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Reaction of Bis(diethyl dithiocarbamato)nickel(II) with 4-Methyl- & 4-Vinyl-pyridines

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Bis(diethyl dithiocarbamato)nickel(II) when reacted separately with 4-methylpyridine and 4-vinylpyridine (L) in ethanolic medium forms compounds having the composition $[\text{Ni}(\text{dtc})_2\text{L}]$. They are diamagnetic and non-electrolytes. Infrared spectra indicate the presence of bonded ligands. The complexes are penta-coordinated, as revealed by their electronic absorption spectra with nickel atom surrounded by four sulphur and one nitrogen donor atoms.

IN Ni(II) complexes tetra- and hexa-coordination is a common feature, and penta-coordination is rare. The preferred coordination number depends upon the polarizability of the ligands reacting with the metal ion. It is, therefore, worthwhile to see whether this less common penta-coordination can be stabilized by providing a hetero-donor atom environment round the nickel ion. With this in view the reaction of bis(diethyl dithiocarbamato)nickel(II) with 4-methyl- and 4-vinylpyridines has been studied and the complexes formed isolated and characterized.

Ethanolic solution of nickel chloride was reacted with ethanolic solution of sodium diethyl dithiocarbamate (Na.dtc) in the ratio 1:2. The precipitated light green compound was suction-filtered, washed with ethanol and dried *in vacuo*. The composition of this compound was established to be $\text{Ni}(\text{dtc})_2$ by elemental analysis and infrared spectral study. This freshly prepared complex was reacted with 4-methylpyridine and 4-vinylpyridine separately in ethanolic medium in the stoichiometric ratios of 1:1 and 1:2. The reaction mixture was refluxed for 6 hr and the resulting products were suction-filtered, washed with ethanol followed by ether and then dried *in vacuo*. (i) $\text{Ni}(\text{dtc})_2\cdot 4\text{-me.py}$ (Found: Ni, 13.6; S, 29.0. Calc.: Ni, 13.4; S, 28.6%), m.p. >300; Λ_M 0.5 mhos. $\text{Ni}(\text{dtc})_2\cdot 4\text{-vi.py}$ (Found: Ni, 12.8; S, 27.8. Calc.: Ni, 12.8; S, 28.2%), m.p. >300; Λ_M 0.6 mhos.

McCormick and Roy¹ have reported that Ni(II) forms stable, planar, diamagnetic and tetracoordinated compounds $[\text{Ni}(\text{dtc})_2]$ with a series of dithiocarbamates. Nickel(II) β -diketonates on reaction with nitrogen² and sulphur³ donor ligands were found by us to give hexacoordinated compounds, $\text{Ni}(\beta\text{-dik})_2\text{L}_2$. Bis(diethyl dithiocarbamato)zinc(II) was reacted⁴ with some substituted pyridines and several penta-coordinated compounds having the composition $\text{Zn}(\text{dtc})_2\text{L}$ were obtained. Dithiocarbamate is a uni-negative, bidentate ligand and so neutral ligands cannot replace it; they can be simply added on if the requirements are satisfied. Neutral bidentate nitrogen donor ligands like α,α' -dipyridyl and *o*-phenanthroline were reacted with $\text{Ni}(\text{dtc})_2$ but with no consequence. So, it is clear that the coordination number cannot be increased to six. In the present investigation when several neutral unidentate nitrogen donor ligands were tried, reaction took place only with 4-methylpyridine and 4-vinylpyridine resulting in the addition of only one mole of the ligand. Even when excess of ligand in the ratio 1:2 was taken, only one mole of the ligand was added. This explains why there was no reaction when a bidentate ligand was used. Very low values of molar conductance, Λ_M (0.5 mhos) in nitrobenzene ($10^{-3}M$ solution) indicate the non-electrolytic nature. The compounds are diamagnetic as expected for a penta-coordinated nickel(II) compound involving $3d4s4p^3$ hybrid orbitals.

In diethyl dithiocarbamate, $\nu(\text{C}-\text{N})$ was reported⁵ at 1480-1550 and $\nu(\text{C}-\text{S})$ ⁶ at 989-1006 cm^{-1} . The sample of $\text{Ni}(\text{dtc})_2$ prepared by us exhibits bands at 1525 and 985 cm^{-1} corresponding to $\nu(\text{C}-\text{N})$ and $\nu(\text{C}-\text{S})$ respectively. In the 4-methylpyridine and 4-vinylpyridine adducts, the $\nu\text{C}-\text{N}$ and $\nu\text{C}-\text{S}$ frequencies are observed at 1520, 1518 and 980, 995 cm^{-1} respectively. It is, therefore, clear that dithiocarbamate ligands in the complex remain undisturbed. In addition to the absorption bands due to diethyl dithiocarbamate, characteristic bands due to 4-methylpyridine and 4-vinylpyridine are also observed in the complexes $\text{Ni}(\text{dtc})_2\text{L}$. There is no evidence, either analytical or spectral, for the presence of a coordinated water molecule. Hence the complexes under report are definite examples of penta-coordination of nickel(II) being surrounded by four sulphur atoms and one nitrogen atom.

Pentacoordination of nickel(II) gains further support from electronic spectral data. Sacconi had shown⁷ that in penta-coordinated configuration, the ground state term of the nickel(II) ion splits into a relatively large number of terms on lowering the symmetry as compared to that of tetrahedral or octahedral configuration. Bertini reported⁸ absorption bands at 8000, 10000, 13000 and 16000 cm^{-1} and postulated the existence of five-coordinate high spin nickel(II) complexes with mixed salicylaldimine ligands. It was also suggested⁹ that four-coordinated planar complexes of nickel(II) do not show appreciable absorption below 18000-20000 cm^{-1} .

In the present investigation, the electronic spectrum of $\text{Ni}(\text{dtc})_2(4\text{-vi-py})$ in CHCl_3 exhibited maxima (ϵ) at 11420 (57), 12500 (51), 16600 (150), 17540 (142) and 21275 (340) cm^{-1} while $\text{Ni}(\text{dtc})_2(4\text{-me-py})$

exhibited maxima at 11765 (107), 13790 (125), 16000 (200) and 23800 (2000) cm^{-1} . These bands are in the same range as reported by Bertini⁸ and further, bands below 20000 cm^{-1} exclude the possibility of any four-coordinated species. Hence it is suggestive that these compounds under report are definitely penta-coordinated. The two preferred geometries for this penta-coordination are square pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}). The exact stereochemistry can be ascertained only by X-ray analysis.

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Hg(II) Complexes with Some Dithioureas

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A number of complexes of Hg(II) with substituted dithioureas having the composition $[\text{HgLX}_2]$ where X is Cl^- , I^- , SCN^- and L = a substituted dithioureas have been synthesized and characterized as octahedral complexes on the basis of analysis, conductance and infrared spectral studies.

ACCORDING to Chatt and Davies¹, mercury(II) belongs to the class (b) acceptors and thus has a strong affinity for sulphur donor ligands. Even though large number of complexes of Zn(II), Cd(II), Hg(II) and other metal ions with simple and substituted thioureas have been reported²⁻⁵, no work has been done on the mercury(II) complexes with dithioureas. This note reports ten complexes of the composition $[\text{HgLX}_2]$ where X is Cl^- , I^- , SCN^- and L is piperazino-1,4-diphenyldithioureas, piperazino-1,4-di-(*m*-tolyl) dithioureas, piperazino-1,4-di-(*o*-chlorophenyl) dithioureas, biphenyl-4,4'-dithioureas and phenyl-1,4-dithioureas.

All the chemicals used were of AR grade.

Preparation of piperaziniodiaryldithioureas — Phenyl isothiocyanate (5.16 g) in ethanol was mixed with

piperazine (4 g) in ethanol, when white precipitate of the dithioureas separated out immediately. These were filtered and recrystallized from dimethyl formamide. Other substituted piperaziniodiaryldithioureas were prepared exactly in an analogous manner by treating stoichiometric amount of substituted phenyl isothiocyanates with piperazine.

Preparation of biphenyl-4,4'-bis-thioureas — To an aqueous suspension of benzidine dihydrochloride (2.56 g), ammonium thiocyanate (2.56 g) was added and heated for 2 hr over a water-bath when the dithioureas separated out which was filtered, washed and recrystallized from dimethylformamide.

Preparation of phenyl-1,4-dithioureas — To an aqueous suspension of *p*-phenel-*n*-diamine dihydrochloride (1.8 g), ammonium thiocyanate (about 2.2 g) was added and heated over a water-bath for 2 hr when the corresponding dithioureas separated out. The composition of the compounds was confirmed by elemental analysis.

Preparation of complexes — To a hot mercury(II) salt solution in ethanol, dimethylformamide solutions of the dithioureas in (1:2) ratio were added slowly with constant stirring. On cooling, complexes separated out, which were filtered, washed in ethanol and dried *in vacuo*.

Metal was estimated complexometrically by EDTA method using Erichrome Black-T as indicator at pH 10.

All the complexes reported (Table 1) in the present investigation have the general composition $[\text{HgLX}_2]$, where X is Cl^- , I^- or SCN^- and L is a substituted dithioureas. The complexes are white to greyish white in colour. Some of the complexes are crystalline, where others are amorphous. These have high melting points, are either insoluble or very sparingly soluble in common organic solvents. Conductance measurement for the complexes which are sparingly soluble in acetone, indicated non-electrolytic nature as Λ_M is around 18-20 mhos cm^2 .

TABLE 1 — ANALYTICAL DATA OF MERCURY(II) DITHIOUREA COMPLEXES

Compounds	Hg (%)		N (%)		S (%)	
	Found	Reqd	Found	Reqd	Found	Reqd
L	—	—	15.38	15.70	17.35	17.69
L ^I	—	—	14.57	14.89	16.79	17.02
L ^{II}	—	—	15.81	16.18	18.28	18.49
L ^{III}	—	—	18.13	18.54	20.87	21.19
L ^{IV}	—	—	24.49	24.76	28.15	28.31
HgLCl ₂	31.65	31.90	8.67	8.93	9.94	10.21
HgLI ₂	16.94	17.1	6.74	6.90	7.68	7.89
HgL(SCN) ₂	25.63	25.9	12.23	12.48	9.33	9.51
HgLCI ₂	29.97	30.48	8.48	8.72	9.51	9.88
HgLI ^I Cl ₂	28.44	28.70	7.97	8.15	9.14	9.32
HgLI ^{II} Cl ₂	36.57	36.78	9.38	9.77	10.94	11.17
HgLI ^{III} I ₂	26.34	26.58	7.17	7.34	8.15	8.39
HgLI ^{III} Cl ₂	40.12	40.39	11.06	11.27	12.63	12.88
HgLI ^{IV} I ₂	29.24	29.57	8.31	8.52	9.24	9.40
HgLI ^{IV} (SCN) ₂	36.63	36.97	15.25	15.47	11.52	11.77

L = Piperazino-1,4-diaryldithioureas; L^I = piperazino-1,4-di(*m*-tolyl)dithioureas; L^{II} = piperazino-1,4-di(*o*-chlorophenyl)dithioureas; L^{III} = biphenyl-4,4'-dithioureas; L^{IV} = phenyl-1,4-dithioureas.