STUDIES ON COORDINATION OF COMPOUNDS

Part I.—Nickel(II) Complexes of Adipyl Dihydrazide

M. Arshad A. Beg and B. Bilquis

P.C.S.I.R. Laboratories, Karachi 32

Adipyl dihydrazide complexes of the type [{ Ni (Adipyldihydrazide).$2H_2O$ } $X_2]_n$ where X is chloride, bromide nitrate or sulfate are reported. Their insolubility in all organic solvents suggests a polymeric nature. Models for the compounds do not support a chelated metal ion. The magnetic data and visible spectra suggest an octahedral structure with tetragonal distortions. The conductivity shows that the anions are outside the coordination sphere. The high value for the ligand field parameter as also the IR spectra indicate that the terminal amino groups are donors and hence form a linear polymer.

Coordination compounds of ligands containing more than one potential donor group have been of great interest during recent years. The preferential bonding of one of the groups has been the subject of discussion in many cases.[1,2] Amino acids, amides and dithiocarbamates are some such ligands. It is proposed to study the chemistry of similar coordination compounds from adipyl diphrazide which has four potential donors.
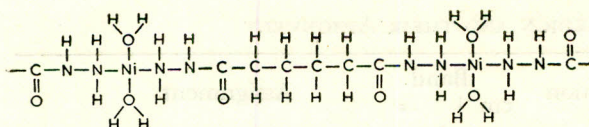
This paper not only describes the nickel complexes but also introduces a new ligand to the already long list of such compounds.

Results

From the analytical data it is apparent that the complexes are formed in the 1:1 proportion with respect to the nickel salt and the adipyl dihydrazide. There are also two molecules of water in the coordination sphere since no loss in weight is observed on storage in vacuum over sulphuric acid. The compounds are insoluble in all organic solvents which suggests a polymeric structure. The IR spectra reveal a decrease in the C—N stretching frequency and a shift of the N—H vibration to lower wavelengths indicating the participation of the amino groups in coordination. These spectra will be discussed separately elsewhere. The visible region spectrum shows three consistent bands which are listed along with their assignments in Table 1. The magnetic measurements, listed in Table 2 indicate paramagnetic behaviour.

Discussion

The assembly of Fischer–Taylor–Hirschfelder model for this series suggests: (1) that the dihydra-zide molecule will have to be considerable twisted in order to act as a bidentate ligand with the terminal amino groups as the donor, (2) the case is identical whether the configuration is octahedral or tetrahedral. A twisted structure is a departure from planarity and consequently it will not impart stability to the chelate structure. The IR spectra are much simpler than that of adipyl dihydrazide itself and hence suggests a higher symmetry for the molecule. Such a system is obtainable if the amino groups are donors to two different nickel ions thus forming a linear chain giving rise to a polymeric structure which is also evidenced by the low solubility.

The IR spectra also do not show any increase in the C—O frequency which is rather unexpected since with the participation of the amino groups the resonance interaction with the lone pair on nitrogen would be disturbed and there would be an increase in the carbonyl frequency as observed in the urea complexes of palladium and platinum.[2] It is possible that the carbonyl group interacts with the yet another neighboring nickel ion in the crystal lattice giving rise to a cross-linked structure. Such an interaction would give an octahedral structure which is supported by the visible spectra and magnetic data. It is, however, also quite likely that the carbonyl group resonance, instead of extending over the entire hydrazide group is now limited to the imino group thus causing no shift in the carbonyl frequency.

Visible Spectra.—The notable features of the spectra are four weak bands occurring at 27100 ± 300 cm^{-1}, $10580 \pm$ cm^{-1}, and 7050 ± 40 cm^{-1}. The fourth band is quite weak and is most likely due to the ligand. The fundamental bands are those occurring at 27000, 16900 and 10580 cm^{-1}. These three absorptions suggest an octahedral structure but since the complexes are of the $MA_2B_2C_2$ $^{2+}$ type a tetragonal structure is

expected with a linear chain of the dihydrazide molecule occupying two *trans* positions and the water molecules taking another two *trans* positions. Using the 10580 cm^{-1} band as the lowest energy transition $3A_{2g} \rightarrow 3T_{2g}$, it is found that the calculated position corresponds to that observed. The D_q value of $\sim$1058 is quite high which is, however, of the same order as in other amines. This therefore again suggests the participation of the terminal amino groups and also the linear polymeric structure. The β value is calculated to be $\sim$19%. β is a measure of the delocalization of the metallic ion electron density into the ligand. The high value therefore, suggests that the electron–electron repulsions among the d electrons in the complexed metal ion are sufficiently reduced. This may among other things, be taken to imply that the amount of distortion from octahedral structure is not large. These conclusions are further supported by the low intensity of the bands which in the tetrahedral and square planar fields should have been much higher.

Magnetic Susceptibility.—The magnetic data (Table 3) also suggest an octahedral framework with tetragonal distortions since the susceptibility

corresponds to 2.72–3.01 BM corresponding to two unpaired electrons. The magnetic moments are either close to or lower than the spin only value. It may be recalled that the D_q value is quite high.

$$\mu = \mu_\circ \left(1 - \alpha \frac{\lambda}{\Delta}\right)$$

From the above relationship where $\mu_\circ$ is the spin only moment, α is a constant whose value in our case is 4, λ is the spin–orbit coupling constant and Δ is the ligand field stabilization energy. Since Δ is large the above relationship gives a low value for λ implying a further quenching of the orbital angular momentum which should be obtained in ligand fields of symmetry lower than octahedral. The magnetic data therefore also suggest tetragonal distortions in an octahedral framework.

Conductivity.—The substances are nonconductors in organic solvents but dissolve in water. Their molar conductivity (Table 3) at Λ_{1000} is $\sim$250 corresponding to the presence of three ions so that the anions are outside the coordination sphere and the complexes may be formulated as [Ni(Adipyldihydrazide).2H$_2$O]X$_2$.

TABLE 1.—Bands in the Visible Region and their Assignment

Compound	Concentration	Band cm^{-1}	ε	Assignment
[(Ni Adipyl dihydrazide.2H$_2$O]Cl$_2$	29.4×10	26880	8.9	$3A_{2g}(F) \rightarrow 3T_{1g}(P)$
		16800	5.9	$\rightarrow 3T_{1g}(F)$
		10640	5.9	$\rightarrow 3T_{2g}(F)$
		7069	3.2	
[(Ni Adipyl dihydrazide.2H$_2$O]Br$_2$	23.3×10	27395	9.1	$3A_{2g}(F) \rightarrow 3T_{1g}(P)$
		16940	5.6	$\rightarrow 3T_{1g}(F)$
		10520	7.6	$\rightarrow 3T_{2g}(F)$
		7092	3.2	
[(Ni Adipyl dihydrazide.2H2O](NO$_3$)$_2$	25.4×10	27775	8.9	$3A_{2g}(F) \rightarrow 3T_{1g}(P)$
		16940	6.8	$\rightarrow 3T_{1g}(F)$
		10750	8.6	$\rightarrow 3T_{2g}(F)$
		7017	4.2	
[(Ni Adipyl dihydrazide.2H$_2$O]SO$_4$	Insoluble			

TABLE 2.—The Calculated Ligand Field Parameters.

Compound	$E(P)E\leftarrow(F)$ cm^{-1}	p term cm^{-1}	D_q	Band II cm^{-1} Observed	Band II cm^{-1} Calc.	β%
[Ni (Adipyl dihydrazide).2H$_2$O]Cl$_2$	14112	13060	1064	16800	17391	17.55
[Ni (Adipyl dihydrazide).2H$_2$O]Br$_2$	14771	12740	1052	16940	16869	19.56
[Ni (Adipyl dihydrazide).2H$_2$O] (NO$_3$)$_2$	14875	12680	1075	16940	17155	19.94

TABLE 3.—MAGNETIC SUSCEPTIBILITY AND CONDUCTIVITY $\wedge$ 1000 OF THE COMPOUNDS.

Compounds	$X_g \times 10^6$	$X_m \times 10^6$	X_m Corrected	μ_{eff}	$\wedge$ 1000
[Ni (Adipyl dihydrazide).$2H_2O$]$Cl_2 q$	10.2	3465.04	3610.94	2.96	239.9
[Ni (Adipyl dihydrazide).$2H_2O$] Br_2	8.07	3472.07	3638.97	3.01	266.4
[Ni (Adipyl dihydrazide).$2H_2O$]$(NO_3)_2$	7.42	2914.00	3057.5	2.76	241.7
[Ni (Adipyl dihydrazide).$2H_2O$]SO_4	8.08	2946.6	3092.6	2.72	insol.

TABLE 4.

Compound	Ni		Anion		M.p.	Colour
	Calc	Found	Calc	Found		
[(Ni(Adipyl dihydrazide).$2H_2O$]Cl_2	17.27	18.15	20.60	20.51	300°C (d)	Yellowish green
[(Ni(Adipyl dihydrazide).$2H_2O$]Br	13.12	13.4	39.29	39.19	295°C (d)	Bluish green
[(Ni(Adipyl dihydrazide).$2H_2O$]$(NO_3)_2$	16.7	16.6			300°C (d)	Light blue
[(Ni(Adipyl dihydrazide).$2H_2O$]SO_4	16.02	16.5	26.32	26.30	290°C (d)	Blue

Experimental

Adipyl dihydrazide was prepared by the method of Leonard.[3] The complexes with the nickel salts, nickel chloride, bromide, nitrate and sulphate were prepared by mixing their solutions in 50% aqueous ethanol and refluxing for 3 hr over a water bath. The solution was then concentrated by evaporation and ether was added. A jelly-like substance obtained at this stage was again refluxed with ethanol. The crystals obtained thereafter were washed with alcohol and dried *in vacuo*. The nickel sulphate complex was obtained by direct mixing and the initial refluxing was not necessary. The analytical data, colour and m.p. are reported in Table 4. The compounds were desiccated over sulphuric acid and no loss in weight was noted even when stored for several days.

The IR spectra were run on a Beckman IR-4 spectrophotometer using KBr pellets and Nujol mulls. The visible range spectra were run on a Beckman DK-2 spectrophotometer using aqueous solutions. Magnetic susceptibility measurements were made on powdered samples, using a Newport single-Temperature Gouy Balance system Type C which was kindly made available to us through the CENTO Aid. The conductivity was measured on a WTW conductivity meter using conductivity water as solvent.

References

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