

Physical Properties of Some Acetylbenzaldehydehydrazone Metal Complexes

M. G. Abd El Wahed,^{*} H. A. Bayoumi,[†] and M. I. Mohammed[‡]*Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt*[†]*Chemistry Department, College for Girls, Ain Shams University, Cairo, Egypt*[‡]*Physics Department, Faculty of Science, Al Azhar University, Cairo, Egypt*

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A series of complexes of bivalent transition metal ions with acetyl benzaldehydehydrazone and its derivatives of general formula ML have been prepared and characterized with the help of conductometric, photometric and infrared studies. The stability constants and related thermodynamic functions of complexes were determined using the potentiometric technique at different temperatures. The formation of complexes is exothermic process with covalency nature. The electrical conductivity of some solid complexes was measured in the temperature range 289-353 K. The results revealed semiconducting properties for the studied complexes.

Key Words : Potentiometric, Conductometric and photometric titrations, IR spectra and conductivity measurements

Introduction

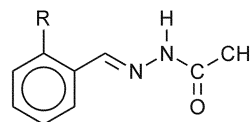
The coordination chemistry of nitrogen-oxygen donor ligands is an interesting area of research.¹ A great deal of attention in this area has been focused on the complexes formed by transition metal ions with hydrazones.²⁻⁷ The complexes obtained are spin free, cationic and octahedrally coordinated. The coordination via the nitrogen and carbonyl oxygen atoms of hydrazone moiety was suggested. Complexes of heterocyclic hydrazones with transition metals were also characterized.⁸ The electrical conductivity and electronic, IR as well as NMR spectra of some phenylhydrazone derivatives and their lanthanide complexes were measured.⁹ Semiconducting behaviour was detected.

The objective of the present study is to establish the thermodynamic, electrical and other physico-chemical properties of complexes of bivalent Mn, Co, Ni and Cu with N-acetylbenzaldehyde-hydrazone (ABH), N-acetyl(o-hydroxy) benzaldehydehydrazone (AHBH) and N-acetyl-(o-chloro) benzaldehydehydrazone (ACBH), respectively. Potentiometric, conductometric and photometric titrations as well as IR measurements were used. The a.c. electrical conductivity of some compounds was followed as a function of temperature (289-353 K) in the frequency range 0.1-20 kHz.

Experimental Section

All the chemicals used were of pure laboratory grade. To prepare the different ligands, acetic acid hydrazide was firstly prepared by refluxing an equimolecular ratio of ethyl acetate and hydrazine hydrate. The product was condensed with benzaldehyde, 2-hydroxybenzaldehyde or 2-chloro-benzaldehyde to obtain the required hydrazones. The products were crystallized from ethyl alcohol (m.p. 180°-

185 °C). The hydrazones prepared have the following structures:



where R = H, OH or Cl.

A digital pH-meter, Nel Electronic, pH 890 with a glass calomel electrode assembly was used for pH measurements. The method of Bjerrum and Calvin as modified by Irving-Rossotti¹⁰ was used to determine the metal-ligand stability constants. It is involved three titrations, viz, titration of i) free HCl, ii) HCl plus hydrazone and iii) HCl plus hydrazone plus metal ion, against KOH. Initial ionic strength of all solutions was maintained at 0.1 M by adding requisite amounts of KCl. The titrations were repeated at different temperatures, 25°, 35° and 45 °C, to determine the thermodynamic functions of the complexing process.

In order to illustrate the molar ratio of complexes, conductometric and photometric techniques were used at room temperature. The conductograms were obtained by titrating 30 mL of 10^{-4} M of metal ions against 10^{-3} M of various hydrazone solutions using a digital conductivity-meter, CMD 830, WPA-Linston, Cambridge. The photometric titration curves of copper complexes were followed by help of Perkin Elmer spectrophotometer, the measurements were carried out under fixed concentration of CuCl_2 , 1.0×10^{-4} M, with different concentrations of hydrazones, 0.25×10^{-4} M to 3.50×10^{-4} M.

Solid complexes were prepared by slight heating of a solution of the metal chloride (1.5 mmol) and ligand (1.5 mmol) in ethanol (10 mL) for some hours. On cooling at 18 °C, the complexes were precipitated, filtered and washed several times to remove the excess of ligand (m.p. 135°-160 °C). Satisfactory microanalysis obtained C \pm 0.40%, H \pm 0.35%

^{*}Corresponding author. E-mail: abdelwahed49@hotmail.com

and $N \pm 0.38\%$. The structure of complexes was characterized using FT-IR I650, Perkin Elmer spectrophotometer.

For the conductivity measurements, the samples were compressed to disks of diameter 13 mm and thickness 1.0 mm sandwiched between two parallel copper electrodes. Silver paste was used to ensure a good contact between the sample and the copper electrodes. The samples were molded under pressure of 4 ton cm^{-2} at room temperature. The two probe technique was used by help of PM 6304 programmable automatic RCL bridge, Philips. Before the measurements, the ohmic behaviour was checked from the linearity of the voltage-current characteristic. A.C. conductivity and capacitance for the investigated samples were obtained in the frequency range 0.1-20 kHz over the temperature range 289-353 K. Sample temperature was measured using a pre-calibrated chromel-alumel thermocouple type K.

Results and Discussion

In order to illustrate the nature of the interaction between metal ions and hydrazones, the protonation and stability constants of free ligands and their complexes were determined. The formation curves of proton-hydrazone systems, using the titration of solutions i) and ii), extend over 0.2 to 0.95 indicating that one proton dissociates from each hydrazone derivative. On other side, from the three titration curves, the number of hydrazone molecules associated with each metal ion at different pH values were calculated. The obtained data, 0.15 to 1.00, suggest the formation of only 1 : 1 complex. The calculated results have been evaluated in Table 1. The trend of stability for all complexes follows Irving-Williams order, *i.e.*, $\text{Mn} < \text{Co} < \text{Ni} < \text{Cu}$. The data reveal also that the complexes of ABH are more stable than those of ACBH, but less stable than the complexes of AHBH. This behaviour is attributed to the effect of presence

Table 1. Protonation and stability constants of metal complexes at different temperatures, ionic strength $I = 0.1 \text{ M KCl}$

Compound	25 °C	35 °C	45 °C
ABH	9.60	7.75	7.00
Mn complex	5.54	4.80	4.20
Co complex	5.60	5.00	4.40
Ni complex	5.70	5.18	4.60
Cu complex	7.20	6.95	6.65
AHBH	7.95	7.30	7.13
Mn complex	6.00	5.75	5.55
Co complex	6.75	6.30	5.85
Ni complex	7.22	6.60	6.05
Cu complex	8.00	7.25	6.62
ACBH	8.48	8.00	7.80
Mn complex	4.75	4.25	3.80
Co complex	5.40	4.80	4.20
Ni complex	5.60	5.20	4.80
Cu complex	6.70	6.30	5.90

Table 2. Thermodynamic data of hydrazone complexes at 298 K

Compound	$-\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
ABH			
Mn complex	31.63	114.89	279.41
Co complex	31.97	111.04	265.43
Ni complex	32.51	107.23	108.41
Cu complex	41.09	72.76	106.32
AHBH			
Mn complex	34.23	57.45	77.86
Co complex	38.53	84.27	153.47
Ni complex	41.21	111.04	234.39
Cu complex	45.65	153.51	362.00
ACBH			
Mn complex	21.67	95.73	248.49
Co complex	26.23	114.89	293.26
Ni complex	29.66	88.07	196.02
Cu complex	33.68	84.22	169.66

ΔG° and ΔH° in KJ mol^{-1} and ΔS° in $\text{J mol}^{-1} \text{ deg}^{-1}$

of -OH or -Cl in the ortho position of the phenyl ring, where the OH group increases the electron density at the hydrazone nitrogen atom whereas the presence of Cl atom decreases the basicity of nitrogen.

The above discussion is confirmed by measuring the stability constants at higher temperatures. The formation of complexes is exothermic process, *i.e.*, the stability is reduced by rising of temperature. The thermodynamic terms, ΔG° , ΔH° and ΔS° , have been computed using the relationships,

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

$$\text{and} \quad d \ln K/d(1/T) = -\Delta H^\circ/R$$

The data are represented in Table 2. It is evident that ΔG° is negative which means that the complexed molecules are thermodynamically stable and the complexing process is a spontaneous process. In spite of the unfavourable entropy change, negative values, the complexes are stabilized by relatively large negative enthalpy changes, *i.e.*, the complexing process is accompanied by evolving of heat.

To investigate the bond character of hydrazone complexes, ionic or covalent, the thermodynamic data can be analysed into two components, electrostatic and non-electrostatic¹¹:

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

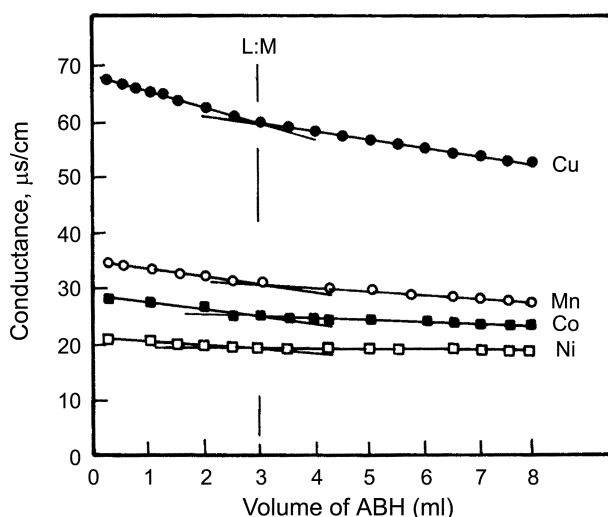
$$\Delta H^\circ = \Delta H^\circ_{\text{el}} + \Delta H^\circ_{\text{non}} = RC[a + (1 - T/\theta)e^{T/\theta}]$$

$$\Delta S^\circ = \Delta S^\circ_{\text{el}} + \Delta S^\circ_{\text{non}} = -nR \ln M - (RC/\theta)e^{T/\theta}$$

where θ is the characteristic temperature of solvent and M is its molality. On the basis of the calculated $\Delta G^\circ_{\text{el}}$ positive values, and $\Delta G^\circ_{\text{non}}$ negative values, it is apparent that the complexes have covalency nature. In view of the comparison of $\Delta H^\circ_{\text{el}}$ and $\Delta H^\circ_{\text{non}}$ for the various complexes, it is clear that

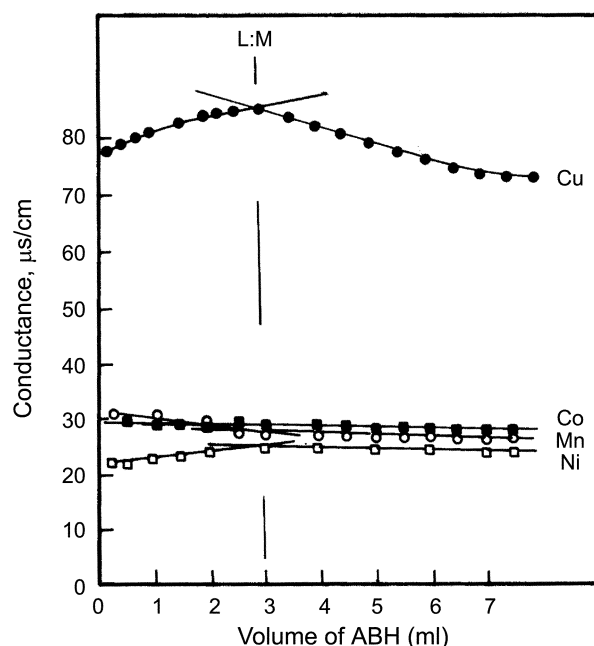
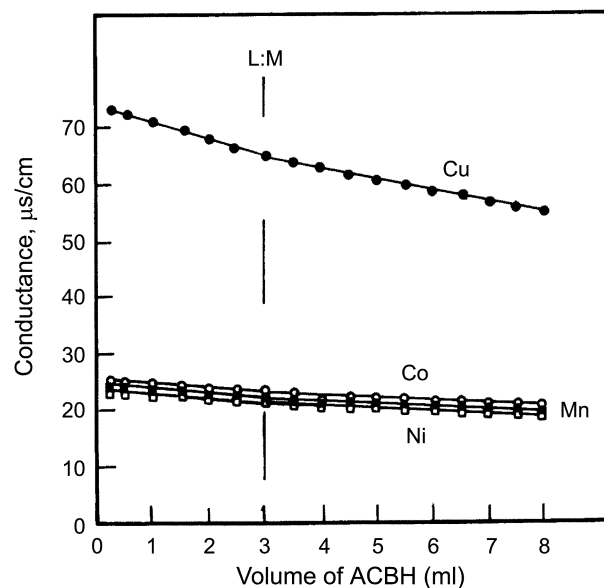
Table 3. Electrostatic and non-electrostatic components of thermodynamic data of complexes

Compound	ΔG_{el}°	$-\Delta G_{non}^{\circ}$	$-\Delta H_{el}^{\circ}$	$-\Delta H_{non}^{\circ}$
ABH				
Mn complex	52.13	83.81	21.17	93.76
Co complex	47.95	81.13	20.00	91.04
Ni complex	15.89	48.41	6.44	100.79
Cu complex	15.44	56.53	6.28	66.48
AHBH				
Mn complex	9.46	43.68	3.85	53.60
Co complex	25.48	64.02	10.33	73.93
Ni complex	42.59	83.81	17.32	93.72
Cu complex	69.66	115.31	28.28	125.23
ACBH				
Mn complex	45.56	67.24	18.54	77.19
Co complex	55.06	81.30	22.38	92.51
Ni complex	34.48	64.14	14.02	74.06
Cu complex	28.91	62.59	11.72	72.51

**Figure 1.** Conductograms of ABH with metal ions.

the negative values of ΔH_{non}° are greater than those of ΔH_{el}° i.e., the formation of complexes is mainly covalent process, as given in Table 3.

On the basis of conductometric and photometric data, the stoichiometry of hydrazone complexes can be estimated.¹² Figures 1, 2 and 3 demonstrate the conductograms of ABH, AHBH and ACBH complexes, respectively. Generally, the conductance values of metal ion solutions are decreased steadily as the hydrazone solutions are added. This behaviour is ascribed to the replacement of metal ions by the complexed molecules with different mobilities. The reduction continues until the equivalent point of titration is reached. With excess addition of titrant, hydrazone molecule remains unreacted and a slight decrease of conductance value may be observed due to the accumulation of excess hydrazone. The conductograms exhibit only one break at molar ratio 1 : 1, as suggested from the potentiometric measurements.

**Figure 2.** Conductograms of AHBH with metal ions.**Figure 3.** Conductograms of ACBH with metal ions.

In the photometric technique, by measuring the absorbance at a constant wavelength ($\lambda_{complex} = 238, 233$ and 232 nm) the equivalent point, i.e., the molar ratio, is the point at which the rate of change of absorbance with concentration of hydrazone is at maximum. The photometric titration curves, as shown in Figure 4, illustrate that the various hydrazone derivatives form stable complexes with a stoichiometric ratio of M:L.

Good evidence for the possible coordination sites of hydrazones can be obtained from IR spectra. The main absorption bands are reported in Table 4. By comparing the spectra of free hydrazones with those of their metal complexes, a slight shift to lower frequency is observed for

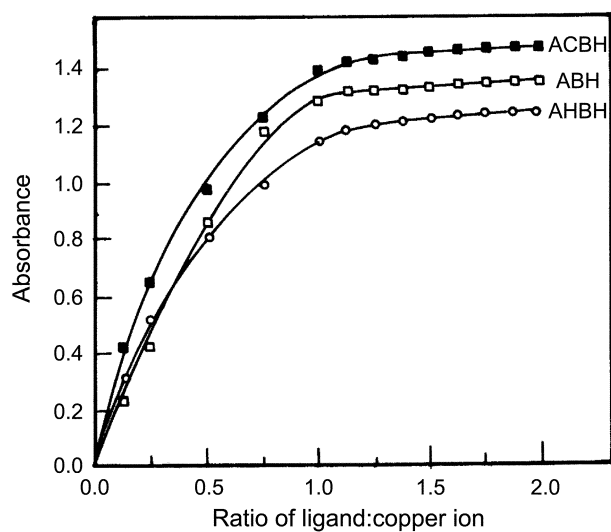


Figure 4. Photometric titration curves of hydrazones with copper ions.

Table 4. Main absorption bands in IR spectra of hydrazones and their copper complexes

Assignment	ABH complex	AHBH complex	ACBH complex
νOH	—	3230	3183
νNH	3075	3069	3072
$\nu\text{CO-CH}_3$	2942	2952	2949
$\nu\text{C=O}$	1673	1626	1673
$\nu\text{C=N}$	1603	1590	1608
M-O	—	420	—
M-N	—	358	—

νNH band. On the other side, a remarkable shift in $\nu\text{C=O}$ and $\nu\text{C=N}$ bands to lower frequencies is observed after complexation. Consequently, the complexing process takes place through the oxygen of carbonyl group and nitrogen of hydrazone, *i.e.*, the ligands are bidentate. The presence of water molecules in the coordination sphere of complexes has been inferred by the appearance of absorption bands at 3200 and 800 cm^{-1} . The new bands in the spectra of complexed molecules around 450 and 350 cm^{-1} are assignable to M-O and M-N bonding.

The presence of chloride ions outside or inside the coordination sphere was determined qualitatively by adding silver nitrate solution to ethanolic solution of complexed hydrazones. A white precipitate was observed suggesting that the chloride ions are present outside the sphere of coordination. Thus, a cationic nature of complexes was suggested.

The main character of a solid organic compound is its electrical conductivity. Many organic complexes, especially compounds containing conjugated bonds, are semiconductors.¹³⁻¹⁹ The a.c. conductivity of hydrazone, ABH, and its copper and cobalt complexes has been measured in the frequency range 0.1–20 kHz and in the temperature range 289–353 K. The frequency dependence on conductivity is

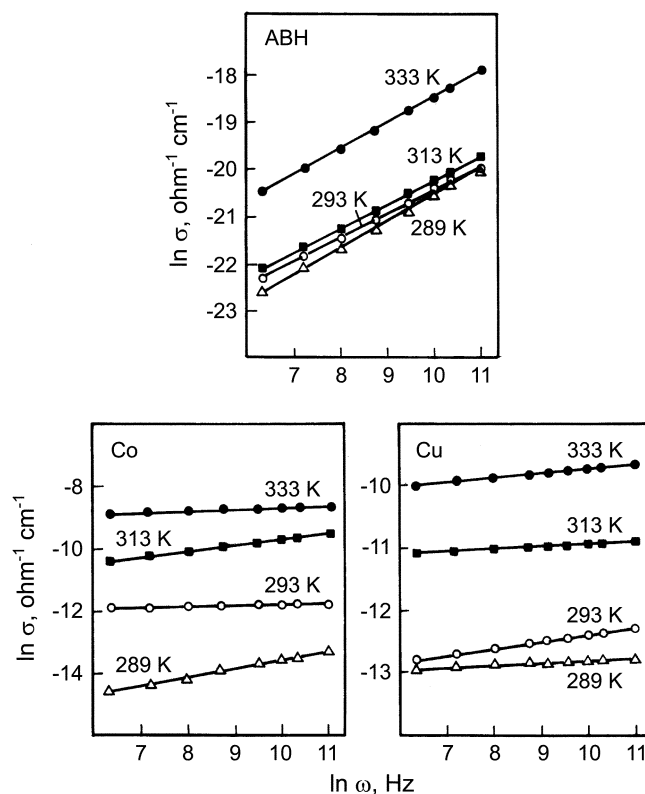


Figure 5. Frequency dependence of conductivity of ABH and its complexes.

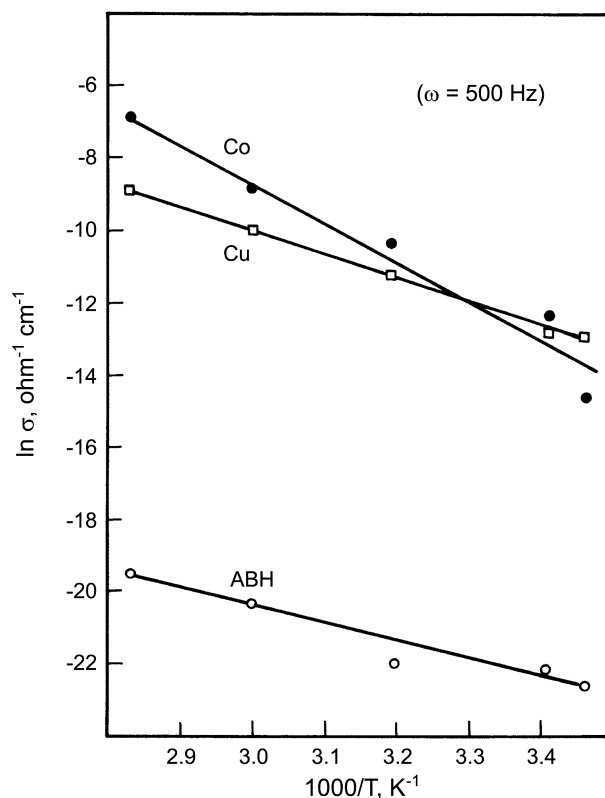


Figure 6. Temperature dependence of conductivity of ABH and its complexes.

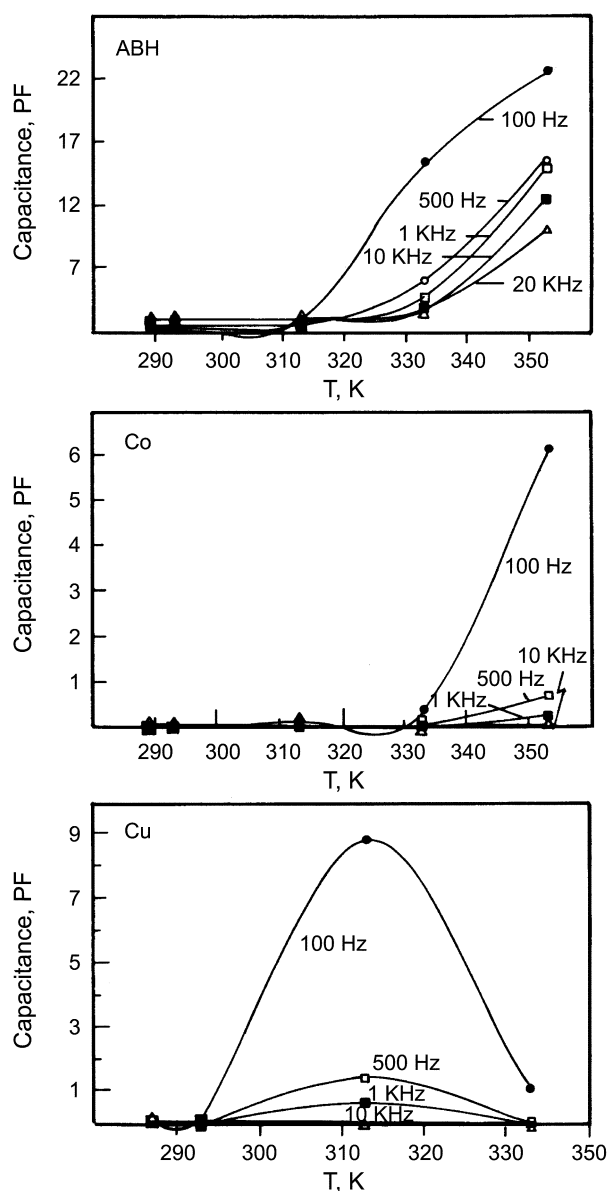


Figure 7. Capacitance dependence of frequency at different temperature of ABH and its complexes.

illustrated in Figure 5. Like many amorphous semiconductors, the obtained data reveal a linear relation between the conductivity measured and the frequency showing the validity of

$$\sigma_{a.c.}(\omega) = \sigma(\omega) - \sigma_{d.c.} = A \omega^s$$

$\sigma(\omega)$ is the frequency dependent conductivity, $\sigma_{d.c.}$ is the different current conductivity, A is constant, ω is the circular frequency, and the exponent s is generally less than or equal to unity. This behaviour is ascribed to relaxation caused by the motion of electrons or hopping between equilibrium sites. The temperature dependence of both conductivities $\sigma_{d.c.}$ and $\sigma_{a.c.}$ obey the well known exponential relation,

$$\sigma = \sigma^0 \exp(-E/KT)$$

where E is the activation energy of conduction.

The results of the temperature dependence of the conductivity $\sigma_{a.c.}(\omega)$ at a fixed frequency (500 Hz) are demonstrated in Figure 6. The plot of $\ln \sigma$ versus $1/T$ is almost linear, i.e., the conductivity of investigated hydrazone and its complexes increases with increasing temperature. It is apparent also that the conductivity of hydrazone is increased in complexation with transition metal cations, e.g. at 293 K, the measured conductivity values are given as: ABH = $2.28 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$, Cu-complex = $2.63 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$, and Co-complex = $4.12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. At the same time, the activation energy between the valence state and the next allowed energy state is raised from 0.22 eV to 0.60-0.76 eV after complexation. This behaviour can be attributed to the strong interaction between the metal ions and hydrazone which leads to an increase in the number of dislocated electrons on hydrazone molecule.

The variation in capacitance with frequency at different temperatures of the investigated compounds is represented in Figure 7. It can be seen that the capacitance decreases with frequency up to 2 kHz, then starts to be almost frequency independent. This may be accounted for by the presence of bounded dipoles. The latter cannot follow the rapid varying field at such high frequencies. This is in fair agreement with observed increase of capacitance by raising temperature. At high temperatures, the flexibility of dipoles increases giving rise to the observed increase in capacitance. It is worthy mentioned that in the investigated complexes, the central metal ions are firmly bound with hydrazone, hence it is not flexible enough to follow rapid fields. In this respect, the flexibility of dipoles in hydrazone is higher than those of complexes. The above argument explains why the capacitance values of hydrazone are higher than those of complexes.

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