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Pyridine: A Useful Ligand in Transition Metal Complexes

Satyanarayan Pal

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Abstract

Pyridine (C_5H_5N) is being the simplest six-membered heterocycles, closely resembles its structure to benzene. The "N" in benzene ring has its high electronegativity influence on resonance environment and produces markedly different chemistry from its carbon analog. The presence of nitrogen and its lone pair in an aromatic environment makes pyridine a unique substance in chemistry. The sp^2 lone pair orbital of "N," directed outward the ring skeleton, is well directed to have overlap with vacant metal orbital in producing an σ bonding interaction. This causes pyridine to be a ligand and has been utilized with all transition metals in producing the array of metal complexes. A rich literature of metal complexes is now available with pyridine and its derivatives. Innumerable complexes have been synthesized with academic as well as industrial importance. To shed a light on ligating capability of pyridine, transition metal complexes with pyridine, and its derivative is presented in this chapter.

Keywords: pyridine, ligand, synthesis, metal complex

1. Introduction

Pyridine is one of the simplest heterocycle known since its discovery in 1849 by Scottish chemist Thomas Anderson. It closely resembles with benzene structure, where a benzene methine (=CH-) group is occupied by "N" to form a six membered aromatic heterocycle of formula C_5H_5N. It is a room temperature colorless, water-soluble liquid with the distinctive pungent smell. The presence of electronegative "N" in ring structure is the sole cause of new properties induced in pyridine differentiating it markedly from benzene. The "N" presence in ring prevents the electron density be distributed evenly over the ring owing to its negative

inductive effect, which also causes the weaker resonance stabilization (117 kJmol^{-1}) than benzene (150 kJmol^{-1}) [1]. This is evident from the shorter C-N bond distance (137 pm) compare to 139 pm of the C-C bond. The other bond lengths satisfy typical aromatic nature of the pyridine ring. Similar to benzene all the pyridine ring atoms are sp^2 hybridized and involve in the π electron resonance. The sp^2 "N" involvements in resonance come through its unhybridized p-orbital rather than involving its lone pair. The lone pair thus in sp^2 orbital remain directed outward of the ring in the same plane without contributing to the aromatic behavior of pyridine but greatly influence the chemical environment of the ring. The available "free" lone pair thus could be utilized by "N" in several ways suiting for chemical reactions either on pyridine ring or as Lewis base to form coordinate bond with Lewis acids (**Figure 1**). It is a weak base reacts with acids to get protonated to pyridinium salt with pK$_a$ of conjugate acid (pyridinium cation) is 5.25. For an illustrative example the pyridine reacts with p-toluenesulfonic acid and gets protonated to pyridinium p-sulfonate salt. The protonated pyridine thus produced is isostructural and isoelectronic with benzene.

The pyridine owing to its Lewis basic character rooted in its nitrogen lone pair qualifies as the ligand for transition metals and able to form metal complexes across the metals in the periodic table. It is usually a weak monodentate ligand having capability to bind metal in different proportions to produce the range of metal complexes. A rich literature of pyridine coordinated complexes of transition metals has grown over the years. Pyridine and its numerous derivatives have been under investigation of inorganic chemists in design and preparation of numerous metal complexes of their interest. The further design of pyridine ligand explored in polypyridine system fusing two or more pyridine moieties to result in chelating multidentate ligands. Such as bipyridine, a fused two pyridine rings system, is a worth mention in transition metal chemistry. The unique photochemistry and luminescent ruthenium bipyridine complexes are a glimpse of bipyridine metal chemistry. Phenanthroline, terpyridine, and other multidentate ligands have been in focus in the transition metal chemistry since long. The discussion of bipyridine and polypyridine complexes is beyond the scope of this discussion. In this chapter, we will have a look of ligating capability of basic pyridine unit to transition metal ions.
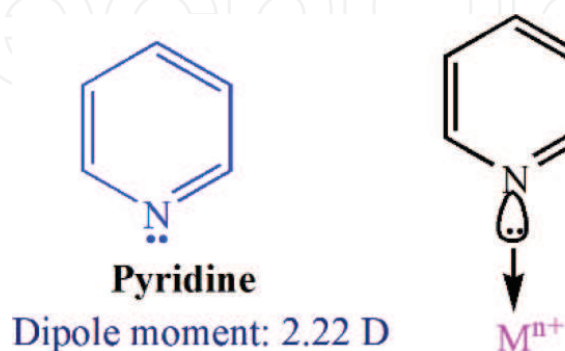
Figure 1. Structure of pyridine and its ligation to metal.

2. Pyridine and its metal complexes

2.1. Ligating power of pyridine

The spectrochemical series of ligands in crystal field theory (CFT), portray ligand arrangement pertaining to their metal d-orbital splitting capability, depicts pyridine as moderately strong ligand [2]. This interprets to strong electrostatic interactions of pyridine lone pair to metal d- orbitals. Despite being neutral, pyridine causes moderately large d-orbital splitting implying to strong bonding interaction to metal centers. Beside the CFT, the valence bond theory (VBT), considers metal pyridine bonding to overlap of sp^2 lone pair orbital of pyridine to hybridized metal orbitals. The extent of overlaps is happened to be highest in first transition metals in comparison to the second and third transition elements owing to the difference of shape, size, and energy of the combining orbitals. Apart from nitrogen lone pair orbitals, the ring π-electron is also capable of bonding interaction to metal ions. Moreover delocalized π* anti-bonding orbitals can act as acceptor of metal electron density (**Figure 2**). The pyridine can also indulge in hydrogen bonding and π-π stacking-like weak interactions. Thus pyridine is enriched with multiple orbitals for bonding interactions with metal ions.

2.2. Pyridine transition metal complexes

The pyridine transition metal complexes have a rich literature. Pyridine found to coordinate all the transition metals producing the variety of metal complexes in their different oxidation states. Efforts were made to incorporate the increasing number of pyridines in metal coordination sphere but exclusive pyridine complexes such as $[M(py)_4]^{n+}$ or $[M(py)_6]^{n+}$ are rare (where M = transition metal). The metal- pyridine chemistry incorporates pyridine and its derivatives with the capability of bidentate or tridentates ligands in the formation of metal complexes. The discussion here to be restricted to the domain of pyridine and it coordination to transition metals. A brief overview of pyridine transition metals complexes is presented here.
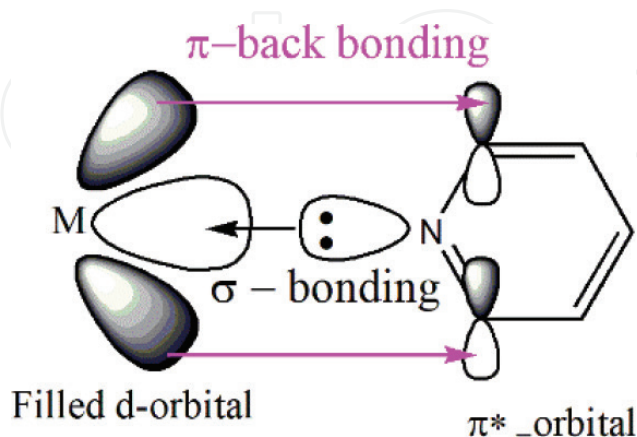

Figure 2. Bonding picture of pyridine.

Scandium and yttrium preferably bind to three pyridine units in a four-coordinated geometry. The coordination number might vary with characteristics of binding ligands. Five and six coordinated complexes are also synthesized in combination of pyridine and thiocyanate (SCN) ligands. The pyridine derivative capable of acting as a bidentate ligand, such as picolinic acid, prefers to produce higher coordination number complexes. A good number of complexes are known with variously substituted pyridines. These complexes are known in +1 and + 3 states of Sc and Y. The example of pyridine coordinated complexes include [Sc(py)$_3$Cl] [3, 4], [Y(py)$_3$Cl] [5, 6], [Sc(py)$_2$(NCS)$_3$] [7], and [Sc(py)$_3$(NCS)$_3$] [8]. These complexes could be derived directly from their metal salt and pyridine at room temperature.

Pyridine complexes of titanium are usually found in Ti(IV) state but could exist in other valence states (II-IV) also. Zirconium also produces pyridine complexes in Zr(III) and Zr(IV) states. Pyridine complexes of Titanium and Zirconium in +4 states are more common. Ti(II) and Ti(IV) pyridine complexes could be prepared along with halogen ligands with formula [Ti(py)$_2$(Cl)$_4$], [Ti(py)$_2$(Br)$_4$] [9]. The Ti(II) complexes use to be tetra-coordinated and those of Ti(III) and Ti(1 V) are hexa- and octa-coordinated [10]. Zr(IV) pyridine complexes have the similar behavior of titanium. A commonly known complex is [Zr(py)$_2$Cl$_4$] [11]. Three representative complexes are depicted in **Figure 3**.

The Ti(II), Ti(III), and Zr(III) pyridine complexes required preparation under inert and moisture free environment. The presence of aerial oxygen facilitates decomposition and formation of +4 states of metal centers. This is evident from preparative methods of Ti(IV) and Zr(IV) pyridine complexes under oxygen. In general, simple pyridine complexes are sensitive to moisture and air [12]. The electron donating substituents at two and four positions help "N" in forming the stronger coordinate bond and enhance the stability of resultant complexes. Beside the chelate pyridine ligands provide appreciably higher stability compare to the monodentate pyridine moiety.

The vanadium, niobium, and tantalum possess rich chemistry of pyridine complexes. The richness arises due to numerous valence states (0-V) of vanadium, which are found to exist with different pyridine complexes. Though pyridine complexes with V (0) and V (I) are very rare. Example of V (0) is [V$_2$ (2-Me-py)$_4$(CO)$_{12}$] [13]. A handful of complexes with other oxidation states are reported. V (II) pyridine complexes were prepared with a range of monodentate and bidentate anionic ligands. Along with basic pyridine moiety, various substituted derivatives were found in the coordination sphere of V (II) centers [14–16]. The simplest
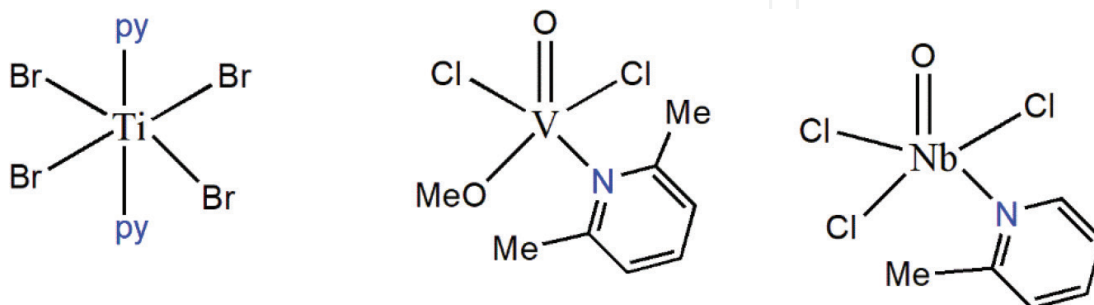

Figure 3. Representative pyridine complexes of Ti, V and Nb.

example of V (II)-pyridine combination includes $[V^{II}(py)_2(acac)_2]$. A similar combination of anionic monodentate and chelate ligands could produce V (III) pyridine complexes, such as $[V(py)(NCS)_3]$ [17]. The inclusion of oxo group helped in stabilizing V(IV) and V(V) states and a range of pyridine complexes were synthesized. A few illustrative examples are $[V^{IV}(O)(4\text{-}Et\text{-}py)_2(acac)_2]$ [14], $[V^{V}O(2,6\text{-}Me_2\text{-}py)(OMe)(Cl)_2]$ [18] (**Figure 3**) and so on. Niobium and Tantalum produce pyridine complexes at +4 and + 5 oxidation states. $[Nb(4\text{-}Me\text{-}Py)_2(Cl)_4]$ [19], $[Nb(py)(OMe)_5]$ [20], $[Nb(O)(2\text{-}Me\text{-}py)(Cl)_3]$ [21], and so on, are few niobium pyridine complexes. Similar combination of Ta complexes are known with halide ligands, for example, $[Ta(py)_2X_4]$ [22] (X = halide), $[Ta(py)(OMe)_5]$ [23] etc.

The complexes could be synthesized from halides salts of respective metals and pyridine in a neutral environment. The tetravalent and pentavalent complexes are harvested in a low-temperature environment to prevent decomposition through disproportionation. The higher valent pyridine complexes possess superior stability than their lower valent counterpart.

Chromium, molybdenum, and tungsten pyridine complexes could be obtained from their inorganic salts as well as carbonyl and nitrosyl complexes. Neutral environment remain a preferred choice to ensure the stability of synthesized complexes. The large range of oxidation states (0-VI) of these metals has produced innumerable pyridine complexes. The tendency of lower valent pyridine complexes, particularly in 0 and + 1 states, get oxidized to higher oxidation states made these complexes sensitive to air and moisture. The common coordination number remains six in Cr and Mo, but it could be in higher numbers in tungsten pyridine complexes.

Cr(0) and Cr(I) pyridine complexes are accompanied with carbonyl and nitrosyl ligands, such as $[Cr(py)(C_5H_5)(NO)(CO)]$ [24] (**Figure 4**). The higher valent pyridine complexes have anionic monodentate and bidentate ligands in Cr(III) and Cr(IV) complexes. The Cr(IV) and upper oxidation state mostly found with an oxo group. The representative chromium-pyridine complexes are $[Cr(py)(acac)_3]$ [25], $[Cr(O)(py)(Br)_3]$ [26], $[Cr(O)_3(py)]$ [27] and so on, reflects the above facts. The oxo group continues to stabilize higher valent molybdenum and tungsten pyridine complexes too. This is evident from the formula of $[Mo(py)(O)_3]$, $[Mo(NCS)_2(O)_2]$ [28], $[W(py)(O)_2(Cl)]$ [29], $[WO(py)(Cl)_4]$ [30] (**Figure 4**) and so on. The +6 state of tungsten-pyridine complexes could also be stabilized by monodentate anionic ligands as it found in $[W(py)F_6]$ [31], and $[WO(py)Cl_4]$ [30].
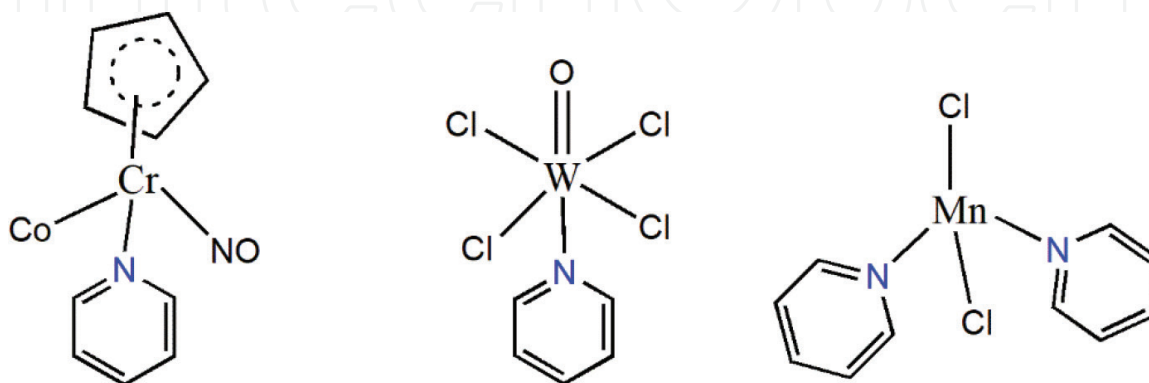

Figure 4. Representative pyridine complexes of Cr, W and Mn.

Manganese and rhenium forms complexes with pyridine in different oxidation states spreading over 0 to VII. The coordination number commonly varied from four to eight. However, the manganese forms pyridine complexes only in zero to quadrivalent oxidation states, whereas rhenium pyridine complexes exist in seven oxidation states. The lower valent pyridine complexes of these metals are composed of carbonyl and nitrosyl counterpart. The higher valent rhenium accommodates oxo ligands along with anionic monodentate and chelating ligands. The Mn(I) complexes quickly react with air and oxygen. Thus their preparation is carried out in a neutral atmosphere. The higher valent pyridine complexes are stable in normal condition and could be prepared in alcoholic or aqueous media. Manganese halides and manganese oxide are remaining preferred starting materials for synthesizing pyridine complexes. Complexes such as $[Mn(py)_2X_2]$, (X = halide) (**Figure 4**), $H[Mn(H)(py)(Cl)_3(OH)]$, and $[Mn(py)_2(thiourea)_4Cl_2]$ [32–34] were obtained from these starting materials. The rhenium-pyridine complex preparation has also origin at rhenium halides, such as ReI_4, $K_2[ReCl_6]$ are few to mention. The higher valent rhenium pyridine compound also derived from $K[ReO_4]$. The examples of rhenium complexes [35–38] are $[Re(4\text{-}Me\text{-}py)(Br)(CO)_4]$, $[Re(py)Cl_2(CO)_2(NO)]$, $[Re(py)(O)(Cl)_4]$ (**Figure 5**), $[Re(py)_2(OH)_2(Cl)_5]$ and so on. Technetium-pyridine complexes are rare [39, 40].

Fe(II) has produced quite a significant number of pyridine complexes with the comparison to other first transition metals. A range of pyridine derivatives were included in these Fe-pyridine complexe. The number of pyridine complexes of Fe(II) are quite high in compare to Fe(0), Fe(III), and Fe(IV). This is due to the higher stability of Fe(II) pyridine complexes than the relevant complexes of Fe(0), Fe(III), and Fe(IV). In case of iron, pyridine coordination to metals center achieved both in mixed ligand and fully pyridine coordinated environment, such as $[Fe(py)_6]^{2+}$ [41] (**Figure 5**). Fe(II), Fe(III), and Fe(IV) pyridine complexes are mostly octahedral. Though four and five coordinated complexes are also seldom found, the pyridine complexes were prepared by interaction of pyridine and an inorganic salt of iron. Few representative iron pyridine complexes [42, 43] of different oxidation states are $[Fe(CO)_4(py)]$, $Na_3[Fe(2\text{-}NH_2\text{-}py)(CN)_5]$, $[Fe(py)_4I_2]$ and so on.

In this group, the versatility of complex formation continues with ruthenium and osmium too. This is evident from numerous pyridine complexes reported with these metals. Ruthenium displays nine oxidation states (0-VIII). Among these +2 and +3 oxidations are most stable. The pyridine complexes of ruthenium contain +I, +II, +III, +IV, +VI, and + VIII states. Few complexes even
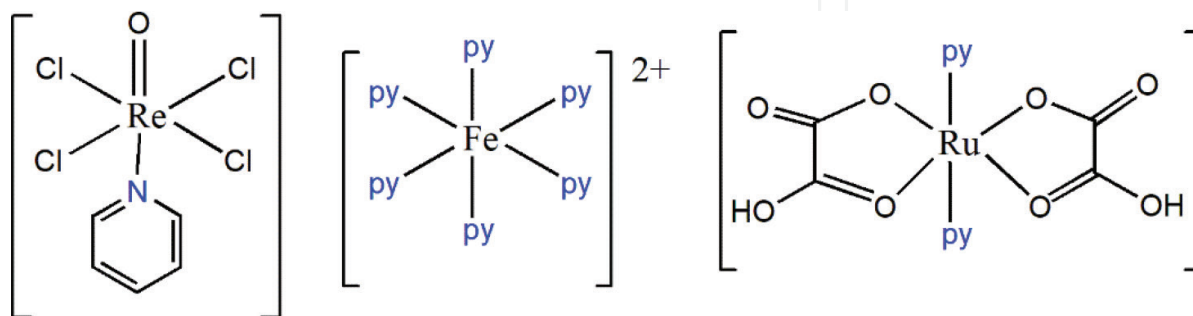

Figure 5. Representative pyridine complexes of Re, Fe and Ru.

reported with fractional oxidation number. Like ruthenium, osmium pyridine complexes found with II-IV, VI, and VIII oxidation states. The common coordination number in such complexes ranges from 4 to 6, though higher coordination numbers are claimed in higher oxidation states.

Ruthenium pyridine complex preparation involves high-temperature reflux of ruthenium salt with pyridine in an organic solvent preferably in the oxygen-free environment. $RuCl_3$, $[Ru(NH_3)_6]Cl_2$, "ruthenium red" $[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$ are the common choice for the synthesis of pyridine complexes. These resultant pyridine complexes are often labile and subject to the decomposition. Ru(III) pyridine complexes often show up disproportion to Ru(II) and Ru(IV) states and this decomposition route appears to be a synthetic procedure for new complex preparation. Few ruthenium complexes [44–47] with varied pyridine numbers are $K[Ru(py)(Cl)_4]$, $K[Ru(py)_2(ox)_2]$ (**Figure 5**), $[Ru(O)_4(py)_2]$, $[Ru(py)_6]$ $(BF_4)_2$ and so on. The coordination of six pyridine ligands to ruthenium, $[Ru(py)_6](BF_4)_2$, is a unique example of "pure" pyridine complex, which is infrequent in metal-pyridine chemistry.

The osmium pyridine complex preparations could be achieved by reaction of $K_2[OsCl_6]$ and pyridine. OsO_4 also proved to react with pyridine and produce higher valent pyridine complexes. In a reaction of $[Os_3(CO)_{12}]$ with pyridine in neat or with a pyridine saturated hydrocarbon solvent resulted series of complexes [48], such as $[HOs_3(py)(CO)_{10}]$, $[HOs_3(py)(CO)_9]$, $[H_2Os_3(py)_2(CO)_8]$, $[Os_2(py)_2(CO)_6]$, and so on, $K[OsCl_4(bpy)]$ gave rise to pyridine complex $[Os(py)Cl_3(bpy)]$ by treatment with aqueous pyridine in boiling condition or treatment in pyridine–glycerol mixture [49]. In Glycerol pyridine mixture $[OsCl_4(bpy)]$ complex reduced to produce $[Os(py)Cl_3(bpy)]$ (**Figure 6**) and $[Os(py)_3Cl_2(bpy)]ClO_4$. These complexes are fairly stable except the labile Os(II) complexes.

Cobalt pyridine complexes were isolated with Co(II) and Co(III) oxidation states. Only few Co(I) and Co(IV) complexes are reported. The Co(II) could accept one to six pyridine ligands in its coordination sphere and the resultant complexes are mostly six coordinated. One such complex contains six pyridine ligands (**Figure 6**) and formulated as $[Co(py)_6]I_2$ [50]. Most of the cobalt pyridine complexes are mixed-ligand molecule.
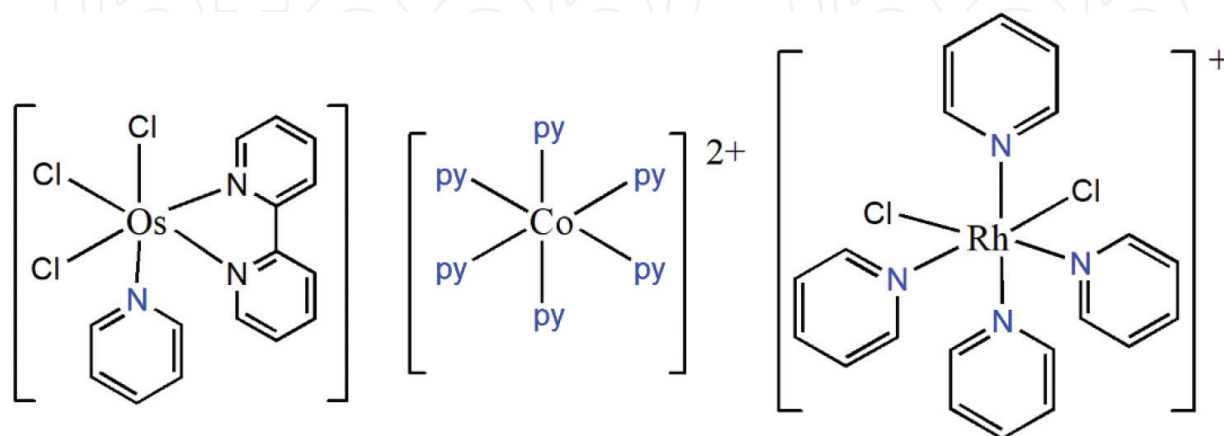

Figure 6. Representative pyridine complexes of Os, Co and Rh.

They could either prepared from alcoholic or aqueous solution with reaction of cobalt salt and appropriate quantity of pyridine. When cobalt iodide treated with excess of 3-ethyl pyridine a brown complex [Co(3-Et-py)$_4$Cl$_2$] resulted [51]. Several other substituted pyridine employed in a similar fashion resulting in numerous complexes. Cobalt(I) complexes usually resulted from reduction of Co(II)-pyridine complexes.

Rhodium also used its various oxidation states to have pyridine coordination. Pyridine complexes are known with +1 to +4 and +6 oxidation states with coordination numbers four to six. Rh(III) dominates the spectra of pyridine complexes with octahedral geometrical preference, whereas square planar geometry is common finding with Rh(I) complexes. RhCl$_3$ is the most common starting material for preparation of pyridine complexes. [RhL$_4$X$_2$]$^+$ (where L = 3 or 4 substituted pyridine, X = halide) type complexes were readily synthesized from rhodium halide and pyridine interaction in aqueous medium [52]. [Rh (PPh$_3$)$_2$(CO)(Cl)] is another starting material for preparation of Rh(I) pyridine complexes.

Iridium also displays eight different oxidation states (−1 to VI) and pyridine complexes are favorably formed with +3 state. Ir(I) complexes can have four and five coordination, whereas Ir(III) and Ir(IV) can extend their coordination number to six. The preparation of iridium pyridine complexes can be achieved from the array of starting materials. Ir$_2$(SO$_4$)$_3$, K$_3$IrX$_6$ (X = halide), K$_2$[Ir(H$_2$O)Cl$_5$] are few to mention. The number of pyridine moiety varies around iridium center and it could reach maximum six. Iridium(IV) pyridine complexes derived from Ir(III) counterpart by oxidation. Few illustrative examples of iridium pyridine complexes [53, 54] are K [Ir(py)$_2$Cl$_4$], [Ir(py)$_3$Cl$_3$] (**Figure 7**), [Ir(py)$_3$(H$_2$O)Cl$_2$] and so on.

The pyridine nickel complexes are mostly found in +2 oxidation states. The other oxidation states, that is, Ni(I), Ni(III), and Ni(IV) are less numerous in nickel-pyridine chemistry. Ni(II) complexes could be tetra, penta, and hexacoordinated. One such octahedral complex is [Ni(py)$_4$X$_2$] [55] (X = halide ion) (**Figure 7**). Ni(II) pyridine complexes offer easy preparation in the organic solvent by the combination of nickel salt and pyridine and are stable against aerial oxidation, but Ni(I) pyridine complexes are sensitive to air and moisture. Though nickel can be coordinated up to six pyridines the stability of these complexes are very low [56].
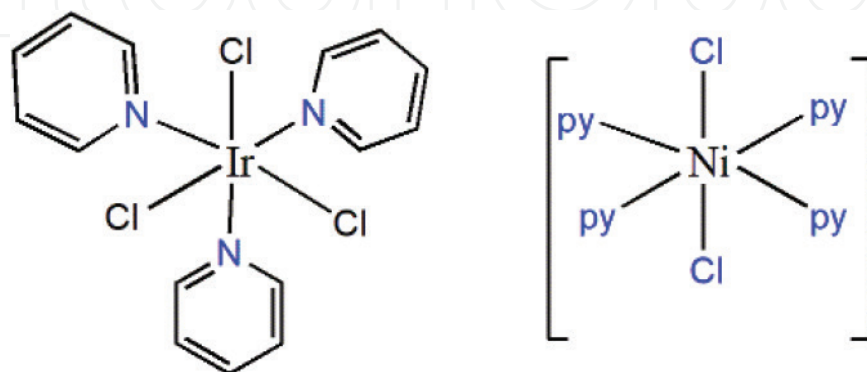

Figure 7. Representative pyridine complexes of Ir and Ni.

The palladium and platinum have many similarities in complex formation. The main oxidation states of these two metals are +II and + IV, yet pyridine complexes are known with Pd(0), Pt(0) Pd(I) and Pt(I) oxidation states. All other pyridine complexes are mostly square planar, though six coordinated complexes are common in +4 oxidation states. Majority of the complex contain one or two pyridine ligand in metal coordination sphere. Tetra pyridine complexes such as $[Pd(py)_4](PF_6)_2$, [57], $[Pt(py)_4Br_2]$ [58] were also synthesized. The examples of four coordinated complexes are $[Pd(py)_2Cl_2]$ [59] (**Figure 8**), $[Pd(py)Br_2\{NH(CH_2CH_2NH_2)_2\}]$ [60], $[Pt(py)(Me)_2(CH_3COO)]$ [61], $[Pt(py)_2X_2]$ [62] and so on, the Pd(IV) and Pt(IV) complexes [63–65] are $[Pd(py)_4Cl_2]^{2+}$, $[PdCl_4(py)_2]$, and $[Pt(py)_2Me_2Cl_2]$ (**Figure 8**).

The palladium-pyridine complexes were derived from $PdCl_2$, $K_2[PdCl_4]$, which reacts with pyridine in the organic solvent or with neat pyridine to provide Pd(II) complexes. A similar procedure was adopted to yield platinum complexes. $PtCl_2$, $K_2[PtCl_4]$, and Zeiss salt were employed in alcoholic, DMSO, and the aqueous medium to combine with pyridine. $[Pt(py)_2Cl_2]$ could be synthesized from $K_2[PtCl_4]$. Pt(IV) complexes are not derived directly from Pt(IV) starting complex such as $K_2[PtCl_6]$, whereas Pt(II) pyridine complexes are oxidized using appropriate oxidizing agents. Hydrogen peroxide could oxidize $[Pt(py)_2Cl_2]$ to $[Pt(py)_2(OH)_2Cl_2]$. The synthesis of Pd and Pt pyridine complexes are governed by trans-effect and the resultant complexes are aptly substituted product on a starting material by pyridine according to this effect.

Both copper and silver are capable to form complexes in three oxidation states (I–III), whereas gold only displays two oxidation states (I and III). The isolated pyridine complexes are either two, three, or four coordinated for +1 state such as $[Cu(py)(PPh_3)_2]$ [66]. But Cu(II), Au(III) complexes could extend their coordination number to six. Among this Cu(II) pyridine complexes are extensively studied. It can have the varied number of pyridine ligand in coordination sphere. Examples are $[Cu(py)_2(ox)]$ [67], $[Cu(py)_3(NCS)_2]$ [68], $[Cu(py)_4(H_2O)_2]^{2+}$ [69] (**Figure 8**) and so on. Complexes with six pyridine ligands, $[Cu(py)_6]Br_2$ [70] is also reported. It was prepared by blending $CuBr_2$ with pyridine in ethanol medium. The compound is stable but readily decompose in presence of moisture resulting $[Cu(py)_2Br_2].2H_2O$
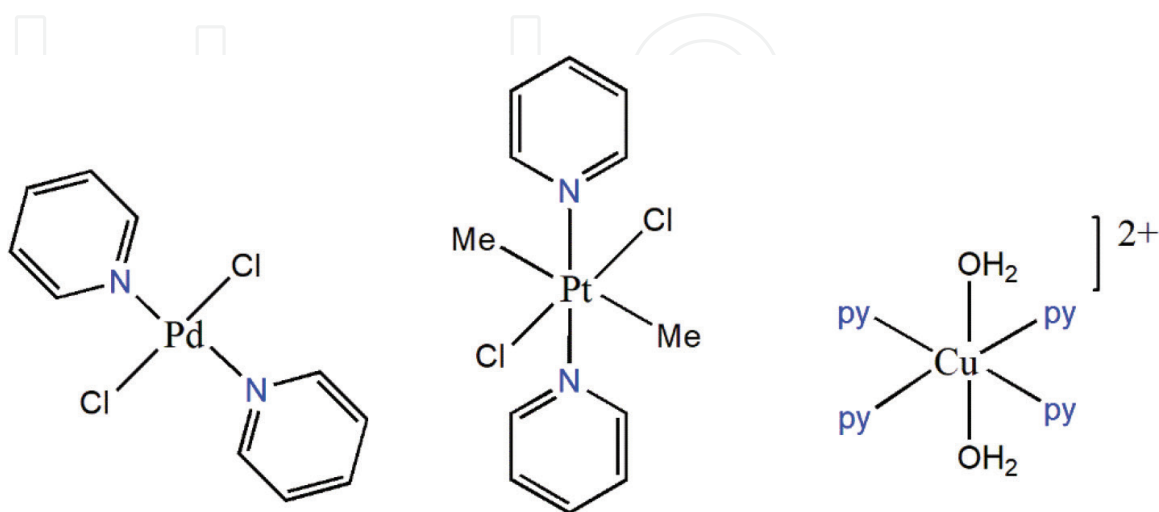

Figure 8. Representative pyridine complexes of Pd, Pt and Cu.

Ag(I) pyridine complexes are usually unstable and difficult to isolate. The coordination number, usually two or three, is another constraint to grow interesting chemistry with silver-pyridine complexes. Ag(I)-pyridine complexes preparation involve reaction of pyridine with Ag(I) salt in the solvent or in neat reactants. Often water remains a preferred solvent for such preparation. The examples include [Ag(py)(SCN)] [71], [Ag(py)(CN)] [72] (**Figure 9**), [Ag(py)$_4$]NO$_3$ [73], and so on. When the picolinic acid (picH) reacted with Ag(I) salt it resulted in a four-coordinated Ag(I) complex of formula [Ag(picH)(pic)] [74]. Ag(II)-pyridine complexes are usually derived from oxidation of Ag(I) counterpart using suitable oxidizing agents. Crystal structure of Ag(II)-bis(pyridine-2,3-dicarboxylate) shows a square planar geometry [75], where silver(II) is coordinated through pyridine nitrogens and two oxygen atoms of carboxylate groups at 2-position.

Compare to silver, gold has more numerous pyridine complexes. It's pyridine chemistry evolves with Au(I) and Au(III) states where pyridine and its various derivative were employed to derive desired complexes. For instance, Au(I) pyridine complexes could be achieved from the reaction of bis(acetonitrile) gold(I) perchlorate and 2-, 3- or 4-cyanopyridine in carbon tetrachloride. The corresponding cyanopyridine was used in the excess amount to produce [Au(n-CN-py)]ClO$_4$ (n = 2, 3, 4) [76]. Au (III) complexes could be prepared from Au(III) starting materials. The common starting materials used are AuCl$_3$ or HAuCl$_4$. [Me$_2$Au(py)X] (X = halide/pseudohalide) (**Figure 9**) type complexes were obtained by blending [Me$_2$AuCl]$_2$ and stoichiometric pyridine in cyclopentane at room temperature [77].

2.3. Application of metal-pyridine complexes

Transition metal pyridine complexes have proved their importance in various applications in different fields. Metal complexes with mixed ligand environment were studied and their applications are reported. Only a few representative complexes and their applications are mentioned here (**Figure 10**). Titanium pyridine complexes of the type [Ti(py)$_x$Cl$_y$] were explored as alkene and alkyne polymerization catalysts. These titanium complexes were used along with various aluminum cocatalyst such as RAlCl$_2$, R$_2$AlCl, and R$_3$Al (R = alkyl groups) as described in Ziegler-Natta catalytic process [78–80]. Pyridine complexes derived from VCl$_3$, VCl$_4$, and VOCl$_3$ act as olefin polymerization catalyst.
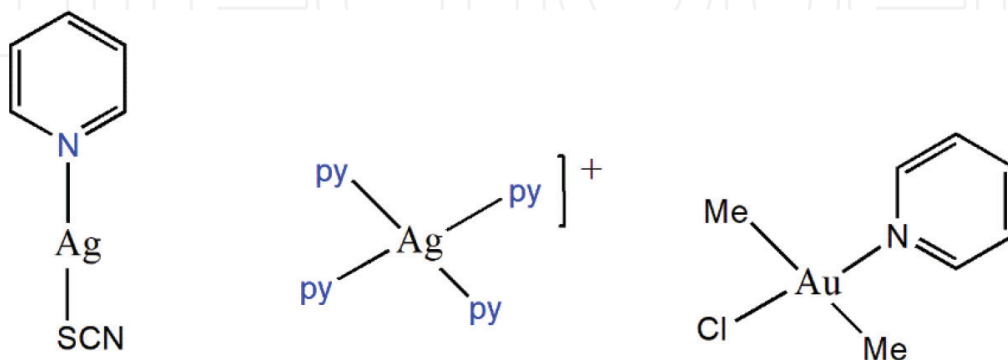

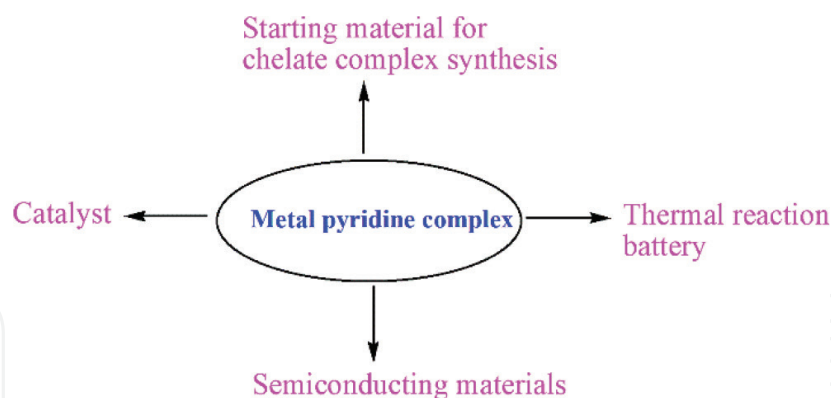**Figure 9.** Representative pyridine complexes of Ag, and Au.

Figure 10. Application of metal pyridine complexes.

Mn(III)-pyridine complexes were found useful in developing photographic images [81]. The Cu (NO_3) complex with pyridine was found as a useful semiconductor for thermistors [82] and was tested to explore as an explosive [83]. [Mn(py)$_4$Cl$_2$] was applied in the thermal reaction battery, where a complex is thermally decomposed into a conducting salt, which forms an electrolyte [84]. The [ReCl$_4$(NO)(py)$_2$] complex showed catalytic activity in the hydrogenation of cyclohexene [85]. Fe(II)-pyridine complexes acts catalyst along with sodium borohydride in the process of selective reduction of nitrobenzene to phenylhydroxylamine [86]. Pyridine ligands are often labile and can be replaced with chelating ligands such as ethylenediamine, oxalate and so on. Fe(II) pyridine complexes used as starting material for synthesis of Fe(II) chelate complexes without pyridine ligands [87]. [Ru(bpy)$_2$(NO)(py)]$^+$ catalyzes the electrochemical oxidation of triphenylphosphine [88], [Ru(py)$_{6-n}$X$_n$] type complexes have a significant amount of π-back donation to the pyridine. This makes the coordinated pyridine suitable for electrophilic substitution. In [RuCl$_3$(py)$_3$], pyridine undergoes nitration to give 3-nitropyridine at elevated temperature [89]. Several Rh(I) and Rh(III) pyridine complexes catalyse hydroformylation of ethylene hydrocarbons [90, 91]. A complex, [RhCl$_2$(BH$_4$)(DMF)(py)$_2$] can act as the homogeneous catalyst for hydrogenation of pyridine to piperidine [92].

Early transition metal pyridine complexes are also explored in catalytic synthesis of amine and N-heterocycles. Quite a few mono (2-aminopyridinate)tris(dimethylamido) titanium complexes were synthesized and explored for intramolecular hydroamination reactivity using aminoalkene substrates. A titanium catalyst capable of room-temperature hydroamination reactivity was identified for the synthesis of *gem*-disubstituted 5- and 6-membered-ring products [93].

A series of 3-substituted-2-pyridonate ligands were employed with titanium and used as ancillary ligands for targeting selectively intramolecular hydroaminoalkylation over hydroamination. It was found that bis(3-phenyl-2-pyridonate)bis(dimethylamido) titanium complex is selective for hydroaminoalkylation over hydroamination. This can selectively α-alkylate primary aminoalkenes with marked substrate-dependent diastereoselectivity [94].

2.4. Theoretical look at metal pyridine complexation

The above discussion brings out the fact that pyridine ligation to metal studied in a mixed ligand environment. Synthesis of "pure" pyridine complexes of the type $[M(py)_4]^{n+}$ and $[M(py)_6]^{n+}$ are difficult. Experimentally sequential addition of pyridine to a particular metal center to its highest coordination number is impractical. Thus theoretical approach adopted to study pyridine binding to metals using pyridine ligands to a group of first transition metals ions in their +2 oxidation states. DFT calculation employed by Rodgers [95] to determine the ground state structure and sequential binding energies of $[M^{2+}(Py)_x]$ complexes, where x = 1–6 and M = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. On gradual addition of pyridine, the metal ion adopts different geometries and the M-Py bond lengths and py-M-py angles got optimized according to the geometrical arrangements. $[M^{2+}(py)_4]$ and $[M^{2+}(py)_5]$ usually adopt distorted tetrahedral and distorted trigonal bipyramidal geometry. $[Cu^{2+}(py)_4]$ exhibits significant distortion from an ideal tetrahedral geometry to close to square planar arrangement, whereas $[Ni^{2+}(py)_5]$ and $[Cu^{2+}(py)_5]$ complexes adopt a square pyramidal geometry. The change of bond distances and bond angles evaluated on the addition of pyridine ligand to the metal are summarized in **Table 1** for $[M^{2+}(py)_x]$ (M^{2+} = Fe^{2+} & Cu^{2+}). In a trend $M^{2+} - N$ bond distances decrease from Fe^{2+}(1.939 Å) to Co^{2+}(1.854 Å) to Ni^{2+}(1.848 Å) to Cu^{2+}(1.844 Å), and then slightly increase for Zn^{2+}(1.870 Å), which is expected on the basis of the sizes of these cations and, consequently, stronger electrostatic contributions to the binding. For a particular M^{2+} center, the bond lengths gradually increase with the increased number of pyridines in the coordination sphere. The Fe-Py distance 1.939 Å in $[Fe^{2+}(py)]$ increases to 2.302(6) in $[Fe^{2+}(py)_6]$. This bond distance enhancement is due to increase in steric crowding around the metal center.

Complex	$M^{2+} - N$ (Å)	$\angle NM^{2+}N$ (deg)
$Fe^{2+}(Py)$	1.939	—
$Fe^{2+}(Py)_2$	1.953 (2)	179.9
$Fe^{2+}(Py)_3$	2.019 (3)	120.0(3)
$Fe^{2+}(Py)_4$	2.079 (4)	108.7 (2), 111.1 (4)
$Fe^{2+}(Py)_5$	2.161 (3), 2.229 (2)	86.5 (2), 90.2 (2), 94.7 (2), 111.1 (2), 137.7, 170.7
$Fe^{2+}(Py)_6$	2.302 (6)	89.3 (6)
$Cu^{2+}(Py)$	1.844	—
$Cu^{2+}(Py)_2$	1.877 (2)	180.0
$Cu^{2+}(Py)_3$	1.910 (2), 1.929	104.8(2), 150.5
$Cu^{2+}(Py)_4$	2.004 (4)	92.8, 97.2(3), 141.9(2)
$Cu^{2+}(Py)_5$	2.065, 2.277 (4)	86.6 (2), 90.2 (4), 96.4 (2), 104.5(2), 159.1(2)
$Cu^{2+}(Py)_6$	2.027 (4), 3.174(2)	89.5 (6), 90.5(6), 179.0 (3)

Values are reproduced from ref. [95].

Table 1. Theoretical bond angle and bond distances of $[M^{2+}(Py)_x]$ (M^{2+} = Fe^{2+} & Cu^{2+}).

Complex	Binding energy (kJ/mol)	Complex	Binding energy (kJ/mol)
$Fe^{2+}(py)$	621.8	$Cu^{2+}(py)$	916.8
$Fe^{2+}(py)_2$	424.9	$Cu^{2+}(py)_2$	395.3
$Fe^{2+}(py)_3$	302.4	$Cu^{2+}(py)_3$	252.8
$Fe^{2+}(py)_4$	170.3	$Cu^{2+}(py)_4$	147.5
$Fe^{2+}(py)_5$	68.1	$Cu^{2+}(py)_5$	65.4
$Fe^{2+}(py)_6$	57.3	$Cu^{2+}(py)_6$	41.8

Values are taken from ref. [95].

Table 2. Sequential binding energy of $[M^{2+}(py)_x]$ (M^{2+} = Fe^{2+} and Cu^{2+}) complexes at 0 K.

The bonding of M^{2+} cations to the nitrogen lone pairs facilitates strong ion-dipole and ion-induced dipole interactions. This is evident from $M^{2+} - N$ bonds orientation along the dipoles of the pyridine ligands. The M^{2+} cation binds the nitrogen lone pair forming M-py sigma bond. The dominant charge transfer involves ligand-to-metal sigma donation from nitrogen lone pairs of pyridine to the vacant valence shell of the metal and the metal-to-ligand charge transfer via π back bonding to the unoccupied π^* orbitals of pyridine ligand.

The strength of binding of the pyridine ligands to the M^{2+} cations decreases gradually with increasing ligation around the metal cation. This decrease in sequential bonding energy contributed to decreased attractive electrostatic interactions, charge transfer from the pyridine ligands to the metal cation, Jahn–Teller distortion, and ligand–ligand repulsion. Binding of the first ligand is comparatively strong as electrostatic interactions and charge transfer are both important contributors to the bonding in the $M^{2+}(py)x$ complexes. The binding energy of the second, third, fourth, fifth, and sixth ligands decrease on sequential ligation of pyridine because the effective charge retained by the metal center decreases, and the $M^{2+} - N$ bond distances increase. The extent of bonding is expected to increase from Fe^{2+} to Co^{2+} to Ni^{2+} to Cu^{2+} following the decrease of ionic radii of the metal cations. The trend is observed as Cu^{2+}-py binding energy (916.8 kJ) in $[Cu^{2+}(py)]$ is greater than the same (621.8 kJ) of $[Fe^{2+}(py)]$ as illustrated in **Table 2**.

3. Conclusion

In this chapter, the capability of pyridine as a ligand to transition metal ions was discussed. It has wealth of orbitals which are utilized in the formation of the bond to metal centers. Both electrostatic interactions and charge transfer are important factors in the bonding of pyridine to metals. The prominent charge transfer interactions make ligand-to-metal σ donation. The metal-pyridine bonding further got boosted by metal-to-ligand charge transfer through π back donation from metal dπ orbitals to the unoccupied π* orbitals of the pyridine ligand(s). The pyridine coordinates to all the transition metals known in the periodic table and hence has a rich literature of chemistry. Most of the complexes accommodate pyridine in a mixed ligand atmosphere

though $[M(py)_x]^{n+}$ type complexes were also characterized. Theoretical studies showed that the stability of pyridine complexes decreases with increasing ligation of pyridines around the metal center. A range of pyridine complexes was found their applications in numerous fields.

Acknowledgements

List of abbreviation and symbols

pm	picometer
Å	Angstrom
py	pyridine
bpy	bipyridine
SCN	thiocyanate
NCS	isothiocyanate
2-Me-py	2-methyl pyridine
4-Me-py	4-methyl pyridine
4-Et-py	4-ethyl pyridine
2, 6 –Me$_2$-py	2, 6 dimethyl pyridine
acac	acetylacetone
ox	oxalate

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