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Structure and Stereochemistry of Vo(IV), Co(II), Ni(II) and Cu(II) Complexes of (N,N,S) Donor Ligands

Satendra Kumar[1*]

[1]*Department of Chemistry, Government Degree College, Hempur, Bisalpur (Pilibhit)*

[*]*Corresponding author, drsatendrakmr@gmail.com*

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Abstract

The transition metal complexes of Vo, Co, Ni and Cu with multidentate ligand is important due to the growing applications in catalysis and therapeutics, Vanadium in traces has multiple biological roles, therapeutic value in small doses and toxic in excess. Vanadium containing compounds have their utility as insulin mimetic and antiamoebic agent. It is also suggested that vanadium could be considered as a representative of a new class of non platinum metal antitumor agents. The studies of these compounds are very important as medicinal properties in correlation with their structure have great interaction.

Keywords: Stereochemistry, Transition metal complexes, Biological activity, vandyl complexes

INTRODUCTION:

The coordination chemistry of oxovanadium(IV) with multidentate ligand is important due to the growing applications in catalysis[1,2] and therapeutics[3], Vanadium in traces has multiple biological roles, therapeutic value in small doses and toxic in excess. Vanadium containing compounds have their utility as insulin mimetic[4,5] and antiamoebic agent[6]. It is also suggested that vanadium could be considered as a representative of a new class of non platinum metal antitumour agents.[7]

The significant correlation between vanadate and phosphate ions at physiological pH− in blood plasma has emerged as a point of interest. Vandate inhibits the phosphate metabolizing enzymes (phosphatases). It also affects the organism by entering through phosphate and sulphate channels[8,9].

V(V)−V(IV)/V(IV)−V(III) redox systems are very significant from reactivity view point. A comprehensive report on biochemical redox profile of vanadium has appeared recently[10]. Vanadium compounds have been utilized in various homogeneous/heterogenous catalytic processes[11] as they exhibit good synthetic potential[12]. Doped vanadium compounds have been used in synthesizing nanoparticles[13].

DISCUSSION:

Distortion in geometry of oxovanadium(IV) complexes from trigonal bipyramidal; square pyramidal to octahedral also a subject of interest for structural studies[14–17]. Sengupta etal[18] and Maurya[19] have reported on diketonate complexes of oxovanadium(IV). Recent reports on oxovanadium(IV) Schiff base and mixed ligand complexes are also available[20–21]. Gillespie[22] studied in detail the stereochemistry of five coordinated complexes of transition metal ions and suggested for transition elements with d^0 and d^{10}–configuration, the trigonal bipyramidal structure on the interaction of five electron pairs of the valency shell of ligands. For other d^1–d^9 configuration the interaction between valency shell electron pairs of the ligands with d–shell electrons generate square pyramid[23] being more stable than the trigonal bipyramid. The ligand field stabilization energies for d^1 to d^9 electrons is less for trigonal bipyramidal arrangement of the ligands than for square pyramid and the interaction between the bonding electron pairs themselves favours a trigonal bipyramidal arrangement. When the interaction of the ligand electron pair is relatively more important than their interaction with the non bonding d–electrons, it is the case in complexes with large amount of covalent character a trigonal bipyramid geometry is expected. However when the interaction between the bonding and the d–shell electrons predominates (in complexes with essentially ionic bonding) then a square pyramid geometry is expected.

In five coordinated vanadyl complexes the interaction of the bond electron pairs with the single non bonding d–electron of vanadium is probably so great that a square pyramidal structure is preferred to a trigonal bipyramid.

Available data show that it is not possible to accept that the complexes which are largely covalent favour a trigonal bipyramidal arrangement and complexes with essentially ionic bonding favour a square pyramidal structure in the case of five coordinated complexes of transition metals. In fact, $VO(acac)_2$ which is an essentially covalent compound, has a square pyramidal structure. Bis oxalate oxovanadium(IV) anion which is fairly covalent has also a square pyramidal structure.

In vandyl complexes the multiple bond of the (V=O) is responsible for the square pyramidal structure rather than the interaction of the bond electron pair with, the single non bonding d–electron. If d^1 electron was mainly responsible for the square pyramidal structure, Ti(III) belong to d^1–system should also favour square pyramidal structure. In practice, titanium(III) generally forms octahedral complexes.[24,25]

The concept of trans effect may be used to explain the stereochemistry of five coordinated complexes of VO(IV). Negatively charged ligands have greater trans effect, so also the ligands which form strong π–bonds. Accordingly one would expect weak bonding of the ligand in the site opposite to the oxide oxygen due to the trans effect of the multiply bonded vanadyl oxygen. As a result of the trans effect of the oxide oxygen the ligand in the sixth place may sometimes be excluded during solidification of the compounds.[26,27] It is to be noted however that such five coordinated square pyramidal structures as in $VO(acac)_2$ and $VO(C_2O_4)_2^{2-}$ are not expected except in the solid. In solution it is likely that the sixth position will be loosely held by a solvent molecule at a longer distance than the other ligands in the square plane.

The trans effect alone, however fails to explain the hexa coordination of vanadium normally observed with monodentate ligands like H_2O, DMSO, NCS^-, CN^- etc. It is therefore worth pointing out from a study of a number of VO(IV)[28–30] complexes that when two or all the four positions in the square plane are occupied by a bidentate ligand(s) the vanadyl complexes are generally penta coordinated. Also it appears that square

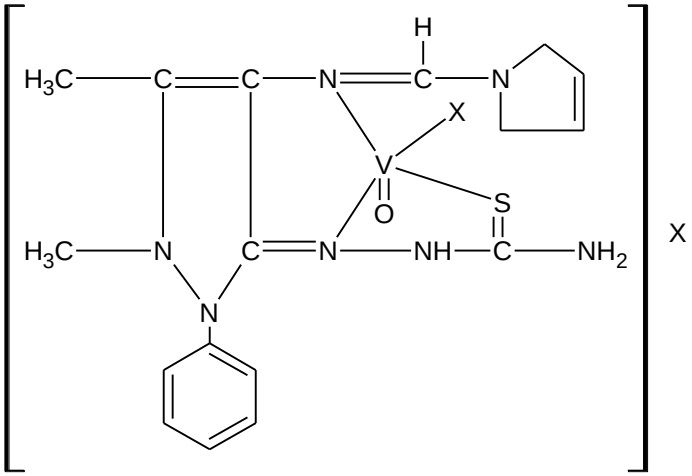
pyramidal complexes of transition metals with monodentate ligands are rare. This indicate that the interaction of the ligands with the metal is of some importance in deciding the stereochemistry of the complexes. It is likely that the interaction is greater in chelates than in monodentate complexes. It is known that the stability of the complexes is greatly increased by the coordination with polydentate ligands. This is also clearly reflected in the structures of $VO(acac)_2$ and $[VOSO_4.4H_2O]H_2O$. In the latter, the metal atom is in the plane formed by the four water oxygens while in the former, the metal atom is above the base of the pyramid formed by the oxygens of acetylacetone ligands. When the vanadium atom is raised above the base of the pyramid, the effective approach of the ligand in the sixth place, trans to the oxide oxygen is hindered as compaired to the metal coplanar with the donor atoms in the square plane. This, in addition to the trans effect is probably responsible for five–coordinated structures in vanadyl(IV) complexes with one or two bidentate ligands. Some exceptions are found to this observations[31,32] e.g., antipyrine (Apy) complex of $VO(ClO_4)_2$, i.e., $[VO(Apy)_4](ClO_4)_2$ contains five–coordinated vanadium(IV) although Apy is a monodentate ligand. Since Apy is a bulky ligand, steric effects may be responsible in deciding the stereochemistry of the complexes. In the case of complex like $VO(Phenanthroline)_2–Cl_2$, where all the four positions in the square plane are occupied by the two bidentates, it is hexa–coordinated, one chloride ion coordinated $[VO(Phen)_2Cl]Cl$. This may be due to the negative charge on the chloride ion and its relatively smaller size. Also in $VO(acac)_2$, the sixth position can be filled by more basic ligands like pyridine, CH_3NH_2 etc. It is found that the ligands occupying the sixth position in such compounds can be removed whereas the bidnetate ligands are strongly bonded. Out ligands like $(CH_3)_3N$, 2,5–dimethylpyridine and acridine do not fill the sixth position due to steric hindrance. Ligands like H_2S, methanol and ethanol could not coordinate due to their lesser basic strength(15).

The stereochemistry of five–coordinated complexes $VOC_2O_4.2H_2O$, $VOC_2O_4.2DMSO$ can have either a trigonal bipyramidal or a rectangular pyramidal arrangement. A trigonal bipyramidal structure is preferred to a tetragonal pyramid for a five–coordinated complex from ligand–ligand repulsion consideration (1). However, X–ray diffraction and e.s.r. studies of five– coordinated bisacetyl acetonato oxovanadium(IV)[33,34], $VO(acac)_2$ and bisoxalato oxovanadium(IV) ion[35], $VO(C_2O_4)^{2-}$, show that they have a rectangular pyramidal structure. By close analogy of the electronic spectra of most of the other oxovanadium(IV) complexes(14,16,19) with these two complexes of VO^{2+}, it was concluded that they also have a square pyramidal structure. Thus with close analogy of the present complexes of VO^{2+} with thiosemicarbazones with earlier studies, it is concluded that these penta coordinated complexes possess square pyramidal structure.[36–40]

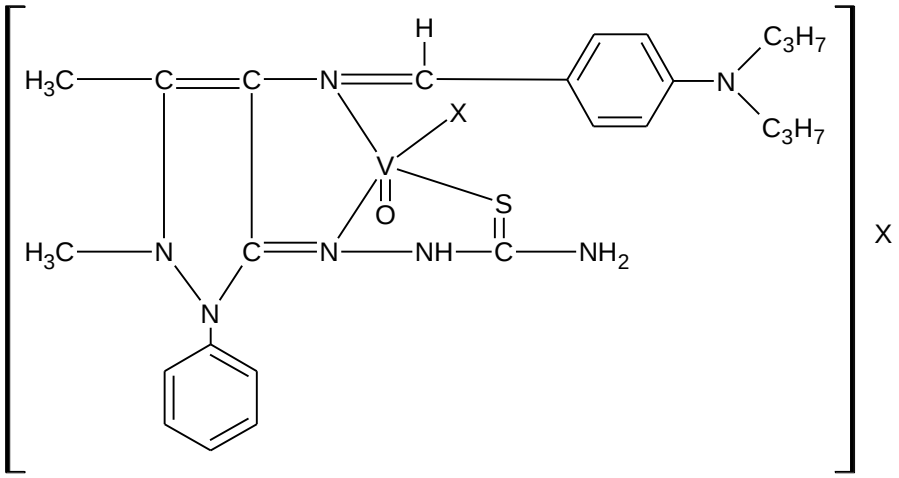
The chemistry of thiosemicarbazone and some of their derivatives has been reviewed by Kurzer and Wilkinson[35].

CONCLUSION:

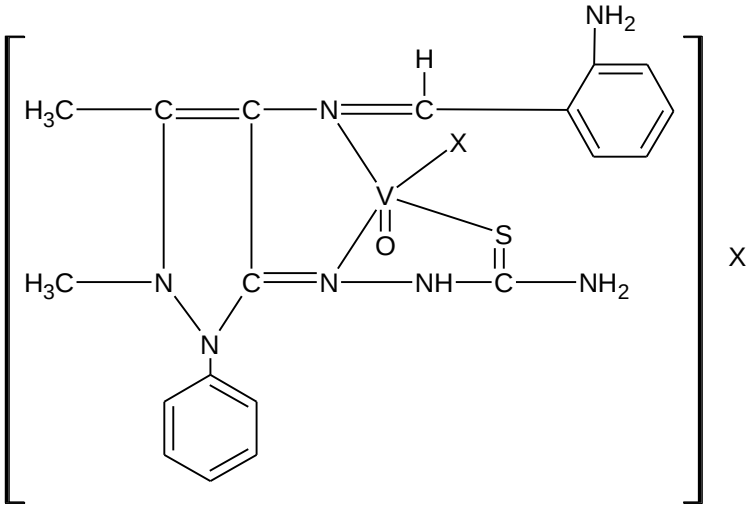
Hydrazine group of these compounds display normal activity towards carbonyl compounds and are expected to yield mono derivatives which contain N, O and S–donor atoms and therefore the derivatives can function as suitable ligands for transition metals. Variety of metal complexes of symmetrical thiosemicarbazones derived from Amino Antipyrine, aldehydes and thiosemicarbazones have been prepared and the isolated ligands, metal complexes of stoichiometry 1:2/1:3 (M : L) have been prepared from the reaction of these ligands with their corresponding metal salt. On the basis of analytical and spectral data octahedral structures have been proposed.



(a) **[VO($C_{17}H_{21}N_7S$)X]X (X= Cl, Br, I, NO_3 or NCS) (C.N. = 5)**

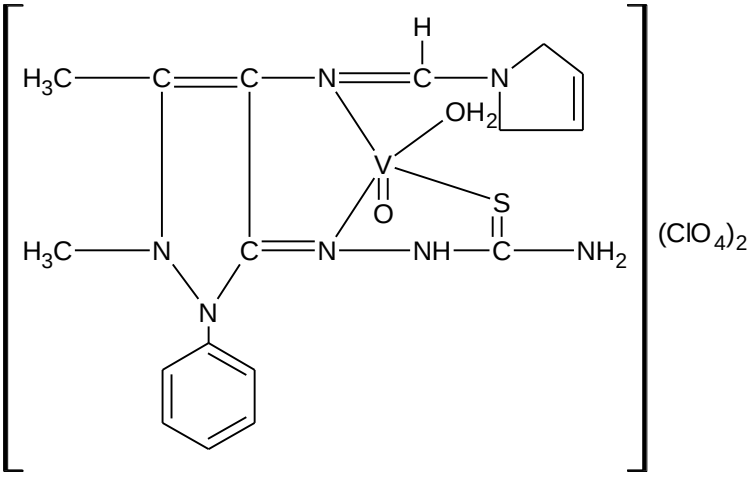


(b) **[VO($C_{25}H_{33}N_7S$)X]X (X= Cl, Br, I, NO_3 or NCS) (C.N. = 5)**

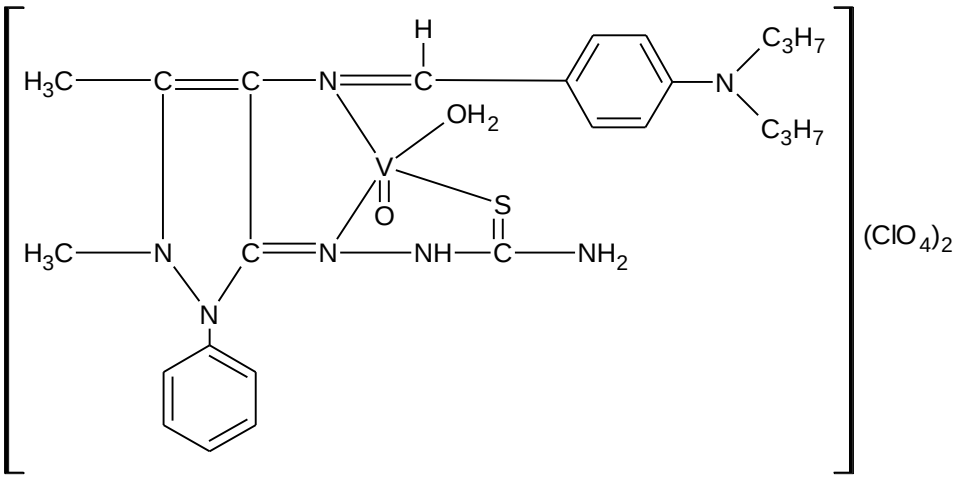


(c) **[VO($C_{19}H_{21}N_7S$)X]X (X= Cl, Br, I, NO_3 or NCS) (C.N. = 5)**

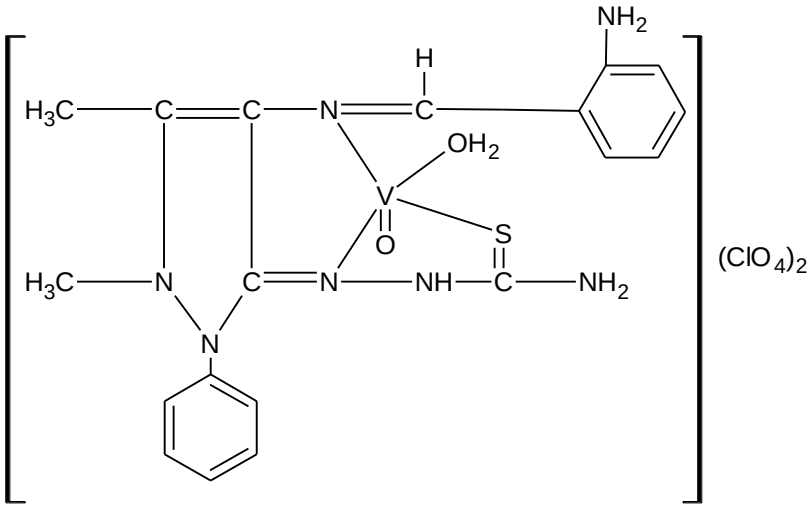
Fig. 7.1 PROBABLE STRUCTURES OF OXO–VANADIUM COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTIPYRINE



(d) **[VO($C_{17}H_{21}N_7S$)H_2O](ClO_4)$_2$ (C.N. = 5)**

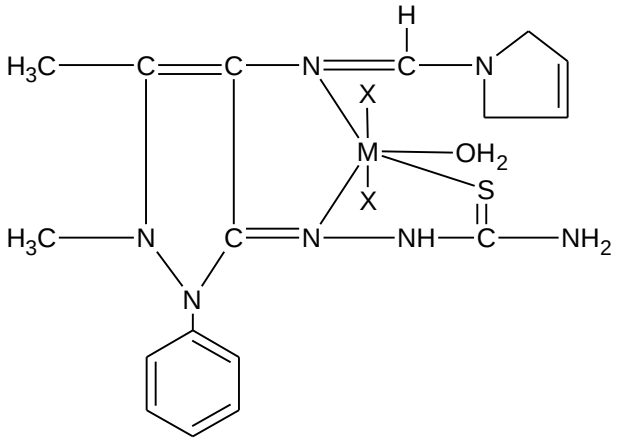


(e) **[VO(C25H33N7S)H2O](ClO4)2 (C.N. = 5)**

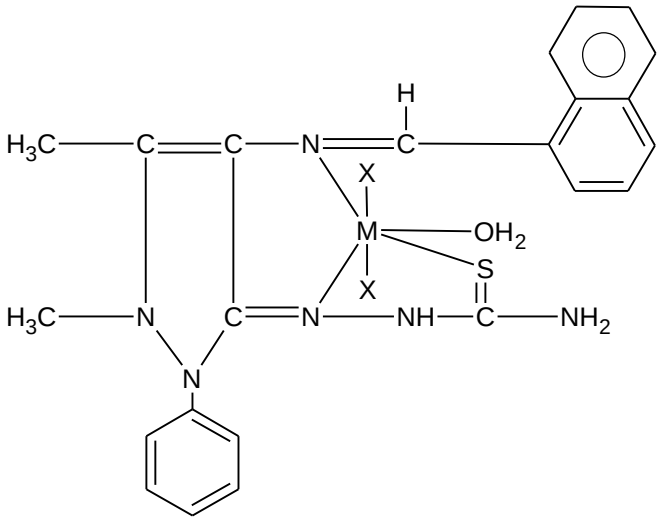


(f) **[VO(C19H21N7S)H2O](ClO4)2**

Fig. 7.2 PROBABLE STRUCTURES OF OXO–VANADIUM COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTIPYRINE

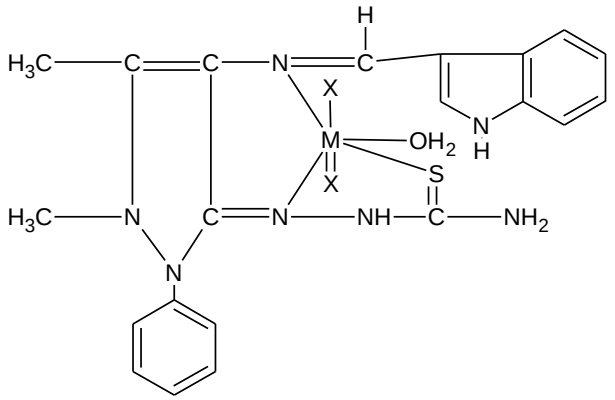


(a) **[M($C_{17}H_{21}N_7S$)H_2O X_2] (M= Co or Ni), (X=Cl, NO_3, NCS or CH_3COO) (C.N. = 6)**

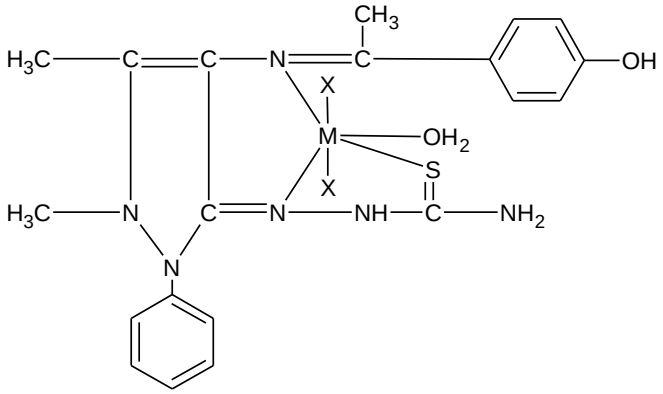


(b) **[M($C_{23}H_{22}N_6S$)H_2O X_2] (M= Co or Ni), (X=Cl, NO_3, NCS or CH_3COO) (C.N. = 6)**

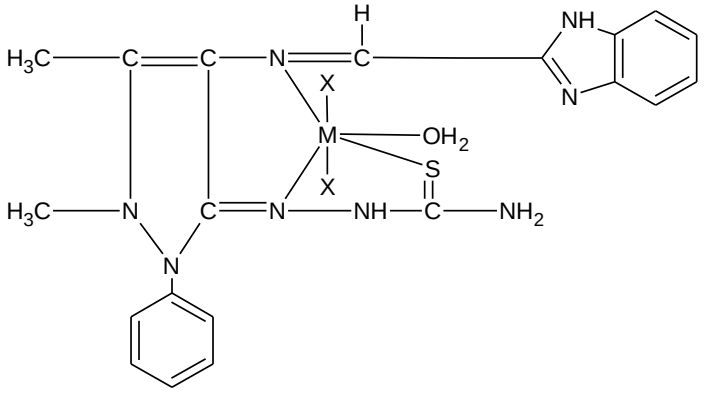
Fig. 7.3: PROBABLE STRUCTURES OF Co/Ni COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTIPYRINE



(c) **[M($C_{21}H_{21}N_7S$)H_2O X_2] (M= Co or Ni), (X=Cl, NO_3, NCS or CH_3COO) (C.N. = 6)**

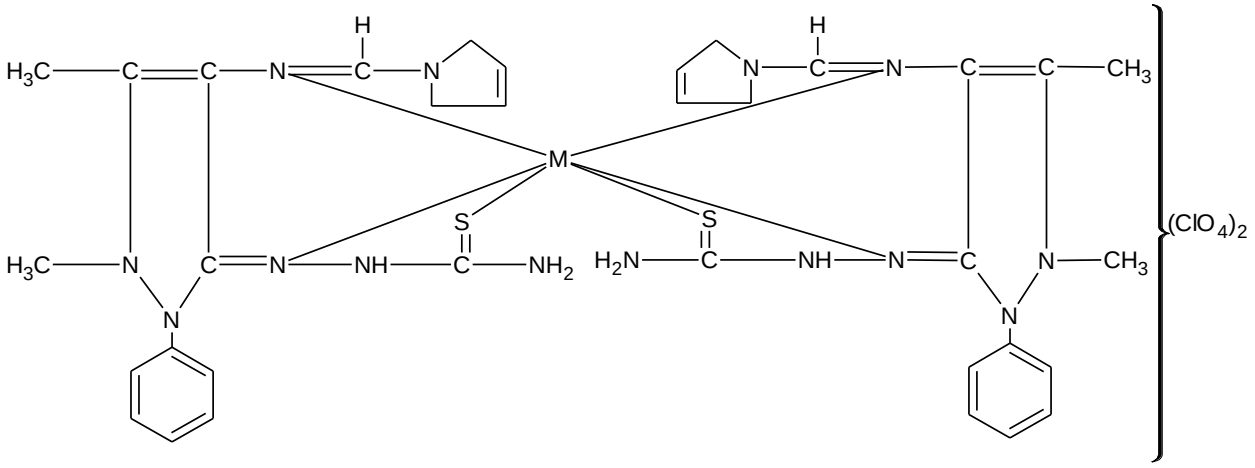


(d) **[M($C_{20}H_{22}N_6OS$)H_2O X_2] (M= Co or Ni), (X=Cl, NO_3, NCS or CH_3COO) (C.N. = 6)**

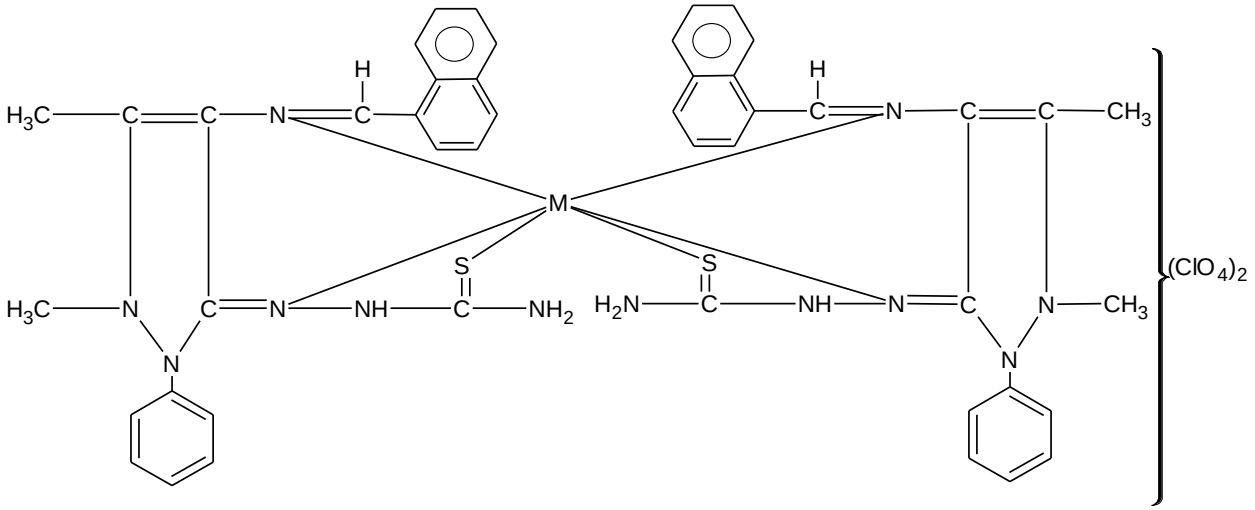


(e) **[M($C_{20}H_{20}N_8S$)H_2O X_2] (M= Co or Ni), (X=Cl, NO_3, NCS or CH_3COO) (C.N. = 6)**

Fig. 7.4: <u>PROBABLE STRUCTURES OF Co/Ni COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTIPYRINE</u>

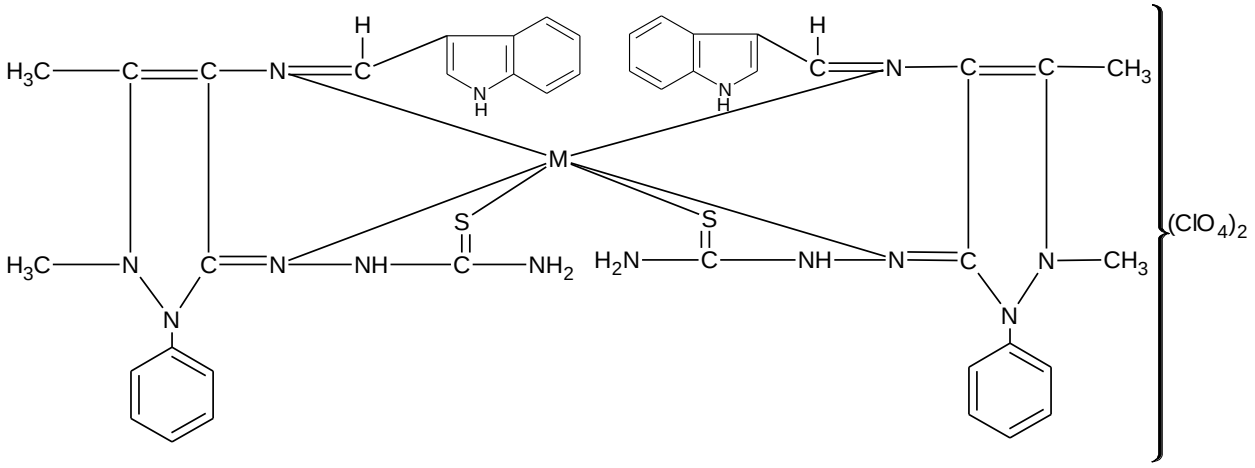


(a) **$[M(C_{17}H_{21}N_7S)](ClO_4)_2$ (M = Co or Ni), (C.N. = 6)**

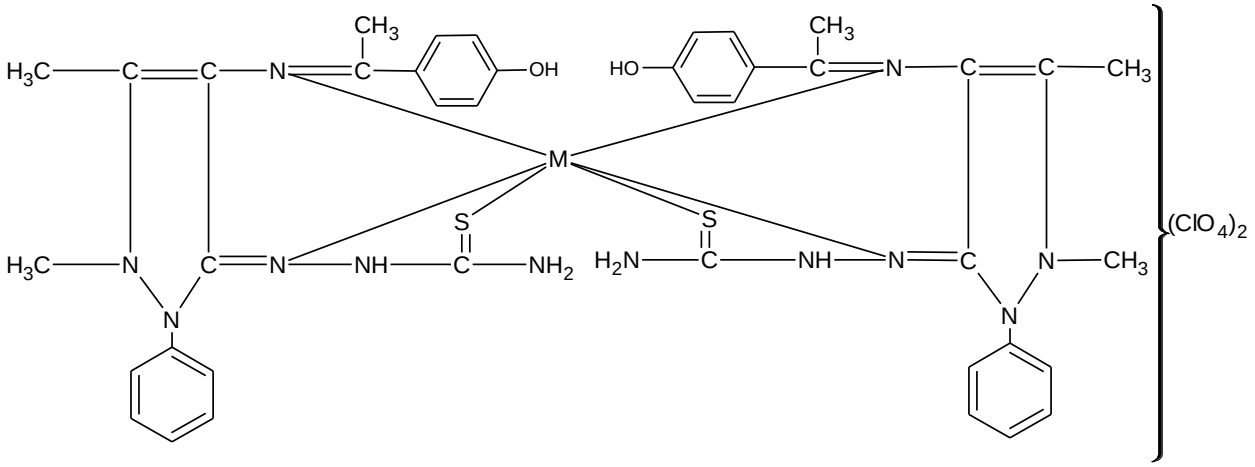


(b) **$[M(C_{23}H_{22}N_6S)_2](ClO_4)_2$ (M = Co or Ni), (C.N. = 6)**

FIG. 7.5: ***PROBABLE STRUCTURES OF Co/Ni PERCHLORATO COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTYPYRINE***

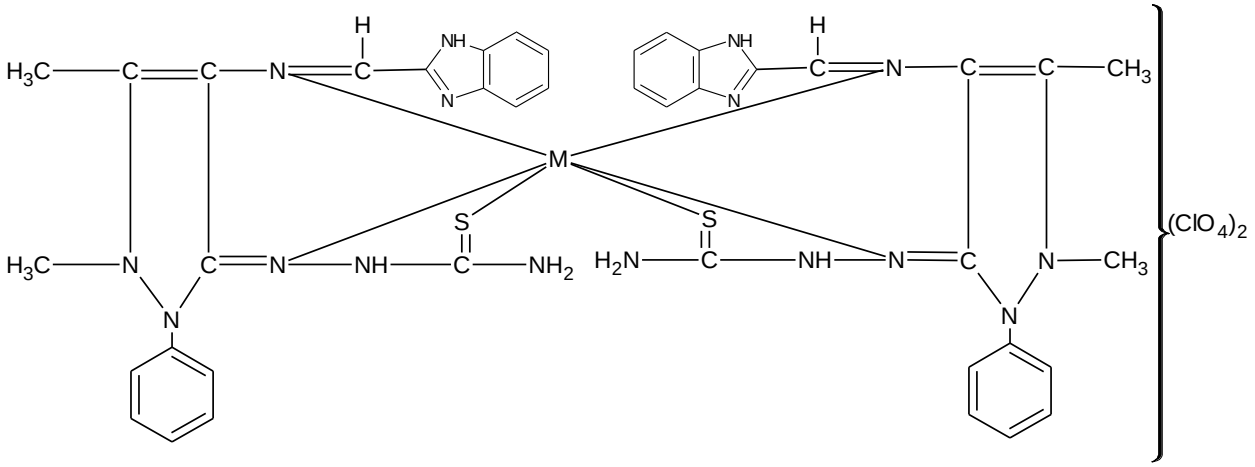


(a) **$[M(C_{21}H_{21}N_7S)_2](ClO_4)_2$ (M = Co or Ni), (C.N. = 6)**



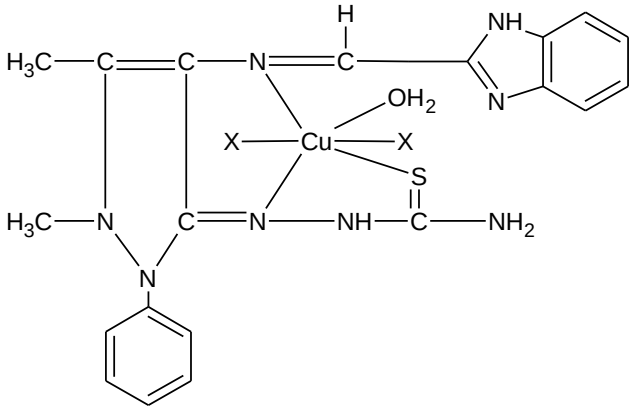
(b) **$[M(C_{20}H_{22}N_6OS)_2](ClO_4)_2$ (M = Co or Ni), (C.N. = 6)**

FIG. 7.6: *PROBABLE STRUCTURES OF Co/Ni PERCHLORATO COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTYPYRINE*



(e) $[M(C_{20}H_{20}N_8S)_2](ClO_4)_2$ (M = Co or Ni), (C.N. = 6)

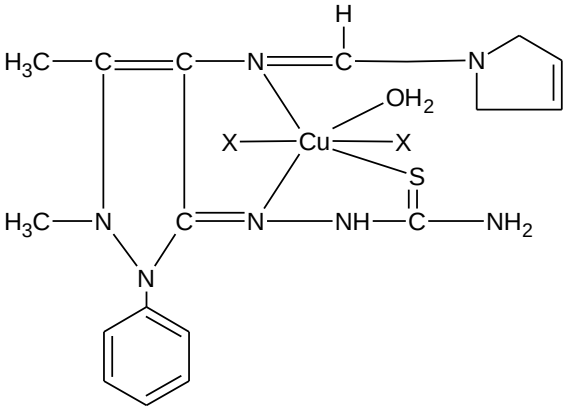
FIG. 7.7: *PROBABLE STRUCTURES OF Co/Ni PERCHLORATO COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTYPYRINE*



(a) $[Cu(C_{20}H_{20}N_8S)H_2O\ X_2]$

(X=Cl, Br, NO_3, NCS or CH_3COO)

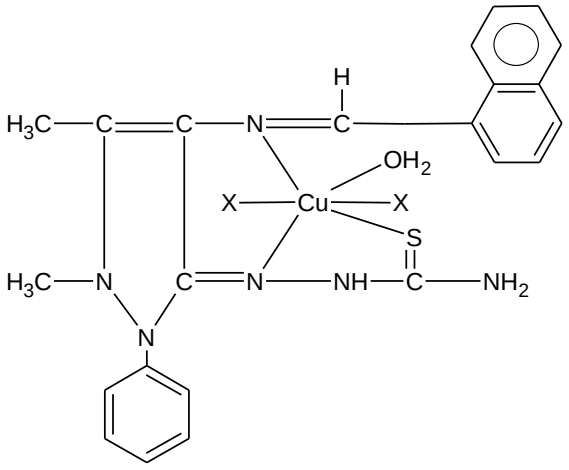
(C.N. = 6)



(b) $[Cu(C_{17}H_{21}N_7S)H_2O\ X_2]$

(X=Cl, Br, NO_3, NCS or CH_3COO)

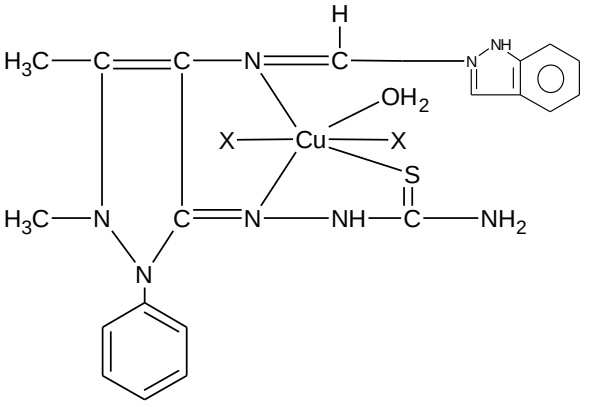
(C.N. = 6)



(c) $[Cu(C_{23}H_{22}N_6S)H_2O\ X_2]$

(X=Cl, Br, NO_3, NCS or CH_3COO)

(C.N. = 6)



(d) $[Cu(C_{21}H_{21}N_7S)H_2O\ X_2]$

(X=Cl, Br, NO_3, NCS or CH_3COO)

(C.N. = 6)

FIG. 7.8: *PROBABLE STRUCTURES OF COPPER(II) COMPLEXES OF VARIOUS THIOSEMICARBAZONES OF 4–AMINOANTYPYRINE*

Declaration of Conflicting Interests

The authors declare no potential conflicts of interest with respect to the research, authorship and publication of this article.

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