Articles

Thermodynamic and Electrical Properties of Aminophenol and Anthranilic Acid Complexes with Some Transition Metals

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Thermodynamic and electrical functions of aminophenol and anthranilic acid complexes with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) were determined. ΔG°, ΔH° and ΔS° were calculated with the help of stability constant values at different temperatures. It was found that the complexing processes have an exothermic nature. The studied complexes behave like semiconductors. The conduction takes place according to hopping mechanism. To show the composition of complexes conductometric and photometric titrations. IR spectra, thermal analysis and X-ray diffraction techniques were employed.

Keywords : Thermodynamic. Thermal stability. Electrical conductivity.

Introduction

In recent years the investigations on organic semiconductors have been much intensified.[1-4] Aminophenol and aminobenzoic acid have aroused interest owing to their utility as starting materials for many azodyes,[5] corrosion inhibitors,[6] bactericides[7] and anti-inflammatory agent.[8] From the complexing point of view, many have taken interest in studying aminophenol and aminobenzoic acid as potential ligands.[9-13]

In the course of our ongoing interest in the area of physical properties of organic complexes, the present work aims to study the thermodynamic and electrical properties of aminophenol and o-amino-benzoic acid (anthranilic acid) complexes with Mn(II). Fe(II). Co(II). Ni(II) and Cu(II). Several techniques such as conductometric and photometric titrations. IR spectra, thermal analysis and X-ray diffraction were used to characterize the composition of complexes.

Experimental Section

All the chemicals used were pure laboratory grade provided by Aldrich. The stability constants of complexes. at constant ionic strength (0.1 M KCl), were determined potentiometrically at 30°. 35°, 40° and 45 °C using Irving-Rossotti pH-titration technique.[2] Three titrations. *viz.* titration of i) HCl. ii) HCl + ligand and iii) HCl + ligand + metal ion. were carried out against 0.01 M KOH. A digit pH-meter. Cole Parmer 5800-05 solution analyzer. fitted with combined glass-calomel electrode was used. All calculations were computed on an IBM 486 Fortran-77 computer.

The composition of complexes was estimated using conductometric and photometric titrations. In the first technique. the conductance of different metal ions (10^{-3} M) was measured during the addition of 10^{-2} M aqueous solution of ligand at room temperature. A digit conductivity meter 5800-

05 solution analyzer was used. In the second technique. absorbance of complexes was measured at constant wavelength (λ_{max}=290 nm for aminophenol complexes and λ_{max}= 250 nm for anthranilic acid complexes) using Milton Roy, Spectronic 1201 spectrophotometer. The concentration of metal ions is kept fixed (0.5×10^{-2} M) and that of ligand is varied (0.25×10^{-2}–2.00×10^{-2} M) to give a series of L/M ratios.

Solid complexes of molar ratio M:2L were prepared by mixing an aqueous solution of the calculated amounts of each ligand with the respective metal chloride. The reaction mixture was refluxed on a water bath for three hours. The complexes formed were filtered. washed with ethanol and dried in vacuum. In order to suggest the correct formula for complexes under investigation. elemental analysis for C, H and N were carried out. The results revealed that the complexes are of general composition $ML_2Cl_2 \cdot nH_2O$.

The infrared spectra of the solid complexes were recorded using a Shimadzu spectrophotometer model 440. Thermal analysis of complexes were carried in the range 20-500 °C using a Shimadzu DTA-TGA, 50 H with a uniform heating rate 10 °C min^{-1}. XRD patterns were obtained using Philips X-ray diffractometer pw 1390 fitted with an ionization detector (CuK$_\alpha$ radiation).

The electrical conductivity of solids was measured, using a d.c. voltage of 10 volts across the cell, on discs of 13 mm diameter and 0.5 mm thickness sandwiched between two parallel copper electrodes.[14] The samples were molded under pressure of 4 ton cm^{-2} at room temperature. The two point probe technique was used by help of Ni/Ni-Cr thermocouple. To exclude the effect of moisture, the conductivity values were determined during the cooling process.

Results and Discussion

In order to understand the interaction between metal ions

with ligands, the proton-ligand, pK, and the metal-ligand, log K, constants were evaluated using the formula of Irving and Rossotti.

$$n_H = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V_o + V_1)T_L}$$

$$n = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V_o + V_1)n_H T_M}$$

$$P_L = \log\left[\frac{B\left(\dfrac{1}{antilogB}\right)^n}{T_L - nT_M} \cdot \frac{(V_o + V_1)}{V_o}\right]$$

V_1, V_2 and V_3 are the volumes of alkali in the three titration curves to reach the same pH value. V_o is the total volume of titrating mixture, N° and E° are the normality of alkali and initial concentration of free acid. Y is the number of dissociable protons attached to ligand. T_L and T_M are the total concentration of ligand and metal, respectively. The proton-ligand constant was obtained by plotting n_H against the corresponding pH values and interpolating at $n_H = 0.5$ and 1.5. The plot is wave-like. The values of metal-ligand stability constants were determined from the graph between the average number of ligands attached by metal ion, n, and the free ligand exponent, P_L.

The calculated values of protonation constant and step-

wise stability constants. log K_1 and log K_2 have been reported in Table 1. The stability constants of complexes follow the order: Mn < Fe < Co < Ni < Cu, which is in accordance with the typical Irving-Williams order. On the other side. it is found that the values of stability constant are reduced with the rising of temperature suggesting an exothermic nature for the complex formation.

Thermodynamic relationships can be applied to complexation reactions.[15] The stability constant is related to the standard enthalpy change. ΔH°, and other thermodynamic function by the equation:

$$\Delta G^\circ = -2.303RT \log K = \Delta H^\circ - T\Delta S^\circ$$

From the values of stability constant at different temperatures. the enthalpy change can be calculated using the equation:

$$\log\frac{K_1}{K_2} = -\frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

The calculated thermodynamic data are collected in Table 2. It is apparent that the formation of complexes takes place spontaneously and is energetically favored. An exothermic behavior, negative enthalpy values, is observed. *i.e.*. low temperature favors the complexing process. The greater value of enthalpy. the more stable of complex is expected to be. Consequently, the complexes of anthranilic acid are more stable than those aminophenol. Finally, the formation of complexes is accompanied by decreasing of entropy, *i.e.*, decrease in the disorder of the complexed molecules.

In order to clarify the complexing process tendency. *i.e.*, ionic or covalent. the thermodynamic functions were ana-

Table 1. Stepwise stability constants of metal complexes at different temperatures

Compound	Stability constant	Temperatures			
		30 °C	35 °C	40 °C	45 °C
Aminophenol	pK$_1$	8.18	7.98	8.02	7.26
	pK$_2$	6.82	7.20	6.78	6.70
Mn complex	log K$_1$	8.98	8.75	8.60	7.95
	log K$_2$	8.50	8.20	7.80	7.90
Fe complex	log K$_1$	9.70	9.45	9.30	9.09
	log K$_2$	8.80	8.60	7.39	7.70
Co complex	log K$_1$	9.80	9.62	9.25	8.70
	log K$_2$	8.20	7.92	7.70	7.50
Ni complex	log K$_1$	10.45	10.35	10.00	9.25
	log K$_2$	7.97	7.75	7.51	7.33
Cu complex	log K$_1$	12.38	13.60	12.20	11.55
	log K$_2$	10.00	8.10	8.80	8.75
Anthranilic acid	pK$_1$	8.37	9.05	7.18	8.00
	pK$_2$	4.45	4.35	4.21	4.20
Mn complex	log K$_1$	–	8.03	7.60	7.41
	logK$_2$	–	7.10	6.70	6.08
Fe complex	log K$_1$	10.39	10.00	9.37	8.25
	log K$_2$	8.42	7.45	6.68	6.45
Co complex	log K$_1$	10.24	11.60	8.92	7.41
	log K$_2$	9.18	7.00	6.83	6.49
Ni complex	log K$_1$	12.39	11.00	10.45	8.45
	log K$_2$	6.92	7.42	5.90	6.10
Cu complex	log K$_1$	12.31	11.20	11.60	9.70
	log K$_2$	10.09	9.70	7.80	8.20

Table 2. Thermodynamic data of complexes at 303 K

Compound	$-\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta G^\circ_{ion}$	$-\Delta G^\circ$	$-\Delta H^\circ_{el}$	$-\Delta H^\circ_{el}$
Aminophenol							
Mn complex	12.45	28.45	52.79	22.27	9.78	24.68	3.76
	11.79	19.51	25.49	15.62	3.84	18.04	1.47
Fe complex	13.45	17.47	13.26	14.61	1.16	17.02	0.44
	12.20	39.91	91.43	30.48	18.28	32.90	7.01
Co complex	13.59	32.25	61.60	25.33	11.74	27.75	4.50
	11.37	20.48	30.06	6.20	4.84	18.62	1.85
Ni complex	14.49	34.64	66.51	27.31	12.82	29.73	4.92
	11.05	19.06	26.42	15.09	4.04	17.51	1.55
Cu complex	17.17	33.76	54.77	27.41	10.25	29.83	3.93
	13.87	27.42	44.74	21.92	8.05	24.33	3.09
Anthranilic acid							
Fe complex	14.41	61.95	156.9	47.02	32.62	49.44	12.51
	11.67	59.11	156.5	44.21	32.53	46.63	12.48
Co complex	14.20	97.66	275.5	72.77	58.58	75.19	22.47
	12.73	73.18	199.5	54.67	41.94	57.09	16.09
Ni complex	17.18	108.9	302.7	81.72	64.54	84.14	24.76
	9.59	35.00	83.85	26.21	16.62	28.63	6.37
Cu complex	17.07	65.29	159.1	50.17	33.10	52.59	12.70
	13.99	66.96	174.8	50.53	36.54	52.95	14.02

ΔG° and ΔH° in Kcal·mol^{-1} and ΔS° in cal·K^{-1}mol^{-1}

lyzed into electrostatic and non-electrostatic terms:[16,17]

$$\Delta G^\circ = \Delta G^\circ_{non} + \Delta G^\circ_{el} = nRT\ln M + RC\left(a + e^{\frac{T}{\theta}}\right)$$

$$\Delta H^\circ = \Delta H^\circ_{non} + \Delta H^\circ_{el} = RC\left[a + \left(1 - \frac{T}{\theta}\right)e^{\frac{T}{\theta}}\right]$$

$$\Delta S^\circ = \Delta S^\circ_{non} + \Delta S^\circ_{el} = -nRT\ln M - \frac{RC}{\theta}e^{\frac{T}{\theta}}$$

where θ is the temperature characteristic of the solvent and M is its molality. The two terms C and a are used to evaluate the separated thermodynamic functions. The obtained results are given in Table 2. It is clear that ΔG°_{non} values are negative compared to those of ΔG°_{el} indicating that non-electrostatic forces are stronger than electrostatic ones, *i.e.*, the formation of all complexes is mainly covalent process. Also, ΔH°_{non} are more negative than ΔH°_{el} reflecting the covalency nature of the bonding of various complexes. However, the comparison of ratio of electrostatic to non-electrostatic data shows that the anthranilic acid complexes are more ionic than those of aminophenol.

Generally, both the free energy and enthalpy changes computed for 1 : 1 complexes were found to be more negative than that for 1 : 2 complexes indicating that the mono-complexes are energetically favored over the di-complexes. This may be attributed to the repulsion between the ligands.

One of the most frequent uses of conductometric titration is the qualitative determination of molar ratio of complexes.[18] It is known that the conductance of a solution at a given temperature is influenced by the number and mobility of the ions present. Thus, the replacement of some ions by others during the complex formation is accompanied by the change in the conductance value. Straight or nearly straight lines intersecting at the molar ratio of complexes formation are obtained. A common behavior of the curves of anthranilic acid complexes is a continuous increase in conductance during the addition of ligands. This behavior is attributed to the liberation of highly conducting hydrogen ions. In contrast to this behavior is the conductograms of aminophenol complexes where there is a continuous decrease in conductance owing to the formation of intramolecular hydrogen bond between the phenolic hydrogen and the amino nitrogen. This leads to the difficulty of the liberation of hydrogen ions. The conductograms exhibit two obvious breaks suggesting that the possible stoichiometric ratios of complexes are M : L and M : 2L.

The photometric titration was also used to determine the molar ratio of complexes.[18] In this method, the absorbance increases linearly up to the ratio of the complex, at which virtually the whole amount of both reactants is complexed. Further addition of ligand can not increase the absorbance and the line becomes horizontal. The results show that both aminophenol and anthranilic acid form stable complexes with stoichiometric ratio M : 2L as obtained previously from the potentiometric and conductometric titrations.

photometric titration was not only used in determining the

stoichiometric ratio of complexes but also used to calculate the stability constants of complexes using the relation.[19]

$$\beta_n = \frac{(A/A_m)}{(1 - A/A_m)^{n-1}c_L^n n^2}$$

Where A is the absorbance at ligand concentration c_L. A_m is the absorbance at full color development and n is the stoichiometric ratio of the complexes. The data obtained at room temperature are smaller than those obtained potentiometrically at the same temperature. This may be attributed to the fact that if the stability constant is small or very large, the evaluation becomes uncertain.[20]

Good evidence for the composition of the solid complexes can be obtained from the comparison between the infrared spectra of ligands and those of metal complexes. Figures 1 and 2 show the spectra of the studied compounds. A strong and broad band appearing in the spectrum of free aminophenol at 3200-2500 cm^{-1} is attributed to stretching vibration of the phenolic OH engaged in intramolecular H-bonding. The disappearance of this band in the spectra of complexes indicates the coordination of aminophenol through deprotonated phenolic oxygen.[21] A medium and broad band in the spectrum of ligand at 1200 cm^{-1} is assigned to the combination of phenolic υ C-O and δ OH vibrations. Another band at 1050 cm^{-1} is of phenolic υ C-O. The bathochromic shift of both bands on complexation suggests that the coordination takes place between oxygen atom and metal ions. On other side, the NH$_2$ bending band, 1580 cm^{-1}, shows blue shift after the complexing process indicating the participation of NH$_2$ group in coordination. The new band observed at *ca.* 400 cm^{-1} may be assigned to υ M-O.

The anthranilic acid band observed at 1645 cm^{-1} is ascribed to C=O. This band shows blue shift of 45-55 cm^{-1}
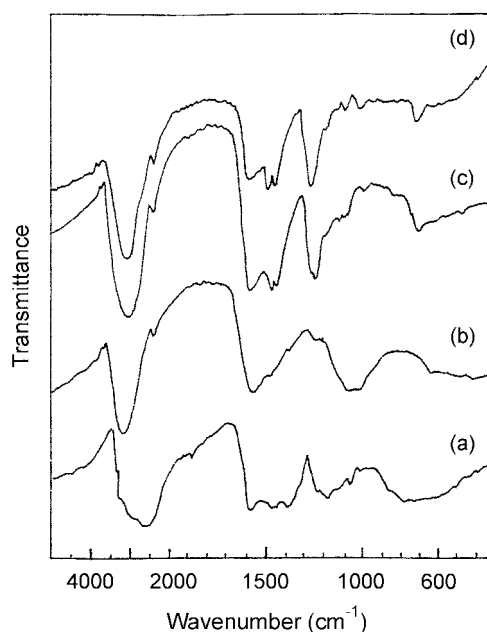

Figure 1. IR spectra of (a) aminophenol and its complexes with (b) Fe, (c) Co and (d) Ni.
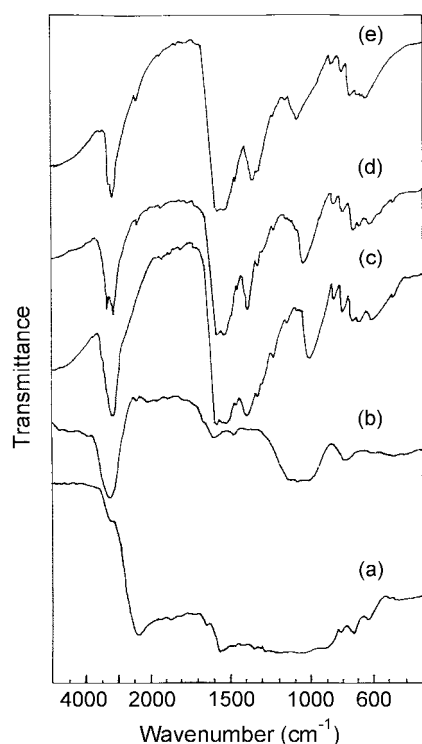
Figure 2. IR spectra of (a) anthranilic acid and its complexes with (b) Fe, (c) Co, (d) Ni and (e) Cu.

in the respective complexes suggesting the involvement of carbonyl group in bonding. The new band at 480 cm^{-1} is attributed to v M-O. A medium band of NH$_2$ at 1570 cm^{-1} demonstrates a blue shift suggesting the coordination through amino group. Thus, the divalent metal ions coordinate with the anthranilic acid molecule through the oxygen of carbonyl group and the nitrogen of amino group forming six-membered ring.[22]

The spectra of all complexes illustrate a strong band around 3000 cm^{-1}, which is attributed to coordinated water molecules. To determine the number of crystalline and coordinated water molecules. definite weights of the samples were heated in an oven, first at 130 °C until constant weights were reached and then at 210 °C. The first weight-loss corresponds to the number of crystalline water, whereas the second weight-loss corresponds to the number of coordinated molecules. The results indicate that manganese and cobalt aminophenol complexes have two crystalline and two coordinated water molecules. while nickel and copper complexes possess one crystalline and two coordinated molecules. Also, manganese and iron anthranilates have two crystalline and two coordinated water molecules. while cobalt complex contains one crystalline and two coordinated molecules. Nickel anthranilate possesses only one crystalline molecule. while copper complex does not have any water molecules.

To show the thermal stability of complexes, the TG for Cu-aminophenol complex and Cu-anthranilic acid complex. was measured as illustrated in Figure 3. On calculation based on the weight loss methods the data for the Cu-aminophenol complex show that there are three bands. the first one
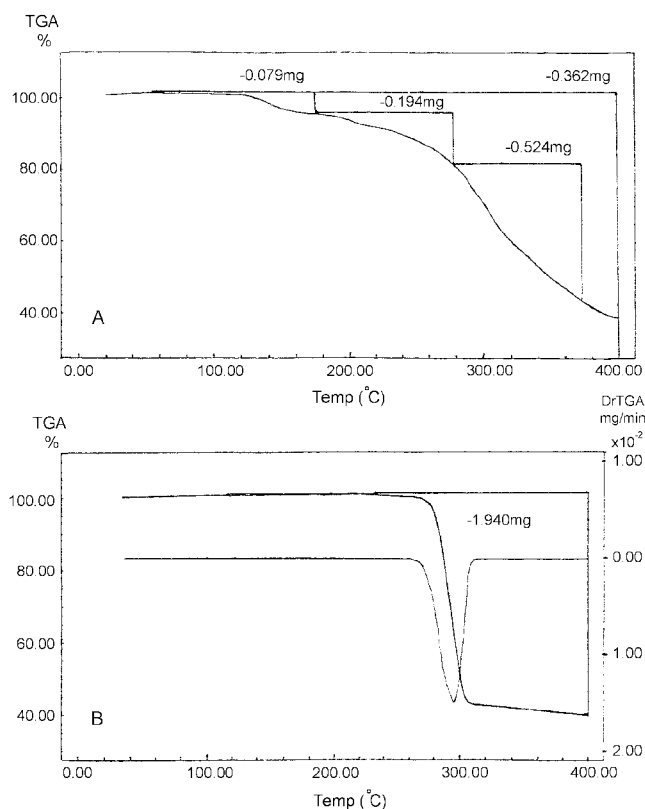

Figure 3. Thermal gravimetric analysis of (a) Cu-aminophenol complex and (b) Cu-anthranilic acid complex.

at about 130 °C attributed to liberation of one crystalline water molecule, while the second band at about 210 °C which is due to liberation of two coordinated water molecules and the third one at about 300 °C for the complete decomposition of the complex to CuO. On the other hand, for Cu-anthranilic acid complex. one band is observed only at about 300 °C which is attributed to the composition of the complex to CuO, *i.e.*. it is anhydrous complex. It is clear that, these results are in a good agreement with the data obtained from heating of a definite weight of the two complexes.

Figures 4 and 5 show the X-ray diffraction patterns of both ligands and their copper complexes. Generally, It can be observed that the patterns of organic ligands differ from those of their complexes. The peaks are broaded after complexation due to the formation of not well defined distorted crystalline structure.

In order to discuss the electrical behavior of aminophenol, anthranilic acid and their complexes, the variation of logarithmic conductivity values as a function of reciprocal temperature was followed as shown in Figures 6 and 7. The linearity of the plots shows the validity of the equation:

$$\sigma = \sigma^\circ \exp(-E/KT)$$

where E is the activation energy for releasing the free charge carriers. The electrical data are reported in Table 3. In general. a reduction of conductivity values was observed in complexation. This means that the conduction pathway is
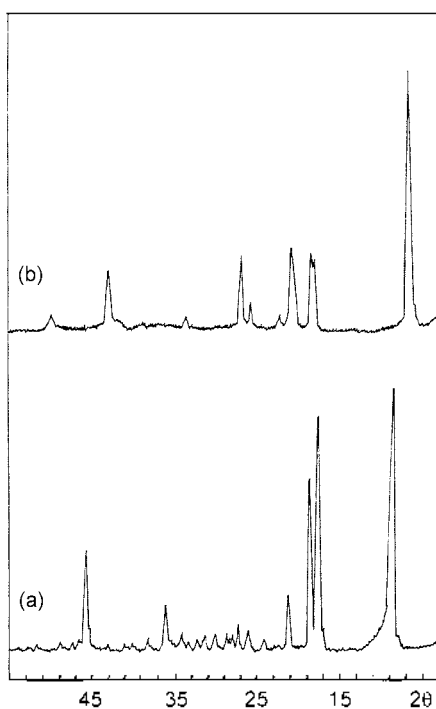
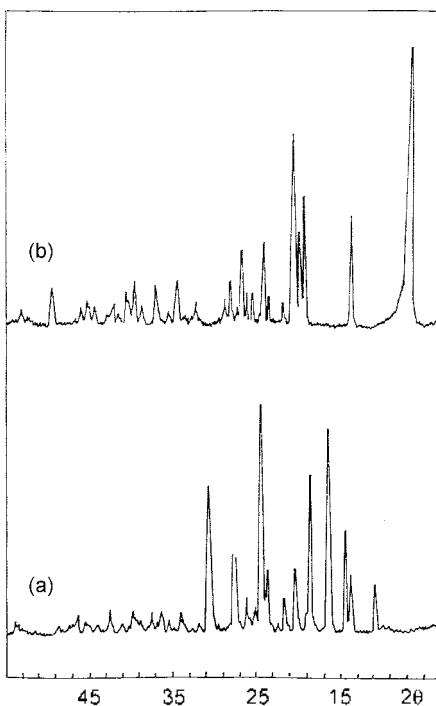**Figure 4.** XRD patterns of (a) aminophenol and its complexes with (b) Cu.

Figure 5. XRD patterns of (a) anthranilic acid and its complexes with (b) Cu.

Figure 6. Electrical conductivity of (a) aminophenol and its complexes with (b) Fe, (c) Co and (d) Ni.
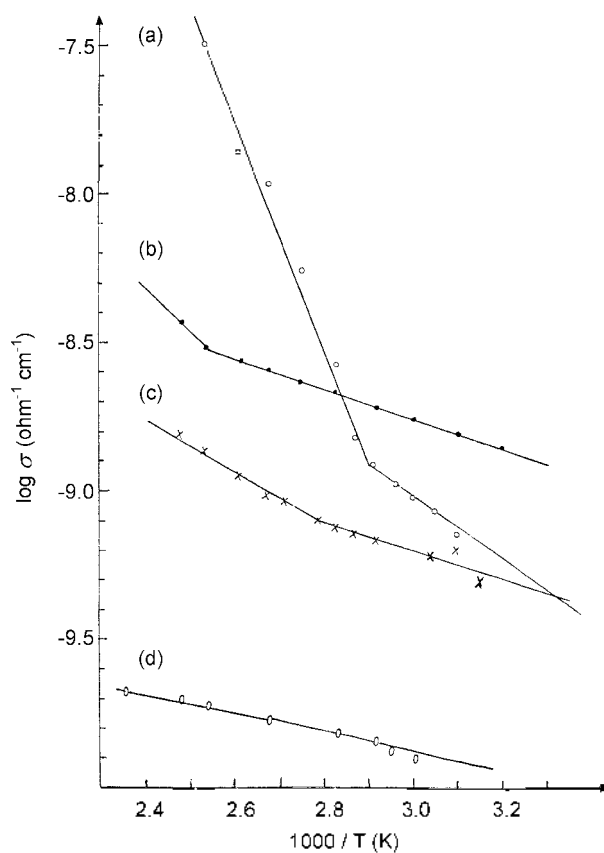
Figure 7. Electrical conductivity of (a) anthranilic acid and its complexes with (b) Fe, (c) Co and (d) Ni.

predominantly via suitable orbitals belonging to the free organic molecules. On complexation, the incorporation of metal ion would destroy or hinder this conduction pathway by increasing the internuclear distance between the organic orbitals leading to lower conductivity values.[23] On the other
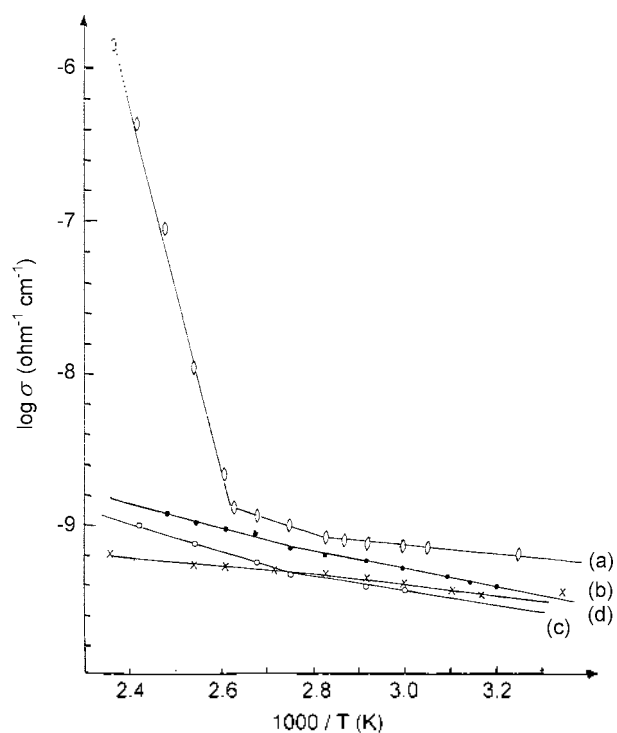
Table 3. Electrical data of complexes at 303 K

Compound	σ, ohm^{-1}cm^{-1} $\times 10^{-10}$	E, eV	n, cm^{-3} $\times 10^{24}$	μ, cm^{2}V^{-1}s^{-1} $\times 10^{-15}$
Aminophenol	5.75	0.061	2.45	1.46
Fe complex	3.31	0.119	0.266	7.79
Co complex	2.54	0.102	0.509	3.12
Ni complex	3.09	0.073	1.55	1.25
Anthranilic acid	4.62	0.210	0.00812	356.00
Fe complex	12.00	0.106	0.437	17.20
Co complex	4.47	0.096	0.641	4.36
Ni complex	1.06	0.063	2.27	0.292

hand, the fact that the complexes prepared are mainly covalent compounds meant that no good results could be expected. The break observed in the conductograms can be attributed to a change from extrinsic to intrinsic conduction mechanism.

The conduction in organic materials takes place according to the band picture or hopping model. To describe the suitable model for the studied compounds. the charge carrier density. n, and its mobility. μ, were calculated using:

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

$$\sigma = ne\mu$$

where m^{-} is the effective mass of charge carrier and e is the charge of an electron. It is clear that all the studied samples are characterized by very small mobility values. For this reason the hopping model. in which the charge carrier can move from one molecule to another by jumping over the barrier *via* an excited state. is preferable for the compounds under investigation.[24]

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