

POTENTIOMETRIC AND THERMAL CONDUCTIMETRIC STUDIES ON SALICYLIDENE GIRARD-P HYDRAZONE COMPLEXES OF DIVALENT Co, Ni, Cu AND Zn SALTS

R. M. El-Bahnasawy

Chemistry Department, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt

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Abstract

Salicylidene Girard-P hydrazone $[H_2L]Cl$ reacts with divalent cobalt, nickel, copper and zinc ions to form mono-ligand complexes of the type $[ML \cdot H_2O]Cl \cdot nH_2O$ and $[(CuL)_2]Cl_2$. The formation constants of the complexes ML were determined in 50% (v/v) aqueous ethanol solution at an ionic strength $I=0.1 M$ KCl and at $25 \pm 0.1^\circ C$. The solid complexes and the ligand were subjected to differential thermal analysis and the DC electrical conductivities were measured at varying temperatures. The results obtained were explained and discussed in terms of the proposed semiconductive behaviour of the complexes and the probable occurrence of a phase transition. The activation energies (ΔE) were calculated for the ligand and the complexes; that of the ligand was higher than those of the complexes.

Keywords: DC electric conductivity, Girard-P hydrazone complexes

Introduction

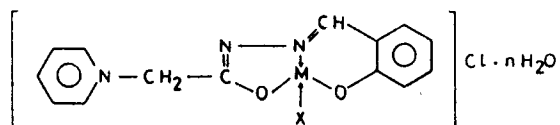
Studies of solid complexes are attracting increasing attention because of their many useful applications. N-Isonicotinoyl hydrazones and many other physiologically active hydrazones exert antibacterial activity *in vitro* against several human pathogenic microorganisms, including those causing mycobacterium tuberculosis [1], leprosy and mental disorder [2]. Hydrazones also act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. In analytical chemistry, hydrazones are extensively used for the detection, determination and isolation of compounds containing carbonyl groups. The kinetic parameters of the thermal decompositions of the zinc, cadmium and mercuric hydrazones of anisaldehyde Girard-T were determined from the corresponding thermal curves [3]. The CD electrical conductivities of the complexes depend mainly on the chemical structure, the mode of bonding and the degree of charge delocalization in the molecule, and the mode of solid packing. Ther-

mal analysis reveals the stability and probable physical and chemical transformations.

As a continuation of our investigations on complexes of hydrazone derivatives with transition metals [4–6], electrical conductivities and thermal reactions of different hydrazones [7], the present article deals with the determination of the stability constants and the thermodynamic, kinetic and electrical parameters of the ligand salicylidene Girard-P hydrazone and its cobalt, nickel, copper and zinc complexes.

Experimental

Salicylidene Girard-P hydrazone was prepared by refluxing salicylaldehyde with Girard-P reagent in a molar ratio of 1:1 in ethanol. The solid complexes of cobalt, nickel, copper and zinc were also prepared by refluxing equimolecular amounts of the ligand and metal acetates in ethanol. The compounds formed were filtered off, washed and dried in a vacuum desiccator over CaCl_2 . The compounds were characterized as previously described [4]. The established molecular structures of the complexes are as follows:



where $x = \text{H}_2\text{O}$ for Co, Ni and Zn, but another ligand molecule for Cu, while $n = 1$ in the case of Ni, but zero in other cases.

For evaluation of the formation constants of the divalent cobalt, nickel, copper and zinc complexes, solutions of the metal chlorides were prepared in bidistilled water. All solutions were standardized by established procedures [8]. An Exttech 671 digital *pH*-meter was used for *pH* measurements, which are devoid of errors arising from the solvent or the ionic strength of the medium. The *pH*-meter readings in aqueous ethanol solvent (*R*) were converted to hydrogen ion concentrations by using the method of Van Uitert and Hass [9]:

$$-\log[\text{H}^+] = R + \log U_{\text{H}} \quad (1)$$

where $\log U_{\text{H}}$ is the correction factor for the meter reading. For this purpose, readings were taken for a series of 50% (*v/v*) aqueous ethanol solutions containing known amounts of HCl and KCl such that the ionic strength (*I*) was 0.1 *M* at $25 \pm 0.1^\circ\text{C}$. The value of $\log U_{\text{H}}$ (Fig. 1) was found to be -0.88 . The dissociation constants of the ligand and the formation constants of the complexes were determined by using the following mixtures:

- i) 2.5 ml of 2 *M* KCl + 1 ml of 0.1 *M* HCl

- ii) mixture (i) + 5 ml of 0.2 M ligand
- iii) mixture (ii) + 1 ml of 0.2 M metal chloride solution.

The total volume of each mixture was made up to 50 ml and each mixture was separately titrated with carbonate-free 0.481 N KOH solution. The titrations were performed under a nitrogen atmosphere at $25 \pm 0.1^\circ\text{C}$ with a Fisher Scientific Isotemp Refrigerated Circulator Model 9000. From the pH -titration curves, the average number of ligands \bar{n} and the free ligand exponent pL were calculated as described previously [10].

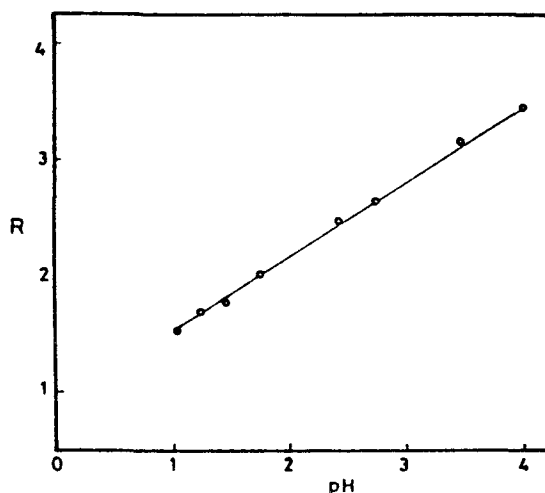


Fig. 1 Values of pH vs. pH-meter reading R , to determine the correction factor for solvent, temperature and ionic strength

Thermogravimetric analysis (TG) was performed manually in an oven by heating 0.1 g of sample at the decomposition temperature, and the percentage mass loss was calculated. Differential thermal analysis (DTA) was carried out with a Shimadzu DT-30 thermal analyser, with heating at $10 \text{ deg}\cdot\text{min}^{-1}$ from 20 to 500°C in air. The DC electrical conductivity was measured as described previously [7] from 20 to 325°C .

Results and discussion

Potentiometric results

a) The ligand

The protonation constants of salicylidene Girard-P hydrazone were calculated from the potentiometric titration curves of HCl in the presence and absence of ligand (curves (i) and (ii) (Fig. 2)), via the method of Nayan and Dey [11]:

$$\bar{n}_H = [(v' - v'')(N^o + E^o)] / [(v^o + v')T_{CL}^o] \quad (2)$$

The protonation curve was extended between 0.3 and 1.8 in the \bar{n}_H scale and from pH 5 to pH 12 and indicated that the ligand contains two dissociable protons. The protonation constants $\log K_1$ and $\log K_2$ were taken directly from the formation curve, as the values of pH at $\bar{n}_H = 0.5$ and 1.5, respectively. It was found that $\log K_1 = 7.2$ and $\log K_2 = 10.8$. The rapid attainment of equilibrium during titration, and the absence of significant drift in the pH -meter readings indicate the absence of hydrolysis in the system [12].

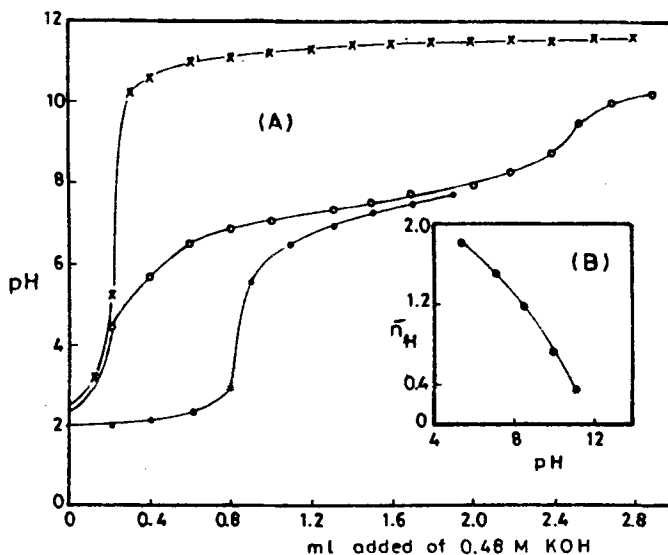
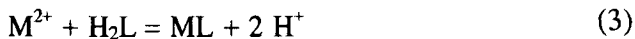


Fig. 2 (A) Titration curves of solutions (i), (ii), and (iii) of copper salt. (B) Formation curve of the ligand

b) The complexes

The metal complex and ligand titration curves in Fig. 2 are well separated, indicating the liberation of protons due to complexation:



The values of \bar{n} and pL were also evaluated by using the method of Nayan and Dey [11].

$$\bar{n} = [(v''' - v'')(N^o + E^o)] / [(v^o + v')T_{CM}^o \bar{n}_H] \quad (4)$$

$$pL = \log[K_1 K_2 [H^+]^2 (v^o + v''')] / [T_{CL}^o - \bar{n}_H T_{CM}^o] v^o \quad (5)$$

where v' , v'' and v''' denote the volume of alkali required to reach the same pH in the titration of mixtures (i), (ii) and (iii), respectively, v^0 is the initial volume of the titrated solution. N^0 is the normality of the alkali; E^0 is the initial concentration of the free acid, T_{CM}^0 is the total metal ion concentration, and T_{CL}^0 is the total ligand concentration. The formation curves for the complexes were obtained by plotting \bar{n} vs. pL (Fig. 3). The curves show that \bar{n} attains a maximum value of 0.85, indicating that in solution only one complex ML is formed. The values of $\log K$ are 6.2, 6.6, 6.9 and 6.0 for the complexes of cobalt, nickel, copper and zinc, respectively. The sequence of the conditional stability constants ($\log K$) was found to be $Cu > Ni > Co > Zn$.

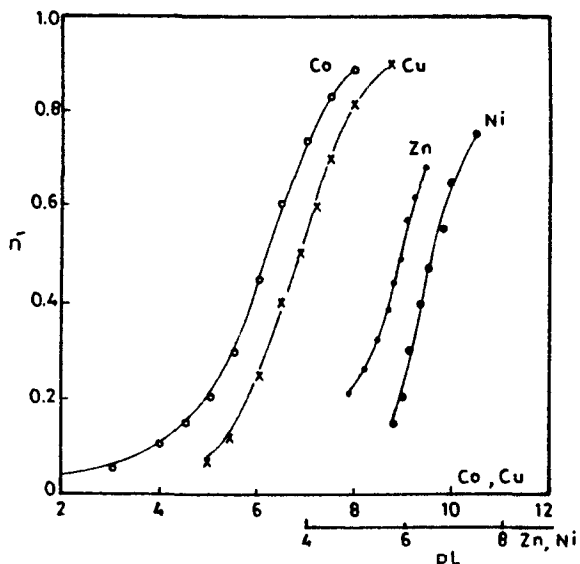


Fig. 3 Formation curves of Co, Ni, Cu and Zn complexes

Thermal analysis

a) The ligand

Figure 4 depicts DTA curves for the ligand salicylidene Girard-P hydrazone and its complexes. The DTA curve of the ligand displays a sharp endothermic peak at 265°C (with no loss in mass), which corresponds to its melting. The activation energy of this thermal changes was calculated by the Piloyan method [13] to be $150 \text{ kJ}\cdot\text{mol}^{-1}$.

b) The complexes

The nickel and copper complexes melted with decomposition at 250°C , whereas the cobalt and zinc complexes did not melt up to 250°C (Table 1). The

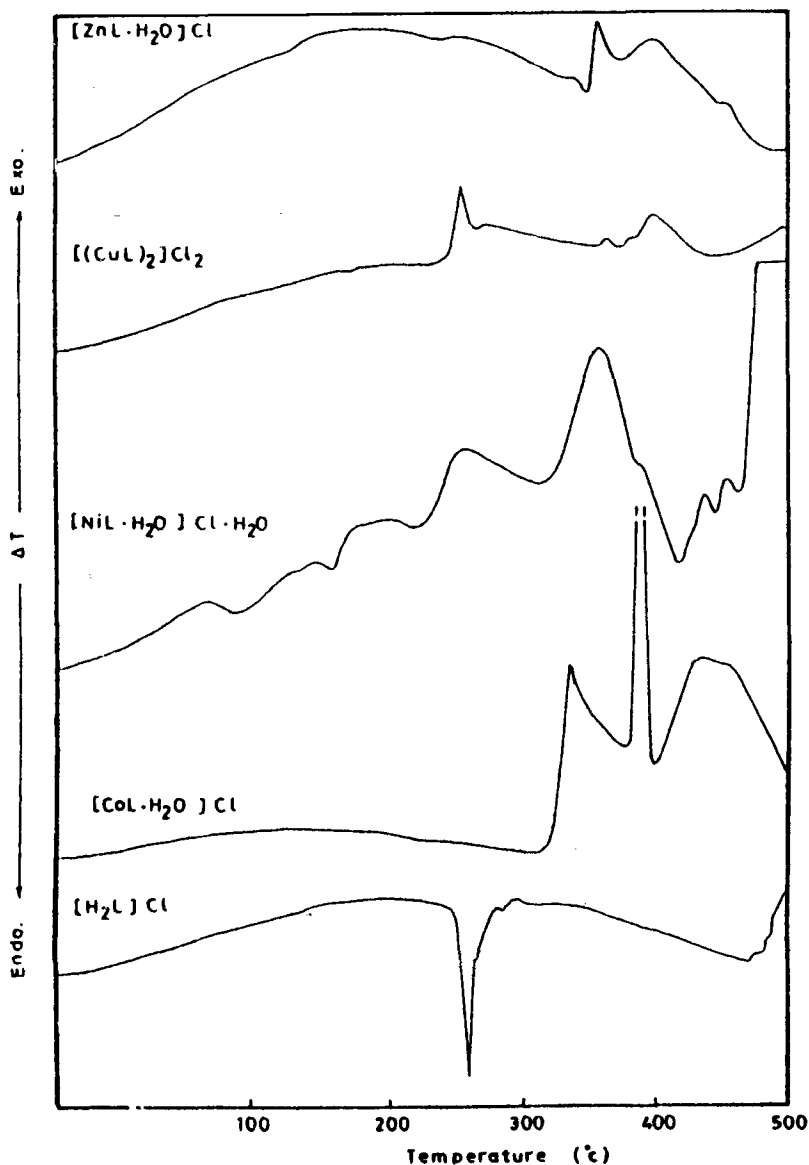


Fig. 4 DTA curves of salicylidene Girard-P hydrazone and its Co, Ni, Cu and Zn complexes (at a heating rate of $10 \text{ deg}\cdot\text{min}^{-1}$)

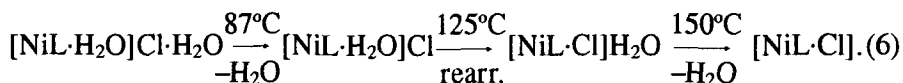
differential thermograph of the nickel complex in Fig. 4 exhibits 4 endothermic peaks before melting. The percentage mass loss in each stage was determined by weighing the sample after heating, as reported in the Experimental part. The

Table 1 Colour, melting points (°C) and molar conductances of salicylidene Girard-P-hydrazone and its complexes as described in Ref. [4]

Compounds	Colour	M.P. / °C	$\Lambda_m^{(a)}$
[H ₂ L]Cl	golden-yellow	270	96
[CoL·H ₂ O]Cl	olive-green	> 250	111
[NiL·H ₂ O]Cl·H ₂ O	orange	250 ^(b)	99
[ZnL·H ₂ O]Cl	dark-white	> 250	107
[(CuL) ₂]Cl ₂	green	250 ^(b)	201

(a) molar conductance (s·cm²·mol⁻¹), (b) melting with decomposition

first peak, at 87°C (3.8% mass loss), corresponds to the loss of one molecule of weakly bonded water of hydration in the outer sphere of the nickel complex, with an activation energy of 180 kJ·mol⁻¹. The second endotherm, at 125°C (with no mass loss), corresponds to rearrangement of the molecule before evolution of the second water molecule, coordinated in the inner sphere of the complex. The third endothermic peak, at 150°C (3.6% mass loss), corresponds to the elimination of the second molecule of water, with a net activation energy of 213 kJ·mol⁻¹. The last endotherm, at 212°C (with no mass loss), with an activation energy of 155 kJ·mol⁻¹, may correspond to lattice rearrangement in the nickel complex molecule after the evolution of H₂O. The decomposition products were confirmed by elemental and IR spectral analyses; the latter did not show any significant change up to 200°C. The previous discussion can be simplified in the following equation:



It is known that melting is an endothermic reaction. However, if melting is associated with an exothermic decomposition reaction (as in our case) the resultant may appear as an exothermic peak in the DTA curves. Hence, the exothermic peaks at 330, 250, 250 and 350°C, could be assigned to melting with decomposition of the Co, Ni, Cu and Zn complexes, respectively. The other exothermic peaks could be assigned to thermal stepwise decomposition, which may end with formation of the corresponding metal oxide.

Electrical conductivity

a) Free ligand

Figure 5 shows the temperature dependence of the conductivity of the ligand, which displays semiconducting behaviour. At low temperature, the conductivity is independent of temperature; a transition takes place at 200°C. At higher temperatures, the conductivity increases with elevation of the temperature.

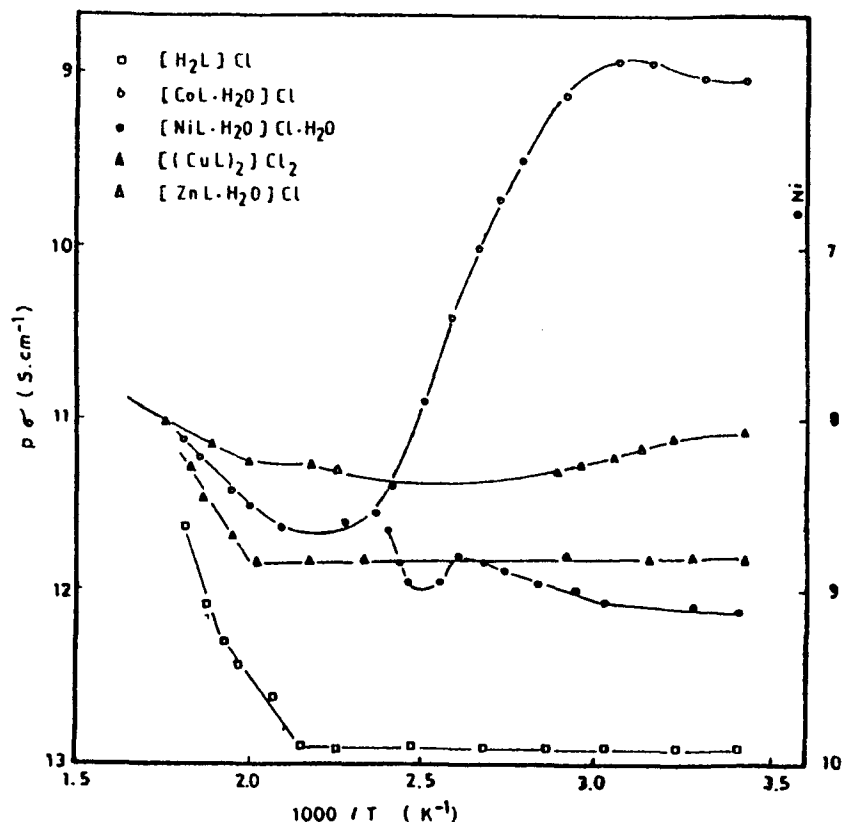


Fig. 5 Electrical conductivity – temperature relationship of Girard-P hydrazone and its Co, Ni, Cu and Zn complexes

At lower temperatures, a pure extrinsic conduction mechanism is predominant; this is attributed to the enhanced delocalization of π -electrons, characterized by low activation energy. At higher temperature, the activation energy is higher and an intrinsic semiconducting conduction mechanism is suggested which can be attributed to the π - π^* transition from the ground state (valence band) to the lowest empty molecular orbital (conduction band). The activation energy (ΔE) was calculated from the Arrhenius relation:

$$\sigma = \sigma_0 \exp(-\Delta E / 2kT) \quad (7)$$

b) The complexes

As a general trend, ΔE for the free ligand decreases upon complexation with Co, Ni, Cu and Zn ions. In Fig. 5, two regions can be recognized, reflecting two different conduction mechanisms. Reference to the DTA curve indicates

that a phase transition is not probable at these temperatures. The low-temperature range is generally related to extrinsic conductivity, where dehydration is probable, as demonstrated in earlier work on similar hydrazone complexes [14].

The curves of the complexes exhibit semiconducting behaviour mainly in the higher temperature range [7], where the mechanism of conduction involves the promotion of electrons from the ground state to the lowest molecular orbital (excited state).

For the cobalt and nickel complexes, inversions in the slope of the $\rho\sigma$ vs. $1000/T$ curve are observed in the ranges 55–200 and 112–135°C, respectively; these are centred at 185 and 125°C, respectively. This may be explained in that heating in this range does not increase the thermal mobility of the electrons, which would increase the conduction, but heat is consumed for dehydration [7].

In the low-temperature range, the conductivity of the copper complex is independent of temperature, but there is a transition at 220°C, and at higher temperature the conductivity increases with elevation of the temperature. The similarity between the ligand and copper complex may be due to the fact that both compounds are anhydrous. However, the relatively high activation energy of this complex $[(CuL)_2Cl_2]$ may be due to dimerization.

From Fig. 5 and Table 1, it can readily be seen that the electrical conductivity is higher and the energy gap is lower for the transition metal complexes relative to the data for the organic ligand. This could plausibly be interpreted in that the transition metal ion may act as a bridge for current transfer throughout the organic ligand molecule. The reaction order (n) was calculated for the ligand and its nickel complex via the Reichs empirical relation [15], where the reaction for the ligand is a melting process, while that for the complex is melting associated with an exothermic decomposition reaction:

$$n = 1.26 S^{1/2} \quad (8)$$

where S is the peak shape factor $=a/b$. Values of a and b were calculated from the profile of the peak in the DTA curve (Fig. 4), as reported in reference [15]. The calculated values of n were found to be ca. 1.0, indicating that the reactions are of the first-order type.

References

- 1 R. Shivhare, K. V. Kale Aron, D. D. Berge and H. R. Gupta, *Indian J. Pharm. Sci.*, **49** (1987) 79.
- 2 Yu. P. Kitaev, B. I. Buzykin and T. V. Trowpul'skaya, *Russian Chem. Rev.*, (1970) 441.
- 3 M. E. M. Emam, M. A. H. Hafez and M. N. H. Moussa, *J. Thermal Anal.*, **32** (1987) 945.
- 4 R. M. El-Bahnasawy, M. M. Abou Sekkina and F. M. Abou El-Ela, *Ain Shams Sci. Bull.*, **27(A)** (1986) 377.
- 5 *Idem*, *Egypt. J. Chem.*, **30** (1987) 159.
- 6 *Idem*, *ibid*, **31** (1988) 227.

- 7 R. M. El-Bahnasawy, E. El-Shereafy, Y. M. Issa and S. El-Meleigy, *Thermochimica Acta*, 173 (1990) 9.
- 8 A. Vogel, 'Textbook of Quantitative Inorganic Analysis', 4th ed., 1985, pp. 433, 447, 462 and 489.
- 9 L. G. Van Uitert and C. G. Hass, *J. Am. Chem. Soc.*, 75 (1953) 451.
- 10 R. M. El-Bahnasawy, M. M. Shoukry and M. M. Hussein, *Proc. Indian Acad. Sci. (Chem. Sci.)* 96 (1986) 309.
- 11 R. Nayan and A. K. Dey, *Indian J. Chem.*, 10 (1972) 109.
- 12 N. T. Abdel-Ghani, Y. M. Issa, M. A. Khaled and M. M. Kottamy, *Thermochim. Acta.*, 163 (1988) 125.
- 13 G. O. Piloyan, J. D. Ryabchikov and O. S. Novikova, *Nature*, 212 (1966) 1229.
- 14 R. M. El-Bahnasawy, E. El-Shereafy and T. I. Kashar, *J. Thermal Anal.*, 39 (1993) 65.
- 15 L. Reich's, *J. Inorg. Nucl. Chem.*, 28 (1966) 1329.

Zusammenfassung — Salicyliden Girard-P Hydrazone $[H_2L]Cl$ reagiert mit zweiwertigen Kobalt-, Nickel-, Kupfer- und Zinkionen unter Bildung der Monoligandenkomplexe vom Typ $[ML \cdot H_2O]Cl \cdot nH_2O$ und $[(CuL)_2Cl_2]$. Die Bildungskonstante der Komplexe ML wurde in einer 50% (v/v) wäßrigen Ethanollösung bei einer Ionenstärke von $I=0.1 M$ KCl und bei $25 \pm 0.1^\circ C$ ermittelt. Die Feststoffkomplexe und die Liganden wurden einer Differentialthermoanalyse unterzogen und die elektrischen Leitfähigkeiten (bei Gleichstrom) wurden bei verschiedenen Temperaturen gemessen. Die erhaltenen Ergebnisse wurden im Hinblick auf das vorgeschlagene Halbleiterverhalten der Komplexe und das wahrscheinliche Vorkommen einer Phasenumwandlung erklärt und diskutiert. Die Aktivierungsenergien (ΔE) wurden für Ligand und Komplexe berechnet; die der Liganden sind höher als die der Komplexe.