

Studies on Ni(II) Complexes of Substituted Thioureas

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Crystalline compounds of the types $[\text{Ni}(\text{ATU})_n\text{X}_2]$ and $[\text{Ni}(\text{PATU})_n\text{X}_2]$ (ATU = N-allylthiourea, PATU = N-phenyl-N'-allylthiourea, X = Cl, Br or I), $[\text{Ni}(\text{ATU})_5\text{NO}_3]\text{NO}_3$, $[\text{Ni}(\text{ATU})_6](\text{ClO}_4)_2$ and $[\text{Ni}(\text{PATU})_4](\text{ClO}_4)_2$ have been prepared. Nickel iodide complexes are diamagnetic and hexa-coordinated. $[\text{Ni}(\text{PATU})_4](\text{ClO}_4)_2$ is diamagnetic and square-planar while the remaining complexes are paramagnetic. Stereochemical assignments are made on the basis of spectral, magnetic, conductance and molecular weight data.

NUMEROUS studies of Ni(II) complexes have been reported in literature¹⁻⁴. The great interest in Ni(II) complexes arises from the possibility of their existence in different stereochemical configurations, octahedral, tetrahedral and planar. These forms are capable of manifesting complicated equilibria which are dependent on the nature of solvent, concentration and temperature. Ni(II) complexes of N-allylthiourea and N-phenyl-N'-allylthiourea have not been previously described. These ligands present several coordination centres, namely, free/substituted nitrogen atoms, allyl group and sulphur. Nitrogen coordination in thiourea or its derivatives is rare except in N-methylthiourea complexes of Pd(II), Pt(II) and Cu(I) (ref. 5). It has been found that sulphur is the typical coordination site in these complexes. In the present paper Ni(II) complexes of N-allylthiourea and N-phenyl-N'-allylthiourea are reported. These have been characterized on the basis of UV, visible and IR spectra and magnetic and conductance studies.

Materials and Methods

N-allylthiourea (ATU) was prepared according to the method of Falke⁶; m.p. 77-78°. N-phenyl-N'-allylthiourea (PATU) was prepared by refluxing an equimolar mixture of aniline and allylisothiocyanate in ethanol. On cooling the white solid separated which was recrystallized from ethanol; m.p. 98°.

Other chemicals used were of reagent grade. Nickel bromide, iodide and perchlorate were prepared from nickel carbonate and the corresponding hydrohalic acids. The solvents were made spectroscopically pure for spectroscopic, conductivity and other physical measurements⁷.

Preparation of the complexes — Ni(II) halide complexes of N-allylthiourea were prepared by mixing dimethoxypropane solution of the nickel salts with the ligand dissolved in minimum amount of the same solvent in the ratio of 1:6 (metal:ligand). The crystalline solids obtained were filtered, washed repeatedly with anhydrous ether and dried *in vacuo*. Ni(II) nitrate and perchlorate complexes of ATU

were prepared by adding an isopropanol solution of the ligand to a paste of the respective metal salt in isopropanol in 1:6 (metal:ligand) ratio. The coloured mass was transferred to a mixture of isopropanol and pet. ether (1:3). The solid obtained was filtered, triturated in a mortar and again similarly treated with the mixed solvent. The solid was filtered and collected as above. Ni(II) complexes of N-phenyl-N'-allylthiourea (PATU) were prepared by adding *n*-butanol solutions of the corresponding metal salt to the ligand dissolved in minimum amount of *n*-butanol, in a 1:6 ratio (metal:ligand). The mixture was warmed on a water-bath for about 30 min. The solid separated on cooling which was collected, washed with cold *n*-butanol, followed by anhydrous ether and dried *in vacuo*. The complexes are soluble in common organic solvents.

Physical measurements were carried out as described in an earlier communication⁸.

Results and Discussion

Analytical data of the complexes are presented in Table 1 along with some of their physical properties. The complexes are susceptible to moisture and hydrolyse in aqueous medium.

ATU shows electronic spectral bands at 217 and 243 nm along with a shoulder at ~310 nm. On complex formation the first band vanishes while the 243 nm band remains unaltered. In PATU complexes, the ligand bands observed at 248 and 273 nm suffer hypsochromic shifts (Table 2).

The IR spectra of the ligands and complexes show a number of bands in the region 3400-3130 cm^{-1} which may be due to the νNH of the primary or secondary amino groups. Bands observed in the region 1650-1550 cm^{-1} may be due to the bending vibrations of the primary and secondary amino groups. Three band positions near 1400, 1000 and 730 cm^{-1} have been suggested for the controversial $\nu(\text{C}=\text{S})$ frequency by various workers⁹⁻¹². Strong bands observed near 1000 cm^{-1} in the spectra of the ligands disappear or get weakened in the spectra of the complexes. The assignment of $\nu(\text{C}=\text{S})$ fre-

TABLE 1 — ANALYTICAL, MAGNETIC SUSCEPTIBILITY AND MOLECULAR WEIGHT DATA OF NICKEL COMPLEXES OF ATU AND PATU

Compound	Colour	m.p. (°C)	Metal* (%)	N* (%)	S* (%)	μ_{eff} (B.M.) (at 303°K)	Mol. wt (Found)
[Ni(ATU) ₄ Cl ₂]	Greenish yellow	77†	9.81 (9.89)	18.99 (18.87)	—	3.29	200
[Ni(ATU) ₄ Br ₂]	Green	69	8.55 (8.60)	16.63 (16.41)	18.51 (18.75)	3.28	237
[Ni(ATU) ₄ I ₂]	do	106	7.79 (7.56)	14.09 (14.42)	16.29 (16.47)	Dia.	245
[Ni(ATU) ₅ NO ₃]NO ₃	Yellow	77-80	7.51 (7.70)	21.91 (22.03)	21.30 (20.97)	3.83	346
[Ni(ATU) ₆](ClO ₄) ₂	Brown	—	5.94 (6.16)	17.82 (17.62)	20.40 (20.13)	3.21	301
[Ni(PATU) ₄ Cl ₂]	Greenish yellow	150*	6.49 (6.54)	12.30 (12.47)	—	3.15	315
[Ni(PATU) ₄ Br ₂]	Green	81	6.15 (5.95)	11.47 (11.35)	13.21 (12.97)	3.42	321
[Ni(PATU) ₄ I ₂]	do	84	5.40 (5.43)	10.51 (10.36)	12.00 (11.84)	Dia.	358
[Ni(PATU) ₄](ClO ₄) ₂	do	136	5.80 (5.72)	11.20 (10.91)	12.71 (12.47)	Dia.	351

*Figures in parentheses indicate the calc. values.

†Decomposition point.

quency has become difficult owing to the significant vibrational mixing of $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{S})$ and $\delta(\text{N}-\text{H})$ vibrations. The nickel nitrate complex shows IR bands assignable to both ionic and coordinated nitrates¹³.

The colour, spectral feature and magnetic susceptibilities of the yellow compounds, [Ni(ATU)₄Cl₂] and [Ni(PATU)₄Cl₂], are identical with dichlorotetrakis(thiourea) Ni(II) which is reported¹⁴ to consist of a *trans*-NiS₄Cl₂ coordination sphere with four sulphur atoms in a square plane about the nickel atom and the two axial positions occupied non-equivalently by two chlorine atoms. Magnetic behaviour of the complexes except the iodo complexes and [Ni(PATU)₄](ClO₄)₂, is typical of octahedral Ni(II) complexes. The high magnetic moments of these octahedral complexes may be due to spin-orbit coupling which causes an orbital contribution in the 'quenched' ³A_{2g} ground state of Ni(II).

An important spectral characteristics of the complexes is the splitting of the spectral bands, which may be due to lowering of symmetry because of tetragonal distortion. [Ni(ATU)₄Cl₂], [Ni(ATU)₄Br₂], [Ni(ATU)₆](ClO₄)₂, [Ni(PATU)₄Cl₂] and [Ni(PATU)₄Br₂] may assume octahedral/pseudo-octahedral configurations with varying degrees of tetragonal distortion. [Ni(PATU)₄](ClO₄)₂ may be considered to have a square-planar configuration on the basis of its diamagnetic character and its spectral band position at 600 nm. The iodo complexes also exhibit split bands and may be tetragonally distorted pseudo-octahedral species similar to the diamagnetic [Ni(diars)₂I₂] (ref. 15). The three bands of [Ni(ATU)₄Cl₂] are close to the split band of octahedral Ni(II) complexes^{16,17}. The complex has a symmetry lower than octahedral as shown by the splitting of the band.

Conductivity measurements show that significant solvolysis takes place in methanol and acetone solutions, solvolysis being greater in the former.

TABLE 2 — VISIBLE SPECTRAL DATA OF THE NICKEL COMPLEXES OF ATU AND PATU

Complex	Medium	Band positions (nm)
[Ni(ATU) ₄ Cl ₂]	Acetone	640 (184.1), 680 (176.2), 950 (29.0), 1060 (41.5), 1100 (41.5)
	DMF	420 (13.8), 610 (4.5), 685 (7.5), 750 (4.7), 1090 (3.0), 1130 (4.7)
[Ni(ATU) ₄ Br ₂]	Acetone	660 (214.0), 710 (208.9), 1000 (42.7), 1090 (41.8)
[Ni(ATU) ₄ I ₂]	do	420 (2273), 630 (220.0), 680 (261.7), 1010 (55.1), 1060 (55.1)
[Ni(ATU) ₅ NO ₃]NO ₃	do	435 (46.7), 610 (8.7), 675 (20.9), 710 (33.8), 750 (34.9), 850 (19.0), 1000 (6.1)
[Ni(ATU) ₆](ClO ₄) ₂	DMF	400 (118.0), 610 (24.7), 710 (7.7), 800 (9.7), 1070 (4.6), 1120 (5.6)
[Ni(PATU) ₄ Cl ₂]	Acetone	620 (173.0), 665 (172.2), 980 sh (34.0), 1070 (43.5)
[Ni(PATU) ₄ Br ₂]	do	650 (401.0), 680 (414.4), ~720 (~321), 1010 (76.2), 1100 (80.2)
[Ni(PATU) ₄ I ₂]	do	420 (1020), 620 (215.4), 680 (220.1), 1020 (50.5)
[Ni(PATU) ₄](ClO ₄) ₂	do	390 (100), 600 (17.5)

Figures in parentheses indicate extinction coefficients.

Solvolysis increases in the order — chloro < bromo < iodo complexes. The iodo complexes behave as strong electrolytes at low concentrations [Λ_M (ohm⁻¹ cm² mole⁻¹) = 50 at 2.5 mM, 132 at 0.25 mM and 229 at 0.025 mM for ATU complex and 52 at 2.54 mM, 100 at 0.6 mM and 303 at 0.025 mM for PATU complex in acetone]. Nickel perchlorate complexes may be viewed as 1:2 electrolytes [Λ_M (ohm⁻¹ cm² mole⁻¹) = 146 at 3.1 mM, 232 at 0.31 mM for ATU complex and 136 at 2.56 mM, 229 at

0.256 mM for PATU complex in acetone]. [Ni(PATU)₄Cl₂] in methanol behaves as a strong electrolyte even at a concentration of 2 mM ($\Lambda_M = 210 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$). The Λ_M values for nickel nitrate complex correspond approximately to a 1:1 electrolyte being 11 at 3.2 mM, 16 at 1.28 mM, 22 at 0.53 mM and 30 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ at 0.32 mM in acetone. Other complexes behave either as weak electrolytes or non-electrolytes.

Ebullioscopic determination of molecular weights in acetone ($K_b = 1.73$) shows that the complexes dissociate into several species in the solvent. The value for the nickel nitrate complex of ATU corresponds to the composition [Ni(ATU)₅NO₃]₂NO₃.

It can be concluded that the type of anion has a profound influence on the structure assumed by the complex and the coordination number of the complex seems to be determined by the type of the anion in terms of its size, charge, electronic configuration and coordinating power.

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Band positions (nm)	Medium	Complex
640 (184.1), 680 (176.5), 720 (139.0), 750 (128.0), 780 (121.5), 810 (116.3), 840 (111.8), 870 (108.0), 900 (104.4), 930 (101.1), 960 (97.9), 990 (94.7), 1020 (91.5), 1050 (88.3), 1080 (85.1), 1110 (81.9), 1140 (78.7), 1170 (75.5), 1200 (72.3), 1230 (69.1), 1260 (65.9), 1290 (62.7), 1320 (59.5), 1350 (56.3), 1380 (53.1), 1410 (50.0), 1440 (46.8), 1470 (43.6), 1500 (40.4), 1530 (37.2), 1560 (34.0), 1590 (30.8), 1620 (27.6), 1650 (24.4), 1680 (21.2), 1710 (18.0), 1740 (14.8), 1770 (11.6), 1800 (8.4), 1830 (5.2), 1860 (2.0)	Acetone, DMF, Acetone, do, do, do, DMF, Acetone, do, do, do, do	[Ni(ATU) ₄ Cl ₂], [Ni(ATU) ₅ NO ₃] ₂ NO ₃ , [Ni(ATU) ₄ Cl ₂], [Ni(ATU) ₅ NO ₃] ₂ NO ₃ , [Ni(ATU) ₄ Cl ₂], [Ni(ATU) ₅ NO ₃] ₂ NO ₃ , [Ni(ATU) ₄ Cl ₂], [Ni(ATU) ₅ NO ₃] ₂ NO ₃

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