# Electrical Conductivity of Some Hydrazones and Binary Complexes with Transition Metals

## M. G. Abd El Wahed, K. A. El Manakhly, A. Barakat, and A. M. Amer

Faculty of Science, Zagazig and Al Azhar Universities, Zagazig, Egypt

**Summary.** The electrical behaviour of some hydrazones was studied in the temperature range of 290–435 K. The effect of complex formation with Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) on the electrical conductivity of the hydrazones was investigated. The structure of the hydrazones was characterized using $^1$H and $^{13}$C NMR spectroscopy. Conductometric titration and IR spectroscopy were used to illustrate the structure of the hydrazone complexes. Both the structures of the hydrazones and the complexation process play an effective role in the conduction process.

**Keywords.** Conductometric titration; Organic semiconductor; Resonance effect; Hopping mechanism.

**Elektrische Leitfähigkeit einiger Hydrazone und ihrer binären Komplexe mit Übergangsmetallen**

**Zusammenfassung.** Das elektrische Verhalten einiger Hydrazone und ihrer Komplexe mit Mn(II), Fe(II), Co(II), Ni(II) und Cu(II) wurde im Temperaturbereich von 290 bis 435 K untersucht. Die Strukturen der Hydrazone wurden mittels $^1$H- und $^{13}$C-NMR-Spektroskopie charakterisiert, jene ihrer Komplexe durch konduktometrische Titration und IR-Spektroskopie. Sowohl die Strukturen der Hydrazone als auch der Komplexbildungsvorgang spielen eine wesentliche Rolle beim Leitungsvorgang.

## Introduction

Much work has been done on the biological activity of hydrazones [1–5]. Most of them are of special interest due to their use in the treatment of diseases such as tuberculosis, leprosy, and mental disorder [6]. This influence has been attributed to the formation of stable complexes with the metal ions present in the cell [7]. The chemistry of hydrazones and their derivatives has thus received a considerable amount of attention due to their applications as complexing agents [8–14].

Complex formation of many organic compounds plays an important role in the field of conduction. An increase in the conductivity values is observed when metal ions are incorporated into the $\pi$ electron delocalization of the organic compound [15]. However, a reduction of conductivity is noted if a localized bond between metal ions and organic compound is created [16].

In continuation of our previous work on the electrical behaviour of solid hydrazides as conducting materials [17], it seemed to be of interest to prepare some new hydrazones and to evaluate their electrical conductivities. The effect of complex

formation with some divalent transition metal ions on the electrical behaviour of the hydrazones has also been studied.

## Results and Discussion

The conductance of a solution at any temperature depends on the ions present and on their concentration. As a result of the complex formation, ions of different mobility appear in the solution. Depending on the nature of these ions, an increase or decrease in the conductance occurs [18]. Thus, to show the various possibilities of stoichiometric ratios of complex formation, the addition of hydrazone 1 to different aqueous solutions containing transition metal ions was followed conductometrically.

Figure 1 shows the different conductograms of hydrazone complexes at room temperature. A common behaviour of these curves is a continuous increase in conductance till a molar ratio of 1:1 is reached. Upon addition of excess hydrazone, a change in the trend is observed till the molar ratio reaches 1:2. Consequently, it is clear that 1:1 and 1:2 metal:hydrazone complexes can be formed.

To identify the structures of complexes of hydrazone 1, their infrared spectra were measured and compared with those of metal free 1. The main characteristic features of the IR spectra are reported as follows:
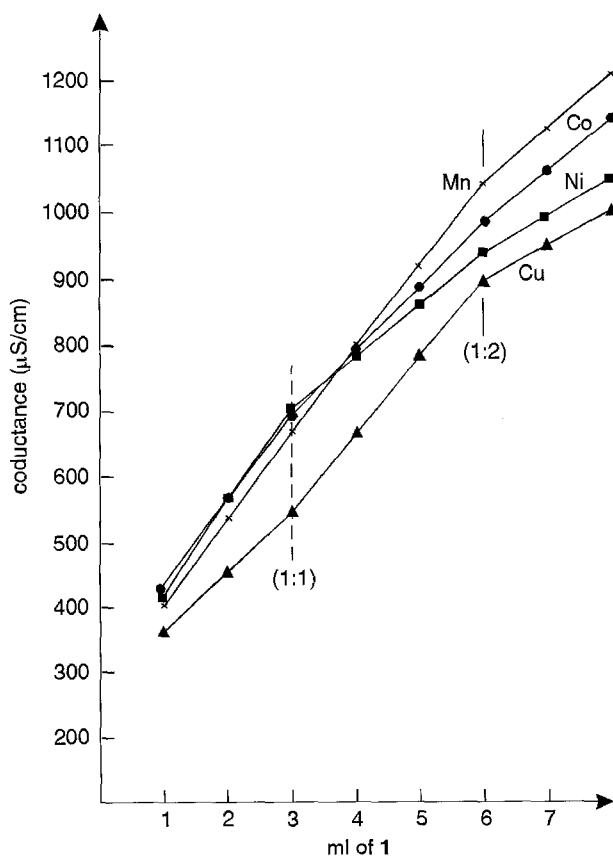


Fig. 1. Conductograms of 1 with transition metal ions

1. A strong and broad band at $3100 \, cm^{-1}$, assigned to coordinated water molecules, is observed in the spectra of all complexes.
2. A strong and sharp absorption band at $1570 \, cm^{-1}$ and a medium one at $1400 \, cm^{-1}$ are obtained in the spectra of both free and complexed hydrazone. These two bands are attributed to the asymmetrical and symmetrical stretching vibrations of $NO_2$ [19]. Thus, the nitro groups of the hydrazone do not participate in the complexation process.
3. The IR spectrum of **1**, shows a weak band at $3300 \, cm^{-1}$ ($\nu_{NH}$) which disappears upon complexing with metal ions. On the other side, another weak band at $1470 \, cm^{-1}$ ($\delta_{NH}$) is shifted towards higher frequency after complexation, suggesting that the complexation takes place through the nitrogen atom of the hydrazide moiety. This is supported by the appearance of a new band of $M-N$ at $590 \, cm^{-1}$. The stretching vibration of $N-N$ in hydrazone complexes appears at $1060 \, cm^{-1}$ [20].

One of the main characteristics of solid organic compounds is their electrical conductivity. Almost all conductivity measurements yield a temperature variation of the form

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

where $E$ is the activation energy of conduction process. The conductivity of the hydrazones prepared was measured in the temperature range of 290–435 K as shown in Fig. 2. An increase in conductivity with rising temperature was observed for hydrazones **2** and **4**, indicating that these compounds behave like semiconductors. On the other hand, the conductivity of hydrazones **1** and **3** is not affected by elevating the temperature, i.e. they behave like insulators.
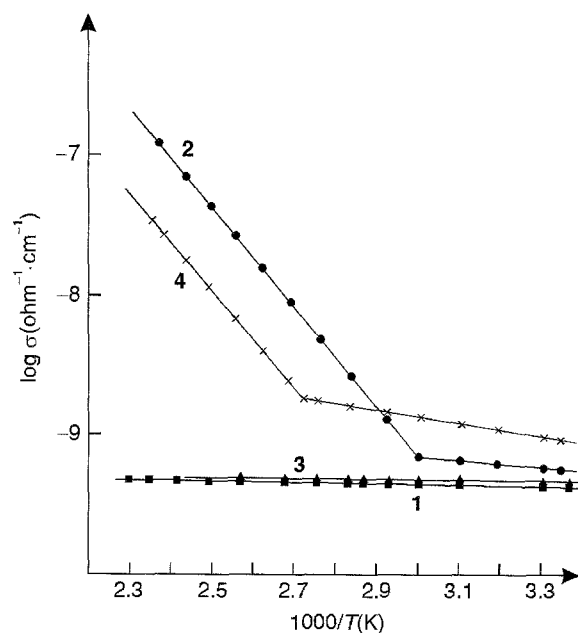


**Fig. 2.** Electrical conductivity of hydrazones

In general, the electrical conduction of a solid organic compound takes place through the movement of charge carriers from one molecule to the other, *i.e.* the conduction takes place through the overlapping of molecular orbitals of neighbouring molecules. Thus, it is expected that the conductance is proportional to the degree of conjugation and coplanarity of substituents. At room temperature, the measured electrical conductivity of the various hydrazones decreases in the order 4 > 2 > 3 > 1. This behaviour can be attributed to the resonance effects of the various hydrazones studied. In hydrazone 4, there is a carbonyl group attached directly to the azo group leading to a high degree of conjugation. In hydrazone 2, the azo group is neighboured by two carbonyl groups, leading to a delocalization of the electrons over the entire molecule. In 3, there is no strong electron withdrawing group attached to the azo group, making delocalization difficult. The same trend is observed for 1 where the presence of two nitro groups inhibits delocalization sterically. In other words, the electrical conductivity of the various hydrazones depends mainly on their degree of conjugation.

It is known that the complexation of organic compounds with transition metals leads to an overlap between $d$ orbitals of the metal and $\pi$ orbitals of the ligand, thereby extending electron delocalization. Therefore, 1 (as a representative compound) has been coordinated with Mn(II), Fe(II), Co(II), Ni(II), and Cu(II). Figure 3 shows the electrical behaviour of the complexes. It is apparent that the conductivity value of the complexes is by 1 to 4 orders of magnitude higher than that of the free hydrazone. The complexes behave like semiconductors.
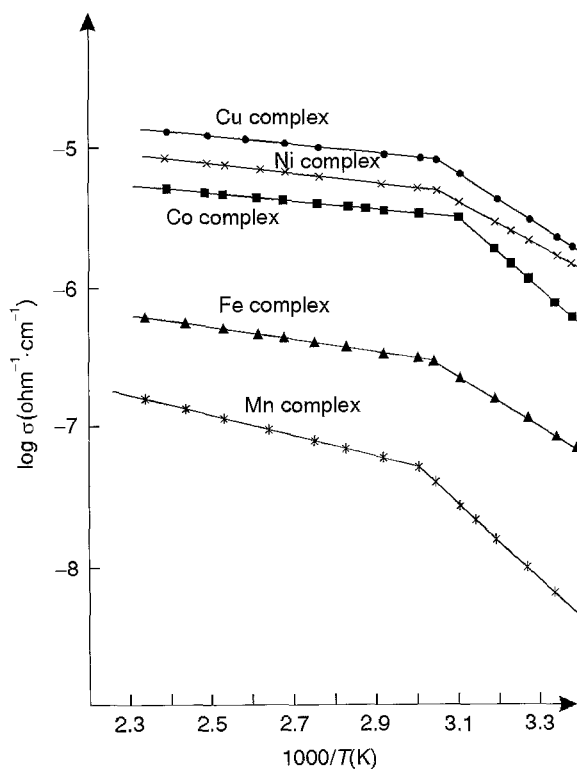


Fig. 3. Electrical conductivity of complexes formed from some transition metal ions with 1

**Table 1.** Electrical data of selected hydrazones and transition metal complexes at 294 K

|  | $\sigma$ (ohm$^{-1}$·cm$^{-1}$) | $E$ (eV) | $W$ (eV) | $n$ (cm$^{-3}$) | $\mu$ (cm$^2$/Vs) |
|---|---|---|---|---|---|
| 1 | $4.89 \times 10^{-10}$ | – | – | – | – |
| 2 | $6.03 \times 10^{-10}$ | 0.044 | 0.069 | $4.267 \times 10^{24}$ | $8.83 \times 10^{-16}$ |
| 3 | $5.07 \times 10^{-10}$ | – | – | – | – |
| 4 | $9.55 \times 10^{-10}$ | 0.109 | 0.135 | $3.269 \times 10^{23}$ | $1.83 \times 10^{-14}$ |
| Mn complex | $4.17 \times 10^{-9}$ | 0.535 | 0.560 | $1.591 \times 10^{16}$ | $1.64 \times 10^{-6}$ |
| Fe complex | $6.46 \times 10^{-8}$ | 0.356 | 0.382 | $1.881 \times 10^{19}$ | $2.15 \times 10^{-8}$ |
| Co complex | $5.25 \times 10^{-7}$ | 0.515 | 0.540 | $3.508 \times 10^{16}$ | $9.35 \times 10^{-5}$ |
| Ni complex | $1.35 \times 10^{-6}$ | 0.301 | 0.327 | $1.654 \times 10^{20}$ | $5.10 \times 10^{-8}$ |
| Cu complex | $1.74 \times 10^{-6}$ | 0.396 | 0.422 | $3.871 \times 10^{18}$ | $2.81 \times 10^{-6}$ |

On the other hand, the conductivity of complexes follows the order Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II). This trend depends heavily on the increasing stability of the complexes formed which increase the number of dislocated electrons.

To determine the density of charge carriers of the investigated compounds, provided that the concentration of electrons is equal to the concentration of holes, the following relation can be used where $m^+$ is the effective mass of the electron.

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

The other characteristic parameter is the carrier mobility $\mu$ which is obtained from the basic equation

$$\sigma = en\mu,$$

e being the charge of an electron. The electrical data hydrazones and metal complexes are summarized in Table 1. The carrier mobility of the complexes is higher than that of the metal free hydrazones. This is attributed to the fact that in organic solids the degree of intermolecular overlap is small and the conduction bands are narrow. In complexation with metal ions, a strong intermolecular overlapping is created. However, in general, the charge carrier mobilities are low enough to suggest that the conduction takes place by a hopping mechanism [21]. According to this mechanism, the conductivity is given by

$$\sigma = \frac{C}{T} \cdot \exp(-W/kT)$$

where $C$ is a constant and $W$ is the activation energy of the hopping process. The difference between activation energies $W$ and $E$ gives the activation energy of mobility which varied from 0.025 to 0.026 eV.

On the basis of the above evidences, it can be assumed that the electrical behaviour of hydrazones depends on their structures and their ability to form metal complexes.

## Experimental

The hydrazones investigated were prepared as follows: 100 mmol of a ketone (acetophenone, ninhyd-rine, p-methoxyacetophenone, or cyclohexanone) were added to 100 mmol of hydrazine (2,4-dinit-rophenylhydrazine, 2,4,6-trichlorophenylhydrazine, or p-methylbenzoylhydrazine) in ethanol (80 ml)/acetic acid (1 ml). Each reaction mixture was boiled under reflux for one hour. Evaporation and crystallization of the residue afforded the pure hydrazone. The hydrazones prepared have the following structures:
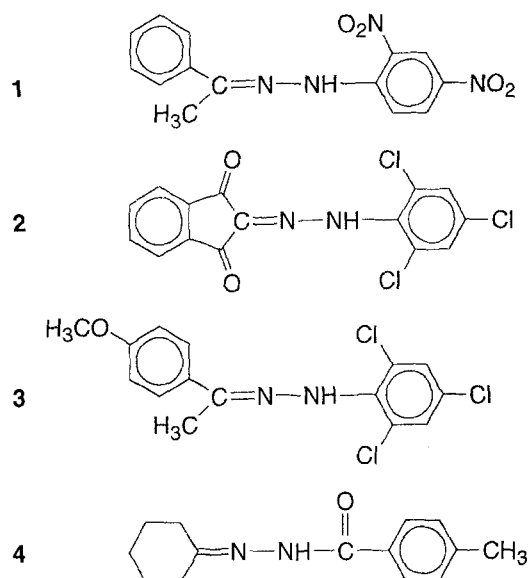


$^1$H and $^{13}$C NMR spectra ($\delta$, ppm) were recorded by means of a Bruker AC 200 (200 MHz) spectrometer at the Institut für Chemie, Johannes-Kepler-Universität Linz, Austria. Melting points were measured on a Kofler apparatus. The physical and spectroscopic data of the hydrazones are given in Table 2.

To determine the probable stoichiometric ratio of hydrazone complexes, conductometric titrations were performed using 30 ml of $10^{-3} M$ metal ion solution against $10^{-2} M$ solution of hydrazone 1 at room temperature. The conductance of the solution was measured by a digital conductivity meter 5800-05 solution analyzer (Cole-Parmer Instrument Co).

The solid complexes were prepared by mixing 20 ml of a $10^{-2} M$ aqueous solution of metal(II)sulfate with 20 ml of 1 dissolved in $DMF$ ($10^{-2}$ M). The mixture was refluxed on a water bath for 3 h. The complexes formed were filtered, washed with ethanol, and dried in vacuum. IR spectra of the solid complexes were obtained on a Shimadzu IR-440 spectrometer (KBr pellets).

The number of coordinated water molecules in the solid complexes was calculated by heating a certain amount of the solid in an oven at 180 °C. After 4 h, the sample was weighed again to determine the number of water molecules lost. The results indicate that each complex has two coordinated water molecules.

The conductivity measurements were carried out in a cylindrical glass furnace in a dry atmosphere on solid discs of 12 mm diameter and 0.4 mm thickness [22]. The discs were molded under a pressure of 5 t/cm$^2$. The conductivity was measured using the two terminal technique (HC-3500 T and Thandar TM digital multimeters) in the temperature range of 290–435 K. A Ni/Ni–Cr thermocouple was used.

**Table 2.** Characterization of selected hydrazones

| | m.p. (°C) | Yield (%) | Colour | $^1$H NMR (CDCl$_3$/$TMS$) ($\delta$/ppm) | $^{13}$C NMR (CDCl$_3$/$TMS$) ($\delta$/ppm) |
|---|---|---|---|---|---|
| 1 | 252 | 95 | orange | 2.48 (s, 3H, CH$_3$); 7.46 (d, 3H, phenyl); 7.85 (m, 2H, phenyl); 8.12 (d, 1H, aromatic); 8.40 (d, 1H, aromatic); 9.17 (s, 1H, aromatic); 11.40 (s, 1H, NH) | – |
| 2 | 264 | 88 | deep red | 7.41 (s, 2H, trichlorophenyl); 7.79–7.97 (m, 4H, aromatic); 13.10 (s, 1H, NH) | 123.25, 123.50, 127.02, 129.10, 132.17, 133.20, 133.97, 135.35, 135.79, 138.91, 140.92, 185.36, 188.30 |
| 3 | 138 | 98 | pale yellow | 2.28 (s, 3H, CH$_3$); 3.80 (s, 3H, OCH$_3$); 6.89 (d, 2H, aromatic); 7.20 (s, 1H, NH); 7.30 (s, 2H, trichlorophenyl); 7.70 (s, 2H, aromatic) | 12.18, 55.18, 113.64, 125.84, 126.91, 127.02, 128.70, 131.05, 138.31, 147.34, 160.03 |
| 4 | 167 | 82 | pale yellow | 1.65 (m, 6H, cyclohexanone); 2.30 (s, 3H, CH$_3$); 2.40 (m, 4H, cyclohexanone); 7.20 (d, 2H, aromatic); 7.55 (d, 2H, aromatic); 9.10 (s, 1H, NH) | 14.80, 25.61, 25.84, 26.40, 26.92, 35, 46, 126.81, 128.85, 133.74, 139.92, 154.92, 162.10 |

# References

[1] Sengupta AK, Bhatnagar A (1987) J Indian Chem Soc **64**: 616

[2] Islam AM, Abdel Halim AM, Salama MA (1986) Egypt J Chem **29**: 405

[3] Molodykh ZhV, Buzykin BI, Bystrykh NN, Kitaev YuP (1977) Khim Farm Zh **11**: 37

[4] Dilworth R (1976) Coord Chem Rev **21**: 29

[5] Aggarwal RC, Yadav BN, Prasad T (1973) J Inorg Nucl Chem **35**: 653

[6] Kitaev YuP, Buzykin BI, Troepol'Skaya TV (1970) Russian Chem Rev 441

[7] Ma TS, Tien TM (1953) Antibiotics and Chemotherapy **3**: 491

[8] Sharma RC, Ambwani J, Varshney VK (1992) J Indian Chem Soc **69**: 770

[9] Sharma RC, Johri RB (1988) J Indian Chem Soc **65**: 792

[10] El Bahnasawy RM, Abou Sekkina MM, Abou El-Ela FM (1987) Egypt J Chem **30**: 159

[11] Dutta RL, Hossain MM (1985) J Sci Ind Res **44**: 635

[12] Demertzi D, Nickolls D (1983) Inorg Chim Acta **73**: 37

[13] Dutta RL, Sarkar AK (1981) J Inorg Nucl Chem **43**: 4757

[14] Pelizzi C, Predier G (1975) Gazz Chem Ital **105**: 413

[15] Abd El Wahed MG, El Manakhly KA, Metwally SM, Hammad HA, Aly SA (1995) Monatsh Chem **126**: 663

[16] Abd El Wahed MG, Aly SA, Hammad HA, Metwally SM (1994) J Phys Chem Solids **55**: 31

[17] Abd El Wahed MG, Hassan AM, Hammad HA, El Desoky MM (1992) Bull Korean Chem Soc **13**: 113

[18] Srivastava AK, Jain PC (1986) Chemical analysis. An instrumental approach. S. Chand, New Delhi, p 276

[19] Kemp W (1988) Organic spectroscopy. ELBS/Macmillan, Hong Kong, p 22

[20] Adams DM (1967) Metal-ligand and related vibrations. A critical survey of the infrared and raman spectra of metallic and organometallic compounds. Edward Arnold, London, p 276, 304

[21] Seanor DA (1982) Electrical properties of polymers. Academic Press, New York, p 38

[22] Abd El Wahed MG (1995) In: Cheremisinoff NP, Cheremisinoff PN (eds) Handbook of advanced materials testing. Marcel Dekker, New York, chapt 16