Heterocyclic Thioamide Derivatives of Palladium and Platinum Metals

(**Technical Report**)

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Final Progress Report 2009-2012

1.	UGC Reference No. & Date	**F. No. 34-307 \ 2008(SR)**
2	Name of the Principal Investigator	Prof. Dr. Tarlok Singh Lobana
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	Residential	(Past)A-6, GND University, Amritsar 143005 (**Present**): SCF 60, Kabir Park, Opposite GNDU, Amritsar 143005.
4.	Department and University where Project work has been undertaken	Department of Chemistry, Guru Nanak Dev University, Amritsar- 143005.
5.	Title of the Project	**Heterocyclic Thioamide Derivatives of Palladium and Platinum Metals**
6.	Date of Implementation	1-2-2009
7.	Tenure of the Project	3½ years upto July 31, 2012
8.	Grants Received	Grants section –sent All information.
9	Objective of the project	To investigate coordination chemistry of heterocyclic thioamide ligands leading to the formation of mononuclear, dinuclear or polynuclear metal complexes
10.	Work done	**See Annexure I**
11	Has the work been according to the original plan	**See Annexure I**

	of work and towards achieving objectives, if not state reasons.	
12.	Please indicate the difficulties, if any, experienced in implementing the project.	**Nil**
13	Collaboration, if any (with Department, University, Industry etc.)	**Nil**
14	Ph. D enrolled, if yes, details	Yes, **Amanpreet Kaur** enrolled wef **March 9, 2010.**
15	Details of the Publications resulting from the project work	**See Annexure II**

Tarlok Singh Lobana - Principal Investigator

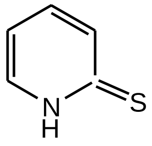
Report of work - Annexure – I

Period : Feb. 1, 2009 - July 31, 2012

Summary : A series of mononuclear, dinucelar and polynuclear metal deivatives of heterocyclic thiomaides have been prepared (30 compounds) and characterized using analytical methods, spectroscopy and using x-ray crsyallography (26 complexes). Some of complexes are mixed valent having Pd^{I}-Pd^{II} pairs, while some other complexes are dinuclear with Pd^{II}-Pd^{II} pairs and involving metallation and heterocyclic thiones as co-ligands (**1, 3-5**, **7-12**). These are prepared for the first time. Platinum and ruthenium gave square planar (**2**) or octahedral (**6**) complexes. Similarly in Cu^{I} , complexes are with and without halogens (**14-22**). In fact, staring salt was $Cu(OAc)(PPh_3)_2$ and capture of halogen was from the laboratory/ solvent in which reaction was carried out. Further copper(I) complexes have shown existence of monomers and dimers in same unit cell as well as shown bond isomerism(**15-17**). Complexes with zinc(II), cadmium(II) and mercury (II) are mononuclear with distorted tetrahedral geometry and are not afftected by the change in substituents at one N atom of the thio-ligands (**23-30**).

Detailed work

Chart 1 shows various thio-ligands which have been used for their interaction with metal salts/precursors. The lignads used are pyridine-2-thione (I, pySH), pyrimidine-2-thione(II, pymSH), benzimidazoline-2-thione (III, bzimSH), purine-6-thione (IV, purSH), imidazoline-2-thione (V, imzSH), 1-methylimidazolidine-2-thione(VI, imdzSH-Me), 1-ethylimid -azolidine-2-thione(VII, imdzSH-Et), 1-n-propyl-imidazolidine-2-thione (VIII, imdzSH-Pr^{n}),1-phenylimidazolidine-2-thione (IX, imdzSH-Ph), thiazolidine-2-thione (X, tzdSH), 1-methylimidazoline-2-thione (XI, mimzSH) and 2, 4, 6- trimercaptotriazine (XII, H_3tmt). The work is discussed under different headings as follows.



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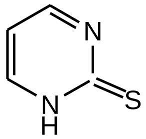

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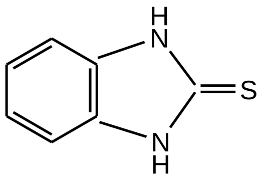

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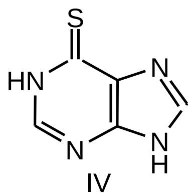

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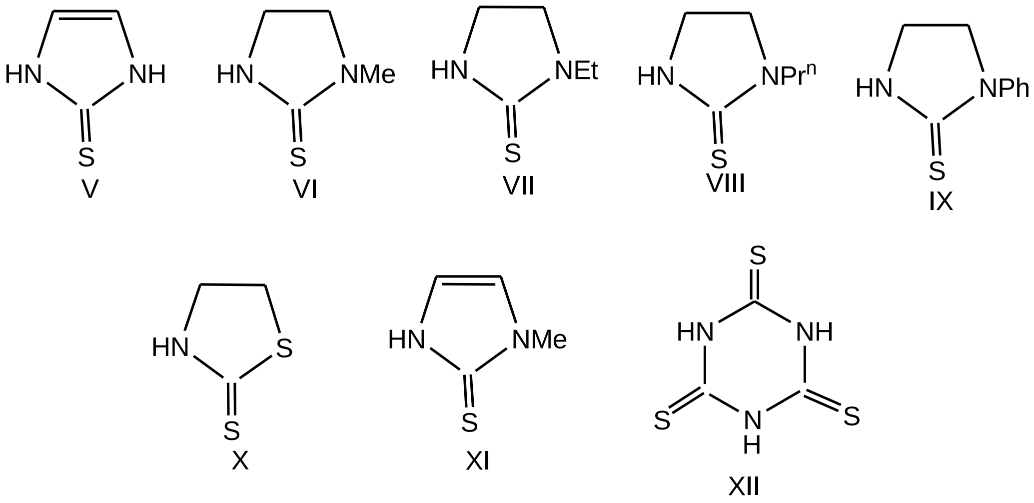


Chart 1

I. Work on phosphine based precursors

Initially the starting compounds, namely, $PdCl_2(PPh_3)_2$, $PdCl_2(L\text{-}L)$ [L-L = $Ph_2P\text{-}CH_2\text{-}PPh_2$, dppm; $Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2$, dppe; cis-$Ph_2P\text{-}CH{=}CH\text{-}PPh_2$, dppen, $Ph_2P\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}PPh_2$, dppp etc.] were prepared by reacting $PdCl_2$ in acetonitrile with stoichiometric amounts of different phosphines as listed above. The objective of the project envisaged the use of the precursors of the type shown in Chart 1, which have P, P-chelation backbone and the pendant pyridyl type groups were believed to react with different Lewis acids for obtaining di-, or poly-nuclear complexes.

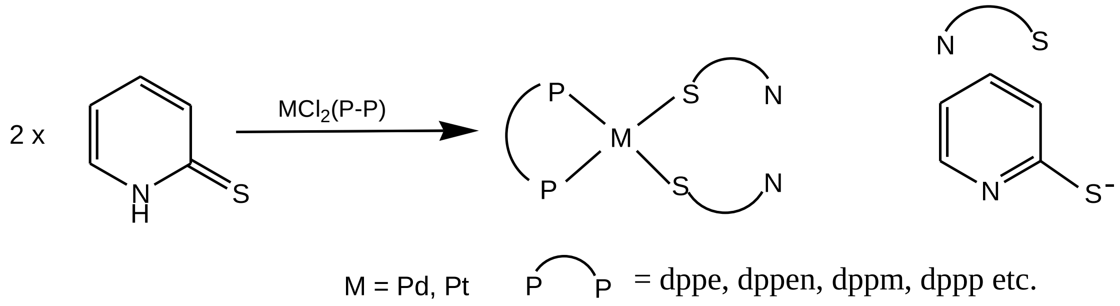
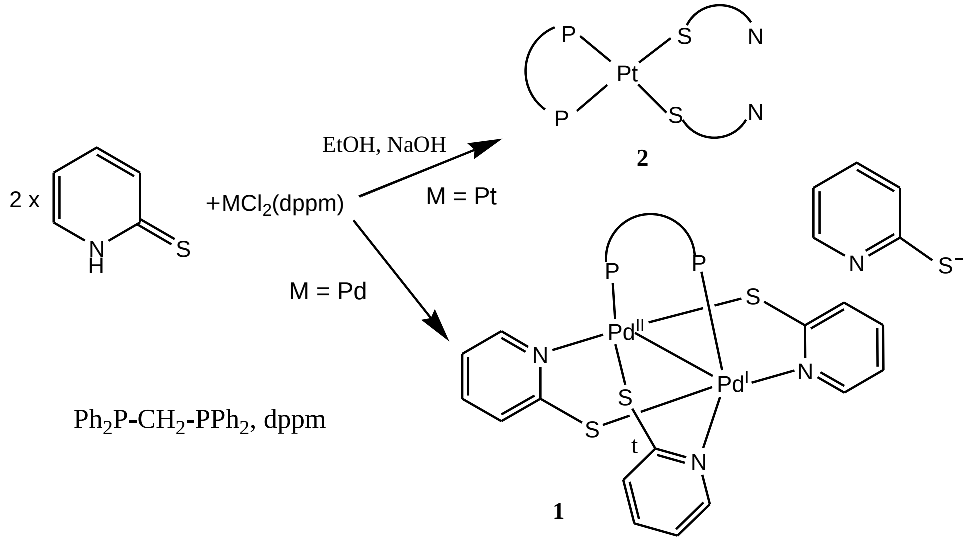


Chart 1

Since the precursors, $[M(L\text{-}L)(\eta^1\text{-}S\text{-}pyS)_2]$ {M = Pd, Pt, L-L= dppe, dppen, pyS^- = pyridine-2-thiolate} have been reported earlier **{[T. S Lobana, Renu Verma, Geeta Hundal and Alfonso Castineiras, Polyhedron 19 (2000) 899}**, efforts were made to prepare these precursors first and then react with different salts /substrates for obtaining their coordination derivaties as bonding was possible through pendant pyridyl moieties Reactions of {M(L-L)(η^1-S-pyS)$_2$] {M = Pd, Pt; L-L = dppe, pyS$^-$ = pyridine-2-thiolate} with a variety of salts such as copper(I) chloride, copper(I) bromide, copper(I) iodide, coper(II) chloride, mercury(II) chloride etc were carried out but no crystallizable product could be obtained, rather thio-ligand was found to shift from Pd to Cu or Hg center and destroying the starting precursors and thus these reactiosn were not successful.

In another reaction PdCl$_2$(dppm) was reacted with two moles of pyridine-2-thione (pySH) in presence of NaOH in ethanol solvent under refluxing conditions and the product characterized using C,H, N analysis, IR, NMR and single crystal x-ray crystallography. It has been found that dppm ligand has yielded rather a different compound of stochiometry, Pd$_2$(pyS)$_3$(dppm) **1 (Scheme 1**), which is a dimer, [Pd^{I}Pd^{II} (κ^2-N,S-PyS)$_3$(dppm)] **1** (Figure 1**)** rather than the expected monomer as shown in Chart 1 with pendant pyridyl groups. It has one Pd^{I} and second Pd^{II} metal centers and such type of mixed valent compounds are not common in metal-heterocyclic thioamide chemistry. The yield of the dimer was high and the reaction clean when only one mole of pyridine-2-thione was used. The substrate PtCl$_2$(dppm) with two moles of pySH was expected to form compound similar to **1**, rather it has formed a monomer, [Pt(dppm)(η^1-S-pyS)$_2$] **2** (Figure 2) with pendant pyridyl groups. This precursor showed behaviour similar to that of [Pt(dppe)(η^1-S-pyS)$_2$]^1**(Scheme 1).**



Scheme 1

The reaction of compound PdCl$_2$(dppp) having chain length 3 connecting PPh$_2$ groups (e.g. dppp) with pySH has not formed expected monomer with pendant pyridyl groups, rather it has formed a dimer Pd$_2$(pyS)$_4$ **3** (Figure 3) **(Scheme 2),** but different from **1** or **2**. The dimer **3** has also been synthesized by an alternative method using Pd$_3$(OAc)$_3$ and pySH **{ K. Umakoshi, A. Ichimura, I. Kinoshita, S. Ooi, Inorg. Chem. 29 (1990) 4005}.** The precursors, [M(L-L)(η^1-S-pymS)$_2$] (L-L= dppm, pymS$^-$ = pyrimidine-2-thiolate) also did not yield mixed metal complexes {T. S. Lobana, P. J. Kaur, Geeta Hundal, Ray. J. Butcher, and A. Castineiras, **Z. Anorg. Allg. Chem.** 634 **(2008)** 747}..

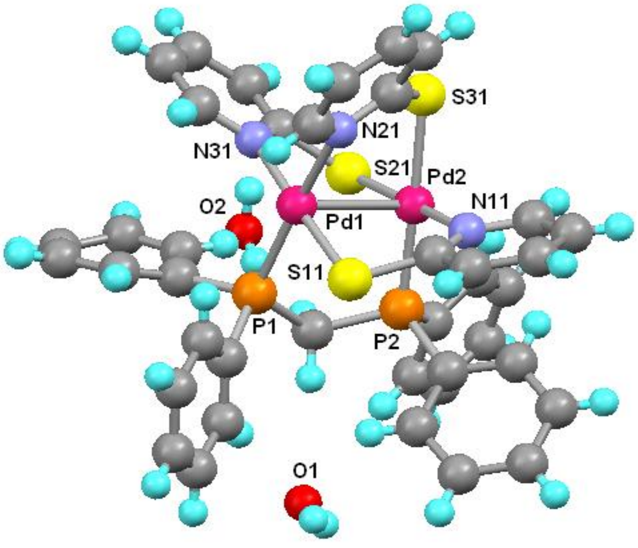


Fig. 1. Structure of [Pd^{I}Pd^{II} (κ^2-N,S-PyS)$_3$(dppm)] **1**

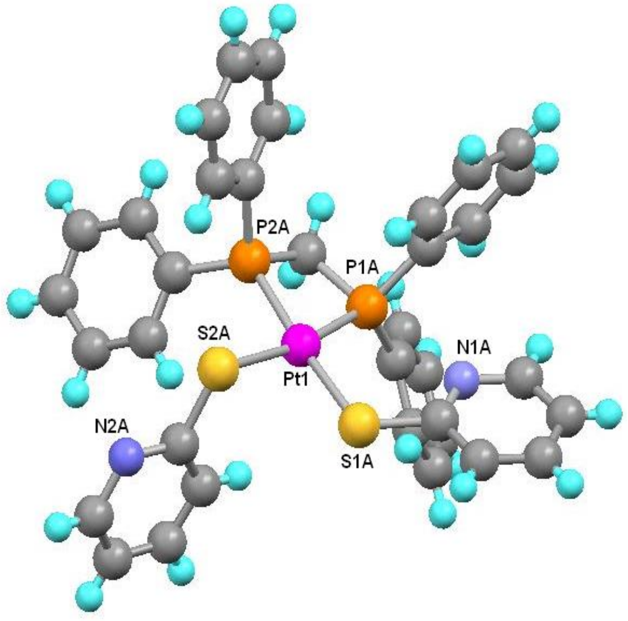
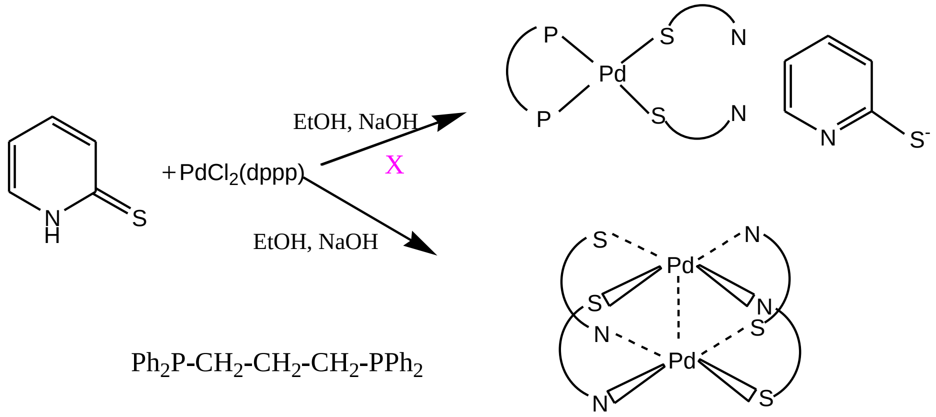


Fig. 2. Structure of [Pt(dppm)(η^1-S-pyS)$_2$] **2**



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Scheme 2

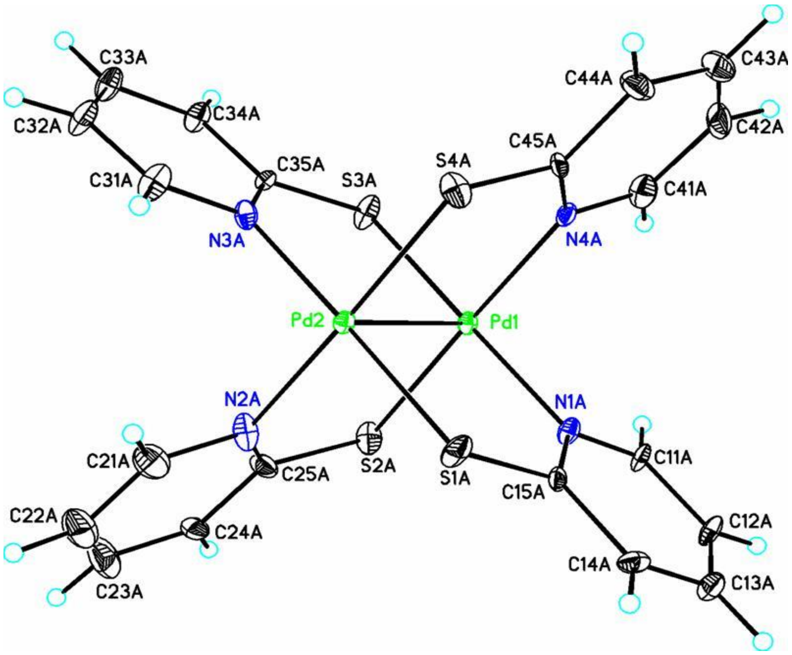
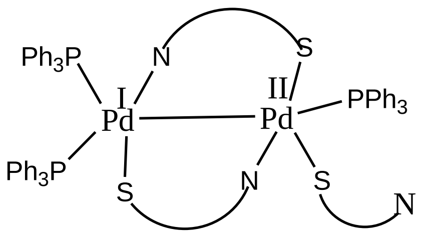


Fig. 3. Molecular structure of compound $[Pd_2((\mu\text{-N, S- pyS})_4]$ **3**

Reaction of $PdCl_2(PPh_3)_2$ with two moles of benzimidazoline-2-thione in acetonitrile in presence of Et_3N base has formed a mixed valence Pd^I-Pd^{II} dimer, $[Pd_2(\mu\text{-N,S-bzimS})_2(\eta^1\text{-S-bzimS})(PPh_3)_3]$ **4** (Figure 4). Similarly, reaction of $PdCl_2(PPh_3)_2$ with two moles of 1,3-imidazoline-2-thione ($imzSH_2$) in acetonitrile in presence of Et_3N base did not form the expected dimer similar to **4**, rather it has formed a different product i.e., square planar monomer, $[Pd(\eta^1\text{-S-imzSH}_2)_4]Cl_2\cdot 2H_2O$ **5** (Figure 5).



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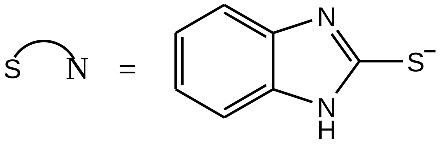

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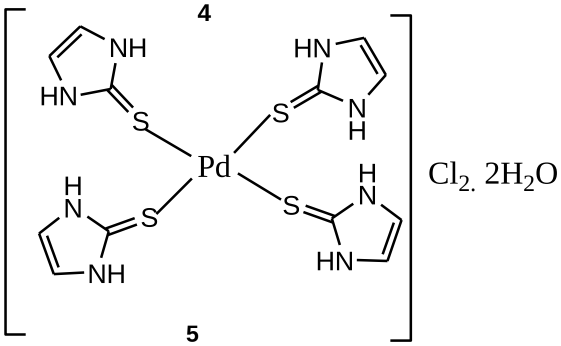

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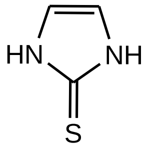

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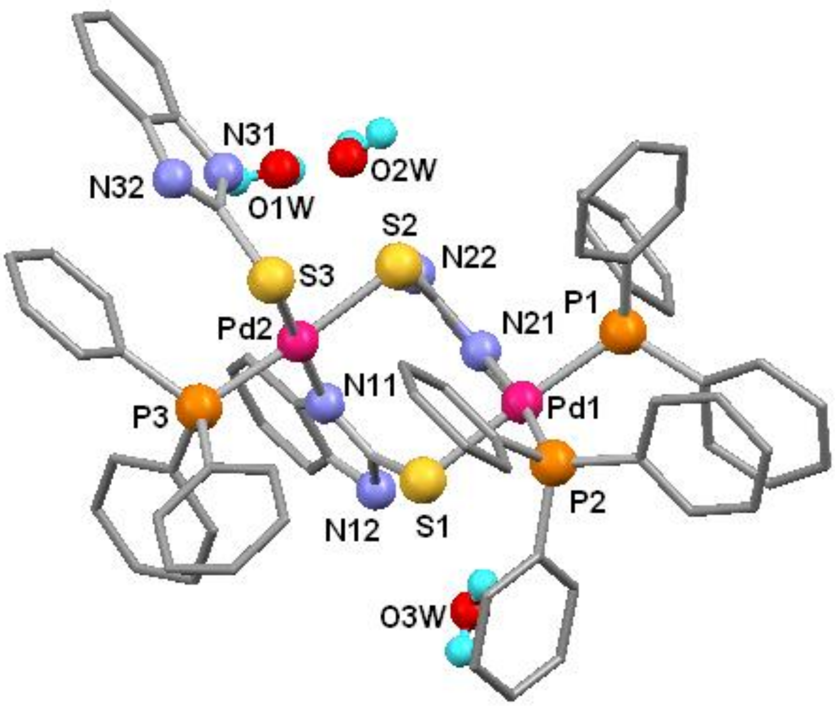


Fig. 4. Molecular structure [Pd$_2$(μ-N,S-bzimS)$_2$(η^1-S-bzimS)(PPh$_3$)$_3$] **4**

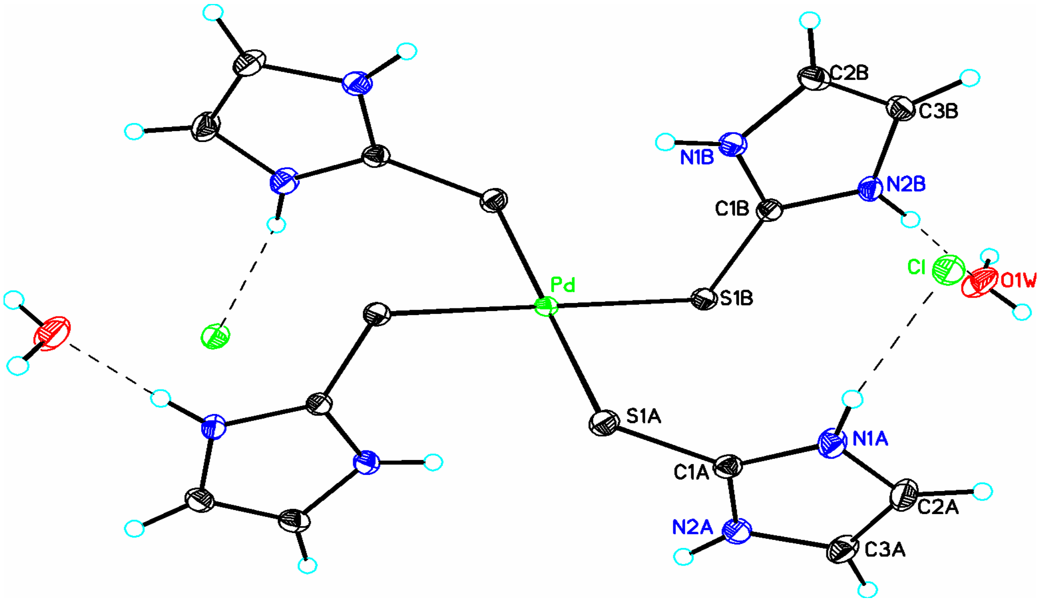


Fig. 5. Molecular structure of $[\mathrm{Pd}(\eta^1\text{-S-imzSH}_2)_4]\mathrm{Cl}_2\cdot 2\mathrm{H}_2\mathrm{O}$ **5**

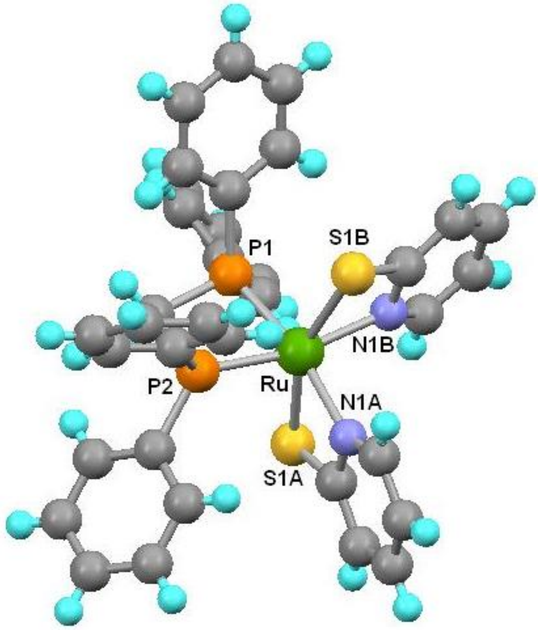


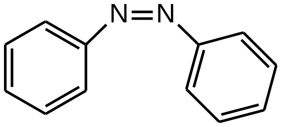
Fig. 6. Molecular structure $[\mathrm{Ru}(\eta^2\text{-N, S-pyS})_2(\text{P, P-dppm})]$ **6**

A precursor based on $\mathrm{Ru^{II}}$, namely, $[\mathrm{Ru}(\eta^2\text{-N, S-pyS})_2(\text{P, P-dppm})]$ **6** was prepared by reacting orange solution of $\mathrm{Ru(dppm)_2Cl_2}$ in toluene with solid pyridine-2-thione and $\mathrm{Et_3N}$. The contents were refluxed for a period of 12 h. The salt $\mathrm{Et_3NH^+Cl^-}$ formed was filtered and filtrate was evaporated. The solid obtained was recrystallised in $\mathrm{CH_2Cl_2}$ – $\mathrm{CH_3OH}$ mixture. Slow evaporation of the solution at room temperature formed light orange crystals. X-ray crystallography of this complex showed an octahedral structure (Fig. 6). Complex **6** represents first example among heterocyclic-2-thione derivatives of ruthenium(II) which has formed first octahedral complex with a central core having three 4-membered rings. However, it did not react further to yield mixed metal complexes.

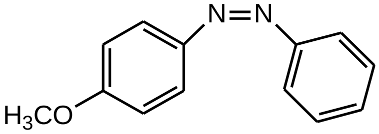
II. Metal derivatives of heterocyclic thiones in presence of azo-ligands

Palladium(II)

In this section, reactions of heterocyclic thioamides with palladiulm(II) in presence of azo-ligands are described. Reaction of $PdCl_2$ with azobenzene and pyridine-2-thione in acetonitrile - DMF mixture has yielded a dinuclear complex, $[Pd_2(\mu\text{-N, S-pyS})_2(\mu\text{-C, N-azobenzene})_2]$ **7** (Fig. 7). Similarly, reaction of $PdCl_2$ with azobenzene and pyrimidine-2-thione in acetonitrile - DMF mixture has yielded a dinuclear complex, $[Pd_2(\mu\text{-N, S-pymS})_2(\mu\text{-C, N- azobenzene})_2]$ **8** (Fig.8).



azobenzene



p-methoxy-azobenzene

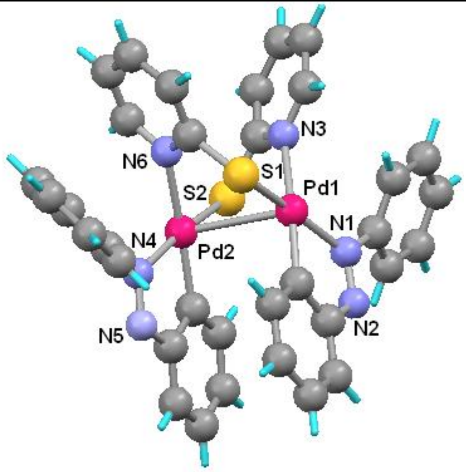


Fig. 7. Structure of compound **7**

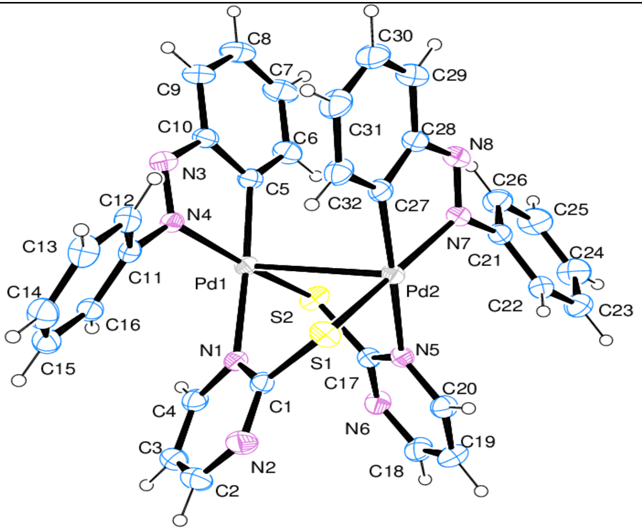


Fig. 8. Structure of compound **8**

Interestingly, similar reaction of $PdCl_2$ with azobenzene and N-methylimidazolidine-2-thione in acetonitrile - DMF mixture has yielded a mononuclear compound, [Pd(η^1-S- imzdSH-Me)(η^2-C, N-azobenzene)Cl] **9**. There is no dimerisation in this case.

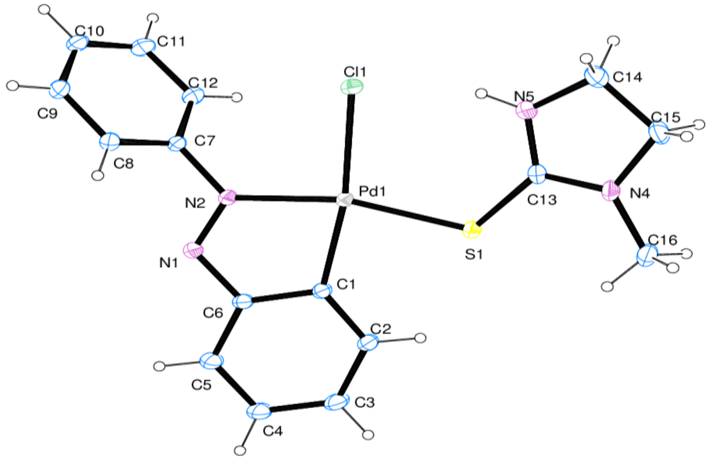


Fig. 9. Structure of compound [Pd(η^1-S- imzdSH-Me)(η^2-C, N-azobenzene)Cl] **9**.

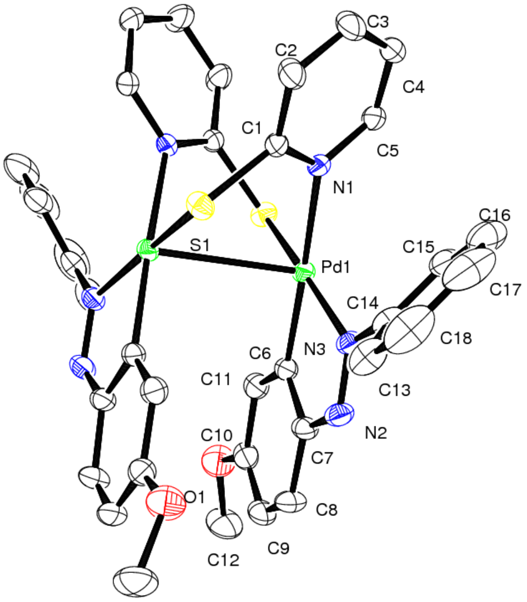
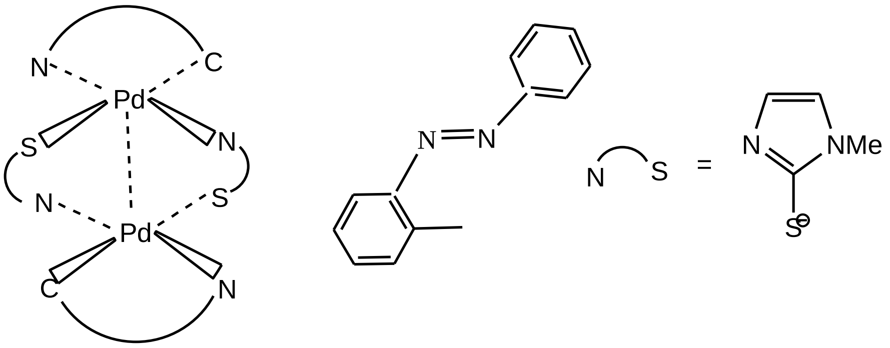


Fig. 10. Molecular structure of [Pd_2(μ-N, S-pyS)$_2$(μ-C, N- p-methoxy-azobenzene)$_2$] **10**

Further, reactions of p-methoxy-azobenzene with palladium(II) chloride in presence of pyridine-2-thione or pyrimidine-2-thione as thiol-ligands have yielded cyclometallated products [Pd$_2$(μ-N, S-pyS)$_2$(μ-C, N- p-methoxy-azobenzene)$_2$] **10** (Fig. 10) and [Pd$_2$(μ-N, S-pymS)$_2$(μ-C, N-p-methoxy-azobenzene)$_2$] **11** (Fig. 11) similar to **8** and **9** respectively. Reaction of palladium(II) chloride with azobenzene in presence of 1-methyl-imidazoline-2-thione in CH$_3$CN yielded compound of composition, Pd$_2$(mimzS)$_2$(azobenzene)$_2$ **12.**



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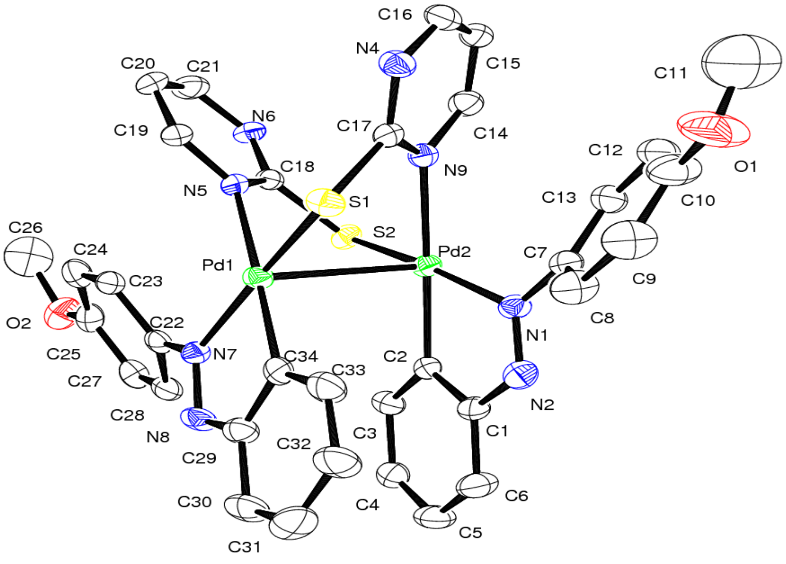


Fig. 11 Molecular structre of [Pd$_2$(μ-N, S-pymS)$_2$(μ-C, N- p-methoxy-azobenzene)$_2$] **11**

Mercury(II)

Reaction of HgCl$_2$ with azobenzene and pyrimidine-2-thione in acetonitrile and DMF was expected to involve metallation similar to that occurred in Pd^{II} case. However it has formed a very unusual polymeric product {Hg(-N=N-Ph)$_2$}$_n$ **13** (Fig. 12). Here a phenyl ring is chopped off and unit {Hg(-N=N-Ph)$_2$} repeats to generate the polymer. The formation of central 6-membered ring with Hg(N$_4$)Hg core is very unusual . Surprisingly, there was no coordination by a thio-ligand.

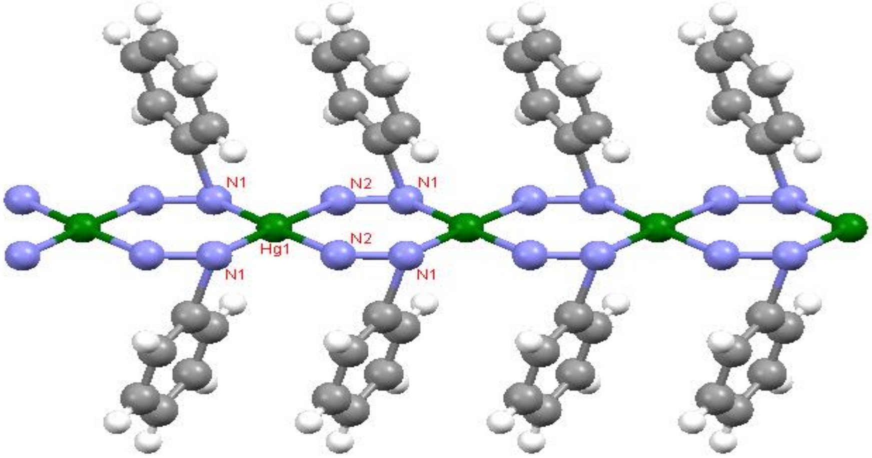
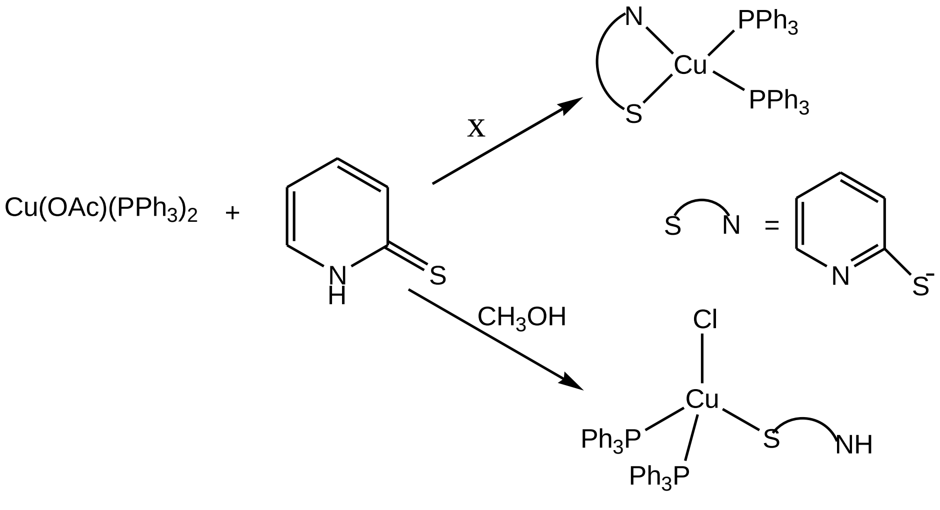


Figure 12. Structure of compound Hg(-N=N-Ph)$_2$}$_n$ **13**

III. Other complexes with Cu^I, Zn^{II}, Cd^{II} and Hg^{II}

Copper(I)

As copper(I) halide chemistry of pyridine-2-thione (pySH) is well documented, the chemistry without halide is less known and so Cu(OAc)(PPh$_3$)$_2$ was chosen as the starting compound. Its reactions with some thio-ligands have been carried out. Treatment of Cu(OAc)(PPh$_3$)$_2$ with pyridine-2-thione (pySH) in methanol was expected to form [Cu(pyS)(PPh$_3$)$_2$]. However, its x-ray has shown that the product is rather, [CuCl(η^1-S-pyS)(PPh$_3$)$_2$] **14** (Fig. 13). This product was same as reported earlier using CuCl Thus it appears that [Cu(pyS)(PPh$_3$)$_2$] when formed has abstracted Cl from the laboratory environment.



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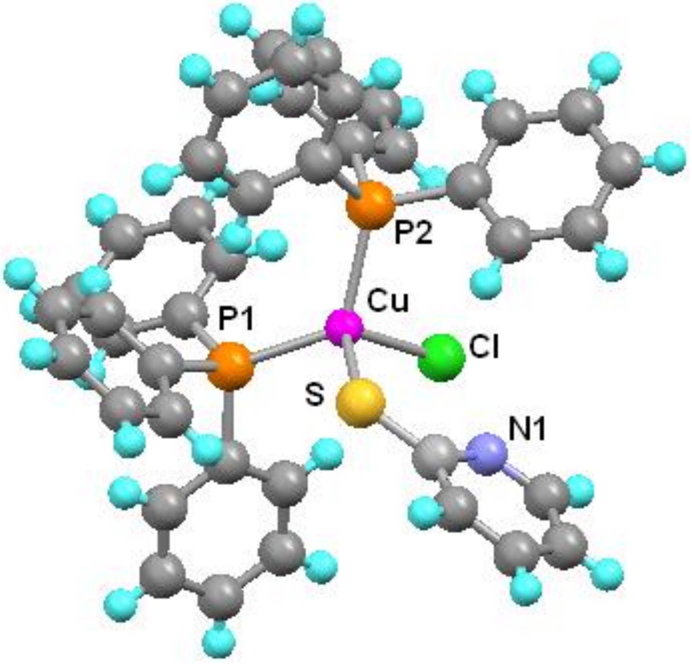
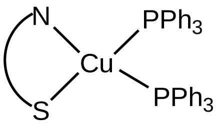


Fig. 13. Molecular structure of [CuCl(η^1-S-pyS)(PPh_3)$_2$] **14**

Interestingly Cu(OAc)(PPh_3)$_2$ with purine-6-thione (purSH) has given two products **15** (Fig. 14) and **16** (Fig. 15) without any abstraction of Cl from the atmosphere or the medium itself. Reaction of Cu(OAc)(PPh_3)$_2$ with trimercaptotriazine (H_3tmt) has formed **17a** and **17b** co-existing in the same crystal as shown by x-ray crystallography (Fig. 16). Treatment of Cu(OAc)(PPh_3)$_2$ with N-methylimidazoline-2-thione (mimzSH) has shown structure **18** (Fig.17) involving abstraction of Cl atom from the atmosphere. Reaction of copper(I) chloride with imdzSH-N-Me in presence of two moles of PPh_3 has yielded mononuclear complex, [CuCl(imdzSH-N-Me)(PPh$_3$)$_2$ **19** (Fig 18). The reaction of copper(I) iodide with a N-phenyl substituted imidazolidine-2-thione has formed a polynuclear complex **20** (Fig. 19).



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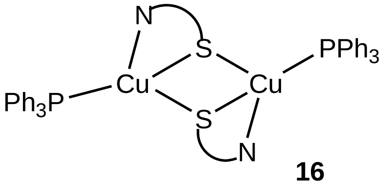

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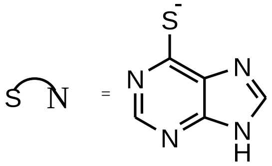
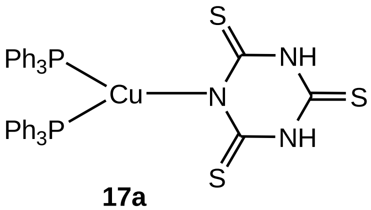
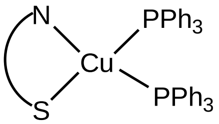
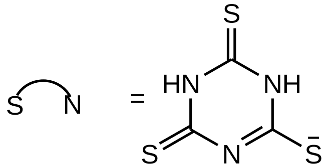


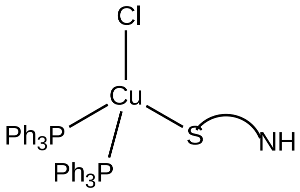


17a



17b





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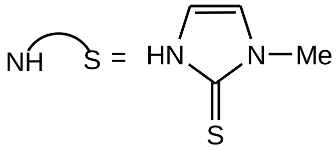


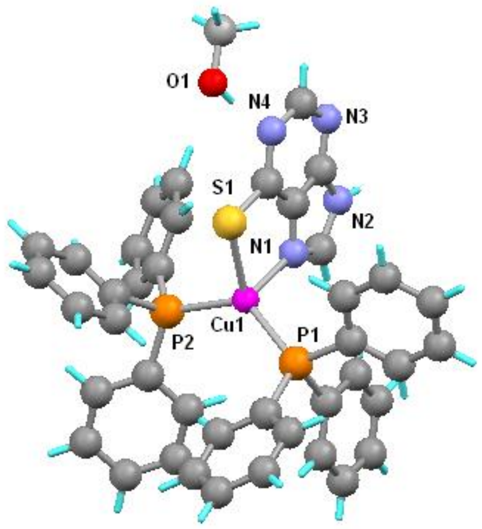


Fig. 14. Molecular structure of Cu(η^2-N,S-purS)(PPh$_3$)$_2$ **15**

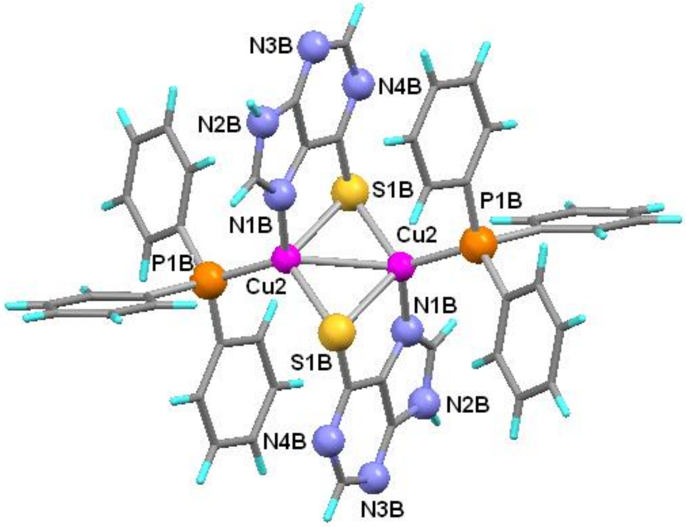


Fig. 15.Molecular structure of Cu$_2$(purS)$_2$(PPh$_3$)$_2$ **16**

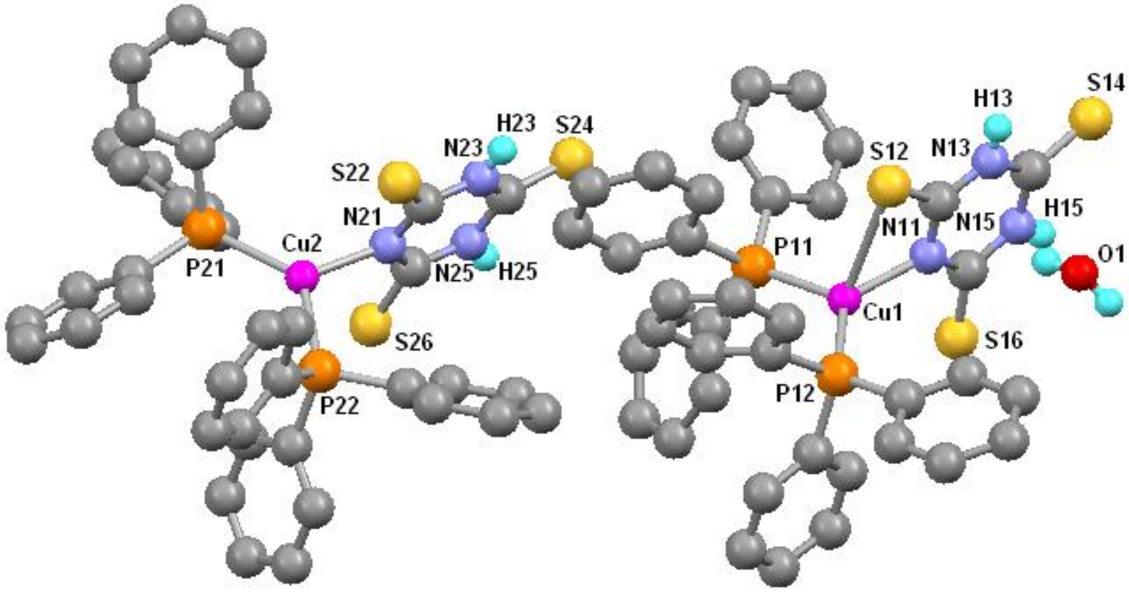


Fig. 16 Molecular structure of Cu(κ^1N-H_2tmt)(PPh_3)$_2$ **17a** and Cu(κ^2-N,S- H_3tmt)(PPh3)$_2$ **17b**
(both co-exist)

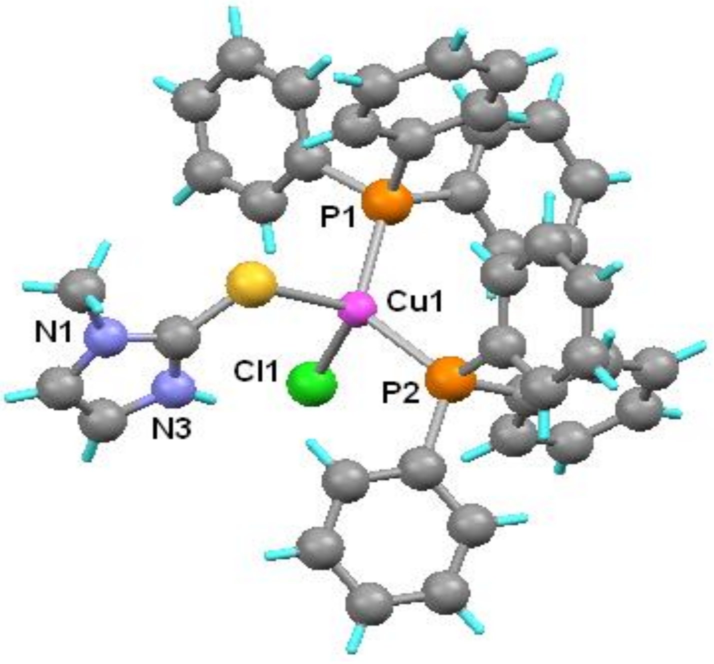


Fig.17. Structure of compound [CuCl(mimzSH)(PPh_3)$_2$ **18**.

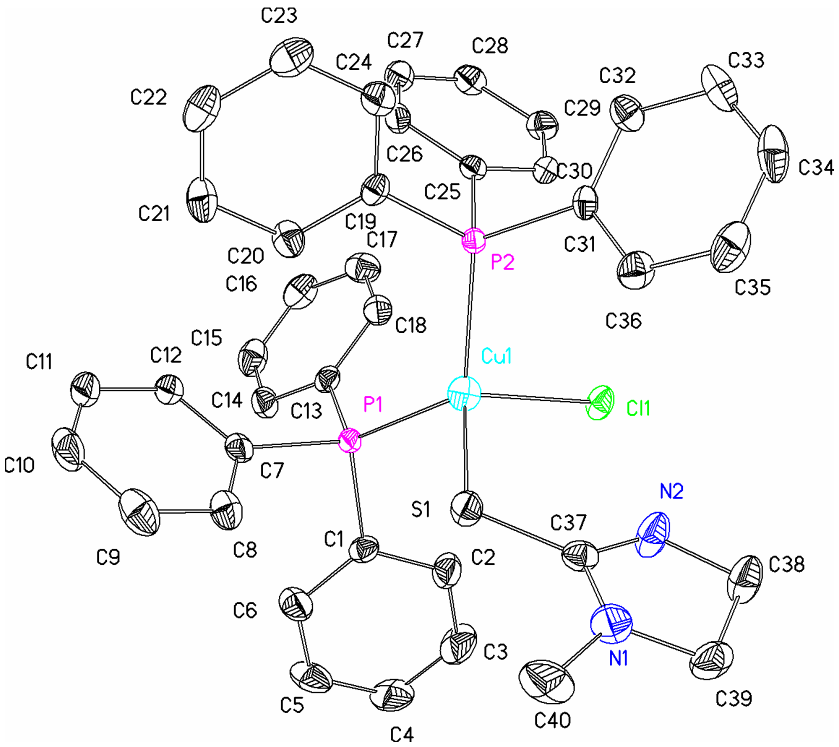


Fig.18. Structure of compound [CuCl(imdzSH-N-Me)$(PPh_3)_2$ **19**.

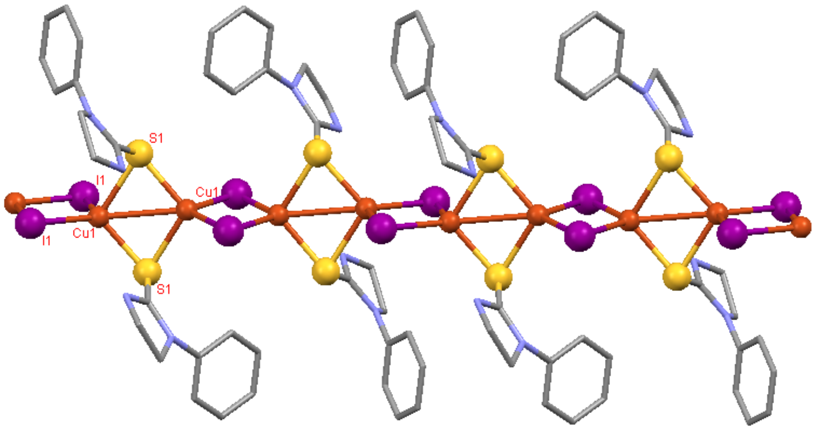
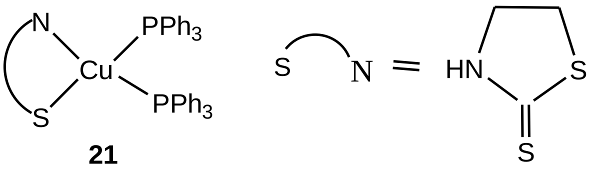
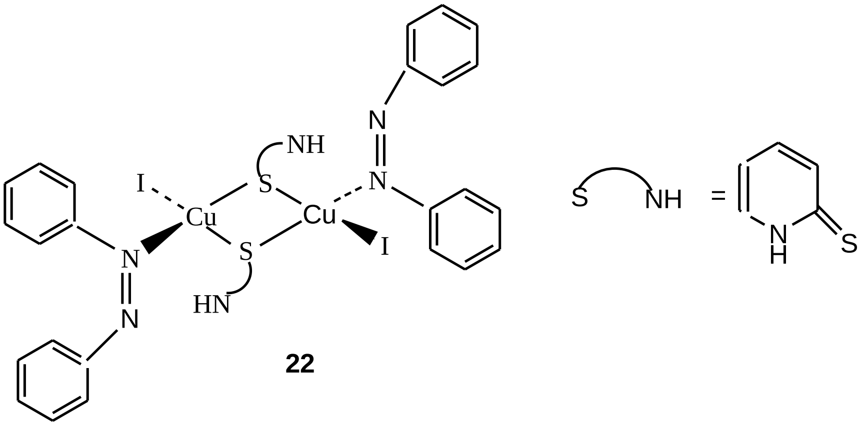


Figure 19. Structure of polymer {CuI(imdzSH-N-Ph}$_n$ **20**.

Treatment of Cu(OAc)$(PPh_3)_2$ with thiazolidine-2-thione in methanol has formed a tetrahedral complex, Cu(tzdS)$(PPh_3)_{2,}$ **21**. Treatment of copper(I) iodide with pyridine-2-thione followed by the addition of azobenzene has formed a dimeric complex, $[CuI(pySH)(azobenzene)]_2$ **22**.



21



22

Zinc, Cadmium and mercury

Here in this section some complexes of heterocyclic thiones with Zn(II), Cd(II) and Hg(II) are described. Among zinc(II) salts, the reaction of zinc(II) iodide with 1-methylimidazolidine-2-thione (imdzSH-N-Me) in 1:2 molar ratio in dry ethanol yielded complex of composition [ZnI$_2$(imdzSH-N-Me)$_2$] **23**. Its x-ray crystal structure has shown that geometry is tetrahedral (Fig. 20). Reaction of zinc(II) chloride with 1-ethylimidazolidine-2-thione (imdzSH-N-Et) in methanol has yielded a tetrahedral complex, Zn(η^1-S-imdzSH-Et)Cl$_2$ **24** (Fig. 21).

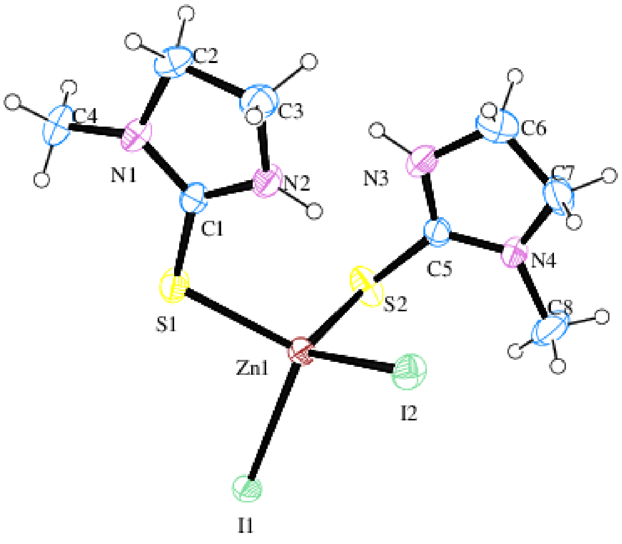


Fig.. 20. Structure of compound [ZnI$_2$(imdzSH-N-Me)$_2$] **23**

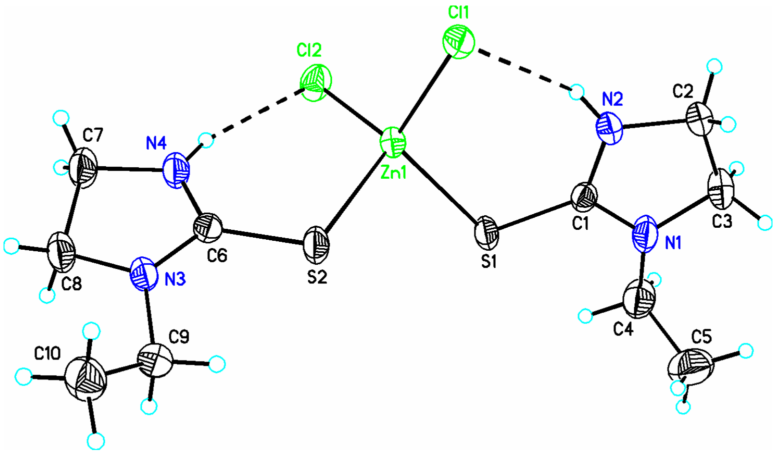


Fig. 21. Molecular Structure of Zn(η^1-S-imdzSH-Et)Cl$_2$ **24**

Similarly, reactions of cadmium(II) bromide/ iodide with imdzSH-N-Et and imdzSH-N-Me respectively have formed complexes of composition, [CdBr$_2$(imdzSH-Et)$_2$] **25** (Fig 22)**,** Cd(η^1-S-imdzSH-Me)$_2$Br$_2$ **26** and [CdI$_2$(imdzSH-N-Me)$_2$] **27** (Fig. 23). The x-ray crystal of these complexes have shown their tetrahedral structures. Finally, mercury(II) chloride/iodide have formed complexes, [HgCl$_2$(imdzSH-N-Me)$_2$] **28** (Fig. 24)**,** Hg(η^1-S-imdzSH-Pr^n)$_2$Cl$_2$ **29** (Fig. 25) and [HgI$_2$(imdzSH-N-Me)$_2$] **30** (Fig. 26).

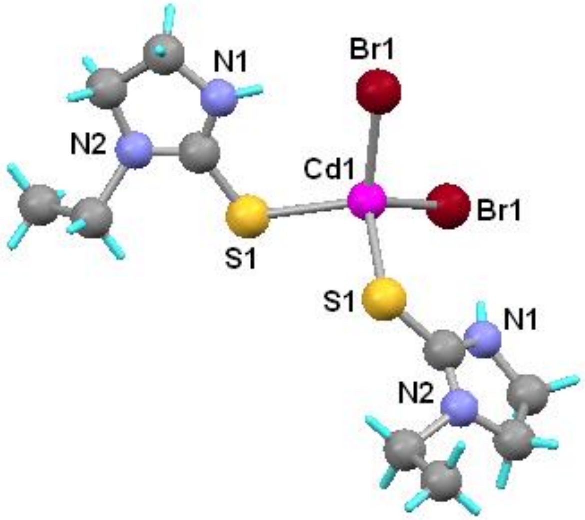


Fig. 22. Molecular structure of Cd(η^1-S-imdzSH-Et)$_2$Br$_2$ **25**

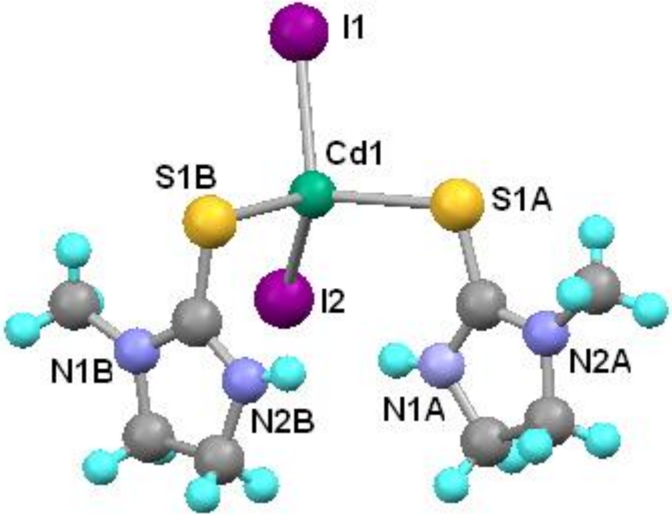


Fig. 23. Molecular structure of Cd(η^1-S-imdzSH-Me)$_2$I$_2$ **27**

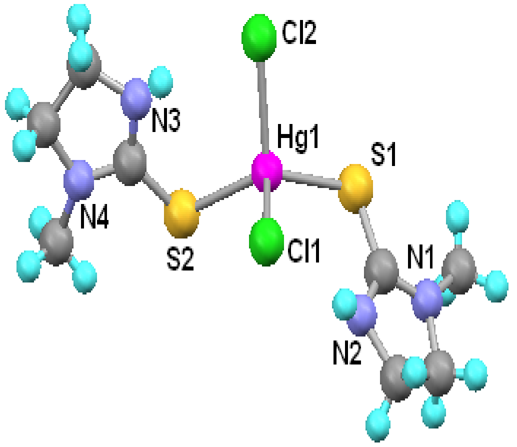


Fig.24.Str.of Hg(η^1-S-imdzSH-Me)$_2$Cl$_2$ **28**

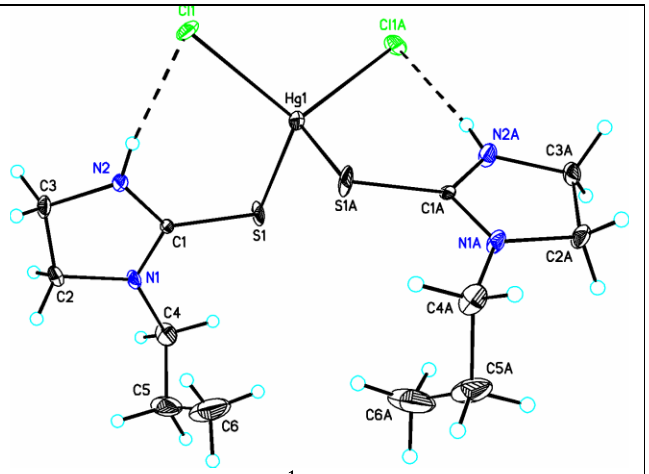


Fig.25.Str.of Hg(η^1-S-imdzSH-Pr^n)$_2$Cl$_2$ **29**

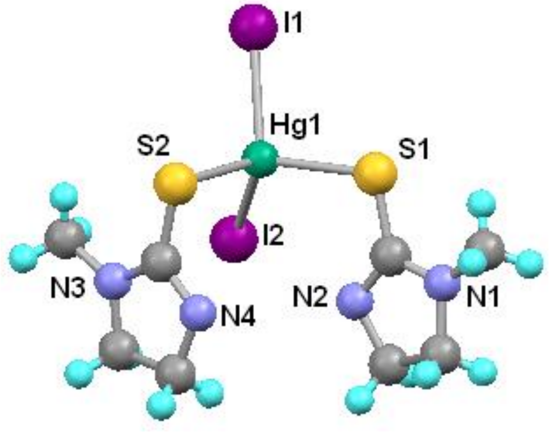


Fig 26. Str. of Hg(η^1-S-imdzSH-Me)$_2$I$_2$ **30**

IV. List of compounds studied.

Table 1. gives a summary of various complexes characterized.

Compd. No.	Formula	Compd. No.	Formula
1	[Pd^{I}Pd^{II} (κ^2-N,S-PyS)$_3$(dppm)]	**16**	Cu$_2$(purS)$_2$(PPh$_3$)$_2$
2	[Pt(dppm)(η^1-S-pyS)$_2$]	**17a**	a. Cu(H$_2$tmt)(PPh$_3$)$_2$ b. Cu(H$_3$tmt)(PPh3)$_2$

3	$[\mathrm{Pd}_2((\mu\text{-N, S- pyS})_4]$	**18**	$[\mathrm{CuCl}(\text{mimzSH})(\mathrm{PPh}_3)_2$
4	$[\mathrm{Pd}_2(\mu\text{-N,S-bzimS})_2(\eta^1\text{-S-bzimS})(\mathrm{PPh}_3)_3]$	**19**	$\mathrm{Cu}(\eta^1\text{-S-imzdSH-Me})(\mathrm{PPh}_3)_2\mathrm{Cl}$
5	$[\mathrm{Pd}(\eta^1\text{-S-imzSH})_4]\mathrm{Cl}_2{\cdot}2\mathrm{H}_2\mathrm{O}$	**20**	$\{\mathrm{CuI}(\text{imdzSH-N-Ph}\}_n$
6	$[\mathrm{Ru}(\eta^2\text{-N, S-pyS})_2(\text{P, P-dppm})]$	**21**	$\mathrm{Cu}(\text{tzdS})(\mathrm{PPh}_3)_2$
7	$[\mathrm{Pd}_2(\mu\text{-N, S-pyS})_2(\mu\text{-C, N-azobenzene})_2]$	**22**	$[\mathrm{CuI}(\text{pySH})(\text{azobenzene})]_2$
8	$[\mathrm{Pd}_2(\mu\text{-N, S-pymS})_2(\mu\text{-C, N-azobenzene})_2]$ **8**	**23**	$[\mathrm{ZnI}_2(\text{imdzSH-N-Me})_2]$
9	$[\mathrm{Pd}(\eta^1\text{-S- imzdSH-Me})(\eta^2\text{-C, N-azobenzene})\mathrm{Cl}]$	**24**	$\mathrm{Zn}(\eta^1\text{-S-imdzSH-Et})\mathrm{Cl}_2$
10	$[\mathrm{Pd}_2(\mu\text{-N, S-pyS})_2(\mu\text{-C, N- p-methoxy-azobenzene})_2]$	**25**	$[\mathrm{CdBr}_2(\text{imdzSH-Et})_2]$
11	$[\mathrm{Pd}_2(\mu\text{-N, S-pymS})_2(\mu\text{-C, N- p-methoxy-azobenzene})_2]$	**26**	$\mathrm{Cd}(\eta^1\text{-S-imdzSH- Me})_2\mathrm{Br}_2$
12	$\mathrm{Pd}_2(\text{mimzS})_2(\text{azobenzene})_2$	**27**	$\mathrm{Cd}(\eta^1\text{-S-imdzSH-Me})_2\mathrm{I}_2$
13	$\{\mathrm{Hg}(\text{-N=N-Ph})_2\}_n$	**28**	$\mathrm{Hg}(\eta^1\text{-S-imdzSH-Me})_2\mathrm{Cl}_2$
14	$[\mathrm{CuCl}(\eta^1\text{-S-pyS})(\mathrm{PPh}_3)_2]$	**29**	$\mathrm{Hg}(\eta^1\text{-S-imdzSH-Pr}^n)_2\mathrm{Cl}_2$
15	$\mathrm{Cu}(\eta^2\text{-N,S-purS})(\mathrm{PPh}_3)_2$	**30**	$\mathrm{Hg}(\eta^1\text{-S-imdzSH-Me})_2\mathrm{I}_2$

List of publications

1. Heterocyclic-2-thione derivatives of metals incorporating cyclopalladated azobenzenes of variable nuclearity and N, S-bridged 1D polymer of [bis(pyridine-2-thiolato)mercury(II)], **T. S. Lobana,** A. K. Sandhu, G. Hundal, J.P. Jasinski, **New J. Chem** 46 (2022) 2722-2729.

2. Synthesis, Spectroscopy, Luminescence and Structures of Trinuclear and Hexanuclear Cu^{I} clusters with 2, 4, 6-trimercaptotriazine, **T.S. Lobana**, Amanpreet Kaur Sandhu, Geeta Hundal, and Jerry P. Jasinski, **J. Chem. Crystallogr.** https://doi.org/10.1007/s10870-021-00897-y; page 1-13, on line, 2021

3. Cyclopalladation of azobenzenes and their reactivity towards N-substituted imidazolidine-2-thiones and allied ligands : synthesis, structures, spectroscopy and ESI-mass studies, Amanpreet Kaur Sandhu, Tarlok S. Lobana, Balkaran S. Sran, Geeta Hundal, Jerry P. Jasinski**, J. Organomet. Chem**. 861 (2018) 112-124.

4. Dinuclear Pd^{II}/Pt^{II} complexes $[M_2(phosphine)_n(thio\text{-}ligand)_3]Cl$ incorporating N, S-bridged pyridine-2-thiolate and benzimidazoline-2-thiolate, Tarlok S. Lobana, Amanpreet Kaur Sandhu, Rakesh K. Mahajan, Geeta Hundal, Sushil K. Gupta, Ray J. Butcher, Alfonso Castineiras, **Polyhedron,** 127 (2017) 25–35.

5. Synthesis, spectroscopy, fluorescence and crystal structures of cyclopalladated dinuclear complexes with C, N-chelating azobenzenes and chelating azobenzenes and N, S-bridging heterocyclic-2-thiolates, T. S. Lobana, Amanpreet.Kaur Sandhu,, A. Kaur, and J. P. Jasinski, **J. Organomet. Chem.** 751 (2014) 519 -524**.**

6. Metal derivatives of heterocyclic-2- thiones:Crystal Structures of [bis(diphenyl -phosphino)-propane][bis(pyrimidine-2-thiolato)] ruthenium(II) and [bis(diphenyl phosphino)methane][bis(pyridine-2-thiolato)]ruthenium(II), T.S. Lobana, P.J, Kaur, Amanpreet Kaur, R.J. Butcher, **Z. Anorg. Allg. Chem**. 638 (2012)195-200.