Articles

The Electrical Conductivity of *O*-amino Benzoic Acid Hydrazide and Its Complexes with Co²⁺, Ni²⁺ & Cu²⁺

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The electrical conductivity of the complexes of Co²⁺, Ni²⁺ and Cu²⁺ with o-aminobenzoic acid hydrazide was measured between 300 and 500 K. It was observed that the conductivity is dependent upon both the cations and anions of the reacted salts. The prepared complexes exhibit typical semiconducting behaviour.

Introduction

The acid hydrazides have special interest due to their use in biological systems[1,2]. As ligands, they form stable complexes with various transition metals[3-5]. Although a lot of work has been done on the electrical behaviour of the solid organic complexes[6-13], there is much less has been done about the electrical characteristics of hydrazide-metal complexes. The aim of this work is to investigate the effect of different anions, such as chloride, nitrate, sulphate and acetate, on the electrical behaviour of complexes of Co²⁺, Ni²⁺ or Cu²⁺ with o-aminobenzoic acid hydrazide.

Experimental

All the chemicals used were of AR grade. The acid hydrazide was prepared by dissolving 10 gm of anthranelic acid in 100 m*l* dry MeOH, then 10 m*l* conc. H₂SO₄ were added. The mixture was refluxed for 4 hr, then cooled in an ice bath and neutralized by adding saturated solution of Na₂CO₃. The ester was extracted by ether and dried using anhydrous Na₂SO₄. One m*l* of hydrazine was added to one gram of the ester and the mixture was refluxed for 3 hr. The product was recrystallized from ethanol.

The solid complexes were prepared by adding dropwise solution of metal (II) chloride, nitrate, sulphate and acetate to a hot aqueous solution of the ligand (o-aminobenzoic acid hydrazide). A complex of stoichiometric ratio 1 : 2 (metal : ligand) was precipitated, then filtered and dried in vacuum. The structure of complexes was characterized on the basis of elemental analysis as listed on Table 1.

Infrared analysis using a Shimadzu IR-440 spectrophotometer and X-ray diffractometer with Philips 1390 of Ni filter have also been used to identify the solid complexes.

All samples studied in the present work were compressed to pellets with diameter of 12 mm and thickness 2 mm. The pressure used was 5 ton/cm². The measuring technique of the electrical conductivity has been described eleswhere[13].

Table 1. Elemental Analysis of Aminobenzoic Acid Hydrazide and Its Complexes

Compound	Elemental	% Calcd.	% Found
Ligand	C	55.60	55.80
(C₇H₉N₃O)	H	5.96	6.00
	N	27.81	27.70
Co-Complex	C	35.91	35.90
Co(C₇H₉N₃O)₂Cl₂·2H₂O	H	4.70	4.80
	N	17.95	18.00
	Cl	15.17	15.10
	Co	12.59	12.40
Ni-Complex	C	35.92	36.20
Ni(C₇H₉N₃O)₂Cl₂·2H₂O	H	4.70	4.90
	N	17.96	18.00
	Cl	15.18	15.10
	Ni	12.55	12.50
Cu-Complex	C	35.55	35.80
Cu(C₇H₉N₃O)₂Cl₂·2H₂O	H	4.66	4.70
	N	17.77	17.30
	Cl	15.02	15.10
	Cu	13.44	13.50

Results and Discussion

The mode of bonding of aminobenzoic hydrazide to the various metal ions (Co²⁺, Ni²⁺ or Cu²⁺) was examined by recording the IR spectra of the complexes compared with that of the free ligand. The IR spectrum of the free ligand shows bands at 3275, 1610 and 1438 cm⁻¹ due to ν NH₂ and δ NH₂ modes of vibration. The complexes show a bathochromic shift and broading in the region 3275-1200 cm⁻¹ indicating that the coordination occurs through the hydrazinic NH₂ group.
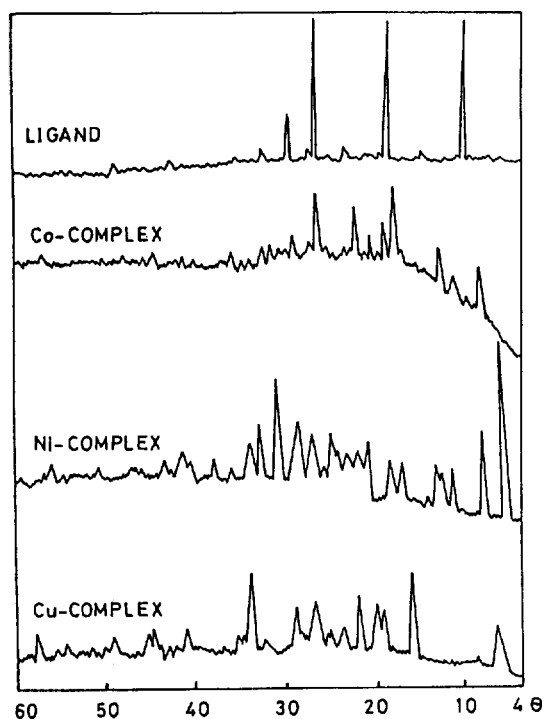
Also, the wavenumber of the strong absorption observed

Figure 1. X-ray diffraction patterns of the investigated complexes at room temperature.

Figure 2. Electrical conductivity of *o*-aminobenzoic acid hydrazide.

at 1608 cm^{-1} due to amide II is red shifted by about 5-10 cm^{-1} upon complexation suggesting the contribution of the carbonyl group in complexation process *via* oxygen atom[14].

Absorption band observed in the range 930-970 cm^{-1} in the spectrum of the ligand is attributed to δ OH. The OH group is formed as a result of the enolisation of the keto group. Enolisation of amide group is supported by the appearance of new bands at 1520-1540 cm^{-1} (ν NCO). The amide group is thus involved in bonding with metal atom through the enolic oxygen.

The coordination of amino group of the ligand to the various divalent metal ions investigated is shown by the red shift in the wavenumber and intensity of δ NH band located at 745 cm^{-1}. The new bands observed at 570-520 cm^{-1} can be assigned to ν M-O vibration[15], whereas the bands appeared in the region 400-450 cm^{-1} were attributed to ν M-N vibration.

Therefore, based on the above discussion the complex formation between aminobenzoic acid hydrazide and the various metal ions under investigation occurs through the hydrazinic NH$_2$ group and the oxygen of the OH group which formed due to the enolization of the keto group of the hydrazide.

Structural information is provided also by X-ray diffraction analysis. Figure 1 shows at room temperature X-ray diffraction patterns of the free ligand as well as of the complexes under investigation. It is clear that new peaks are observed in the diffractograms of complexes which are not present in the diffractogram of aminobenzoic acid hydrazide. These new peaks can be assigned to formation of M-H$_2$O, M-N and M-O bonds. The term isomorphous is used for compounds having the same crystalline but different ions. For the investigated complexes which contain water molecules incorporated in their coordination sphere, the peaks broaden ap-
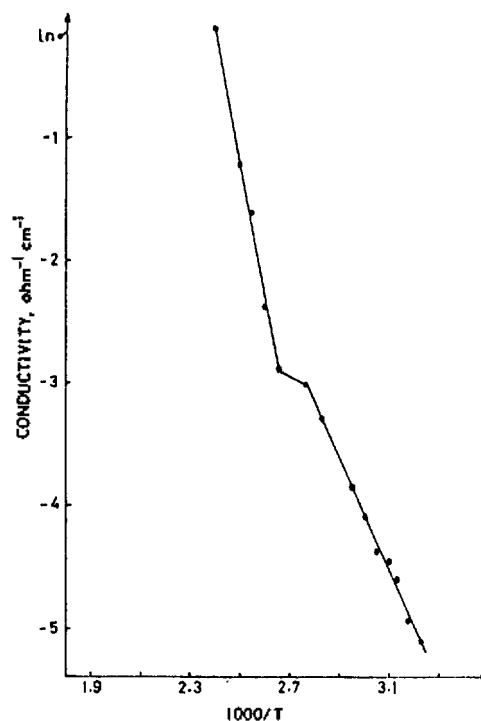
proaching the amorphous phase. This is correlated with interaction of water molecule in the coordination sphere forming ligand crystals having amorphous phase[16].

The electrical conduction may occur through the movement of either electrons or ions. In each case, however, a suitable starting point for discussion of the conduction process is the basic equation.

$$\sigma = q\, n\, \mu$$

where the conductivity σ is resolved into three factors: the charge *q*, concentration *n* and the drift mobility μ of the charge carriers. The latter parameter characterizes the ease with which the charged species will move.

Figure 2 represents the dependence of ln σ on 1/T for aminobenzoic acid hydrazide. The observed linear dependence indicates that the conductivity of the free ligand obey the relation:

$$\sigma = \sigma° \exp\ (-E/KT)$$

where σ° is a constant and *E* is the activation energy. It is clear that the conductivity increases as the temperature rises. *i.e.*, the organic compound under investigation is typical semiconductor.

The mechanism of conduction of aminobenzoic acid hydrazide can be discussed in the light of its molecular nature. In this picture, the charge carriers are mostly due to the activation of either the non-bonding or π-bond electrons. It is expected that there are two pathways of conduction: One, along the horizontal planes and the othere perpendicular to the molecular planes through intervening the organic group inspite of the interlayer spacing. Thus, one can safely say that the major class of organic semiconductors include stacked planar or π-electron systems.
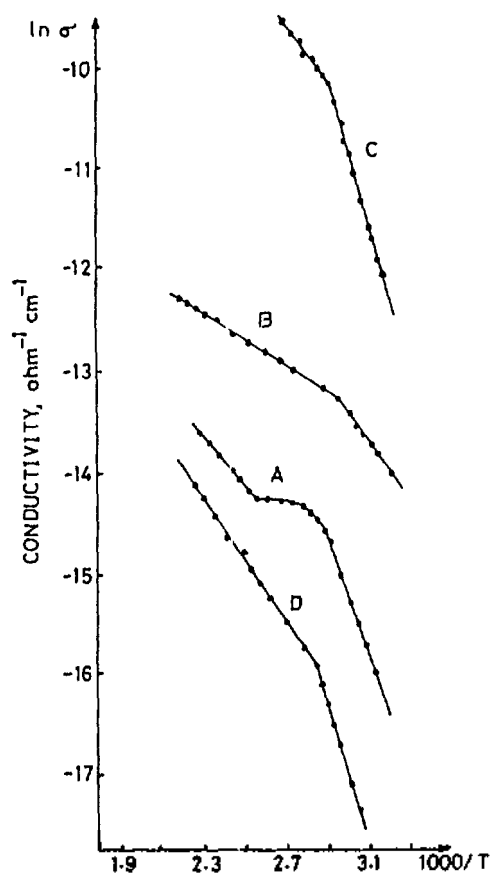
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Figure 3. Electrical conductivity of cobalt-hydrazide complex. A) Co as chloride, B) Co as nitrate, C) Co as sulphate, D) Co as acetate.
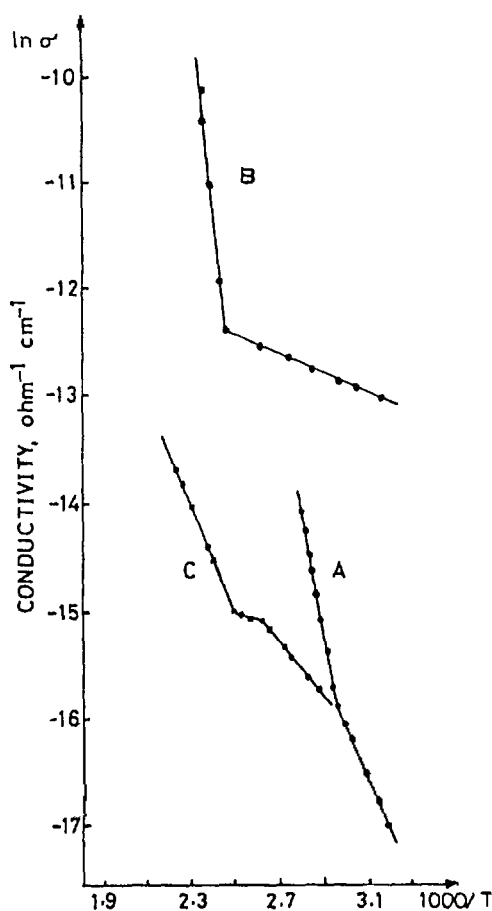

Figure 5. Electrical conductivity of copper-hydrazide complex. A) Cu as nitrate, B) Cu as sulphate, C) Cu as acetate.
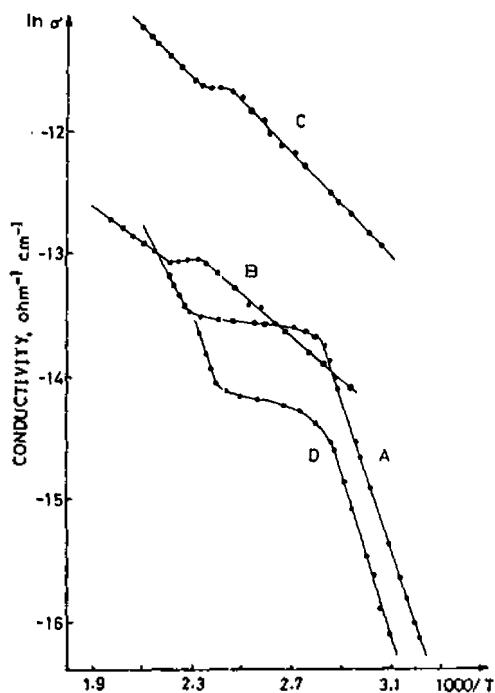

Figure 4. Electrical conductivity of nickel-hydrazide complex. A) Ni as chloride, B) Ni as nitrate, C) Ni as sulphate, D) Ni as acetate.

Figures 3-5 show the measured temperature dependences of the electrical conductivities for cobalt, nickel and copper complexes, respectively. It is found that the conductivity of the various complexes for a given anion depends on the different central metal ions suggesting the importance of complex stability. Increasing the complex stability results in decreasing the conductivity due to a decrease in π-electron mobility.

A phase transition was observed in all the investigated compounds. These phase transitions may be attributed to a change in the type of packing which leads to a change in the singlet-triplet separation energy. The calculated activation energy, in case of the free acid hydrazide, is found to be greater than that of complexed. It is consistent with the idea that the interaction between the electrons in the anti-bonding π-orbitals of hydrazide and the empty d-orbitals of the metal ions, i.e., the π-electronic charge delocalized on the hydrazide molecule. Generally, the activation energies E_1 below the transition temperatures are greater than in the high temperature ranges E_2 by a factor ranging from 2.6 to 1.3 for both cobalt and nickel complexes, respectively. The data obtained for copper complexes are inverse. This might be due to the difference in configuration between copper on one side and cobalt and nickel on the other. The former might be forming a square planar while the latter might be forming octahedral complexes. The electrical data

Table 2. The electrical data of o-amino benzoic acid hydrazide compexes, at 400 K

Compound	δ, chm^{-1}	E_1, eV	E_2, eV	n, cm^{-3}	μ, cm^2/V.s.
Ligand	2.70×10^{-1}	0.56	0.64	5.97×10^{19}	2.8×10^{-2}
CoL$_2 \cdot$Cl	6.88×10^{-7}	0.58	0.23	1.05×10^{19}	4.1×10^{-7}
$\cdot$SO$_4$	1.90×10^{-4}	0.55	0.21	3.34×10^{19}	3.6×10^{-5}
$\cdot$NO$_3$	4.00×10^{-6}	0.24	0.11	3.62×10^{23}	6.9×10^{-11}
$\cdot$acetate	1.20×10^{-6}	0.57	0.21	1.40×10^{19}	5.4×10^{-7}
NiL$_2 \cdot$Cl	1.85×10^{-6}	0.51	0.31	1.43×10^{20}	8.1×10^{-8}
$\cdot$SO$_4$	3.37×10^{-6}	0.20	0.15	1.16×10^{24}	1.8×10^{-11}
$\cdot$NO$_3$	1.52×10^{-6}	0.15	0.12	4.94×10^{24}	1.9×10^{-12}
$\cdot$acetate	1.28×10^{-6}	0.56	0.52	1.87×10^{19}	4.3×10^{-7}
CuL$_2 \cdot$SO$_4$	3.78×10^{-5}	0.10	1.51	2.11×10^{25}	1.2×10^{-11}
$\cdot$NO$_3$	6.81×10^{-7}	0.39	1.02	4.65×10^{21}	9.2×10^{-10}
$\cdot$acetate	8.32×10^{-7}	0.21	0.43	8.66×10^{23}	6.0×10^{-12}

are summarized in Table 2.

Also, it is observed that the value of conductivity for a given complex changes with the type of the anion present (chloride, nitrate, sulphate or acetate). The measured conductivity of the various complexes decreases in general in the order:

sulphate complex>nitrate complex>acetate complex

This behaviour can be attributed to the different sizes, electronegativities and inductive effect of the anions suggesting also the applicability of the mechanism of the ionic conducting. Ionic conduction is the process in which electric current is carried by the motion of ions. This could arise in two different manners; in an ionic crystal where the basic constituents are ions, and physical imperfections alone can be responsible for mechanism of current flow, while in a non-ionic substance chemical imperfection is required to supply the mobile species. The data obtained are in a good agreement with the latter type.

In order to calculate the mobility of charge carriers, the density of carriers was determined using the relation

$$n = 2\left(\frac{2 \pi m^+ KT}{h^2}\right)^{3/2} e^{-E/KT}$$

where m^+ is the effective mass of charge carrier. The obtained results are given in Table 2. It is apparent that the carriers mobility is very low $(10^{-2}\text{-}10^{-12} \text{ cm}^2/\text{V.s.})$, suggesting that the conductions of the studied complexes takes place mainly by hopping mechanism in which disorder in a lattice affects both the energetic and spatial distribution of electronic states. For a random distribution of atoms the density of electronic energy states tails into what is normally the forbidden zone and the electrons in these tails are localized. There is then not so much energy gap as a mobility gap. In other words, there is an intermediate range of electronic energy states in which mobilities are very low[17].

Conduction *via* localized electrons implies discrete jumps across an energy barrier from one site to the next. Then, an electron may hop over the top of the barrier. It is apparent that the hopping conduction mechanism can be used to describe the electrical behaviour of the aminobenzoic acid hydrazide-metal complexes.

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