

# ELECTRICAL CONDUCTIVITY, ELECTRONIC ABSORPTION, IR AND NMR STUDIES ON SOME ETHYL CYANOACETATE PHENYLHYDRAZONES AND THEIR LANTHANIDE COMPLEXES

A. A. Salem\*, Y. M. Issa and E. E. El-Shreafy<sup>1</sup>

Department of Chemistry, Faculty of Science, Cairo University, Giza

<sup>1</sup>Department of Chemistry, Faculty of Science, Menoufia University, Shebin Elkom, Egypt

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## Abstract

The electrical conductivities and the electronic, IR and NMR spectra were measured for some ethyl cyanoacetate phenylhydrazone derivatives and their lanthanide complexes in the temperature range 20–200°C. Semiconducting behaviour was detected for these systems (positive  $d\sigma/dT$ ). A correlation was established between the electrical properties and the structures of the free ligand molecules and their complexes. The mechanism of the conduction process was evaluated. The electronic absorption spectra in ethanol were measured and are discussed. Elemental analyses were performed and the IR and NMR spectra (of the diamagnetic complexes) were measured to throw more light on the structures of these complexes.

**Keywords:** activation energy, electrical conductivity, hydrazones, Ln(III) complexes

## Introduction

Hydrazo and azo compounds are involved in a number of important biological reactions [1]. They have been used as antidepressants and as antitubercular agents (hydrazo monoamine oxidase). Some hydrazoalkanes are known to be alkylating agents with carcinogenic properties (tumour inducers) [2]. Others are reported to be antifungal agents [3]. A number of ethyl cyanoacetate arylhydrazones have been prepared and characterized by El-nagdi [4], Siddiqui [5] and Borovikov [6]. El-nagdi *et al.* prepared  $RC_6H_4NHN:CN$ , where  $R=H$ , 2-, 3- or 4- Me, Cl, Br or MeO; and  $X=CN$  or  $CO_2Et$ . Their IR and UV spectra were measured, and the dissociation constants and isomerization rate constants were determined. The hydrazone rather than the azo structure was confirmed. Siddiqui prepared a series of hydrazones by the reaction of  $o-H_2NCOC_6H_4N_2^+$  with  $\alpha,\beta$ -unsubstituted esters [5]. Borovikov and his coworkers [6] calculated the dipole moments from dielectric data

\* Author to whom all correspondence should be addressed.

in benzene or in the molten state for  $RC_6H_3NHN:CClCO_2-Et$ , with R selected from H and variously placed Me, F, Cl, Br, I,  $CF_3$ ,  $NO_2$ ,  $CHF_2$ ,  $SO_3$ , MeO, EtO and  $EtO_2C$ , and it was shown that such esters are weakly associated in solution through intermolecular hydrogen bonding. In the liquid phase, they exist in a single conformation and those with an ortho substituent show a rotation of the aryl group at the C-N bond to some degree. The electron density distribution differs from that found in the less complex analogues of such esters.

The major goal of the present investigation is to study the mechanism of electrical conductivity of some hydrazone ligands and their lanthanide complexes in the temperature range 20–200°C, the effects of different substituents on the aryl group and the effect of coating the sample pellet with Ag film on the conductivity values and the activation energy. Conduction mechanisms were related to the physico-chemical properties of the ligands and complexes.

## Experimental

The ligands were prepared by direct diazotization of arylamines and coupling of the produced diazonium salts with ethyl cyanoacetate in sodium bicarbonate [7]. The complexes were prepared by mixing the calculated amounts of ligands and lanthanides perchlorate in ethyl alcohol, refluxing the mixtures on a water bath for several hours and precipitating the products by adding alcoholic ammonium hydroxide solution. The structures of the produced ligands and complexes were confirmed by elemental analysis and IR and NMR spectral measurements. The metal contents of the prepared complexes were determined with EDTA, using Arsenazo I as indicator [8].

Compressed pellets of the prepared compounds about 1 cm<sup>2</sup> in area and 0.2–0.3 cm in thickness were moulded for conductivity measurements without silver paste. The experimental technique was reported previously [9].

## Results and discussion

### *Electrical conductivity*

#### Free ligands

Figure 1 shows the temperature dependence of the conductivity of the investigated dyes ( $I_a-I_e$ ) (Table 1). It is evident that all samples show typical semiconducting behaviour. In a previous investigation [10], some of these compounds were measured to study the effects of substituents on the conductivity, the pellets being coated with silver paste. It was found that coating the pellets with silver paste greatly enhanced the conductivity and decreased the activation energy values ( $\Delta E$ ), which can be attributed to the diffusion of silver ions in the organic material. In the case under investigation, no silver paste was used in order to avoid such interferences. At low temperature, the conductivity is independent of increasing temperature, except for  $I_f$  (*p*-AsO(OH)<sub>2</sub>) and  $I_j$  (*o*-OH), where a transition takes place at 140°C for the former and at 81°C for the latter (Fig. 1b).

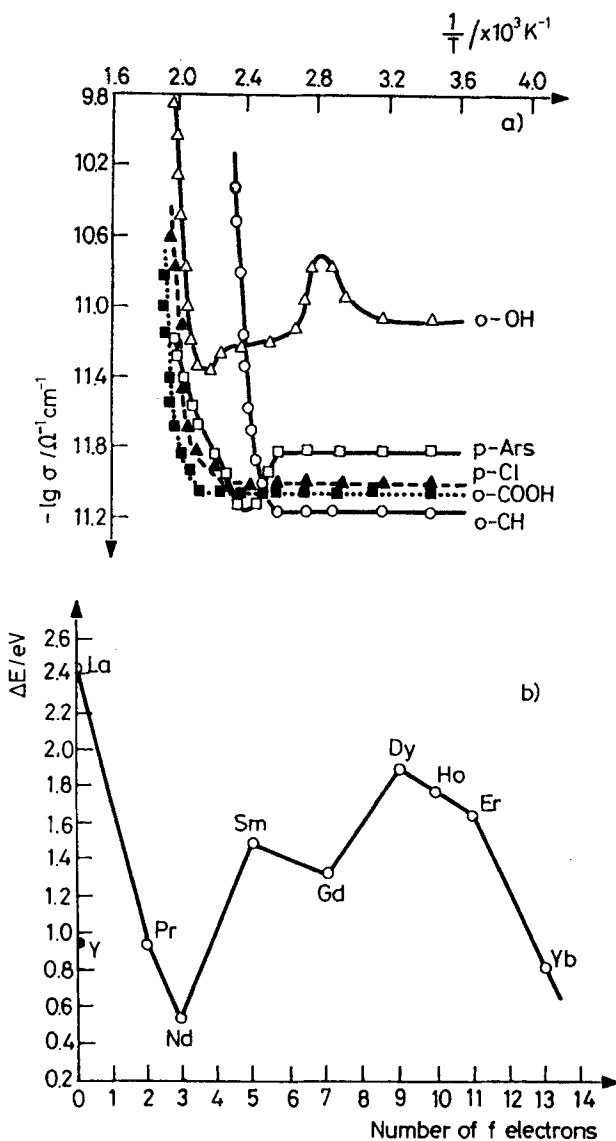


Fig. 1 Electrical conductivity-temperature relationship of the hydrazones ( $I_2$ - $I_1$ ) ligands

This can be attributed to arsanilic acid splitting and hygroscopic water dissociation, respectively. At high temperature, the conductivity increases with elevation of the temperature. This indicates two different mechanisms of conduction [11]. At low temperature, a pure extrinsic mechanism is predominant, where the conduction is mainly due to the empty states (positive holes) formed by the transition of elec-

trons to the acceptor levels. This process is strongly attributed to the enhanced delocalization of  $\pi$ -electrons, usually characterized by low activation energy. At higher temperature, the activation energy is higher and the intrinsic semiconducting conduction mechanism is the predominant one. This can be attributed to the transition of  $\pi$ -electrons from the valence band to the lowest empty  $\pi$ -states in the conduction band.

The substituent on the phenyl moiety may facilitate the conduction process by decreasing the activation energy or *vice versa*. For electron-withdrawing groups, it was found that  $\Delta E$  decreases, whereas for electron-donating groups it increases (Table 1). This can be attributed to the enhancement of electron (charge) delocalization in the direction of the phenyl moiety from the ethyl cyanoacetate residue, and consequently the positive holes in the opposite direction. The opposite can account for the increase in  $\Delta E$  in the case of electron-donating substituents. The flow of charge will be from the phenyl moiety to the rest of the molecule. This will increase the energy gap between the valence and conduction bands ( $E_v$  and  $E_c$ ) and consequently  $\Delta E$  increases.

Table 1 Melting points, electrical and electronic activation energies of the prepared hydrazones

Compound	<i>m.p.</i> / °C	$\Delta E/\text{eV}$		$\Delta E/\text{elec.}$	$\log \sigma$ 30°C
		$\Delta E_1$	$\Delta E_2$		
I <sub>a</sub> H	118	4.33 (0.50)	- (0.37)	3.52	-12.72 (-9.45)*
I <sub>b</sub> <i>p</i> -COOH	140	0.77	-	2.44	-12.39
I <sub>c</sub> <i>p</i> -OH	150	0.71 (0.13)	0.11 (0.13)	3.26	-11.50 (-12.45)
I <sub>d</sub> <i>p</i> -NO <sub>2</sub>	172	2.88 (0.01)	- (0.12)	3.37	-12.12 (-8.47)
I <sub>e</sub> <i>p</i> -Cl	205	3.18 (0.18)	- (0.20)	3.44	-12.01 (-12.37)
I <sub>f</sub> <i>p</i> -AsO(OH) <sub>2</sub>	-	0.78	-	3.54	-11.84
I <sub>g</sub> <i>p</i> -CH <sub>3</sub>	105	5.07 (0.08)	- (0.18)	3.41	-12.18 (-12.41)
I <sub>h</sub> <i>p</i> -OCH <sub>3</sub>	110	4.50	-	3.28	-11.48
I <sub>i</sub> <i>o</i> -COOH	245	3.45 (0.15)	- (0.22)	3.54	-12.06 (-10.05)
I <sub>j</sub> <i>o</i> -OH	195	3.46 (0.17)	- (0.25)	3.26	-11.10 (-12.68)
I <sub>k</sub> <i>m</i> -NO <sub>2</sub>	130	3.96 (0.03)	2.0 -	3.54	-12.19 (-9.50)
I <sub>l</sub> <i>m</i> -Cl	205	-	-	3.5	-

\*The values in parentheses were obtained during measurements with silver paste [10]

A comparison of the  $\Delta E$  values with those calculated from the electronic absorption spectra (Table 1) reveals an agreement in the values obtained, which confirms that the predominant mechanism at high temperature is the  $\pi$ - $\pi$  transition from the ground state (valence band) to the lowest empty molecular orbital (conduction band).

### Solid complexes

Figure 2 shows the variation in the logarithmic electrical conductivity values for some  $I_b$  complexes (given in Table 2) as a function of the reciprocal absolute tem-

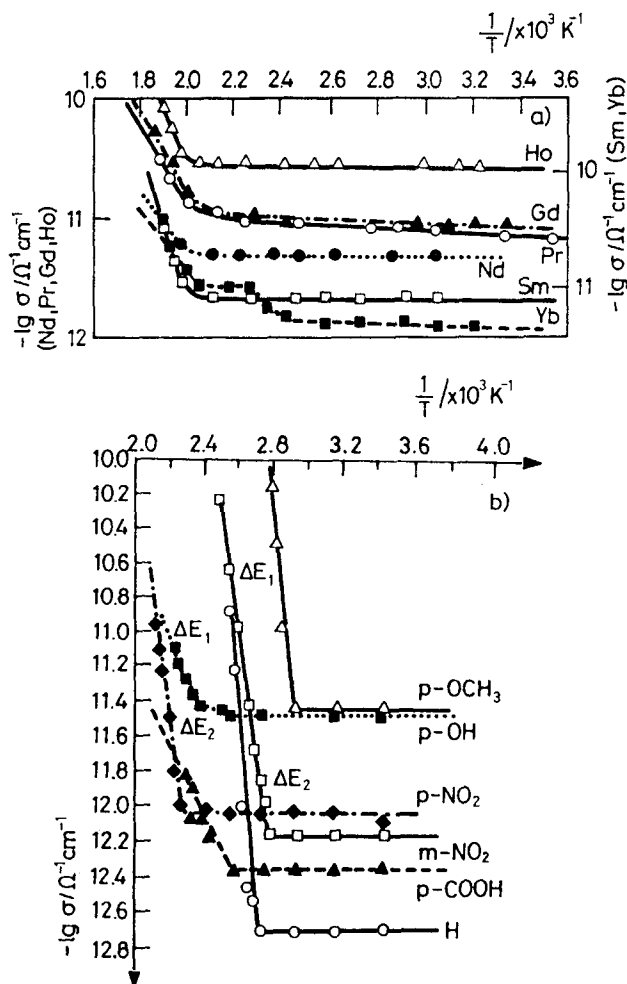


Fig. 2 a) Electrical conductivity-temperature relationship of  $I_b$  ( $p$ -COOH) ligand complexes with some Ln(III) ions; b) Dependence of activation energy  $\Delta E$  of the solid complexes on the number of  $f$  electrons of Ln(III) ion

perature. Two regions can be recognized, again reflecting two different conduction mechanisms. At low temperature, the conductivity is constant with temperature and an extrinsic semiconducting mechanism is the predominant one [12]. At moderate temperature, the mechanism is inverted to an intrinsic mechanism where the carriers (electrons) are excited from the donor localized levels to the conduction band. However, such a donor band is assumed to involve a number of delocalized energy states [13]. The dependence of the activation energy  $\Delta E$  on the number of f electrons is shown in Fig. 2b and Table 2. The 4f orbitals are shielded from the influence of external forces by the overlying  $5s^2$  and  $5p^6$  shells. Hence, the states arising from the various  $4f^n$  configurations are only slightly affected by the surroundings of the ions and remain invariant for a given ion in all of its compounds [14]. Thus, as the f orbitals are shielded from the ligand molecules, the various states arising from the  $f^n$  configuration being splitted by external fields are close in energy (up to  $\sim 100 \text{ cm}^{-1}$ ) and consequently the f-f electronic transition that occurs from one J state to another does not give a high change in  $\Delta E$ . Thus, the discrepancies in the

**Table 2** Elemental analysis, electrical activation energies and conductivity at room temperature for the prepared solid complexes

Complex	No. of f electrons	C% H% M%			$\Delta E/eV$	$\log \sigma$ 20°C
		calc.(found)				
$\text{LnL}(\text{C}_2\text{H}_5\text{OH})_2(\text{OH})_2$						
Y-I <sub>b</sub>	0	40.34 (41.2)	5.25 (4.81)	18.68 (17.90)	0.96	-12.02
La-I <sub>b</sub>	0	36.51 (38.6)	4.75 (3.90)	26.41 (25.90)	2.43	-11.69
Pr-I <sub>b</sub>	2	36.37 (37.5)	4.74 (4.10)	26.69 (26.69)	0.96	-11.20
Nd-I <sub>b</sub>	3	36.14 (35.2)	4.70 (3.90)	27.15 (26.80)	0.56	-11.38
Sm-I <sub>b</sub>	5	35.73 (35.0)	4.65 (3.30)	27.99 (26.80)	1.50	-11.13
Gd-I <sub>b</sub>	7	35.28 (33.8)	4.59 (3.90)	28.89 (27.60)	1.34	-11.14
Dy-I <sub>b</sub>	9	34.94 (34.1)	4.55 (3.90)	29.57 (28.80)	1.93	-11.58
Ho-I <sub>b</sub>	10	34.79 (32.9)	4.53 (3.60)	29.88 (28.90)	1.80	-10.62
Er-I <sub>b</sub>	11	34.64 (33.8)	4.51 (3.80)	30.18 (29.30)	1.69	-11.17
Yb-I <sub>b</sub>	13	34.28 (33.28)	4.46 (4.20)	30.90 (29.50)	0.84	-11.37

Table 2 Continued

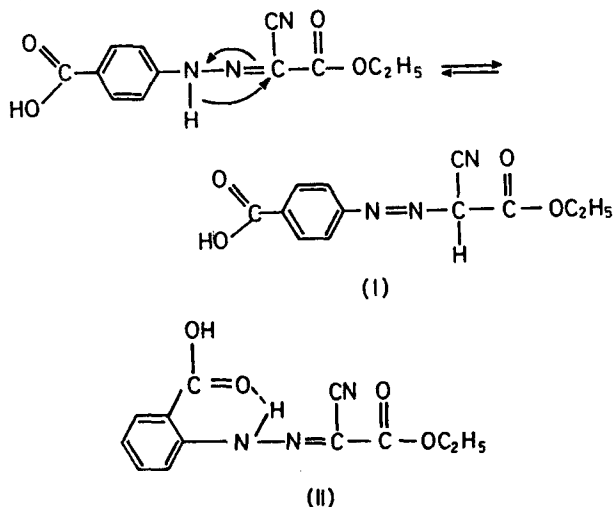
Complex	No. of f electrons	C%	H%	M%	$\Delta E$ / eV	log $\sigma$ 20°C
		calc. (found)				
LnL(C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> (OH)						
Y-I <sub>i</sub>	0	41.84 (41.5)	5.23 (4.30)	19.37 (18.40)	2.53	-12.50
Nd-I <sub>i</sub>	3	37.34 (36.3)	4.67 (3.90)	28.05 (27.30)	3.09	-12.24
Dy-I <sub>i</sub>	9	36.06 (35.3)	4.51 (3.70)	30.52 (29.30)	0.95	-11.23
Yb-I <sub>i</sub>	13	35.36 (34.2)	4.42 (4.20)	31.87 (29.80)	1.74	-11.50
LnL(C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> (OH) <sub>2</sub>						
La-I <sub>h</sub>	0	37.51 (36.9)	4.88 (4.20)	27.13 (26.80)	0.39	-8.48
LnL(C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> (OH) <sub>2</sub>						
La-I <sub>e</sub>	0	37.18 (36.5)	4.84 (4.20)	26.90 (26.1)	1.91	-11.58
LnL(C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> (OH) <sub>2</sub>						
La-I <sub>g</sub>	0	38.72 (37.1)	5.04 (4.30)	-	1.04	-8.54

points on the line in Fig. 2b may be attributed to the complicated interaction between the ligand and the metal ion.

The general trend observed is that the  $\Delta E$  of the free ligand decreases upon complexation with the Ln ions. This can be attributed to the enrichment of electrons by the metal ion and the partial ionic bond character in such complexes, which leads to an increase in electrical conductivity and a decrease in the energy of activation. A comparison of the  $\Delta E$  values for the free I<sub>i</sub> (*o*-COOH) molecule and its complexes (Table 2) demonstrates that  $\Delta E$  (3.45 eV) decreases upon complexation to 0.95–3.0 eV. This is the opposite of the situation for the *p*-COOH (I<sub>h</sub>) derivative, where  $\Delta E$  is 0.77 eV for the free ligand and 0.56–2.43 eV for its complexes.

This can be explained in that the presence of the COOH group in the *p*-position will facilitate the electron delocalization within the whole molecule and consequently decrease  $\Delta E$ . For the *o*-COOH, the lone pair of electrons will be stabilized by hydrogen bonding, which will favour an increased energy gap and thus  $\Delta E$  [10]. Complexation of *p*-COOH takes place on the N=N and hence the resonating system is captured by the metal ion, which will decrease the energy gap between  $E_v$  and  $E_c$  (i.e.  $\Delta E$ ). On the other hand, for *o*-COOH, the carboxyl group is involved in chelation, resulting in increasing  $\Delta E$ . All other *p*-derivatives will provide more carriers upon complexation and consequently decrease  $\Delta E$  (Table 1).

Thus, at high temperature, the mechanism of conduction involves the promotion of electrons from the ground state (upper most filled orbital) to the lowest  $\pi$  molecular orbital (excited state) all over the molecule.



### Infrared spectra

The IR absorption spectra of the hydrazones were recorded (1) for assignment of the IR bands involved in the hydrazone molecular structure, and (2) for correlation of these band positions and intensities with the corresponding ones in the solid complexes. This may facilitate the elucidation of the molecular structures of the solid complexes under investigation. Table 3 shows the IR bands of the hydrazones; the NH, COOH, C $\equiv$ N, C=C, ... group absorption bands are assigned.

The IR spectra of some 1:1 (M:L) lanthanide hydrazone complexes are shown in Fig. 3. The NH group band is still observed in the spectra of the chelates, but it is shifted to higher frequency. This gives an indication that the NH proton is not removed during chelate formation for some lanthanide complexes, whereas the shift in the N-H frequency ( $\sim 20$   $\text{cm}^{-1}$ ) indicates the involvement of the :NH lone pair of electrons in the coordination. The absence of the NH band from the spectra of some other complexes indicates that the complex formation takes place with the displacement of the NH hydrogen from the NH group by the metal ion.

The spectra of the Ln-I<sub>1</sub> (*o*-COOH) complexes show that the characteristic bands of the COOH group at 1250 and 790  $\text{cm}^{-1}$  have disappeared. Also, the intensity of the C=O stretching band at 1730  $\text{cm}^{-1}$  is decreased. This indicates that the COOH group is involved in the chelation process. However, for the *p*-COOH derivative (I<sub>b</sub>) this group is far from the chelation centre and consequently is not involved in the chelation process. On the other hand, some new bands appear upon chelation, such as the broad bands at 870, 1400, 1550, 1490 and 1595  $\text{cm}^{-1}$ , which can be attributed to C-O bending, and to the symmetric and asymmetric [(COO)-Ln], and COO<sup>-</sup> stretching frequencies, respectively.



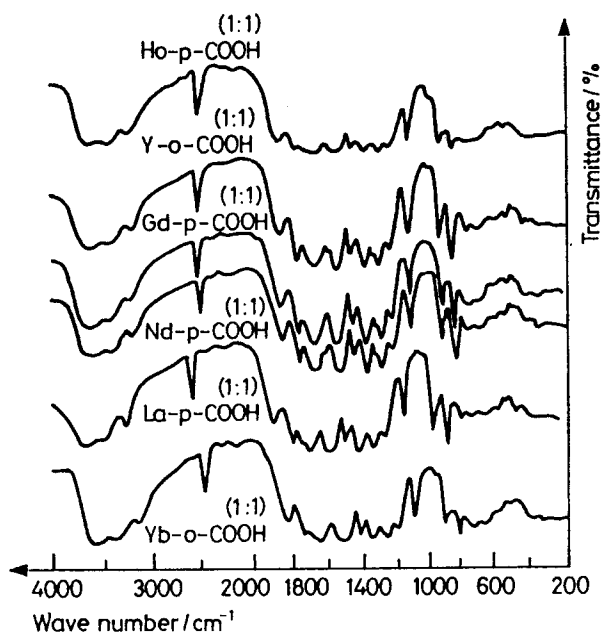


Fig. 3 IR spectra of  $I_b$  and  $I_i$  solid complexes with some Ln(III) metal ions in (1:1) molar ratio

The spectra also show that the  $C\equiv N$  ( $\sim 2200\text{ cm}^{-1}$ ) band is still present for all complexes. On the other hand, the  $N=N$  band is shifted to lower frequencies. This gives an indication that the acetate ( $C=O$ ) and the azo ( $N=N$ ) or hydrazo ( $C=N-N$ ) groups are involved in the chelation process with the central metal ion [15].

Charge balance for the trivalent positive lanthanide metal ions can be achieved by participation of  $OH^-$  from solution in the coordination sphere of the metal ion [16]. The existence of this ion in the complexes could be proved by comparing the results of experimental elemental analysis of the different complexes with those calculated on the basis of different suggested formulae for the molecular structures of the complexes (Table 2). Additional evidence was provided by the absence of bands of the perchlorate ion in the IR spectra. Chloride ion could not be detected by elemental analysis.

The presence of  $OH^-$  to complete the coordination number of the lanthanide metal ion is also indicated by the presence of a broad band at  $3300\text{--}3660\text{ cm}^{-1}$  due to the OH stretching vibration. However, ethanol solvent molecules are assumed to satisfy the metal ion coordination number requirements and also give an O-H stretching vibration in this wavenumber region (Table 3).

The IR spectra of the complexes contain bands at  $500$  and  $510\text{--}700\text{ cm}^{-1}$ , which can be attributed to the  $M-N$  and  $M-O$  stretching frequencies, respectively [17, 18]. This confirms that the coordination is taking place by O and N electron pair addition to the partially filled lanthanide  $f$  orbital. In accord with the above discussion, the proposed formulae III and IV can be assigned to the 1:1 (M:L) Ln-hydrazone complexes.

Table 3 IR band assignment of ( $I_a$ - $I_l$ ) hydrazones in  $\text{cm}^{-1}$ 

$I_a$	$I_b$	$I_c$	$I_d$	$I_e$	$I_f$	$I_g$	$I_h$	$I_i$	$I_j$	$I_k$	$I_l$	Band assignment
$p\text{-H}$	$p\text{-COOH}$	$p\text{-OH}$	$p\text{-NO}_2$	$p\text{-Cl}$	$p\text{-AsO(OH)}_2$	$p\text{-CH}_3$	$p\text{-OCH}_3$	$o\text{-COOH}$	$o\text{-OH}$	$m\text{-NO}_2$	$m\text{-Cl}$	
3220	3200	3290	3210	3190	3200	3220	3220	3220	3300	3320	3220	N-H stretching
3060	-	3080	-	-	-	-	3080	3080	-	3100	3090	aromatic C=H str.
3000	3000	2990	-	3000	3000	2990	3000	2995	3000	3000	3000	aliphatic C=H str.
2220	2200	2200	2210	2210	2210	2210	2210	2210	2220	2210	2210	C $\equiv$ N str.
1740	1670	1710	1690	1740	1710	1690	1730	1740	1690	1735	1700	C=O str.
1600	1610	1605	1600	1610	1600	1605	1610	1610	1600	1690	1600	aromatic C=C str.
1550	1520	1520	1530	1530	1530	1540	1540	1545	1530	1530	1540	aromatic C=C str.
1480	1450	1460	1490	1450	1480	1485	1480	1490	1465	1470	1460	aromatic C=C str.
1545	1590	1545	1550	1520	-	-	1510	-	-	-	1500	C=N str.
1450	1420	1430	1400	1420	1410	1405	1400	1425	1420	1420	1400	N=N str.
1370	1375	1375	1340	1370	1370	1370	1330	1320	1350	1350	1330	sym. CH <sub>3</sub> bending
1250	1250	1270	1250	1235	1240	1280	1250	1260	1230	1250	1260	asym. C-N str.
1180	1170	1150	1180	1170	1150	1140	1130	1170	1185	1180	1160	sym. C-N str.
1130	1120	1110	1130	1120	1110	1110	1110	1120	1150	1140	1120	arom. C-H-plane bending
850	860	840	850	850	830	840	830	860	860	880	870	arom. C-H out of plane bending

### Nuclear magnetic resonance spectra

Additional support for the results obtained from the IR spectra and electrical conductivity measurements is provided by considering the changes in the NMR spectra of some complexes in comparison with their ligands. Only the diamagnetic lanthanum complexes were investigated.

The NMR spectra were measured in chloroform. The ligand spectra exhibit a triplet band at  $\delta = 1-1.5$  ppm, which can be assigned to the  $\text{CH}_3$  of the ethyl group. The aromatic protons of the phenyl group display a multiple signal at  $\delta = 7.3-8.0$  ppm. The integration curves reveal four protons for all substituted derivatives and five protons for the unsubstituted one. The multiple band at 4.2–4.6 ppm is attributed to the  $\text{CH}_2$  protons of the ethyl group.

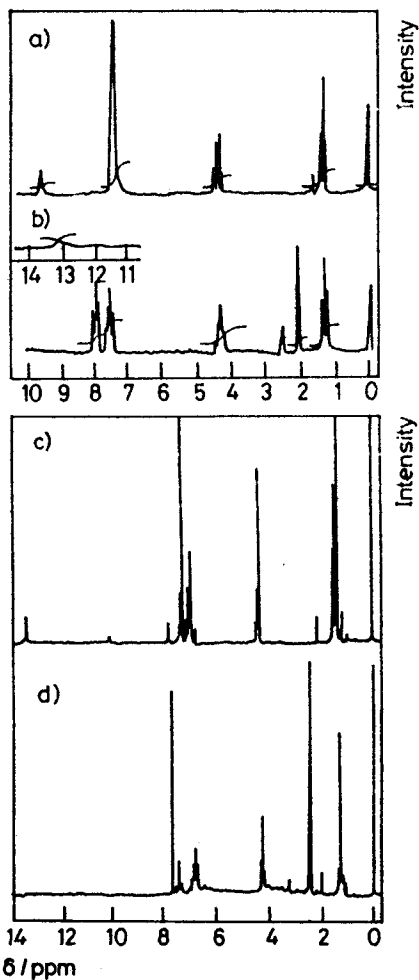
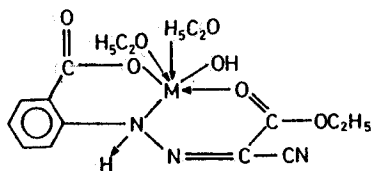
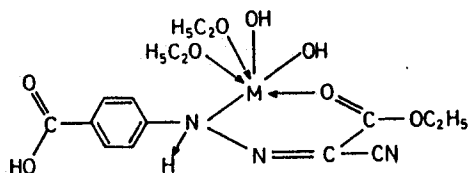


Fig. 4 Proton NMR spectra of unsubstituted  $\text{I}_2$  a),  $\text{I}_1$  b),  $\text{I}_0$  c) and  $\text{La(III)-I}_1$  complexes d)

The NH proton shows a signal at 9.5 ppm for the unsubstituted derivative (I<sub>a</sub>) (Fig. 4a). The COOH proton exhibits a single band at  $\delta=13.2-13.6$  ppm, whereas the NH proton disappears for the *p*-COOH compound, which may be explained in that the resonance effect will favour the presence of the azo tautomer (Fig. 4b) and formulae I and II. In the case of *o*-COOH, the NH proton signal is shifted to  $\delta=10$  ppm because of the intermolecular hydrogen bonding (Fig. 4c). Upon complexation (La-I<sub>1</sub>, Fig. 4d), the NH and COOH protons disappear, indicating that these protons are involved in the chelation process and consequently supporting the structural formulae proposed for the complexes given below (III and IV).

(III, *o*-substituted)(IV, *m, p*-substituted)

## Conclusions

The hydrazones and their lanthanide complexes under investigation exhibit semi-conducting behaviour. This behaviour can be correlated with the structures expected for the free ligands and their complexes. Further evidence is provided by IR and NMR measurements.

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