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MINI REVIEW

Biological Applications of Co(II) and Ni(II) Complexes of Semicarbazones and Thiosemicarbazones

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Due to their borad profiles of biological activities, transition metal complexes containing semicarbazones and thiosemicarbazones become largely appealing. This mini review focused on the recent developments in last 5 years on the biological applications of Co(II) and Ni(II) complexes of semicarbazones and thiosemicarbazones.

Keywords: Schiff's base, Thiosemicarbazones, Semicarbazones, Cobalt(II), Nickel(II) complexes, Biological properties.

INTRODUCTION

The chemistry of thiosemicarbazones and semicarbazones with transition metals has been investigated long years back. Semicarbazones are the derivatives of urea which performs a vital role in the metabolism of nitrogen-containing compounds in animals and are considered as significant pharmacophores in the look for novel drugs [1]. Thiosemicarbazones are the derivatives of thiourea and structurally differs from semicarbazones only *via* replacing the oxygen atom with a sulphur atom.

According to IUPAC guidelines, semicarbazones and thiosemicarbazones may be named through including the class name 'semicarbazone' after the call of the condensed aldehydes or ketones. It additionally consists of derivatives with substituent at the amide nitrogen in this class. Semicarbazones are oxygen-nitrogen based ligands whereas thiosemicarbazones are sulphur-nitrogen based ligands [2]. The condensation reaction of an aromatic, aliphatic or hetrocyclic ketones or aldehydes with semicarbazide or thiosemicarbazide is employed to form semicarbazones or thiosemicarbazones, respectively.

Stereochemistry of semicarbazones and thiosemicarbazones: The stereochemistry of semicarbazones and thiosemicarbazones seems to be very interesting. It depends upon the charge on the ligand, presence of additional bonding site on the compound after the interaction with metal cation and finally influenced by tautamerism form of both the chelates. An exciting fact is that the semicarbazones found predominantly in the amido form in solid state, while it exhibits an amido-iminol tautomerism in solution state [3] (Fig. 1). Semicarbazones in amido state acts as neutral chelates and the iminol form serves as anionic chelates in complexes of metal. Thus, semicarbazones are flexible and versatile chelates in both neutral and anionic forms.

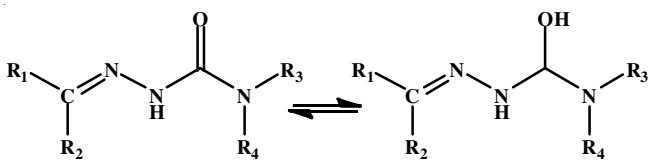


Fig. 1. Amido-iminol tautomerism of semicarbazones

Both amido and iminol tautomeric form of semicarbazone compounds exhibit an excellent and efficient electron delocalization capacity [4]. The addition of the substituents on the semicarbazone compounds boosts the delocalization of electron charge density. Thiosemicarbazones generally exists in two forms and are known to possess thione-thiol tautomerism. The thiosemicarbazones occurs primarily in thione form in solid state, whereas it tautomerize into the thiol form in solution (Fig. 2).

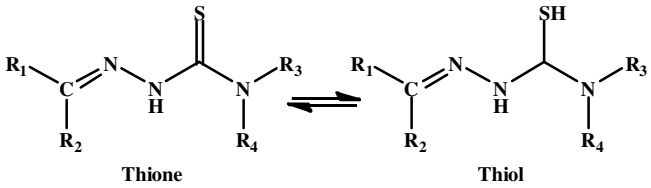


Fig. 2. Thiol-thione tautomerism thiosemicarbazones

These compounds commonly react with metal cations forming metal complexes wherein the semicarbazones and thiosemicarbazones behave as chelating ligands. Upon coordination to a metallic center, delocalization is further improved *via* metallic chelate rings. The coordination opportunities are further accelerated, if the substituent has extra donor atoms [5]. Both semicarbazones and thiosemicarbazones exhibit several donor atoms and normally behave as bidentate or tridentate ligands. It also behaves as monodentate ligands.

Biological importance of semicarbazones and thiosemicarbazones

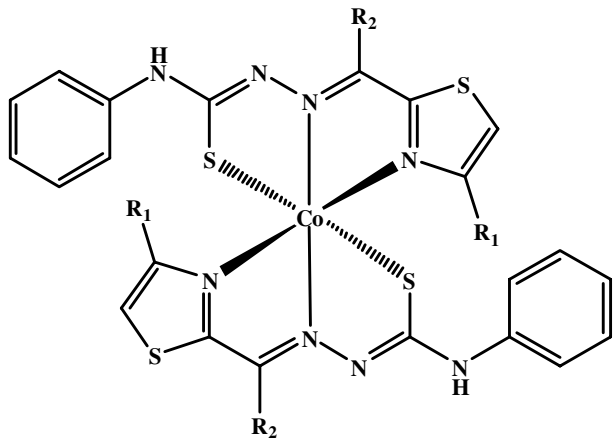
The extensive and diversified biological and pharmacological applications of Schiff's base metal complexes of semicarbazone [6,7] and thiosemicarbazone [8] attracted a number of researchers [9,10]. These transition metal complexes of Schiff's base with different chemical, physical and structural properties provide the platform for research to the number of researchers [11]. The structure and the composition of the complex directly depend on the type and the nature of ligand. The nature implies the total number of atoms which can donate electrons and the tendency to coordinate with metal ions. The superior biological activities of semicarbazones [12] and thiosemicarbazones are because of the substituent of atoms at N_4 position. The substituent of phenolic groups at N_4 position enhances the biological significance of thiosemicarbazones [13]. Likewise, substitution at N_4 position accelerates the antiproliferative capacity of 2-hydroxy-5-methoxyacetophenone thiosemicarbazone [14] and 2-pyridinecarboxaldehyde thiosemicarbazone metal complexes [15].

The biological importance of these Schiff's base chelates of thiosemicabazides involved the researchers greater than before to develop fresh ligands as antibacterial [16], antimicrobial [17-19], antifungal [20,21], antiparasitic [22], antitumor [23], anticancer [24-26], antioxidant [27,28], anti-inflammatory [29], anti-HIV [30], antiproliferative [31], antileishmanial activities [32] and antiviral [33]. Tetradentate thiosemicabazone with strong DNA-binding ability was isolated after the condensation of pyruvaldehyde with 4-(aryl)-thiosemicarbazones [34]. The use of thiosemicarbazones are also utilized as catalyst [35,36] and possess significant mushroom tyrosinase inhibiton activities [37]. A variety of thiosemicarbazone [38-40] have been involved in the treatment of trypanosomiasis caused by *Trypanosoma cruzi* parasite.

Thiosemicarbazones after coordination with transition metals results in the formation of metal complex of corresponding ligand and shows better biological properties because of chelation and overtone's theory. A lot of work proving the biological importance of thiosemecarbazones and their transition metal complexes have been already reported [41-46] and still the efforts to develop more active thiosemicarbazone based drugs goes on. Due to the outstanding and diversified properties, these thiosemicarbazones are employed in pharmacological as well as in food industries [47]. These are also utilized as incomparable option for fluorescent imaging agents [48]. Thiosemicarbazone complexes are capable of detecting divalent mercury as fluorescent chemodosimeters [49,50].

Co(II) is the active center of coenzymes and in inorganic form is a source of micronutrient for algae, bacteria and fungi. Co(II) complexes have been studied and synthesized widely [51,52]. The miscellaneous biological actions of Co(II) complexes have developed the concern of researchers and chemists to design such complexes with more properties. With this aim, a number of Co(II) complexes of semicarbazones and thiosemicarbazones have been isolated having potential anticancer [53-55], antiproliferative activities [56], antioxidant [57], antibacterial [58], *etc*.

Co(II) complexes (Fig. 3) of three different thiosemicarbazone based ligands [59] were prepared by condensation of 4-phenylthiosemicarbazide with 2-thiazolecarboxaldehyde (L_1), 4-phenylthiosemicarbazide with 4-methyl-2-thiazolecarboxaldehyde (L_2), 4-phenylthiosemicarbazide with 2-acetylthiazole (L_3), respectively and characterized. The spin state of complexes was indicated by magnetic susceptibility and EPR measurements. The complexes have considerable solution stability which provides processability to solution and is perfect for the advancement of superior supramolecular materials as per UV-visible and ^{1}H NMR data.



where R_1= H, R_2= H (L_1), R_1= CH_3, R_2= H (L_2) and R_1= H, R_2= CH_3 (L_3)

Fig. 3. Structure of Co(II) complex of thiosemicarbazones

Chen *et al.* [60] reported Co(II) complex of 3-ethyl-2-acetylpyrazinesemicarbazone (Fig. 4) and examined by XRD technique. The activity of complex on cell proliferation, Patu-8988, SGC-7901 and SMMC-7721 cell lines had been evaluated by Annexin V/PI double staining flow cytometry, MTT assay and TUNEL assay. The results confirmed the good inhibitition activity of complex against cell proliferation of SGC-7901, Patu-8988 and SMMC-7721 cells. Furthermore, complex was found to be more biologically active than ligand.

Todorovic *et al.* [61] prepared Co(II) complexes with semi- and thiosemicarbazones of 8-quinolinecarboxaldehyde and characterized by XRD analysis. These novel complexes were found to be active against different human tumor cell lines and normal human cell line. Co(II) complexes (Fig. 5) *i.e.*,

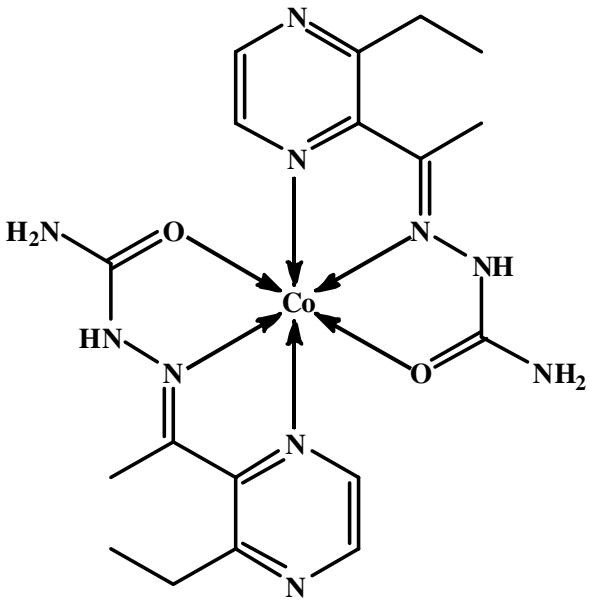


Fig. 4. Structure of Co(II) complex of 3-ethyl-2-acetylpyrazinesemicarbazone

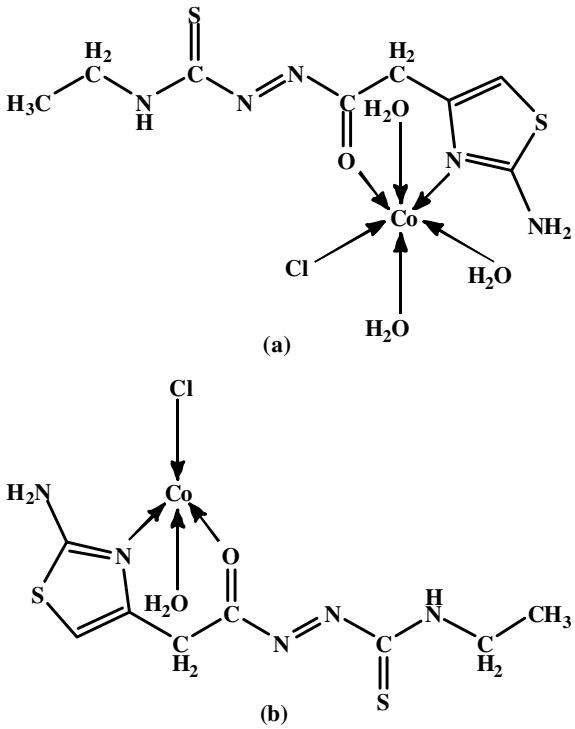


Fig. 5. Structure of (a) $[Co(HTAET)(H_2O)_3Cl]\cdot 2H_2O$ (b) $[Co(HTAAT)(H_2O)Cl]\cdot 2H_2O$

$[Co(HTAET)(H_2O)_3Cl]\cdot 2H_2O$ and $[Co(HTAAT)(H_2O)Cl]\cdot 2H_2O$ of two different ligands were synthesized. The ligands H_2TAET and H_2TAAT were prepared after the addition of 2-(2-aminothiazol-5-yl)actahydrazide in ethyl isothiocyanate and allyisothiocyanate, respectively and characterized by various techniques. The DFT analysis confirmed the octahedral and tetrahedral geometry of $[Co(HTAET)(H_2O)_3Cl]\cdot 2H_2O$ and $[Co(HTAAT)(H_2O)Cl]\cdot 2H_2O$, respectively. All the compounds were tested for antioxidant, antimicrobial, and antitumor activity and found to be possess low biological activity [62].

N_4-morpholinyl isatin-3-thiosemicarbazone and its Co(II) complex (Fig. 6) were obtained and structurally confirmed that ligand is tridentate in nature and coordinated through three different atoms *i.e.*, O, N and S. This metal complex possessed better biological activities due to complexation and chelation as compared to free ligand [63].

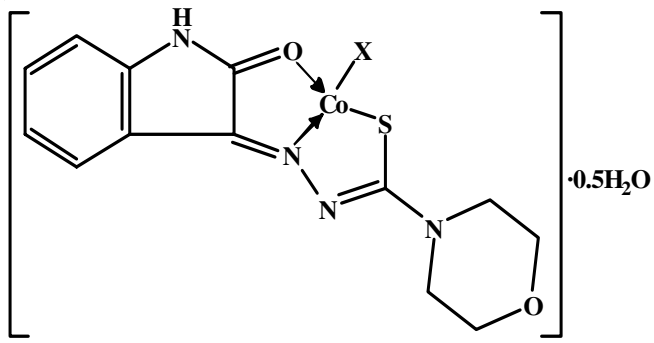


Fig. 6. Structure of Co(II) complex of N_4-morpholinyl isatin-3-thiosemicarbazone

Co(II) complex of 1-(amino-N-methyl-N-phenylmethanethio)(diphenylmethylene)thiocarbonohydrazide (Fig. 7) were reported by Sangeetha and Aravindakshan [64]. As per the experimental results, the ligand behaved as monoanionic bidentate in complex. In addition, the complexes showed tetrahedral geometry.

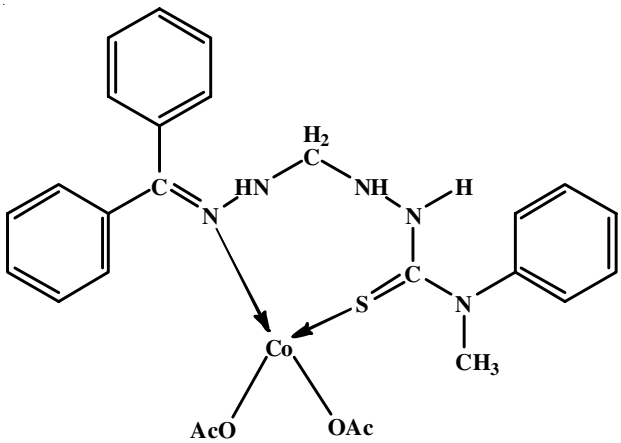


Fig. 7. Structure of Co(II) complex of 1-(amino-N-methyl-N-phenylmethanethio)(diphenylmethylene)thiocarbonohydrazide

Co(II) complexes of two newly formed *vic*-dioxime ligands L_1 & L_2, having 4-methoxy or 4-ethoxy thiosemicarbazone moieties, respectively synthesized (Fig. 8) and characterized. Results confirmed that (*E*) configuration of both the oxime moieties and thione form of ligands. Disc diffusion method was employed to detect the antimicrobial activities of ligands and complexes against 12 different bacteria strain and 4 yeasts. The tested compounds showed fair antimicrobial activity [65]. Similarly, another Co(II) complex (Fig. 9) of thiosemicarbazone ligand *i.e.*, 2-(4-ethylphenylamino acetyl-N-phenyl hydrazine carbothioamide shows significant antibacterial activity against *S. pyogenes* and *E. coli* [66].

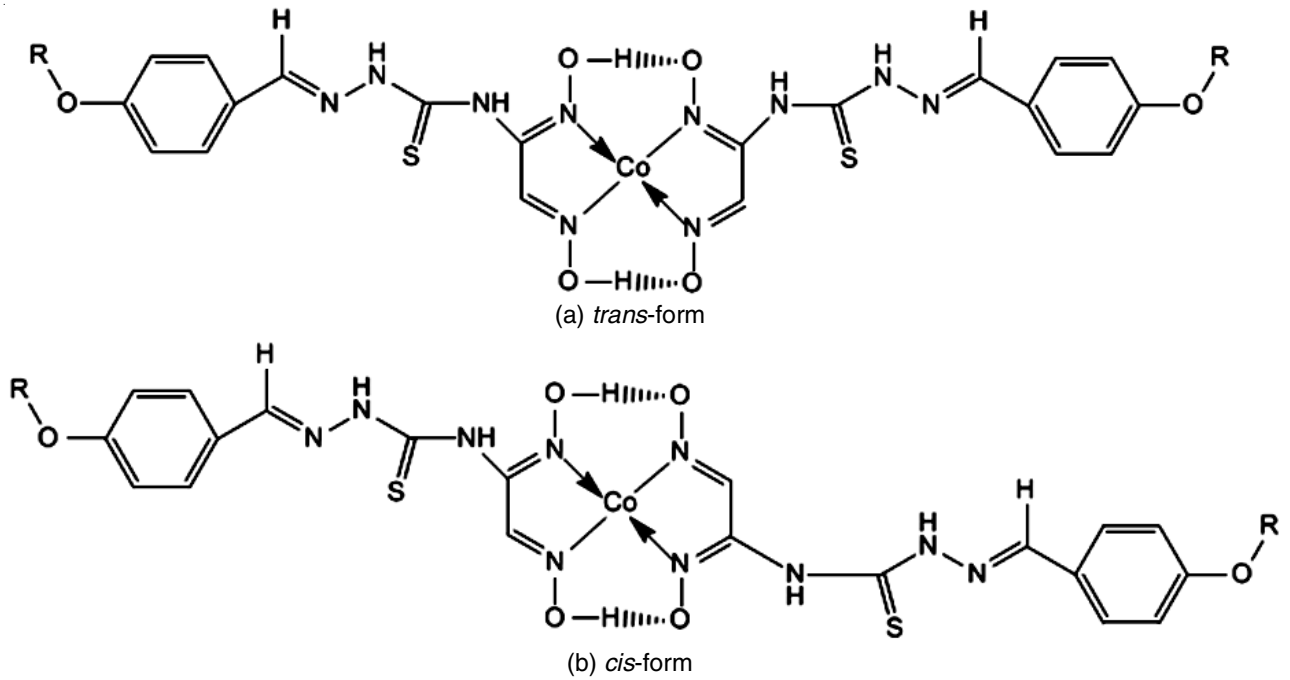


Fig. 8. Structure of Co(II) complex of *vic*-dioxime ligands L^1 (R= CH_3) & L^2 (R= C_2H_5), having 4-methoxy or 4-ethoxy thiosemicarbazone moieties

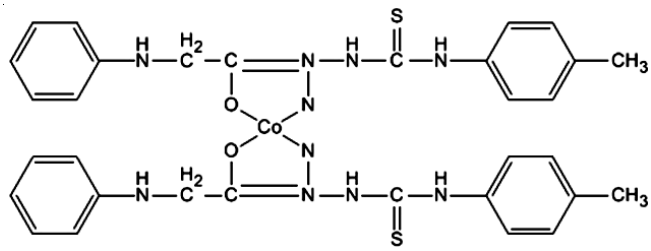
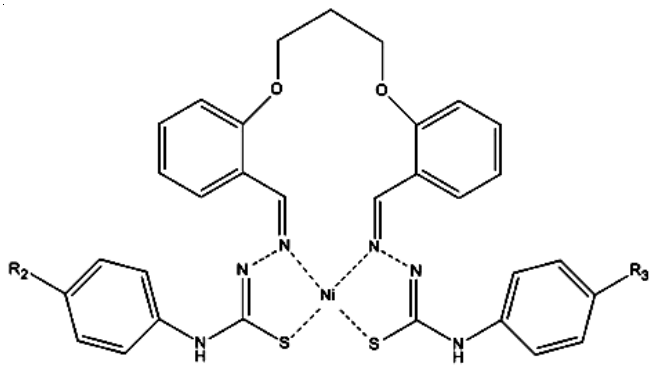


Fig. 9. Structure of Co(II) complex of 2-(4-ethylphenylamino acetyl-N-phenyl hydrazine carbothioamide

Nickel(II) complexes of semicarbazones and thiosemicarbazones: Nickel(II) along with Cu(II), Co(II) and Mn(II) is an essential trace element of human nutrition. It is also an essential trace element for many of the species of bacteria, archea and plants. Ni(II) when gets bonded with RNA, then it shows specific affinity for bones and skin and performs significant role in pigmentation. Apart from being important trace nutritional element, Ni(II) can lead to allergic reactions and few of its complexes found to be carcinogenic in nature [67].

The complexes of Ni(II) have been studied continuously for its biological activities [68-75] and attracted the attention of researchers to develop and design such more these complexes [76]. Various Ni(II) complexes with thiosemicarbazide and semicarbazide moiety [77-80] have been reported with increased antioxidant [81], anticancer [82], antiproliferative activities [83,84], antimicrobial [85], antibacterial [86], *etc*.

Hosseinpour *et al*. [87] synthesized two Ni(II) complexes of potent and asymmetrical tetradentate thiosemicarbazone ligands (Fig. 10) by condensing 4-chlorophenylthiosemicarbazide and 4-phenylthiosemicarbazide with 2-[3-(2-formylphenoxy)propoxy]benzaldehyde (L_1) and 4-chlorophenylthiosemicarbazide and 4-bromophenylthiosemicarbazide with 2-[3-(2-formylphenoxy)propoxy]benzaldehyde (L_2).



where R_2= Cl, R_3= H (L_1) and R_2= Cl, R_3= Br (L_2)

Fig. 10. Structure of Ni(II) complexes of tetradentate thiosemicarbazones

Muralisankar *et al*. [88] prepared Ni(II) complex of N-ethyl-2-(phenyl(pyridin-2-yl)methylene)hydrazinecarbothioamide (Fig. 11) after the condensation of 4-ethyl-3-thiosemicarbazide with 2-benzoylpyridine. The interaction between the complexes and calf thymus DNA (CT-DNA) and bovine serum albumin (BSA) has been studied through UV-visible and synchronous fluorescence spectra. The interaction modes between Ni(II) complex and DNA was found to be mainly intercalative. The complex has been assayed for anticancer activity *in vitro* against A549 and L929 cell lines and confirmed good activity of complex against lung cancer line.

Selvamurugan *et al*. [89] synthesized three Ni(II) complexes (Fig. 12) of 4-chromone-4-methylthiosemicarbazone (L_1), 4-chromone-4-phenylthiosemicarbazone (L_2) and 4-chromone-4-cyclohexylthiosemicarbazone (L_3). The interaction between the complexes and DNA/protein has been studied by means of UV-visible and fluorescence spectra which showed strong binding with bovine serum albumin. The complexes have good anticancer activity against MCF-7 cancer cell line because of terminal substitution.

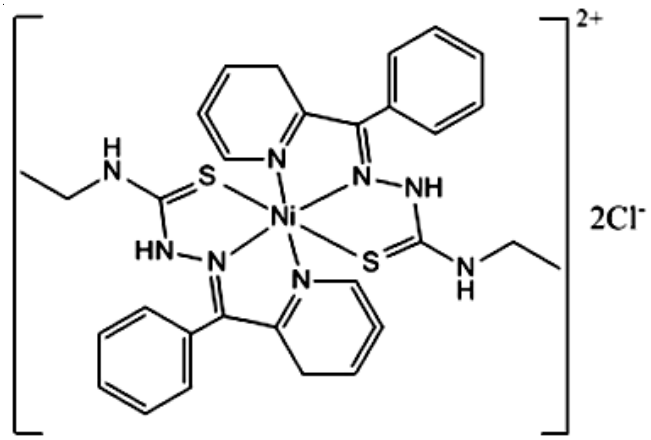
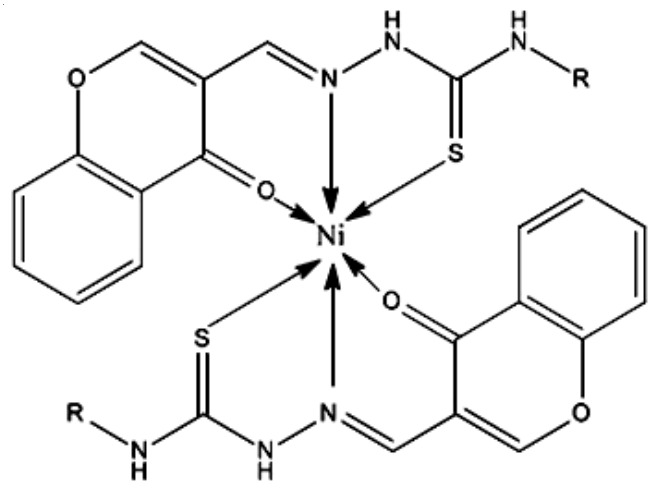


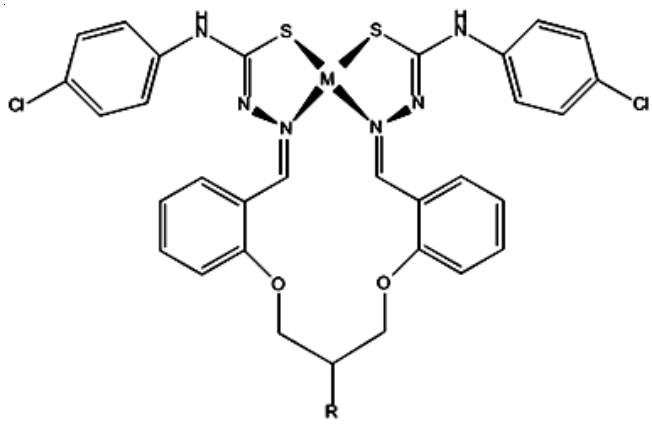
Fig. 11. Structure of Ni(II) complex of N-ethyl-2-(phenyl(pyridin-2-yl)methylene)hydrazinecarbothioamide



where, R= CH_3 (L_1), R=C_6H_5 (L_2), R=C_6H_{11} (L_3)

Fig. 12. Structure of Ni(II) complexes of 4-chromone-4-methylthiosemicarbazone (L_1), 4-chromone-4-phenylthiosemicarbazone (L_2), 4-chromone-4-cyclohexylthiosemicarbazone (L_3)

Hosseini-Yazdi *et al*. [90] synthesized Ni(II) complexes (Fig. 13) of 2-[1-(2-{3-[2-({2-[(4-chloroanilino)carbothioyl]-



where, R = H (L_1), R = OH (L_2) and M = Ni

Fig. 13. Structure of Ni(II) complexes of 2-[1-(2-{3-[2-({2-[(4-chloroanilino)-carbothioyl]hydrazono}ethyl)phenoxy]propoxy}phenyl)ethylidene]-N1-(4-chlorophenyl)-1-hydrazinecarbothiamide (L_1) and 2-[1-(2-{3-[2-({2-[(4-chloroanilino)carbothioyl]hydrazono}methyl)-phenoxy]-2-hydroxypropoxy}phenyl)methylidene]-N1-(4-chlorophenyl)-1-hydrazinecarbothiamide (L_2)

hydrazono}ethyl)phenoxy]propoxy}phenyl)ethylidene]-N^1-(4-chlorophenyl)-1-hydrazinecarbothiamide (L_1) and 2-[1-(2-{3-[2-({2-[(4-chloroanilino)carbothioyl]hydrazono}methyl)-phenoxy]-2-hydroxypropoxy}phenyl)methylidene]-N^1-(4-chlorophenyl)-1-hydrazinecarbothiamide (L_2). The ligands and complexes were characterized and confirmed the ability of both the complexes to stabilize low oxidation states of Ni(I).

Two novel Ni(II) complexes (Fig. 14) of 5-bromosalicylidene-N-methyl-S-methyl-isothiosemicarbazone and 5-bromosalicylidene-N-methyl-thiosemicarbazone with triphenylphosphine were prepared and characterized [91].

Wang *et al*. [92] reported Ni(II) complex of 2-thiophene N(4)-phenylthiosemicarbazone (Fig. 15). The ligand and complex were found to be potent for anticancer activities *in vitro* against QSG7701 and HepG2 carcinoma cells. Shirode *et al*. [93] reported Ni(II) complex (Fig. 16) of a mixed ligand by the reactions of Ni(II) chlorides with pyruvic acid semicarbazone and acetone semicarbazone in 1:1:1 molar ratio. The Schiff's

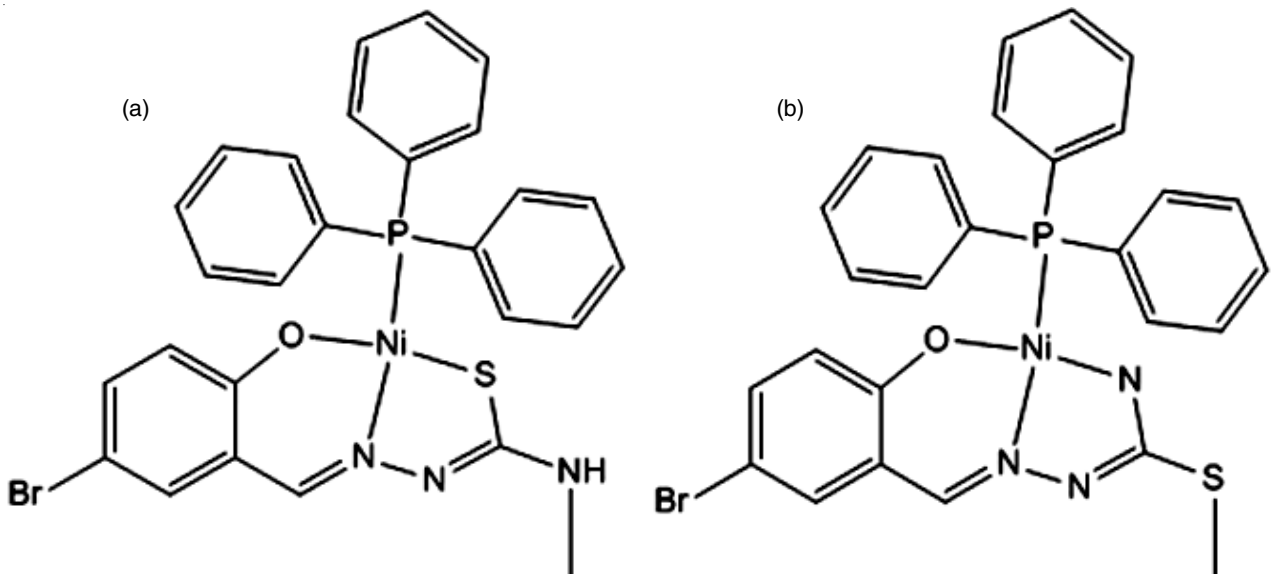


Fig. 14. Structure of Ni(II) complexes of (a) 5-bromosalicylidene-N-methyl-S-methyl-isothiosemicarbazone (b) 5-bromosalicylidene-N-methyl-thiosemicarbazone

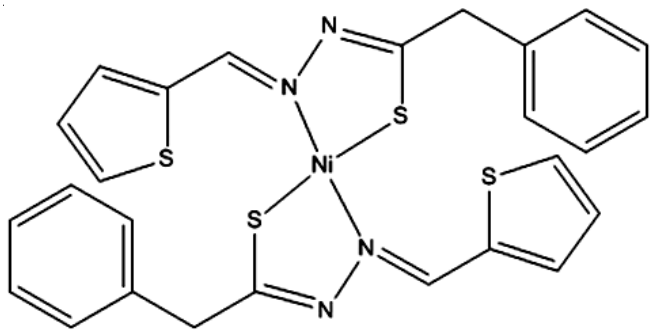


Fig. 15. Structure of Ni(II) complex of 2-thiophene N(4)-phenylthiosemicarbazone

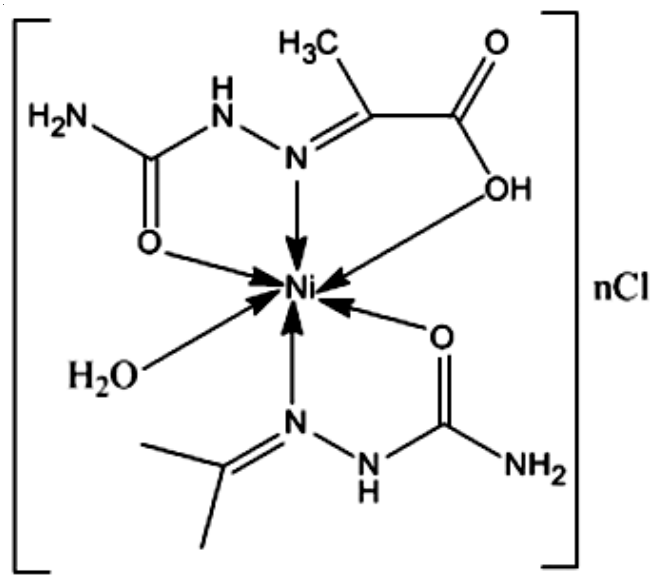


Fig. 16. Structure of nickel complex of mixed semicarbazone

base ligand and its complex were found to be biologically active against the bacteria *E. coli* and *P. aeruginosa.*

The two Ni(II) complexes of quinoline-2-carboxaldehyde with thiosemicarbazone (Fig. 17) *i.e.*, $[Ni(HL_1)_2]$ (**1**) and $[Ni(HL_2)(L_2)]$ (**2**), where HL_1 = (*E*)-N-methyl-2-(quinolin-2-ylmethylene)hydrazinecarbothioamide and HL_2 = (*E*)-N,N-dimethyl-2-(quinolin-2-ylmethylene)hydrazinecarbothioamide demonstrated efficient binding activity with CT-DNA *via* inter-calative mode. These complexes were also efficient in converting super-coiled pBR322 plasmid DNA in open circular form. The complex **2** was stronger in DNA binding and DNA cleavage capability as compared to complex **1**. The stronger activity of complex **2** is due to the substitution of methyl of complex **1** by dimethyl in complex **2** [94].

Conclusion

Semicarbazones and thiosemicarbazones played a key role in the development of coordination chemistry, but also proved their importance for the advancement of inorganic chemistry for biological activites. These chelates have been known to possess a broad range of biological and medicinal activities for a long-time due to the presence of nitrogen, oxygen and sulphur donor atoms. They proved outstanding pharmalogical actions such as antimicrobial, antituberclosis, antiplatelet, antioxidant, anti-inflammatory, anticancer, antimalarial, analgesi. The biologically active Schiff's base ligands have also proved their action against mobilization of enzymes and when bonded to metal ions, shows enhanced biological action and are widely used in versatile fields.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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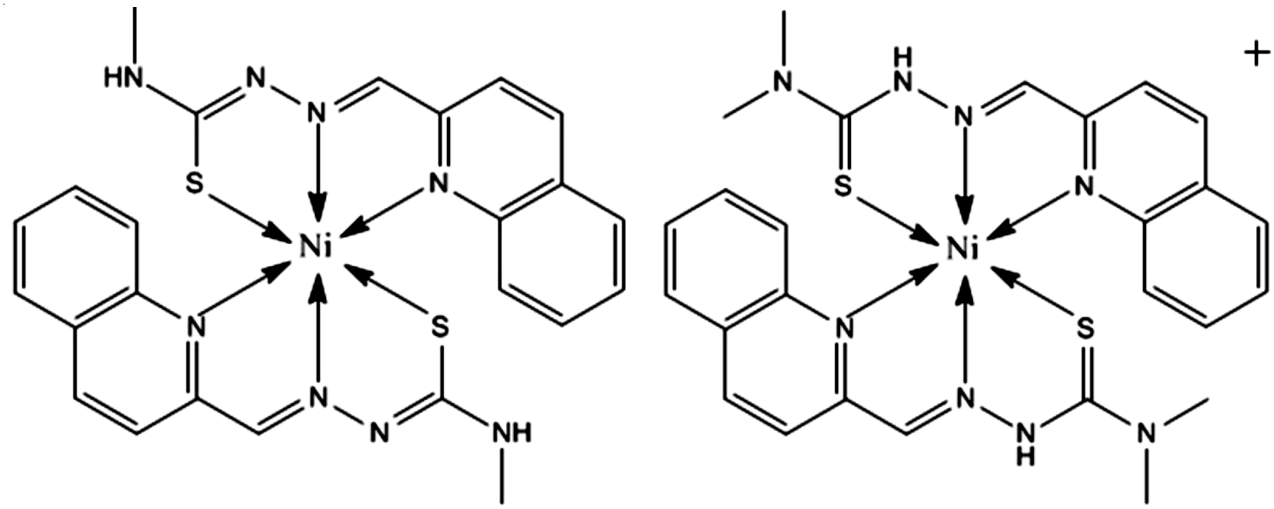

Fig. 17. Structure of Ni(II) complex of quinoline-2-carboxaldehyde with thiosemicarbazone

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