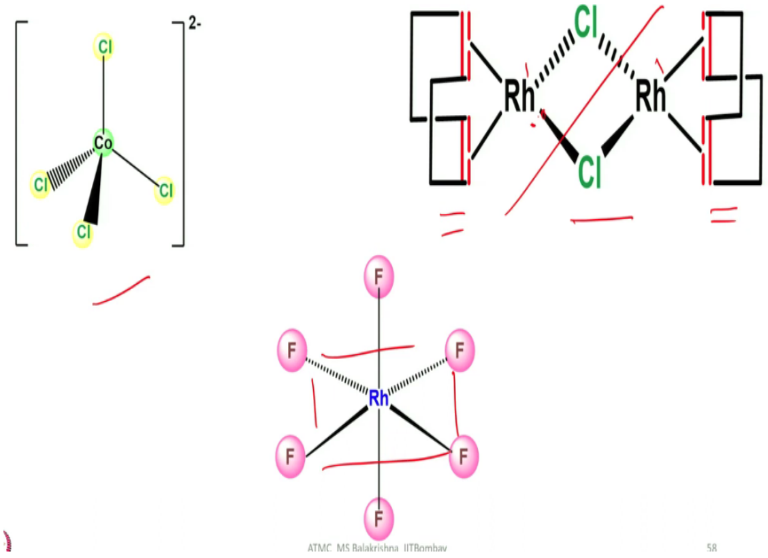

So, this is tetrahedral, tetrachlorocobaltate and in this case we have rhodium is in +1 state and we have here cyclooctadiene. With olefins, whether you take norbornadiene and cyclooctadiene or two ethylene, this is the preferred geometry here. And of course one can break this one symmetrically and vacate this coordination site to add another stronger ligand since chloride or in general halides are weak ligands, you can always anticipate the cleavage of this bond when we use strong field ligands to coordinate here to form two independent molecules. And of course, with 6 we have octahedral geometry here.

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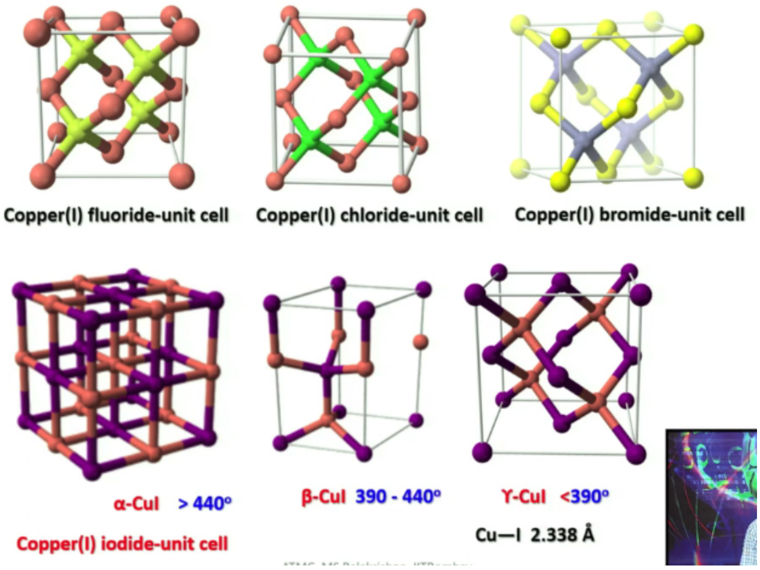

With copper with different halides, we come across a different type of arrangement in the unit cell. You can see here CuF, we have this kind of arrangement there. When you have chloride, this is slightly different, more or less similar, whereas in case of CuI we have this kind of arrangement. And for example, α-copper, this one is β-copper, this one in case of iodide and we also have γ-copper in this kind of. And of course, one can also see at what temperature one can convert alpha into beta or beta back into alpha something like this. And the average copper to iodide bond distance is about 2.338 Å.

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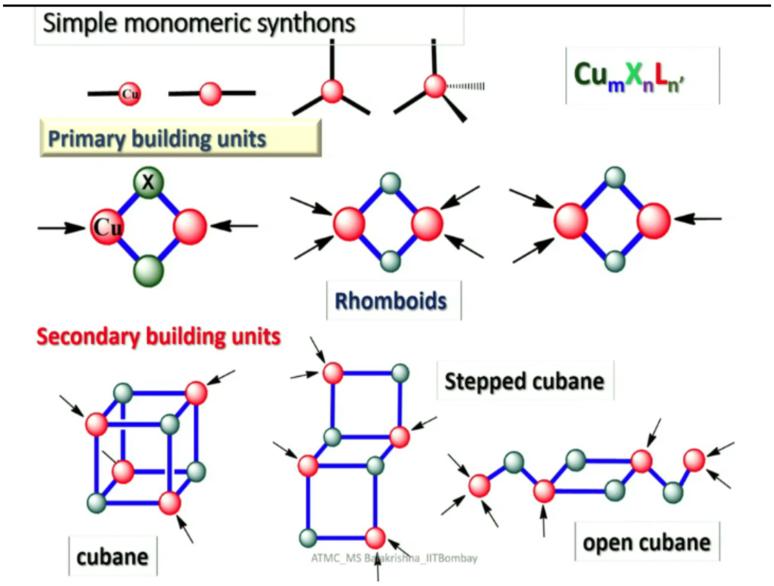

Another interesting thing is depending upon what kind of ligands we have, copper, especially cuprous halides have remarkable ability to undergo association to give a series of structures we will not come across, we cannot see with other metal halides that is the interesting aspect of cuprous halides here. So, for example: you can have simple CuX or you can have two Cl in a linear fashion or you can also have three in this fashion or you can have four and also these units can combine to form a dimeric species.

This is called rhombic unit where we have two bridging halogens. When you have bridging halogens, now other ligands can come here something like this or you can have unsymmetrical coordination, one side three, one side two coordination or one side four, one side three coordination and these units again combined to form a cubane type, very rare. And you can also see once cubane is formed, one of these faces can open up in this fashion.

One can also have open cubane, that I will show you here in this cartoon how these things arrange depending upon the ligand structure. You should remember all these arrangements. I am going to show you how they are dictated by the ligand structure, especially with bidentate ligands and in particular I am talking about bisphosphines here.

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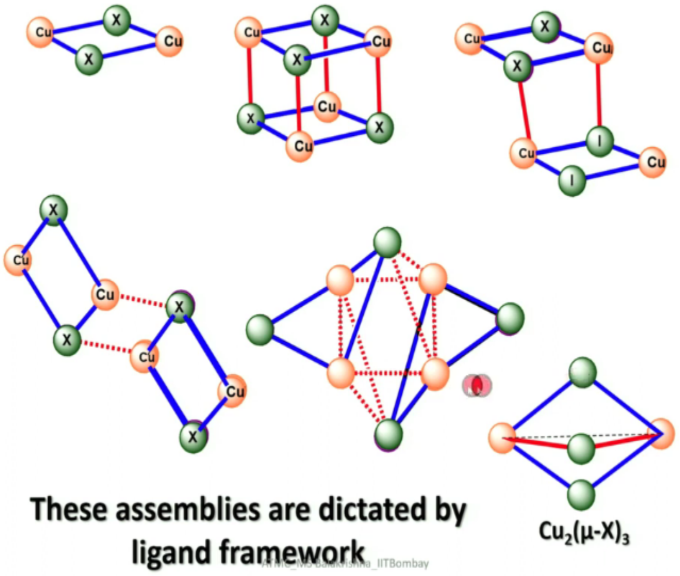

These assemblies are dictated by ligand framework

For example, you take this one, of course if you take a CuX moiety, two CuX moieties come in this kind of arrangement to establish bridging, this is how usually happens. For example, if there is a lack of another ligand and then vacant site is there, this is what exactly happens. This is how we come across many dimeric species. For example, you take $AlCl_3$ same thing happens and it is supposed to have 4 coordination, but we have 3, as a result, it undergoes dimerization.

Now, you take this one, and another one can come something like this. Now two such units can establish a new geometry called cubane, where alternate corners are occupied by copper and halogens, this is true in case of chloride, bromide and iodide as well. On the other hand, if you just slip one of the rhombic units and then you get some sort of stairstep or if you do something like this in a different fashion, you can get a ladder type.

Or if you arrange a little bit, pull them apart a little bit to have some distortion at copper and then bring another one to visualize central symmetry now you can see 4 copper atoms are in the plane, now we have two types of binding here. This halogen is bridging all the four metals, that means all four pairs of electrons are utilized here and it is bridging here, simply two bridging.

This is a rare example which shows two bridging as well as four bridging. You can see here three bridging is there. So, these assemblies you should remember are dictated by the ligand framework depending upon what type of ligands you have, how much separation is there, how much bulkiness is there that would decide how this individual CuX series have to assemble in one of these arrangements.

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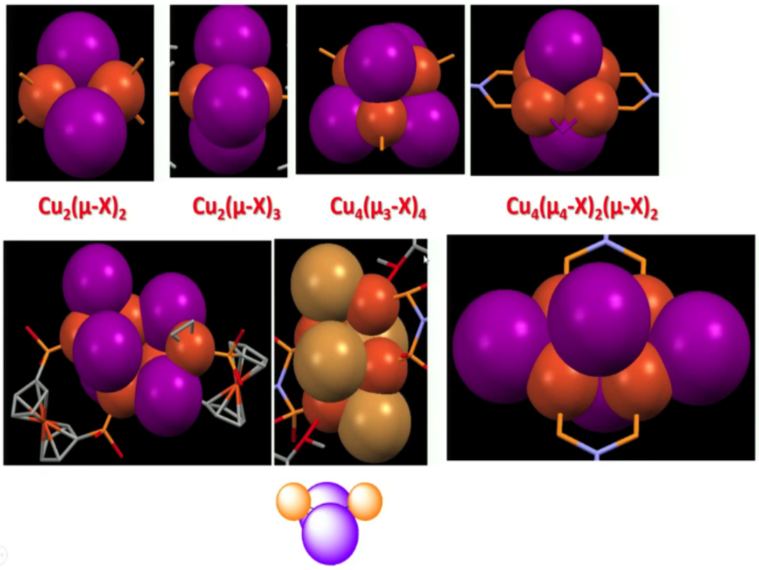

You can see here, these are all examples from my own laboratory with different ligands. Now, you can see here the dark purple ones are halogens here and reddish ones are copper. Copper(I) system you can see here in the space filling model, how this is bridging and, whereas here three such bridges are there, 2 copper units. Here we have 4 copper atoms, one is other side and three bridging, tribridging halogens are there.

And this is an example where you can see one halogen bridging all the 4 metals, that means it is establishing bonds; one covalent bond and three coordinate bonds with all the metals and these all four metals copper 1 ions are in the plane, this is again very interesting and they show very interesting for the physical properties, photoluminescence. And then you can see this one space filling model, I have just expanded, how this is bridging 2 metals and this is bridging 4 metals. So, this shows how much versatility is there in case of halogens as ligands.

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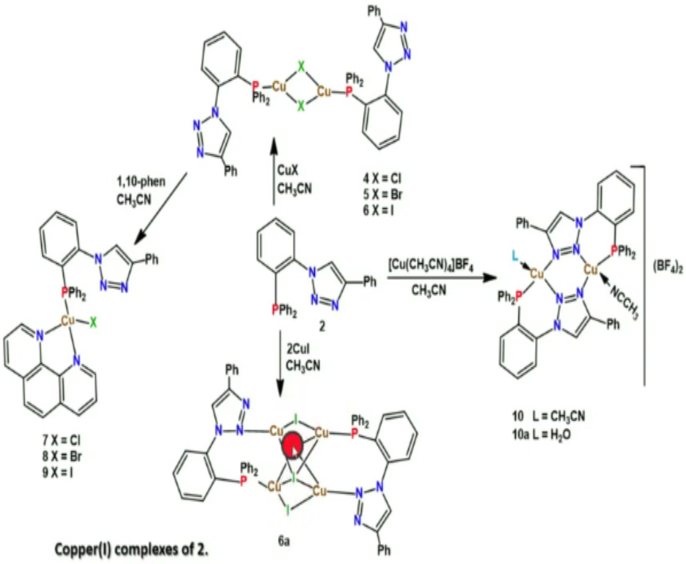

Copper(I) complexes of 2.

When we have something like this, you can see especially with copper(I) system the type of coordination we come across and how some of these moieties are arranged. I have shown here. You can see these 4 copper atoms are in the plane and this one is bridging above and this one is bridging below and these are in the sides acting as μ^2, whereas these ones are μ^4.

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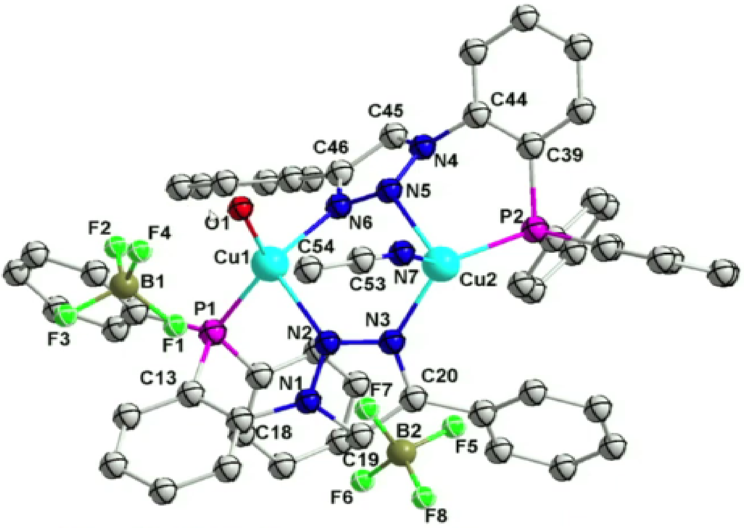

Figure 5. Molecular structure of 10a.

This is some unusual structure, to make you familiar with structures of molecules here, is a copper(I) system.

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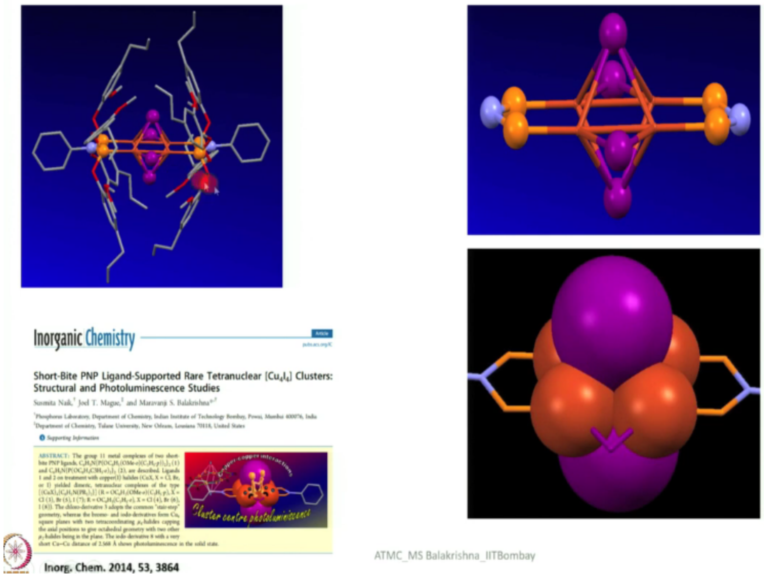

Inorganic Chemistry

Short-Bite PNP Ligand-Supported Rare Tetranuclear [Cu_4I_4] Clusters: Structural and Photoluminescence Studies

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Supporting Information

ABSTRACT: The group 11 metal complexes of two short-bite PNP ligands, $C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2$ (1) and $C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2$ (2), are described. Ligands 1 and 2 on treatment with copper(I) halides (CuX, X = Cl, Br, or I) yielded dimeric, tetranuclear complexes of the type $[(CuX)_2\{C_6H_5N(PR_2)_2\}]_2$ (R = $OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p)$, X = Cl (3), Br (5), I (7); R = $OC_6H_4(C_3H_5\text{-}o)$, X = Cl (4), Br (6), I (8)). The chloro-derivative 3 adopts the common "stair-step" geometry, whereas the bromo- and iodo-derivatives form Cu_4 square planes with two tetracoordinating μ_4-halides capping the axial positions to give octahedral geometry with two other μ_2-halides being in the plane. The iodo derivative 8 with a very short Cu–Cu distance of 2.568 Å shows photoluminescence in the solid state.

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You can see the entire two ligands, bidentate ligands, bisphosphines are there binding in this fashion as bridged bidentate ligands and then we have one below four bridging, and on the sides, one in front, one backside acting as μ^2 halides. This is true in case of how both bromides and iodides and also chlorides.

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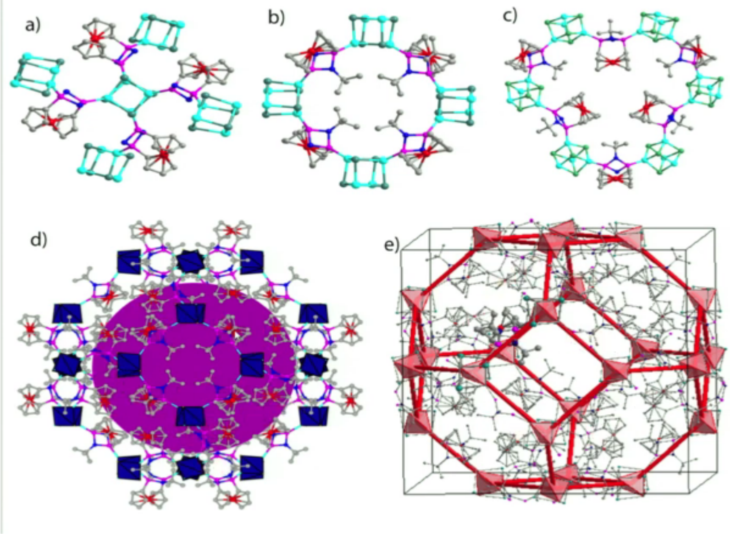

Not serendipitous molecules or serendipitous approach was followed

And also very interesting compounds were made having sodalite topology, you can see here. And this one as shown is like Cu_4X_4 moiety, where 4 copper atoms are there in the alternate corners and then we have 4 halogens on other corners and then this is a bidentate ligand, you can see, you can count how many, so each one is 4 copper atoms are there and 4 halides are there and you can see how many are there in monomeric unit. It has this kind of space inside.

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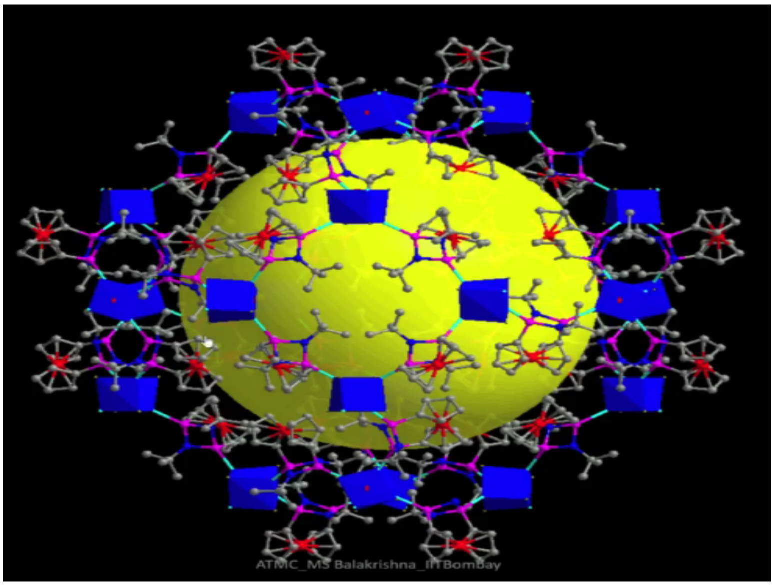

And this is how it looks like, that means very interesting compounds can be made.

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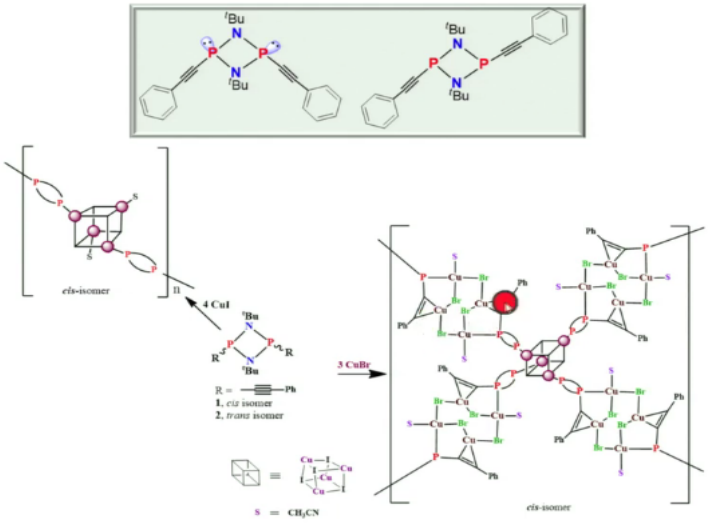
Alkyne derivatives of cyclodiphosphazane



Just to make you familiar with the versatile chemistry, one can think of with cuprous halides with bidentate ligands of different types, I am showing these things here. You can see here how they interact. So cubane is formed and they act as monodentate ligand each towards one and that means, essentially monodentate with respect to one unit, but they are bridging two such units in this one and this propagates to form something like this. One cubane is there and also one open cubane is there here.

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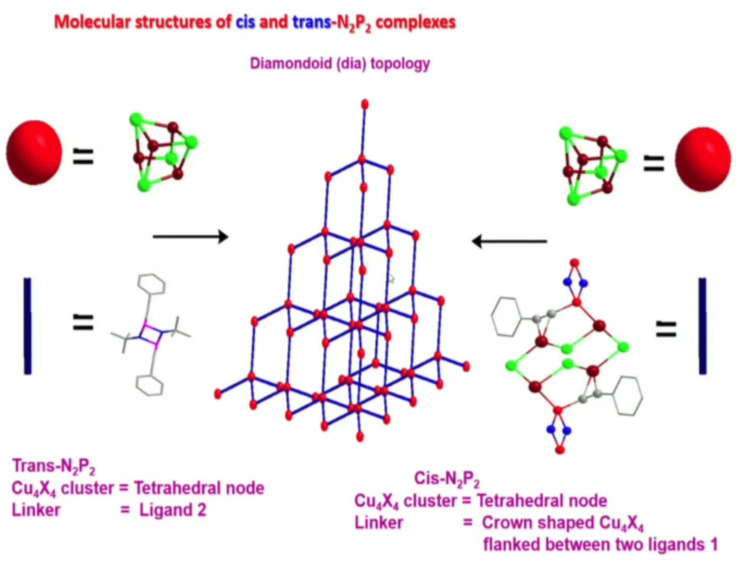

Molecular structures of cis and trans-N_2P_2 complexes

Diamondoid (dia) topology

Trans-N_2P_2
Cu_4X_4 cluster = Tetrahedral node
Linker = Ligand 2

Cis-N_2P_2
Cu_4X_4 cluster = Tetrahedral node
Linker = Crown shaped Cu_4X_4 flanked between two ligands 1

This is called diamondoid structure.

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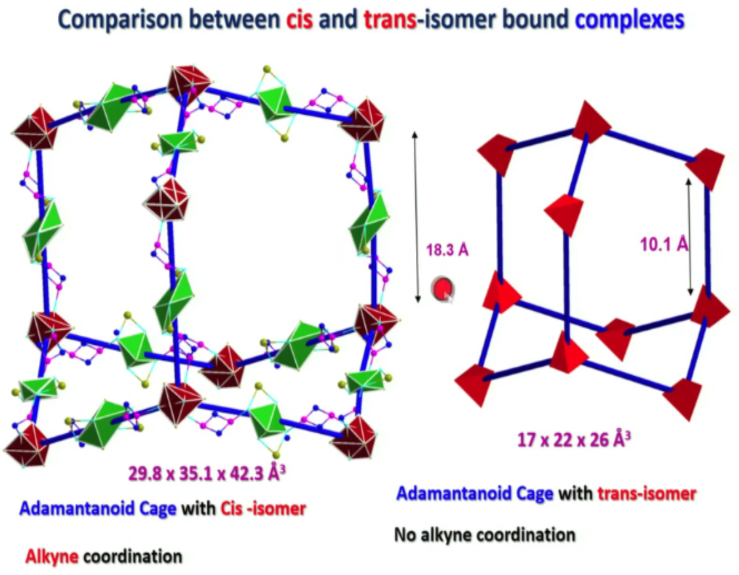

Comparison between cis and trans-isomer bound complexes

29.8 x 35.1 x 42.3 Å^3

Adamantanoid Cage with Cis -isomer

Alkyne coordination

17 x 22 x 26 Å^3

Adamantanoid Cage with trans-isomer

No alkyne coordination

In the diamondoid structure you can see, we have two types here. This is an extended diamondoid and this is another one all are diamondoid here, here is extended because we have cubane and open cubane is also there. So, all these compounds also behave very similar to zeolite molecules in terms of gas absorption, reversible absorption properties.

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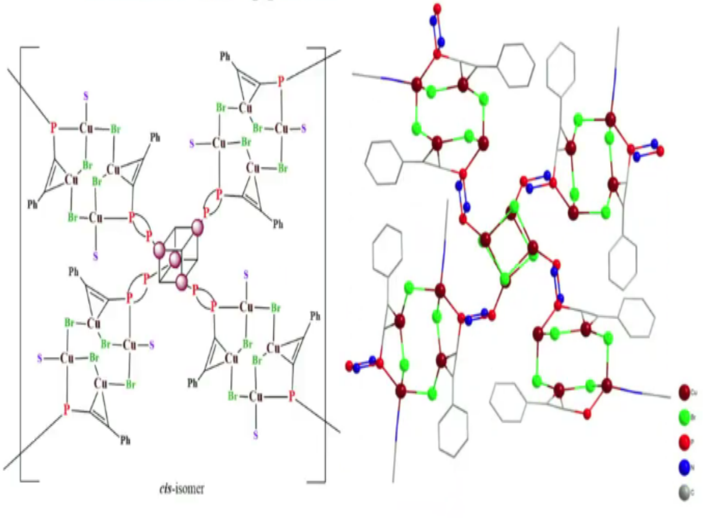
Repeating unit in *cis* –N_2P_2 complex



Just I am showing you all these things to show versatility.

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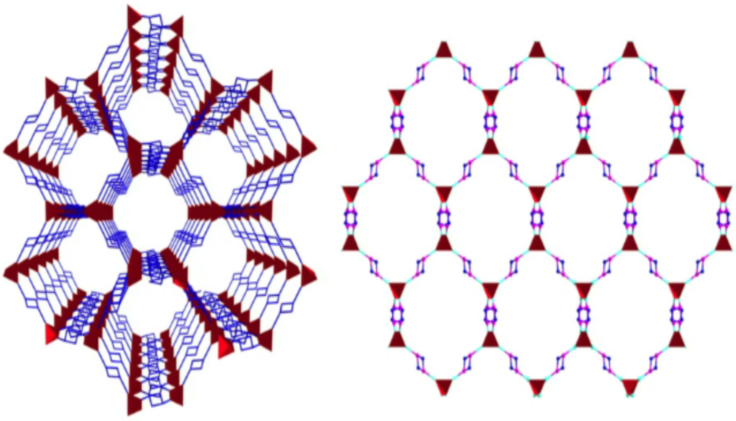
2D and 3D- view of cis-isomer complex



3D view of basic core of framework
Substituents have been omitted for clarity

2D sheet view

This is how the 3-dimensional view looks like. This is a 3-dimensional coordination polymer. We have some of these cavities, you recall your visualization of zeolites, they look very similar, with cavities, very interesting chemistry.

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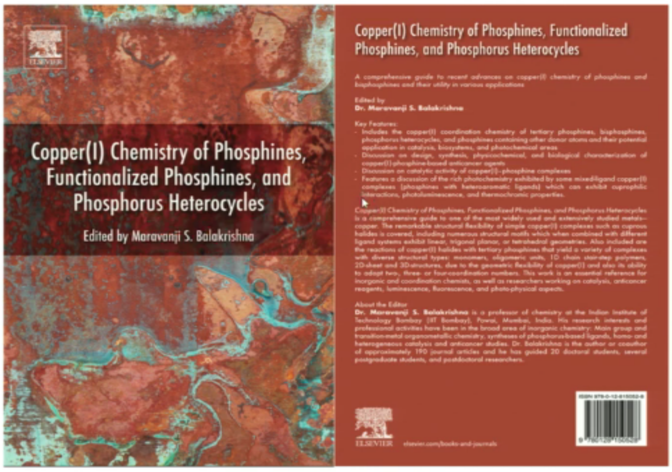
Copper(I) complexes



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Copper(I) Chemistry of Phosphines, Functionalized Phosphines, and Phosphorus Heterocycles

Edited by Maravanji S. Balakrishna

Copper(I) Chemistry of Phosphines, Functionalized Phosphines, and Phosphorus Heterocycles

A comprehensive guide to recent advances on copper(I) chemistry of phosphines and bisphosphines and their utility in various applications

Edited by
Dr. Maravanji S. Balakrishna

Key Features:
- Includes the copper(I) coordination chemistry of tertiary phosphines, bisphosphines, phosphorus heterocycles, and phosphines containing other donor atoms and their potential application in catalysis, biosystems, and photochemical areas
- Discussion on design, synthesis, physicochemical, and biological characterization of copper(I)-phosphine-based anticancer agents
- Discussion on catalytic activity of copper(I)–phosphine complexes
- Features a discussion of the rich photochemistry exhibited by some mixed-ligand copper(I) complexes (phosphines with heteroaromatic ligands) which can exhibit cuprophilic interactions, photoluminescence, and thermochromic properties.

Copper(I) Chemistry of Phosphines, Functionalized Phosphines, and Phosphorus Heterocycles is a comprehensive guide to one of the most widely used and extensively studied metals—copper. The remarkable structural flexibility of simple copper(I) complexes such as cuprous halides is covered, including numerous structural motifs which when combined with different ligand systems exhibit linear, trigonal planar, or tetrahedral geometries. Also included are the reactions of copper(I) halides with tertiary phosphines that yield a variety of complexes with diverse structural types: monomers, oligomeric units, 1D chain stair-step polymers, 2D-sheet and 3D-structures, due to the geometric flexibility of copper(I) and also its ability to adopt two-, three- or four-coordination numbers. This work is an essential reference for inorganic and coordination chemists, as well as researchers working on catalysis, anticancer reagents, luminescence, fluorescence, and photo-physical aspects.

About the Editor
Dr. Maravanji S. Balakrishna is a professor of chemistry at the Indian Institute of Technology Bombay (IIT Bombay), Powai, Mumbai, India. His research interests and professional activities have been in the broad area of inorganic chemistry: Main group and transition-metal organometallic chemistry, syntheses of phosphorus-based ligands, homo- and heterogeneous catalysis and anticancer studies. Dr. Balakrishna is the author or coauthor of approximately 190 journal articles and he has guided 20 doctoral students, several postgraduate students, and postdoctoral researchers.

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And of course, I edited a book on copper 1; complexes of different phosphines in 2019. If you are interested, you can just look into the book. With this, I complete discussion on classification of ligands. So, we learned starting from hydrogen and then we moved on to carbon donor atoms. Under carbon donor atoms, we came across many interesting ligand systems and also we look into the reactivity that can be performed on coordinated ligands and eventually that leads to some organic products coming out, all those things we saw.

In case of nitrogen also how a coordinated nitrogen can be activated through different type of reactions, that means you can perform nucleophilic substitution reaction or electrophilic substitution reaction or in some cases you can also perform coupling reactions. All these things when we understand thoroughly and if you see we can regenerate these things and try to make it reversible and then the utility comes in organic transformations.

And of course, with phosphorus they are very versatile and also I showed you how they stand out among all sigma donor and pi acceptor ligands. And especially how a bidentate ligand is preferred in catalytic reaction compared to monodentate ligands and how a bulky ligand can dictate reaction and how it can stabilize coordinatively unsaturated and electronically rich metals and then it can allow dissociation of ligands for preparing that complex for oxidative addition, all those things interesting aspects we discussed.

And wherever appropriate I also brought molecular orbital diagrams to show the binding properties and binding modes. In my next lecture, I shall begin the discussion on two important reactions when it comes to the utility of organometallic compounds and coordination compounds in homogeneous catalysis that is oxidative addition reaction and reductive elimination reactions. So, let us discuss those things in my next lecture. Until then have a good time reading chemistry.