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Studies on Nickel(II) Complexes of N-Aryl Thioureas

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The preparation and properties of the crystalline compounds of the type NiL_4Cl$_2$, NiL_2Cl$_2$ and NiLCl$_2$ (L = N-aryl thioureas) are described. Analytical, conductometric, magnetic and spectral data (infrared and electronic) show that complexes of the type NiL_4Cl$_2$ possess octahedral structure and those of NiL_2Cl$_2$ and NiLCl$_2$ are characterised as distorted octahedral in solid state. The ligand field parameters D_q, B and β calculated from electronic spectral data, suggest a weak field for all the ligands. Metal sulphur bonding for all ligands is adduced from infrared and far infrared spectral studies.

[Keywords: Conductometric; Ligand field parameters; Nickel(II) complexes; Thioureas]

Untersuchungen an Nickel(II) Komplexen von N-Aryl-thioharnstoff Derivaten

Darstellung und Eigenschaften der kristallinen Verbindungen vom Typ NiL_4Cl$_2$, NiL_2Cl$_2$ und NiLCl$_2$ (L = N-Arylthioharnstoff) werden beschrieben. Magnetische Eigenschaften, Leitfähigkeitsmessungen, analytische und spektroskopische Daten beweisen, daß die Komplexe vom Typ NiL_4Cl$_2$ oktaedrische Struktur besitzen; die Komplexe vom Typ NiL_2Cl$_2$ und NiLCl$_2$ weisen eine verzerrt oktaedrische Geometrie auf. Die Ligandenfeld-Parameter D_q, B und β, die aus Elektronenanregungsspektren berechnet wurden, zeigen ein schwaches Feld für alle untersuchten Liganden an. Aus Untersuchungen der Spektren des IR und fernen IR folgt, daß die Komplexe eine Metall—Schwefel-Bindung aufweisen.

Introduction

N-substituted thioureas form a great variety of complexes with transitional metal ions[1–3]. These ligands confer several stereochemical configurations on Nickel(II) such as octahedral, tetrahedral and planar[4–6]. The existing literature covers the two main types of

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paramagnetic complexes, presumably the tetrahedral NiL_2X_2 and pseudooctahedral NiL_4X_2 (L = thiourea and its derivatives). The latter dissolves in suitable solvents giving off two L molecules, thus behaving again as pseudotetrahedral NiL_2X_2[4,6]. So attempts are made to synthesize and study the properties of Nickel(II) halide with other substituted thioureas in order to understand the behaviour of this class of substances and to gain more data for possible correlation between substituent nature and electronic structure of the complexes.

The present communication deals with the preparation and properties of Nickel(II) chloride complexes of type NiL_4Cl_2, NiL_2Cl_2 and $NiLCl_2$ (L = N-aryl-thiourea). These have been characterized on the basis of data obtained from spectral (UV-visible and IR), magnetic susceptibility, conductivity and molecular weight measurements.

Experimental

Preparation of Complexes

All chemicals used were of *BDH* grade. The ligands were prepared according to the published procedures[8,9] employing freshly purified anilines.

Tetrakis (o-chlorophenyl-thiourea) nickel(II) chloride

The hot ethanolic solution of metal salt $NiCl_2 \cdot 6\,H_2O$ and *o*-chlorophenyl-thiourea in acetone were mixed in 1:4 mole ratio and then heated on water bath with constant stirring until a very small volume was remaining. The yellow coloured complex was isolated by stirring with petroleum ether (40-60 °C). The complex was filtered, washed successively with acetone and petroleum ether and dried over P_2O_5 in vacuum. A similar procedure was adopted for the synthesis of other complexes of nickel(II) chloride with the ligands viz *m*-chlorophenyl-thiourea (-Cl-ptu), *m*-bromophenyl-thiourea (-Br-ptu), *o* and *m*-hydroxyphenyl-thiourea (-HO-ptu), *o* and *m*-nitrophenyl-thiourea (-NO_2-ptu) *o*-methoxy phenyl-thiourea (-MeO-ptu) and *m*-tolyl-thiourea (-totu). The metal ligand ratio was changed to 1:2 for the synthesis of *o*-tolyl-thiourea (-totu) and 2-bromo-4-methylphenyl-thiourea (2-Br-4-Me-ptu) complexes, other wise the procedure remained the same. The yield of the complexes varied in the range 40-60%.

p-Chlorophenyl-thiourea nickel(II) chloride

The hot metal chloride solution in ethanol was treated with hot ligand solution in acetone (1:2 mole) and refluxed for 5-6 hrs. After cooling, the yellow coloured complex was filtered and washed successively with acetone and diethyl ether. The complex was further purified by soxlet extraction in acetone and dried over P_2O_5 in vacuum. A similar method was used for the compounds obtained from ligands viz. *p*-bromophenyl-thiourea and *p*-tolyl-thiourea. The yield of the complex was about 40%.

The complexes were analysed for nickel as dimethyl glyoximate and for nitrogen by the semimicro *Kjeldahl* method. Sulphur was estimated as barium sulphate and chloride as silver chloride[10].

Physicochemical Measurements

The molar conductance measurements of the complexes in acetone and DMF at a concentration $\sim 1 \times 10^{-3} M$ were taken on an ELICO conductivity bridge type CM-82 having a cell constant 0.61.

The molecular weight was determined ebullioscopically in acetone ($K_b = 1.72$) with the aid of a *Beckmann* thermometer graduated to 0.01 °C.

Magnetic susceptibility measurements were performed at room temperature (300 K) on a *Gouy* balance, using mercury tetrathiocyanato cobaltate(II) as the magnetic susceptibility standard. The magnetic moments of the complexes are given in Table 3.

Infrared absorption spectra (4,000-400 cm^{-1}) were recorded on a Carl-Zeiss UR-10 instrument by the Nujol mull method. Far infrared spectra (650-200 cm^{-1}) were taken from a Beckmann IR-12 instrument for solid samples suspended by polythene plates in nujol mull. Electronic spectra were recorded on a DMR-21 instrument in nujol mull and in acetonitrile solution.

Results and Discussion

The analytical data are presented in Table 1. The colour of the solid complexes varies from yellow to green. The complexes of the type NiL_4Cl_2 are soluble in common organic solvents like acetone, acetonitrile, ethanol, methanol, nitromethane etc. imparting bluish green colour to the solution; the complexes of type $NiLCl_2$ are insoluble in above solvents. The high decomposition point and insoluble nature of latter complexes may be related to their polymeric nature in the solid state. Conductance values in DMF lie in the range 43-55 mho $cm^2 M^{-1}$ (Table 1). According to previous reports 1:1 and 1:2 electrolytes in DMF will have molar conductances in the range 70-80 and 135-175 mho $cm^2 M^{-1}$ respectively[4, 5]. In the view of above facts these complexes are classified as nonelectrolytes and thus both chlorides are expected to be bonded to central metal ion.

Infrared Spectra

Thiourea and its derivatives can coordinate to the central metal through sulphur and/or nitrogen. Recent studies on the complexes of Co(II), Ni(II), UO_2^{2+}, Zn(II) chlorides etc. with thiourea and its derivatives clearly indicate coordination through sulphur[2, 3, 11–14]. However, metal nitrogen bonding is observed in Sn(IV), Ti(IV), Cu(I), Pt(II) complexes[15]. It is significant to note that Hg(II) coordinates through both sulphur and nitrogen of ethylene thiourea[16].

The frequency assignments for various bands have been made according to the conventions made by *Jensen et al.*[17] (Table 2). The bands observed in the 3 μ region are attributed to νNH vibration and these bands are not so sharp as those of simple thiourea. In the case of complexes this band undergoes a blue shift to the extent of 5-30 cm^{-1}, except in the case of *o*-chlorophenyl-thiourea complex, where the shift

Table 1. *Physical and analytical data of* Ni(II) *complexes with N-aryl thioureas*

Complex	M.P. °C	λ_M (mho cm^2 M^{-1})	% of Metal		% of Nitrogen		% of Chloride		% of Sulphur	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Ni(*o*-Cl-ptu)$_4$Cl$_2$	150—151	11.96	6.85	6.70	12.33	12.75	8.11	8.09	14.45	14.61
Ni(*m*-Cl-ptu)$_4$Cl$_2$	106—108	13.53	6.57	6.70	12.58	12.75	8.22	8.09	14.72	14.61
Ni(*m*-Br-ptu)$_4$Cl$_2$	106—107	14.77	5.50	5.56	10.41	10.65	6.75	6.72	12.29	12.14
Ni(*o*-HO-ptu)$_4$Cl$_2$	96—98	13.73	7.26	7.31	14.12	13.95	8.76	8.83	15.81	15.95
Ni(*m*-HO-ptu)$_4$Cl$_2$	98—100	4.10	7.41	7.31	14.27	13.95	8.78	8.83	15.78	15.95
Ni(*o*-NO$_2$-ptu)$_4$Cl$_2$[a]	120—121	40.24	6.52	6.38	18.22	18.31	7.87	7.73	14.12	13.95
Ni(*m*-NO$_2$-ptu)$_4$Cl$_2$[a]	98—100	43.08	6.58	6.38	18.42	18.31	7.67	7.73	14.02	13.95
Ni(*o*-MeO-ptu)$_4$Cl$_2$	143—145	3.94	7.00	6.84	13.23	13.05	8.32	8.26	14.36	14.58
Ni(*m*-totu)$_4$Cl$_2$	152—153	24.43	7.56	7.38	13.98	14.09	8.78	8.92	16.25	16.11
Ni(2-Br-4-Me-ptu)$_2$Cl$_2$	120—122	15.49	9.20	9.47	9.25	9.03	11.32	11.44	10.27	10.32
Ni(*o*-totu)$_2$Cl$_2$	124—125	11.62	12.52	12.70	12.11	12.02	15.48	15.34	13.78	13.85
Ni(*p*-Cl-ptu)Cl$_2$[a]	250—251[b]	54.62	18.20	18.57	8.62	8.85	22.43	22.51	10.22	10.16
Ni(*p*-Br-ptu)Cl$_2$[a]	360—361[b]	55.29	16.37	16.22	7.80	7.75	9.75	9.61	8.91	8.85
Ni(*p*-totu)Cl$_2$[a]	295—296[b]	52.24	19.70	19.84	9.43	9.25	24.12	23.96	10.73	10.81

[a] Conductance in DMF. [b] Decomposition temperature.

Table 2. *IR and Far-IR absorption bands of* Ni(II) *complexes with N-aryl thioureas*

Ligand/Complex	ν_{asy}NCN	ν_{sym}NCN + νCS + ρNH_2	νCS + νCN	νM—S	νM—Cl
o-Cl-ptu	1566 w	1133 s	725 s	—	—
Ni(*o*-Cl-ptu)$_4$Cl$_2$	1575 ms	1133 w	716 ms	245 ms	320 s
m-Cl-ptu	1531 s	1060 s	704 s	—	—
Ni(*m*-Cl-ptu)$_4$Cl$_2$	1533 ms	1060 ms	700 ms	260 ms	300 s
m-Br-ptu	1583 ms	1054 ms	670 ms	—	—
Ni(*m*-Br-ptu)$_4$Cl$_2$	1570 s	1054 ms	662 w	245 ms	300 s
o-HO-ptu	1525 s	1000 ms	733 s	—	—
Ni(*o*-HO-ptu)$_4$Cl$_2$	1541 s	1010 ms	729 s	245 ms	290 ms
m-HO-ptu	1545 s	1154 s	689 s	—	—
Ni(*m*-HO-ptu)$_4$Cl$_2$	1554 s	1162 s	689 w	240 ms	350 s
o-NO$_2$-ptu	1500 ms	1100 ms	670 ms	—	—
Ni(*o*-NO$_2$-ptu)$_4$Cl$_2$	1508 s	1108 ms	665 ms	245 ms	275 s
m-NO$_2$-ptu	1532 sh 1500 mbr	1075 ms	730 ms	—	—
Ni(*m*-NO$_2$-ptu)$_4$Cl$_2$	1541 s	1087 ms	725 w	245 ms	320 ms
o-MeO-ptu	1533 s	1062 s	773 ms	—	—
Ni(*o*-MeO-ptu)$_4$Cl$_2$	1566 ms	1066 w	766 s	265 ms	300 ms
m-totu	1537 s	1100 ms	754 s	—	—
Ni(*m*-totu)$_4$Cl$_2$	1558 s	1091 w	748 w	225 s	320 s
2-Br-4-Me-ptu	1477 s	1070 s	741 ms	—	—
Ni(2-Br-4-Me-ptu)$_2$Cl$_2$	1483 ms	1070 w	720 ms	220 mbr	330 mbr
o-totu	1501 s	1112 s	716 s	—	—
Ni(*o*-totu)$_2$Cl$_2$	1545 s	1125 ms	712 w	275 ms	315 s
p-Cl-ptu	1520 mbr	1087 s	689 ms	—	—
Ni(*p*-Cl-ptu)Cl$_2$	1545 s	1085 ms	662 w	270 ms	355 s
p-Br-ptu	1504 s	1066 s	675 s	—	—
Ni(*p*-Br-ptu)Cl$_2$	1533 s	1070 w	643 ms	245 ms	340 ms
p-totu	1537 s	1075 s	708 s	—	—
Ni(*p*-totu)Cl$_2$	1566 s	1108 w	700 w	225 ms	335 s

s = sharp, ms = medium sharp, sh = shoulder, mbr = medium broad, w = weak.

to higher frequency is of the order of 70 cm^{-1}. The bands observed in the complexes are broader than those of free ligands. This may be due to intense intramolecular hydrogen bonding which is also apparent from slight blue shift for $\delta(NH_2)$ (A band) in the region of

1,595-1,615 cm^{-1} compared to free ligand[18]. The increased double bond character of CN (B band) indicated by blue shift (5-30 cm^{-1}) in the region 1,500-1,550 cm^{-1} and small shift for ν_{sym}NCN + δ(NH$_2$) + νCN (C band) around 1,380 cm^{-1} clearly show sulphur coordination of the ligand to the metal. Practically no shift is observed for a composite band at 1,050-1,110 cm^{-1} but a decrease in intensity of the band may be due to equal contribution of ν_{sym}NCN and νCS. The bands observed in the region 700-800 cm^{-1} and 670-600 cm^{-1} are assigned to νCS with slight contribution of νCN and νCS respectively. The red shift (5-25 cm^{-1}) with reduction in intensity of these bands indicates that sulphur is involved in coordination. Far infrared spectral data also supports sulphur coordination of ligand to the central metal ion.

Far Infrared Spectra

According to *Flint et al.*[19] and *Adams et al.*[20] the νM-S is related to the strong band observed at ~ 220 cm^{-1}. The band observed by us in the range 220-275 cm^{-1} is assigned to νM-S (Table 2) for nickel(II) complexes with *N*-aryl-thioureas. The medium strong band in the region 330-290 cm^{-1} has been assigned to νM-Cl for the above complexes.

Magnetic Data

The magnetic moments obtained at room temperature for these Ni(II) complexes are listed in Table 3. The μ_{eff} value falls in the range of 2.84-3.64 BM, which is the expected range for octahedral Ni(II) complexes. The high magnetic moments of these complexes may be due to spin-orbital coupling which causes an orbital contribution in the quenched $^3A_{2g}$ ground state of Ni(II).

Electronic Spectra

Electronic spectra were recorded in solid state as nujol mull (Table 3) and also in acetonitrile solution for some samples. The band in the region 25 to 20 kK is assigned to ν_3 arising from the transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$; in the region 16.26 to 12.90 kK to ν_2 from the transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and in the region 8.30 to 8.16 kK to ν_1 arising from the transition $^3A_{2g} \rightarrow {}^3T_{2g}(F)$; the last one directly yields the $10\,D_q$ value. The solution spectra of the complexes of type NiL_4Cl$_2$ show a splitting of ν_2 band which may be due to lowering of symmetry because of tetragonal distortion[21]. The electronic spectra in solid state could not be easily interpreted since they present characteristics common to tetrahedral, square planar and tetragonal chromophores. However,

Table 3. *Magnetic moment, UV-visible spectra and ligand field parameters*

Complex	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ ν_1 kK	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ν_2 kK	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ν_3 kK	B (cm^{-1})	β	ν_2/ν_1	μ_{eff}(B.M.)
Ni(*o*-Cl-ptu)$_4$Cl$_2$	8.23	12.90	22.99	719	0.744	1.66	3.35
Ni(*m*-Cl-ptu)$_4$Cl$_2$	8.26	13.33	23.26	806	0.765	1.61	3.17
Ni(*m*-Br-ptu)$_4$Cl$_2$	8.23	13.51	24.10	869	0.823	1.64	3.18
Ni(*o*-HO-ptu)$_4$Cl$_2$	8.25	13.74	25.00	935	0.885	1.73	2.93
Ni(*m*-HO-ptu)$_4$Cl$_2$	8.26	13.51	23.81	844	0.799	1.63	3.11
Ni(*o*-NO$_2$-ptu)$_4$Cl$_2$	8.23	13.99	20.20	552	0.523	1.70	3.64
Ni(*m*-NO$_2$-ptu)$_4$Cl$_2$	8.20	13.85	21.98	706	0.671	1.70	3.54
Ni(*o*-MeO-ptu)$_4$Cl$_2$	8.30	16.26	23.81	841	0.796	1.95	2.97
Ni(*m*-totu)$_4$Cl$_2$	8.26	13.70	20.00	537	0.505	1.65	—
Ni(2-Br-4-Me-ptu)$_2$Cl$_2$	8.16	13.33	22.22	733	0.696	1.63	2.96
Ni(*p*-Cl-ptu)Cl$_2$	8.26	13.51	22.47	740	0.701	1.63	2.84
Ni(*o*-totu)$_2$Cl$_2$	8.30	13.42	25.00	930	0.885	1.61	3.41
Ni(*p*-Br-ptu)Cl$_2$	8.20	13.16	24.69	919	0.870	1.60	3.23
Ni(*p*-totu)Cl$_2$	8.23	13.25	24.69	914	0.865	1.61	3.08

magnetic and spectral data, usually employed in conjunction with ligand field theory, have enabled us to determine such structures with fair certainty[4]. The band position and shape of the bands for NiL_2Cl_2 and $NiLCl_2$ type complexes are similar to those of the NiL_4Cl_2 type, hence a polymeric pseudooctahedral structure is proposed for the former type of complexes in solid state. The D_q value ranges from 830-816 cm^{-1} (Table 3) which may be very well compared to that of $[Ni(tu)_4Cl_2]$, (798 cm^{-1}) and $[Ni(entu)_4Cl_2]$, (782 cm^{-1}). The ν_2/ν_1 value lies in the range 1.60 to 1.95 which is expected for an octahedral stereochemistry for the central Ni(II) ion. This value agrees well with previous reports for octahedral complexes (1.7 to 1.8) but not for tetrahedral species (2.2)[21–24].

Molecular weight determination data for tetrakis *o*-chlorophenyl-thiourea nickel(II) chloride (Found 273 ± 10, calcd. 876.3) and tetrakis *m*-chlorophenyl-thiourea nickel(II) chloride (Found 283 ± 10, calcd. 876.3) indicate the presence of three particles in solution (acetone) instead of the one expected. The complex may undergo dissociation yielding free ligands but not the halide ions.

$$NiL_4Cl_2 \rightarrow NiL_2Cl_2 + 2\,L.$$

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