CHALCOGENATED SCHIFF BASES: DESIGNING, METAL COMPLEXES AND APPLICATIONS IN ORGANIC SYNTHESIS

By

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Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

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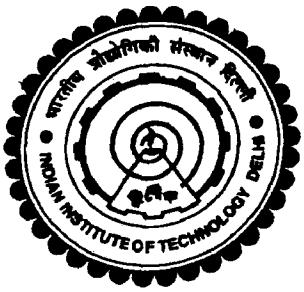

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CERTIFICATE

This is to certify that the thesis entitled, **"CHALCOGENATED SCHIFF BASES: DESIGNING, METAL COMPLEXES AND APPLICATIONS IN ORGANIC SYNTHESIS"** being submitted by **Mr. ARUN KUMAR** to the Indain Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Arun Kumar has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

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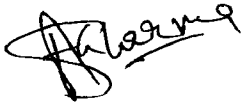


ARUN KUMAR

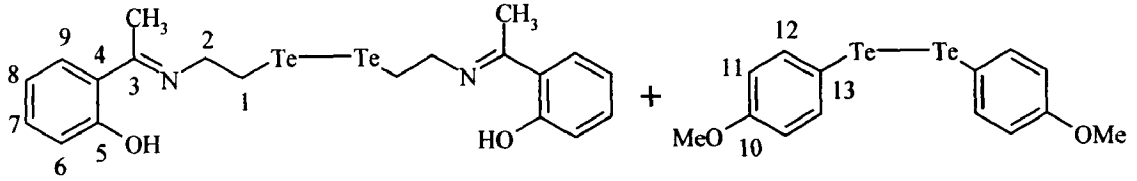
ABSTRACT

Chalcogenated Schiff bases of mono ketones or aldehydes particularly selenated and tellurated one are little explored. There is possibility of significant modification in the known catalytic roles of Schiff bases by the presence of S, Se or Te as a donor site in them. Therefore, such systems are worth exploring. Phosphine based catalysts are often water– and air–sensitive. Therefore, catalysis under phosphine–free conditions is a challenge of high importance and palladium complexes of phosphine–free ligands which have promising catalytic activity for C—C coupling reactions are of current interest. The chalcogenated Schiff bases may deal with this challenge because generally the chalcogen based catalysts are air stable and also moisture insensitive. The objectives of present thesis are mainly focused on designing of chalcogenated Schiff bases i.e. ligands containing Te, Se and S along with N and O donor sites and exploring their ligand chemistry and applications of their metal complexes as homogeneous catalysts for C—C coupling reactions (Heck and Suzuki). A detailed account of results is given in the Chapters 3–6.

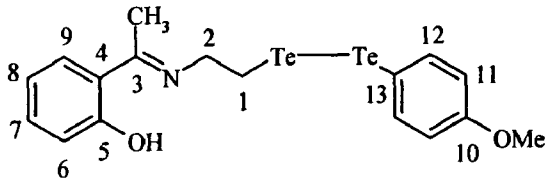
Chapter 3 Tellurides and Ditellurides containing Schiff Base Functionality

Tellurated alkyl amines, $NH_2(CH_2)_2–Te–(CH_2)_2NH_2$ and $NH_2(CH_2)_2–Te–Te–(CH_2)_2NH_2$ have been prepared by reacting appropriate organic halide with nucleophile Te^{2-} and Te_2^{2-} generated in situ by borohydride reduction of Te powder. Reactions of these amines with *o*-hydroxyacetophenone, 1'–hydroxy–2'–acetonaphthone and 2–hydroxybenzophenone in dry ethanol under appropriate conditions gave $HO–2–C_6H_4C(CH_3)=N(CH_2)_2–Te–(CH_2)_2N=C(CH_3)C_6H_4–2–OH$ (**1**), $HO–2–C_6H_4C(CH_3)=N(CH_2)_2–Te–Te–(CH_2)_2N=C(CH_3)C_6H_4–2–OH$ (**2**), $HO–2–C_{10}H_6C(CH_3)=N(CH_2)_2–Te–(CH_2)_2N=C(CH_3)C_{10}H_6–2–OH$ (**3**), HO–2–

$C_{10}H_6C(CH_3)=N(CH_2)_2-Te-Te-(CH_2)_2N=C(CH_3)C_{10}H_6-2-OH$ (**4**), $HO-2-C_6H_4C(Ph)=N(CH_2)_2-Te-(CH_2)_2N=C(Ph)C_6H_4-2-OH$ (**5**) and $HO-2-C_6H_4C(Ph)=N(CH_2)_2-Te-Te-(CH_2)_2N=C(Ph)C_6H_4-2-OH$ (**6**) respectively. All these compounds **1–6** were characterized by ^1H, $^{13}C\{^1H$, ^{125}Te NMR, FT–IR spectroscopy, elemental analysis and mass spectrometry. $^{125}Te\{^1H\}$ NMR data of **2**, **4** and **6** have been compared with those of corresponding monotellurides **1**, **3** and **5**. Instantaneous ligand exchange reaction of **2** with bis(4–methoxyphenyl)ditelluride (**2a**) shown below has been followed with ^{125}Te NMR spectroscopy. The equilibrium shown below is



(**2**) (**2a**)



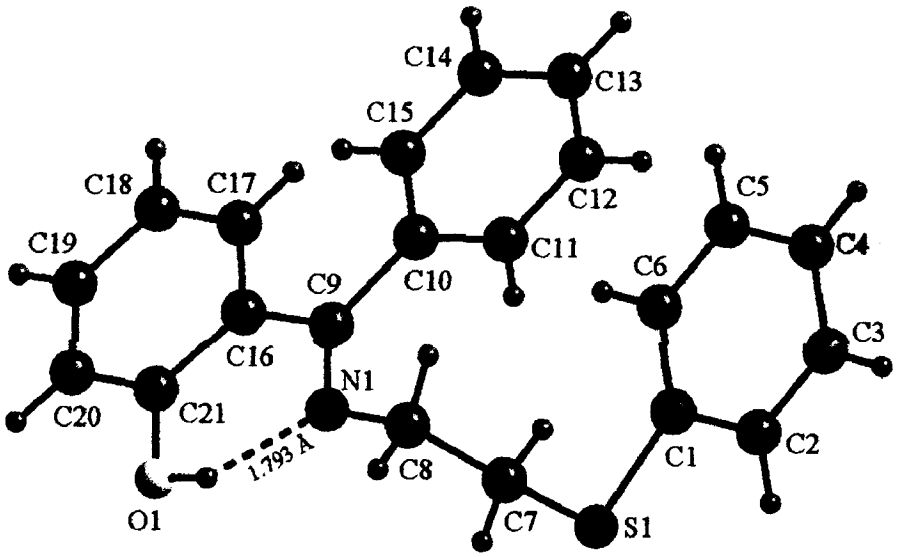
(**2b**)

established readily. The compounds **2**, **4** and **6** are of high significance in the context of development of tellurium ligands further as they can generate by borohydride reduction first examples of (N, O, Te^-) ligands, which can be reacted further with a variety of functionalized organic halides to prepare diverse multidentate hybrid organotellurium ligands.

Chapter 4 Sulphated Schiff Bases: Complexation and Applications

(2-Aminoethyl)phenylsulphide $C_6H_5-S-(CH_2)_2NH_2$ and (3-Aminopropyl)phenylsulphide $C_6H_5-S-(CH_2)_3NH_2$ were prepared by the reaction of

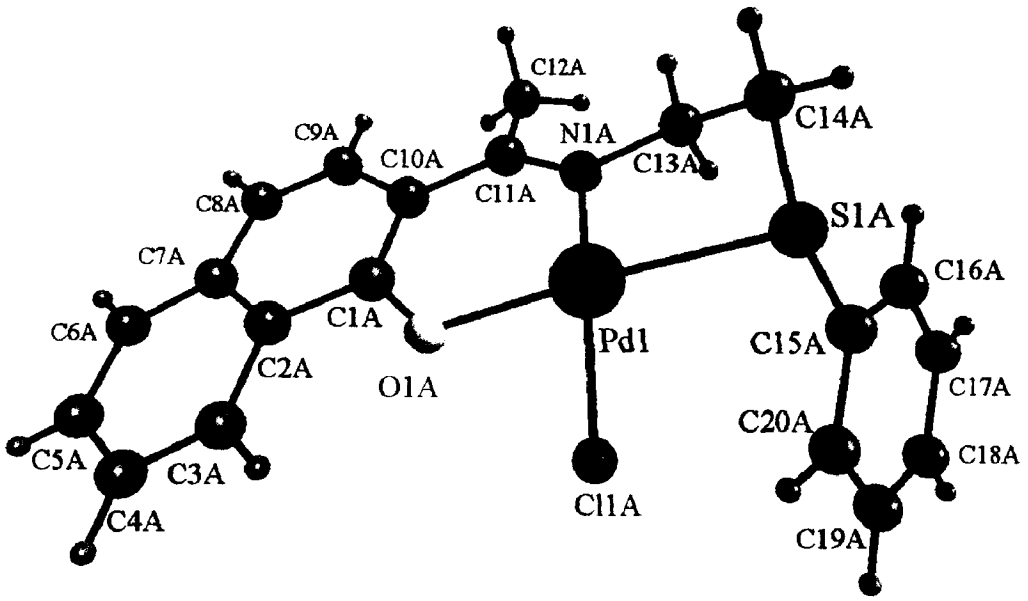
choloroethylamine hydrochloride and choloropropylamine hydrochloride with sodium phenylsulphide in ethanol (95%) as a solvent. These amines were reacted with 1'–hydroxy–2'–acetonaphthone and 2–hydroxybenzophenone in dry ethanol to give Schiff bases PhS–$(CH_2)_2$N=C$(CH_3)C_{10}H_6$–2–OH ($\mathbf{L^1}$), PhS–$(CH_2)_3$N=C$(CH_3)C_{10}H_6$–2–OH ($\mathbf{L^2}$), PhS–$(CH_2)_2$N=C$(Ph)C_6H_4$–2–OH ($\mathbf{L^3}$) and PhS–$(CH_2)_3$N=C$(Ph)C_6H_4$–2–OH ($\mathbf{L^4}$) respectively. All of them were characterized by ^{1}H, ^{13}C{^{1}H} NMR and FT–IR spectroscopy and elemental analyses. The single crystal structures of $\mathbf{L^1}$ and $\mathbf{L^3}$ were determined by X-ray diffraction. The N—H···O intramolecular hydrogen bonding (See Molecular Structure of $\mathbf{L^3}$) was observed in the molecules of $\mathbf{L^1}$ and $\mathbf{L^3}$.



Molecular Structure of $\mathbf{L^3}$

The Pd(II) complexes [PdCl($\mathbf{L^1}$–H)] (**7**), [PdCl($\mathbf{L^2}$–H)] (**8**), [PdCl($\mathbf{L^3}$–H)] (**9**) and [PdCl($\mathbf{L^4}$–H)] (**10**) of these Schiff bases have been synthesized by their reaction with Na_2PdCl_4. The single crystal structures of **7**, **8** and **9** were determined by X-ray diffraction. All the ligands are coordinated with Pd(II) in tridentate (S, N, O^-) mode (See Molecular Structure of **7**). The use of **7**, **8** and **9** has been studied as catalysts in Heck (between alkenes and aryl halides) and Suzuki (between phenyl boronic acid

and aryl halides) C—C coupling reactions. The yields are upto 80 %. For Heck reaction it is highest for ArI.

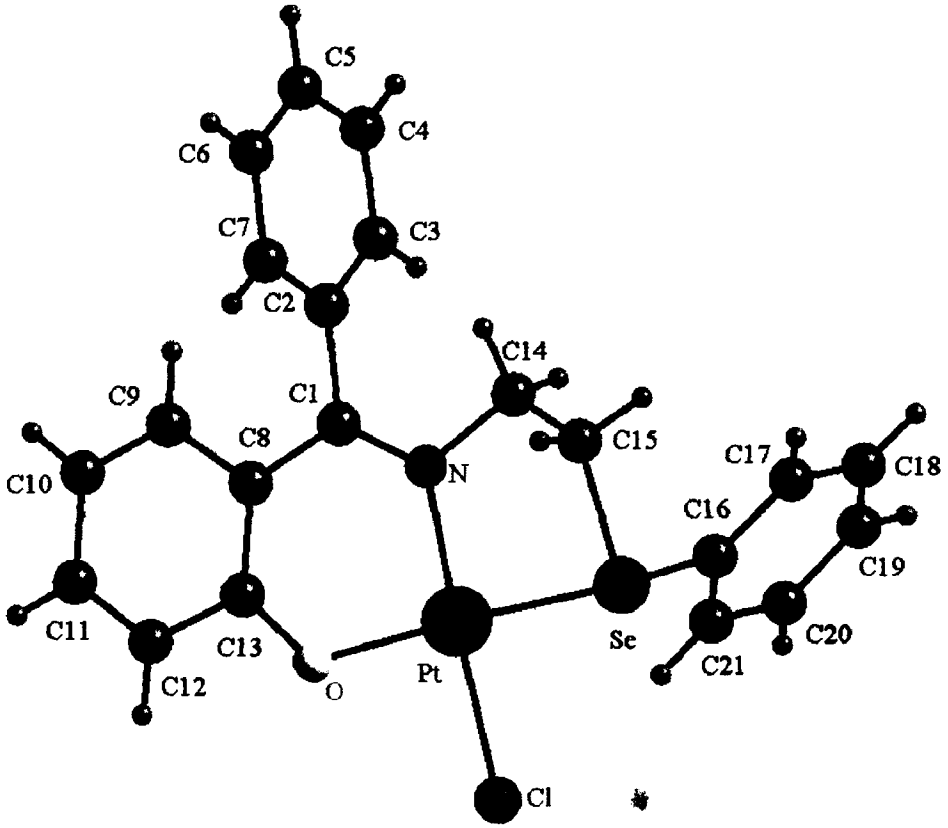


Molecular Structure of PdCl($\mathbf{L^1}$–H) (**7**)

Chapter 5 Selenated Schiff Bases: Complexation and Applications

(2–Selenophenyl)ethylamine C_6H_5–Se–$(CH_2)_2NH_2$ and (3–selenophenyl) propylamine C_6H_5–Se–$(CH_2)_3NH_2$ prepared by the reaction of choloroethylamine hydrochloride and 3–choloropropylamine hydrochloride with nucleophile $C_6H_5Se^-$ generated in situ by borohydride reduction of diphenyl diselenide in dry ethanol as a solvent, were reacted with 2–hydroxyacetophenone, 1'-hydroxy-2'-acetonaphthone and 2–hydroxybenzophenone to give Schiff base PhSe–$(CH_2)_2$N=C$(CH_3)C_6H_4$–2–OH ($\mathbf{L^5}$), PhSe–$(CH_2)_3$N=C$(CH_3)C_6H_4$–2–OH ($\mathbf{L^6}$), PhSe–$(CH_2)_2$N=C$(CH_3)C_{10}H_6$–2–OH ($\mathbf{L^7}$), PhSe–$(CH_2)_3$N=C$(CH_3)C_{10}H_6$–2–OH ($\mathbf{L^8}$), PhSe–$(CH_2)_2$N=C$(Ph)C_6H_4$–2–OH ($\mathbf{L^9}$) and PhSe–$(CH_2)_3$N=C$(Ph)C_6H_4$–2–OH ($\mathbf{L^{10}}$) respectively. The $\mathbf{L^5}$–$\mathbf{L^{10}}$ were characterized by ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ NMR and FT–IR spectroscopy, elemental analyses and mass spectrometry. The single crystal structures of $\mathbf{L^5}$, $\mathbf{L^6}$ and $\mathbf{L^7}$ were determined by X–ray diffraction. They also have N—H···O intramolecular hydrogen

bonding as in case of L^1 and L^3. The Pd(II) and Pt(II) complexes of these Schiff bases have been synthesized by their rection with Na_2PdCl_4 and K_2PtCl_4 respectively. Pd(II) forms complexes of type PdCl(L–H) (L = L^5–L^{10}) whereas Pt(II) forms complexes analogous to those of Pd(II) and also of type $PtCl_2(L)_2$ (L = L^6, L^8 or L^{10}).



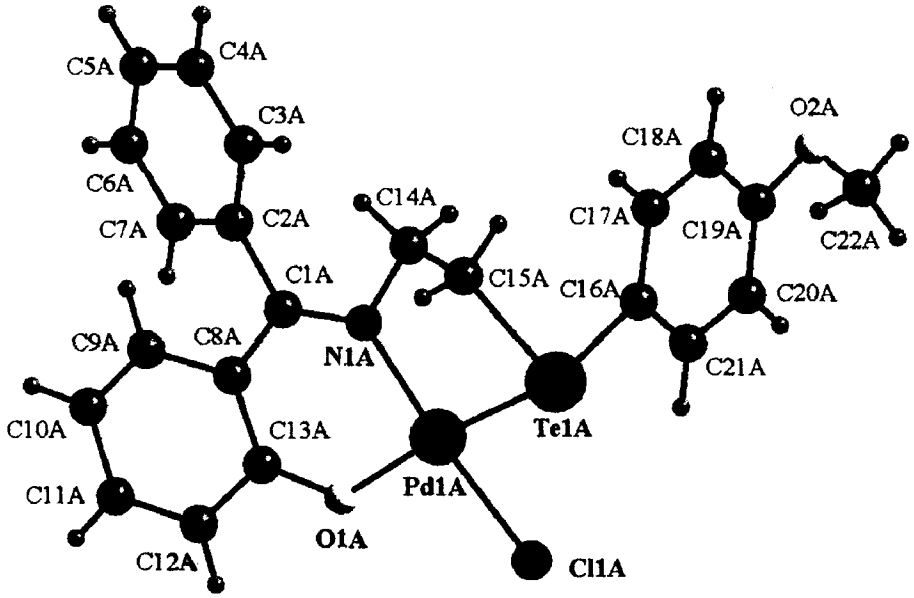
Molecular Structure of PtCl(L^9–H)

The single crystal structures of [PdCl(L^5–H)], [PtCl(L^5–H)], [PdCl(L^7–H)], [PdCl(L^9–H)], [PtCl(L^9–H)] and [PdCl(L^{10}–H)] were determined by X-ray diffraction. The ligands were found to be coordinated with metal in monoanionic tridentate (Se, N, O^-) coordination mode in these structures [See Molecular Structure of PtCl(L^9–H)]. The structures of **11**, **12** and **21** comprise of two independent molecules in the unit cell. The Pd(II) complexes of L^5, L^7, L^8, L^9 and L^{10} have been studied as catalysts in C—C coupling (Heck and Suzuki) reactions. They were found better than those of corresponding sulphated analogues as revealed by higher percentage yields under same conditions.

Chapter 6 Tellurated Schiff Bases: Complexation and Applications

Tellurated alkyl amines, $4\text{-}CH_3O\text{-}C_6H_4Te\text{-}CH_2CH_2NH_2$ and $4\text{-}CH_3O\text{-}C_6H_4Te\text{-}CH_2CH_2CH_2NH_2$ prepared by reaction of appropriate organic halide with nucleophile $4\text{-}MeOC_6H_4Te^-$, were reacted with 1'–hydroxy–2'–acetonaphthone and 2-hydroxybenzophenone to give Schiff bases $ArTe\text{-}(CH_2)_2N{=}C(CH_3)C_{10}H_6\text{-}2\text{-}OH$ ($\mathbf{L^{11}}$), $ArTe\text{-}(CH_2)_3N{=}C(CH_3)C_{10}H_6\text{-}2\text{-}OH$ ($\mathbf{L^{12}}$), $ArTe\text{-}(CH_2)_2N{=}C(Ph)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^{13}}$) and $ArTe\text{-}(CH_2)_3N{=}C(Ph)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^{14}}$) respectively. The ligands $\mathbf{L^{11}}$–$\mathbf{L^{14}}$ were characterized by ^1H, $^{13}C\{^1H\}$, $^{125}Te\{^1H\}$ NMR and FT–IR spectroscopy and elemental analysis. The single crystal structure of $\mathbf{L^{12}}$ was determined by X-ray diffraction. It contains N–H···O intramolecular hydrogen bonding. The Pd(II), Pt(II), Ru(II) and Hg(II) complexes of these Schiff bases have been synthesized. All the four (Te, N, O) ligands form Pd(II) complexes of type [PdCl(**L**–H)] in which they coordinate in monoanionic tridentate (Te, N, O^-) mode. Their single crystal structures were determined when **L** = $\mathbf{L^{11}}$ and $\mathbf{L^{13}}$. But their complexation with Pt(II) becomes different when value of '*n*' in the ligand backbone >C=N–$(CH_2)_n$–Te changes from 2 to 3. So two type of Pt-complexes are formed. The PtCl(**L**–H) type of complexes **24** and **32** are formed by $\mathbf{L^{11}}$ and $\mathbf{L^{13}}$ respectively on coordination with Pt(II) in monoanionic tridentate (Te, N, O^-) mode and $PtCl_2(\mathbf{L})_2$ type of complexes **28** and **36** are formed by $\mathbf{L^{12}}$ and $\mathbf{L^{14}}$ respectively on coordination with Pt(II) in monodentate mode (via. Te only). The **28** and **36** exist in solution as the mixture of *cis*- and *trans*-isomeric forms. All the four ligands (L = $\mathbf{L^{11}}$–$\mathbf{L^{14}}$) form [(*p*–cymene)RuCl(**L**)]Cl type of Ru(II) complexes. In mercurry complexes formed by all the four ligands ($\mathbf{L^{11}}$–$\mathbf{L^{14}}$) coordination with Hg(II) is probably in a monodentate mode. For Hg-complexes of $\mathbf{L^{11}}$–$\mathbf{L^{14}}$, the $^{125}Te\{^1H\}$ NMR signals show shielding with respect to those of corresponding ligands which is in

contrary to deshieldings observed in $^{125}Te\{^{1}H\}$NMR signal of $\mathbf{L^{11}}$ to $\mathbf{L^{14}}$ on complexation with Pd(II), Pt(II) and (*p*–cymene)Ru(II). The Pd(II) complexes of $\mathbf{L^{11}}$



Molecular Structure of PdCl($\mathbf{L^{13}}$–H) (**31**)

[PdCl($\mathbf{L^{11}}$–H)] and $\mathbf{L^{13}}$ [PdCl($\mathbf{L^{13}}$–H)] have been studied as catalysts in C–C coupling (Heck and Suzuki) reactions. The performance of these Pd(II) complexes were found to be almost similar to those of corresponding sulphated analogues. So far no investigation on Pd(II) complexes of tellurated Schiff bases for Heck reaction have been made and present results show promise of such species.

Some more observations about ligation of chalcogenated Schiff bases are as follows. It is observed that in case of Pt(II) the coordination mode of selenated and tellurated Schiff bases ($\mathbf{L^{5}}$–$\mathbf{L^{14}}$) changes when there are three CH_2 groups between >C=N group and Se / Te. When the chalcogenated Schiff bases act as a tridentate uninegative ligand the binding with the Pd or Pt is very strong as indicated by various M–L distances which are shorter than the sum covalent radii. The Pd(II) complexes of chalcogenated Schiff bases are thermally and air stable and moisture insensitive, and offer the advantage of successful coupling of aryl bromides and the synthesis of biaryls under aerobic conditions (Suzuki-Miyaura cross-coupling). Optimum catalyst :

aryl halide molar ratio was found be 1:1000 for Heck and Suzuki reactions both. A good selectivity for *trans*–products has been observed. In $^{125}Te\{^{1}H\}/^{77}Se\{^{1}H\}$ NMR spectra of Pd(II) / Pt(II) complexes, the shift of signal relative to free ligand depends on the size of chelate ring formed around the central metal atom (5-membered > 6 membered).

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