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# Synthesis and Characterisation of Some Nickel(II) Complexes with 3-Aryl Substituted Amidinothioureas

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A series of novel complexes of nickel(II) with the 1-amidino-3-phenyl thiourea (HPATU), 1-amidino-3-*p*-tolyl thiourea (HPTATU), 1-amidino-3-*p*-chlorophenyl thiourea (HPCATU) and 1-amidino-3-*p*-anisyl thiourea (HPAATU) have been prepared and characterized using elemental analysis, magnetic moment measurements and electronic, infrared, pmr, mass and X-ray spectroscopic techniques. The electrochemical behaviour of the complex is followed using cyclic voltammetry and it is seen that the nickel-sulphur linkage is having more covalent nature. The complexes are crystalline in nature and have a tetragonal unit cell and the unit cell parameters have been calculated from the powder X-ray diffraction pattern. The complexes are neutral and have a square planar structure. The complexes were screened for their antistaphylococcal activity by administering the complexes in liquid culture medium containing *S. aureus* and assessed the activity by turbidimetric method.

**Key Words: Amidinothiourea, Deprotonation, Square planar, Cyclic voltammetry, X-ray, NMR, Antibacterial.**

## INTRODUCTION

Amidinothioureas are a group of compounds, which are very much related to biguanides in structure and reactivity and are their immediate precursors. The chemotherapeutic applications of biguanides are invaluable.[1] Hence a large number of amidinothioureas have been synthesized and screened for their antiviral activity[2]. Some amidinothioureas and compounds derived from them are used in the treatment of heart diseases, hypertension, etc[2]. Amidinothioureas and some of their complexes have been screened for their potential antifungal activity[2]. 1-Phenyl-3-amidinothiourea has been shown to be effective in the removal of methylmercury(II) chloride from wastewater by floatation method[3]. It was established earlier that the antibacterial activity of any organic compound enhances, as it forms complex with metal ion[4]. The present report includes the preparation, characterisation and antistaphylococcal activity of four complexes of Ni(II) with 1-amidino-3-aryl substituted thioureas, 1-amidino-3-phenyl thiourea (HPATU), 1-amidino-3-*p*-tolyl thiourea (HPTATU), 1-amidino-3-*p*-chlorophenyl thiourea (HPCATU) and 1-amidino-3-*p*-anisyl thiourea (HPAATU).

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## EXPERIMENTAL

**Preparation of amidinothioureas:** The required amidinothioureas were prepared by the reaction of guanidine carbonate with the appropriate isothiocyanate in presence of an alkali[5]. As a representative experiment the preparation of 1-amidino-3-phenyl thiourea is described below.

To a suspension of guanidine carbonate (1 g) in acetonitrile (5 mL), two equivalents of powdered KOH (0.7 g) were added and stirred well. One equivalent of phenylisothiocyanate in 2 mL acetonitrile was added in drops with stirring in about 30 min. When the pungent smell of isothiocyanate vanished, the mixture was poured into water with stirring; the amidinothiourea separated as a white precipitate. It was filtered and washed with water and dried.[5-7] (Yield 0.85 g).

**General method for the preparation of amidinothiourea complexes:** To a boiling solution of the ligand (0.01 mol, 1.94 g) in 50 mL methanol, a solution of the nickel salt (0.005 mol) in 50 mL aqueous methanol was added. There was a sudden colour change indicating the formation of the complex. Since the complex was soluble in methanol, the solvent was removed by distillation and the residual orange red complex was filtered, washed repeatedly with water and crystallised from methanol or acetone and dried.

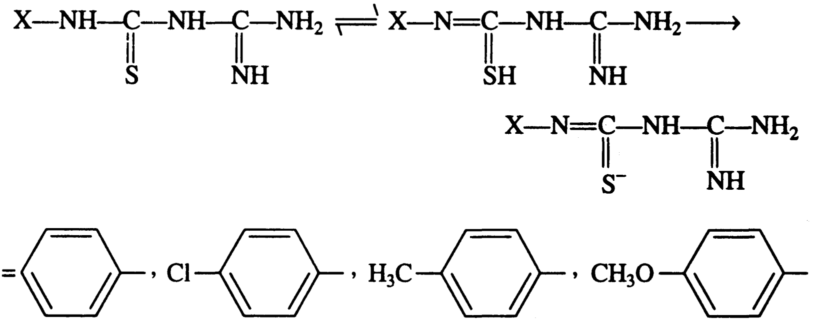
CHN analysis of the samples was done by the micro-analytical technique at RSIC, NEHU, Shillong. Nickel and sulphur were estimated gravimetrically[8] and nickel percentage was confirmed by atomic absorption spectroscopy at the GSI Laboratory, Trivandrum. Conductance measurements were carried out on a digital control dynamics conductivity meter (APX 185). Magnetic susceptibility measurements were made using a Gouy balance at room temperature using $Hg[Co(CNS)_4]$ as calibrant and also by the vibrating sample magnetometer method. The electronic spectra of the ligands and complexes were recorded on a Shimadzu UV-1601 spectrophotometer in methanol. The IR spectra of the ligands and complexes were taken on a Perkin Elmer RXI FTIR spectrophotometer using KBr disc technique. Cyclic voltammetric studies of the complexes were done in deaerated methanol solution on a Cypress model CS-1090/CS-1087 computer controlled electroanalytical system. The proton NMR of the ligands and complexes were recorded on a Jeol 300 MHz machine in DMSO-$d_6$. The mass spectrum of one of the phenyl substituted ligand and its complex was taken on a 70 eV, Varian VG 70-70H spectrometer using the electron impact technique. The powder X-ray diffraction pattern of $Ni(PTATU)_2$ was recorded on a Philips analytical X-ray diffractometer PW 1710 using Cu (40 kV 20 mA) X-ray of wavelength 1.54060 Å.

## RESULTS AND DISCUSSION

The mass spectrometric details of a few amidinothioureas have been reported[2]. The 70 eV mass spectrum of the ligand *p*-tolyl amidinothiourea have been taken and the fragmentation pattern is the same as reported earlier. In addition to the molecular ion peak for *p*-tolyl amidinothiourea, an intense peak seen at 206 can be attributed to the oxidation product of amidinothiourea, *viz.*, thiadiazole.[2] The other prominent peaks are at m/z 149 due to $CH_3—C_6H_4—NCS$, m/z 91, due to the tropilium ion formed from the *p*-tolyl group. This can further eliminate an acetylene molecule giving a peak at m/z 65.

The 300 MHz ${}^1$H NMR of the ligand phenylamidinothiourea in DMSO-$d_6$ have been recorded and the following peaks are observed. A singlet centered at δ 2.8 due to the $NH_2$ protons, a multiplet at δ 6.9–7.1 due to the three imino protons, a multiplet at δ 7.2–7.8 due to the phenyl protons and a singlet centered at δ 8.4 due to the SH proton[9–11].

It has been reported that thiourea and amidinothiourea can exhibit tautomerism as shown below.[12–15] So these ligands can exist in both the thiol and thione forms both of which are capable of complexation.



$$X{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH_2 \rightleftharpoons X{-}N{=}\underset{\underset{SH}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH_2 \longrightarrow X{-}N{=}\underset{\underset{S^-}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH_2$$

The complexes of the four ligands were prepared using nickel salts with different anions and their composition determined. In all cases the analytical data show that the metal-ligand ratio is 1 : 2 (Table-1).

TABLE-1
ANALYTICAL DATA OF THE NICKEL(II) AMIDINOTHIOUREA COMPLEXES

| Complex | m.w. | % Analysis: Found (Calcd.) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Ni | C | H | N | S | Cl |
| $Ni(PATU)_2$ | 444.69 | 13.04 | 43.22 | 4.07 | 25.00 | 14.15 | — |
| | | (13.19) | (43.17) | (4.04) | (25.18) | (14.39) | |
| $Ni(PTATU)_2$ | 472.69 | 12.39 | 45.19 | 4.60 | 23.34 | 13.36 | — |
| | | (12.41) | (45.69) | (4.66) | (23.69) | (13.30) | |
| $Ni(PCATU)_2$ | 513.59 | 11.56 | 37.45 | 3.18 | 21.84 | 12.38 | 13.59 |
| | | (11.42) | (37.37) | (3.09) | (21.80) | (12.46) | (13.50) |
| $Ni(PAATU)_2$ | 504.69 | 11.54 | 42.86 | 4.42 | 22.12 | 12.60 | — |
| | | (11.62) | (42.79) | (4.35) | (21.19) | (12.68) | |

The molar conductance data show that all the complexs are non-electrolytes. Magnetic moment measurements show that the complexes are diamagnetic.

The electronic spectral bands of the ligands and complexes were taken in methanol. The complexes show two overlapping bands around 430 nm and 475 nm. The two transitions can be attributed to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transitions characteristic of square-planar complexes.[16]

The IR spectral bands of the ligands and their nickel(II) complexes have been recorded and their tentative assignments are also made. The ligands and their nickel(II)complexes show strong bands in the region 3450–3160 $cm^{-1}$. This can be assigned to the symmetric and asymmetric stretching vibrations of the NH and $NH_2$ groups.[17]

The bands at 2350 $cm^{-1}$ and 1250 $cm^{-1}$ in the spectra of the ligands are due to the S—H stretching and bending vibrations[18] and that at 1070 $cm^{-1}$ can be assigned to the C═S group of the thione form[19]. The S—H bands are not seen in the complexes indicating that complexation has occurred in the thiol form of the ligand after deprotonation. The ligands having an absorption around 760 $cm^{-1}$ assigned to ν(C—S) is found in the complex around 710 $cm^{-1}$ further indicating the coordination through the sulphur atom.[20, 21] This is further confirmed by the appearance of ν(Ni—S) band around 365 $cm^{-1}$ in the complexes.[22]

The strong ligand bands in the region 1640 $cm^{-1}$ can be assigned to the C═N stretching vibrations.[17] But in the complexes a new band originates at 1620 $cm^{-1}$ in addition to the band at 1640 $cm^{-1}$ which can be accounted on behalf of one of the C═N groups which is involved in coordination.[23] This is further confirmed by the appearance of the band around 460 $cm^{-1}$ which can be assigned to ν(Ni—N)[24]. All other bands in ligands remain unchanged in the spectra of complexes.

The electrochemical behaviour of the amidinothiourea complexes of nickel was followed using cyclic voltammetry. Only quasi reversible peaks are seen in the case of these complexes[25]. Two anodic peak currents are seen at 265 mV and 723 mV suggestive of the two one electron reduction of $Ni^{2+}$. A small cathodic peak is seen at –484 mV. The quasi-reversible equilibria can be attributed to the added covalency of the metal-sulphur bond.[26] The small peak at –484 mV is suggestive of a Ni(II) → Ni(III) oxidation.[27]

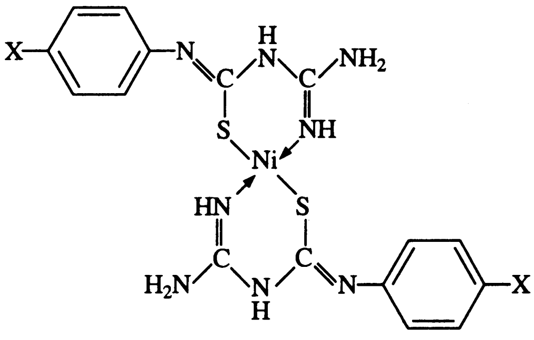
The mass spectrum of the *p*-tolylamidinothiourea complex was taken and it gives a very weak peak at m/z 472. The next peak is at m/z 207, formed by the breaking of the ligand from the metal. The next strong peak is at m/z 206, which can be due to the oxidation of the ligand unit to thiadiazole. The subsequent peaks at 149 ($CH_3$—$C_6H_4$—NCS), 91 ($CH_3$—$C_6H_4$) and the one at 65 are all seen in the mass spectra of the complex. So it can be postulated that the ligands are removed from the coordination sphere by the 70 eV electron impact. Then the fragmentation of the ligands will take place, which is exactly the same as that of the free ligand mass spectra profile[2].

The 300 MHz NMR of the ligand phenylamidinothiourea is compared with that of its Ni(II) complex[9, 10]. The spectrum was recorded in DMSO-$d_6$. The peak at δ 8.4 of the ligand disappears in the complex, showing that the ligand is coordinated to the metal through the thiol-S after deprotonation[11]. The peak centred at δ 2.8 due to the $NH_2$ group is unaffected. The complex also gives the multiplet in the region δ 7.2–7.8 due to the phenyl protons and another multiplet centred at δ 6.9–7.1 due to an NH proton. In the complex, a sharp singlet appeared at δ 5–4. This can be assigned to an NH proton, which has undergone a downfield shift from δ 6.9 due to complexation. In the ligand there were three NH protons. Only one remains intact. One NH proton is absent in the thiol form and another undergoes downfield shift due to complexation. So the proton NMR data is in agreement with the proposed structure.

The X-ray powder diffraction pattern of the complex $Ni(PTATU)_2$ showed fortytwo reflections in the range of 2θ from 5–45° and twenty reflections were successfully indexed. Indexing was done by a trial and error method.[28, 29] It is seen that the tetragonal system gave the best fit. The sample is found to have a tetragonal unit cell with the cell edges as $a = b = 16.54$ Å and $c = 9.94$ Å. The volume of the unit cell is 2719.30 $Å^3$.

**Antibacterial activity against *S. aurenus*:** The ligands, their nickel(II) complexes and nickel chloride were screened for their antistaphylococcal activity by administering them at a concentration of 0.05 mg $mL^{-1}$ in a homogeneous liquid culture medium containing *S. aureus* and assayed by turbidimetric method[30]. The complexes were found to be more antistaphylococcal than the free ligands probably due to the inhibiting involvement of metal ion or complex as a whole in the growth of *S. aureus*[31]. However, activity of nickel chloride was higher than that of the complexes. This is likely to be due to its greater hydrophilicity than the complexes so that the salt can diffuse rapidly, rupture the cell membrane and prevent RNA synthesis in bacteria[32].

On the basis of the above discussion, it can be concluded that nickel amidinothiourea complexes have a square-planar geometry. The ligands function as anionic bidentate ligands coordinating through a terminal nitrogen and a thiol sulphur after deprotonation.



X = H, $CH_3$, Cl, $OCH_3$

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