

Physico-chemical studies of some aminobenzoic acid hydrazide complexes

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Abstract: The stability constants and related thermodynamic functions characterizing the formation of divalent Ni, Cu, Zn, Cd and Hg complexes with *o*- and *p*-aminobenzoic acid hydrazide were determined potentiometrically at different temperatures. The formations of the complexes are endothermic processes. The formed bonds are mainly electrostatic. Conductometric titration was carried out to determine the stoichiometry and stability of the formed complexes. The structures of complexes were characterized by their IR, ¹H-NMR and ¹³C-NMR spectra, as well as X-ray diffractograms. The coordination process takes place through the carbonyl group and the terminal hydrazinic amino group. The thermal stability of the complexes was followed in the temperature range 20–600 °C.

Keywords: potentiometry, conductometry, stability constants, thermodynamic parameters, structure and thermal stability of complexes.

INTRODUCTION

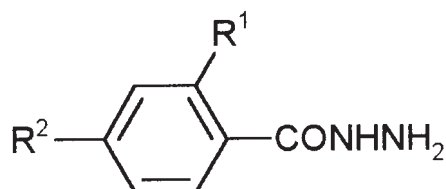
As a result of their antimicrobial, antifungal and antibacterial properties,^{1–3} acid hydrazides are of great biological importance. The formation of metal complexes plays an important role in the growth of their biological activity.^{4–8} Hydrazides successfully provide various active potential donor sites, namely C=O, N-H and NH₂. Therefore, many metal complexes of benzoic acid hydrazides have been synthesized and characterized on the basis of spectral, magnetic and electrical measurements.^{9–12} The coordination process takes place through the carbonyl oxygen and the amino nitrogen atoms. 1:1 and 1:2 M:L molar ratios can be formed.

The present work considers the preparation and characterization of the complexes of *ortho*- and *para*-aminobenzoic acid hydrazides (ABAH) with Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) using potentiometric, conductometric, spectral (IR, ¹H-NMR and ¹³C-NMR), X-ray diffraction and thermal measurements.

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EXPERIMENTAL

All chemicals used were of the purest laboratory grade provided by Aldrich. The ligand solutions were freshly prepared in 80 % (v/v) aqueous-ethanolic medium. The hydrazides provided have the following structures:



(where $\text{R}^1 = \text{NH}_2$ and $\text{R}^2 = \text{H}$ or $\text{R}^1 = \text{H}$ and $\text{R}^2 = \text{NH}_2$)

The potentiometric measurements were carried out using a digital Microprocessor pH meter, HI 9321 fitted with a combined glass/calomel electrode. To determine the dissociation ($\log K_{\text{H}}$) and stability constants ($\log K_1$ and $\log K_2$) of ABAH and their complexes, the following series of solution (total volume 25.0 ml in each case) were titrated against 0.01 M KOH at 298, 308, 318 and 328 K; i) 2.5 ml HCl (0.01M), ii) 2.5 ml HCl + 2.5 ml hydrazide (0.01 M) and iii) 2.5 ml HCl + 2.5 ml hydrazide + 0.5 ml metal ion (0.01M). An appropriate quantity of KCl was added to maintain the ionic strength of all the solutions at 0.1 M. The different stability constants were calculated according to the Irving and Rossotti's method.^{13,14} A 54 X IBM computer using the Excel program was employed.

The conductometric titration measurements were carried out using a digital conductometer, Consort K 120. All measurements were done in aqueous solution adjusted thermostatically to 298 K with constant stirring. The conductance value were measured during the titration of 0.001 M metal ion solution (30.0 ml) against a 0.01 M hydrazide solution. The conductance values were recorded after each addition and then corrected to avoid the effect of dilution during the titration by multiplying the measured values by $(v^0 + v_1)/v^0$, where v^0 is the original volume of the titrand (metal ion solution) and v_1 is the volume of titrant (ligand solution).

The solid metal complexes were prepared by mixing a hot ethanolic solution 80 % (v/v) of the ligand (0.02 M) with that containing the required amount of the appropriate metal chloride (0.01 M). The reaction mixture was continuously refluxed on a water bath for 5.0 – 8.0 hours. In each case, a fine solid product was obtained on cooling which was washed with the solvent and dried over anhydrous CaCl_2 . Brownish black powder of the copper complex, deep green crystals of the nickel complex, white powder of the zinc complex, faint brown crystals of the cadmium complex and fine white crystals of the mercury complex were prepared. All complexes melted above 573K and were insoluble in common organic solvents.

The infrared spectra of the studied free hydrazides and their complexed molecules were recorded on a computerized Genesis- II-F- I spectrometer in the range $4000 - 400 \text{ cm}^{-1}$. The KBr disc technique was employed. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured after dissolution in deuteriated DMSO using a JEOL EX 400 spectrometer at 400 and 100 MHz, respectively (Chemistry Department, Torino University, Italy).

X-Ray powder patterns were obtained using a Philips X-ray diffractometer Pw 1390 fitted with an ionization detector. $\text{CuK}\alpha$ radiation was used at 40 kV and 20 mA.

A Shimadzu DTA-TGA, 50 H, thermal analyzer was used to collect thermogravimetric data in the range $20-600 \text{ }^\circ\text{C}$, at a uniform heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Nitrogen was used as a dynamic atmosphere (flow rate $30 \text{ cm}^3 \text{ min}^{-1}$).

RESULTS AND DISCUSSION

In order to clarify the stability and behaviour of the complexing process of both *ortho*- and *para*- aminobenzoic acid hydrazide (ABAH) with divalent metal

ions Ni, Cu, Zn, Cd and Hg, the method of Bjerrum-Calvin, modified by Irving and Rossotti, was used at different temperatures.^{13,14} The titration curves were separate from each other each taking on an almost S-shape. The end point for the titration of the three mixtures increased in the order: i > ii > iii. Also, the maximum value of n (the average number of ligand molecules attached to a metal ion) did not exceed two for all complexes, suggesting the formation of M:L and M:2L complexes. The calculated data are presented in Table I. It is apparent that the values of the stability constants of *ortho*-aminobenzoic acid hydrazide are greater than those of the *para*-derivative. This may be attributed to the fact that the electron-donation ability of the amino group in the *ortho*-position is greater than that in the *para*-position. On other hand, the dissociation and stability constant values increase with increasing temperature, meaning that the complexation is an endothermic process. The order of the overall stability constants are: Cu(II) > Cd(II) > Zn(II) > Ni(II) > Hg(II), which is in good agreement with the order found by Irving and Williams.

TABLE I. Protonation constants of *o*- and *p*-ABAH and their stability constants with different metal ions at different temperatures and 0.1 M ionic strength.

Compound		Temperature			
		298 K	308 K	318 K	328 K
<i>o</i> -ABAH	$\log K_H$	10.01	10.15	10.20	10.30
1-Ni-Complex	$\log K_1$	6.85	7.05	7.30	7.49
	$\log K_2$	3.48	3.80	4.07	4.35
2-Cu-Complex	$\log K_1$	7.80	8.23	8.65	8.97
	$\log K_2$	5.67	6.00	6.20	6.44
3-Zn-Complex	$\log K_1$	6.35	6.67	7.05	7.38
	$\log K_2$	4.00	4.21	4.50	4.72
4-Cd-Complex	$\log K_1$	6.65	6.83	7.10	7.31
	$\log K_2$	4.30	4.50	4.85	5.08
5-Hg-Complex	$\log K_1$	5.43	5.62	5.95	6.15
	$\log K_2$	3.46	3.80	4.20	4.50
<i>p</i> -ABAH	$\log K_H$	10.08	10.15	10.26	10.32
1-Ni-Complex	$\log K_1$	6.40	6.69	7.00	7.24
	$\log K_2$	3.38	3.75	4.07	4.40
2-Cu-complex	$\log K_1$	7.83	8.05	8.40	8.65
	$\log K_2$	5.18	5.70	6.00	6.45
3-Zn-Complex	$\log K_1$	6.21	6.57	6.85	7.15
	$\log K_2$	3.85	4.05	4.38	4.57
4-Cd-Complex	$\log K_1$	6.40	6.71	7.00	7.26
	$\log K_2$	4.21	4.42	4.65	4.79
5-Hg-Complex	$\log K_1$	5.21	5.40	5.65	5.84
	$\log K_2$	3.30	3.73	4.02	4.35

The thermodynamic functions of the studied complexes were evaluated using the relations:

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

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

TABLE II. Thermodynamic parameters of *o*- and *p*-ABAH complexes with different metal ions at 298 K.

Compound	$-\Delta G^\circ$	ΔH°	ΔS°	$\Delta G^\circ_{\text{non}}$	$-\Delta G^\circ_{\text{ele.}}$	$\Delta H^\circ_{\text{non}}$	$\Delta H^\circ_{\text{ele.}}$	$\Delta S^\circ_{\text{ele.}}$
<i>o</i> -ABAH								
1. Ni-complex	39.10	54.67	314.62	34.66	73.76	24.70	29.97	348.02
	19.88	51.36	239.06	44.96	64.80	25.03	26.33	305.75
2. Cu-Complex	44.54	74.01	397.80	46.84	91.38	36.88	30.98	431.20
	32.36	46.13	263.47	37.63	69.99	17.71	24.95	330.28
3. Zn-Complex	36.25	60.95	326.17	39.93	76.19	30.01	30.97	359.58
	22.86	43.53	222.74	38.51	61.37	18.63	24.95	289.55
4. Cd-Complex	37.97	39.18	258.82	23.99	61.91	14.02	25.16	292.22
	24.53	47.89	243.08	41.11	65.68	21.22	26.66	309.89
5. Hg-Complex	30.47	53.12	280.55	36.04	66.52	26.08	27.04	313.95
	19.76	64.42	282.51	54.29	74.01	34.37	30.10	349.32
<i>p</i> -ABAH								
1. Ni-Complex	36.54	52.24	297.88	33.66	70.20	23.73	28.51	331.28
	19.30	60.07	266.31	51.32	70.58	31.40	28.67	333.12
2. Cu-Complex	44.71	49.65	316.55	29.47	74.18	19.51	30.14	349.95
	29.55	71.41	338.81	56.39	85.94	36.46	34.91	405.62
3. Zn-Complex	35.46	55.72	305.95	36.46	71.92	26.50	29.22	339.36
	21.98	46.13	228.60	40.60	62.58	20.72	25.45	295.41
4. Cd-Complex	36.54	52.24	297.88	33.66	70.20	23.73	28.51	331.28
	24.03	40.23	215.62	35.83	59.86	15.91	24.32	282.43
5. Hg-Complex	29.76	42.15	241.20	28.46	58.19	18.50	23.65	274.64
	18.84	62.71	273.60	53.29	72.12	33.40	29.30	341.62

ΔG° and ΔH° values in kJ mol^{-1} and ΔS° value in $\text{J mol}^{-1} \text{K}^{-1}$

The computed results were collected in Table II. The negative values of ΔG° show the high ability of the studied hydrazides to form stable metal complexes and the process tends to proceed spontaneously. However, the obtained positive values of ΔH° means that the complexation process is endothermic and that enthalpy is not the driving force for the formation of the complexes. On other hand, the positive values of ΔS° indicate that entropy is responsible for the complexing process. An analysis of the thermodynamic data into electrostatic (ionic) and non-electrostatic (covalent) components can give a good indication as to the nature of the formed bonds.¹⁵ The evaluated data are reported in Table II. The large negative values of $\Delta G^\circ_{\text{el}}$ compared to the positive values of $\Delta G^\circ_{\text{non}}$ means that the formed bonds are mainly electro-

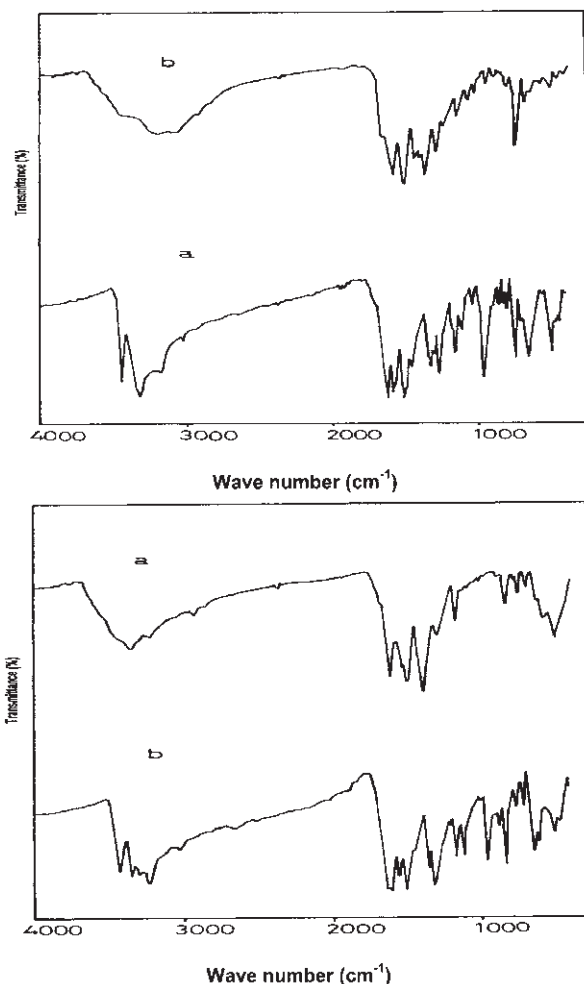


Fig. 1. A: Infrared spectra of *o*-ABA (a) and its copper complexes (b); B: Infrared spectra of *p*-ABA (a) and its copper complexes (b).

static. This is supported by the comparison of $\Delta H^\circ_{\text{non}}$ and $\Delta H^\circ_{\text{el}}$. Finally, it is confirmed by the large positive values of $\Delta S^\circ_{\text{el}}$. This is in a good agreement with the fact that if a ligand is charged and multidentate the formation of complexes is mainly entropically favored.¹⁶ Bond formation between the metal ion and the ligand donors is possible only after the rupture of their bonds with water molecules and so it is not surprising that a positive enthalpy change was observed.

The stoichiometry of the complexes existing in solution was estimated using the conductometric titration technique.¹² The general trend of the conductograms is a steady decrease of the conductance values of the solution after each addition of the ligand. The resulting conductograms are composed of straight lines intersecting at the probable ratio of the formed complexes. Two significant intersections are observed, indicating the formation of 1:1 and 1:2 (metal : ligand) species as was suggested by the results of the potentiometric measurements.

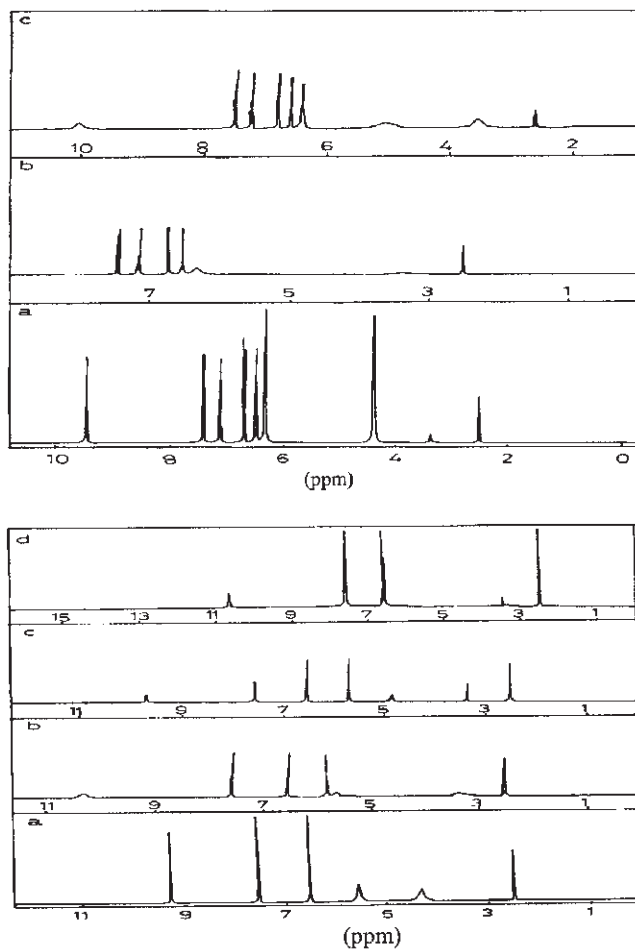


Fig. 2. A: $^1\text{H-NMR}$ spectra for *o*-ABAH (a) and its zinc (b) and cadmium complexes (c) in $[\text{d}_6\text{DMSO}]$. B: $^1\text{H-NMR}$ spectra for *p*-ABAH (a) and its zinc (b), cadmium (c) and mercury (d) complexes in $[\text{d}_6\text{DMSO}]$.

This technique was also used to elucidate the stability constants of the complexes with the help of the relation¹⁸:

$$K_x = \frac{1}{[\text{L}]^x} \frac{\Lambda_{\text{exp.}} - \Lambda_{\text{M}^{+n}}}{\Lambda_{\text{M}^{+n}\text{L}_x} - \Lambda_{\text{exp.}}}$$

where $\Lambda_{\text{exp.}}$, $\Lambda_{\text{M}^{+n}}$, $\Lambda_{\text{M}^{+n}\text{L}_x}$ are the conductance values of the solution, uncomplexed and complexed metal ion, respectively. $[\text{L}]$ is the concentration of the hydrazide and x is its coordination number. The calculated values at 298 K confirmed the values obtained potentiometrically.

Different spectral techniques were used to identify the potential active sites of the studied hydrazides, see Figs. 1–3. The characteristic IR absorption bands assigned to the stretching vibration of NH_2 were found at $3443\text{--}3428\text{ cm}^{-1}$, while the

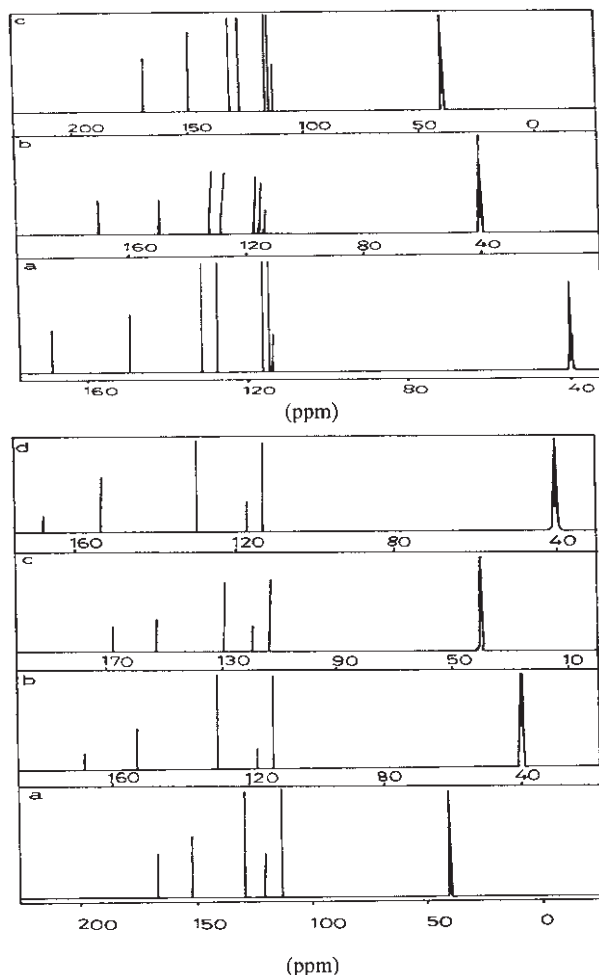


Fig. 3. A: ¹³C-NMR spectra for *o*-ABAH (a) and its zinc (b) and cadmium (c) complexes in [d₆DMSO]. B: ¹³C-NMR spectra for *p*-ABAH (a) and its zinc (b), cadmium (c) and mercury (d) complexes in [d₆DMSO].

band of the hydrazinic amino group was observed at 3180.5 cm⁻¹. As expected, ν NH was found at 3325–3347 cm⁻¹ and ν (C=O) at 1620 cm⁻¹. The observed ¹H-NMR signals were one signal at δ = 4.4 ppm due to the NH₂ of the hydrazinic group and another signal at δ = 6.3 ppm from the NH₂ group attached to the benzene ring. Four signals were found at δ = 6.48, 6.70 and 7.1 ppm attributed to the four protons attached to the benzene ring and one signal of NH at δ = 9.46 ppm.

On complexation of the hydrazide derivatives, the characteristic band of the hydrazinic amino group was shifted to higher frequencies (3204–3300 cm⁻¹) with a broadening and shifting of its ¹H-NMR signal to δ = 9.46 ppm. On the other hand, the band of the carbonyl group completely disappeared and a cyano group (enol-form) was formed (ν = 1587–1600 cm⁻¹ and δ = 170 ppm signals for IR and ¹³C-NMR, respectively). The remaining characteristic bands and signals of free hydrazides were not affected by the complexing process suggesting that the ligands were bonded to the metal

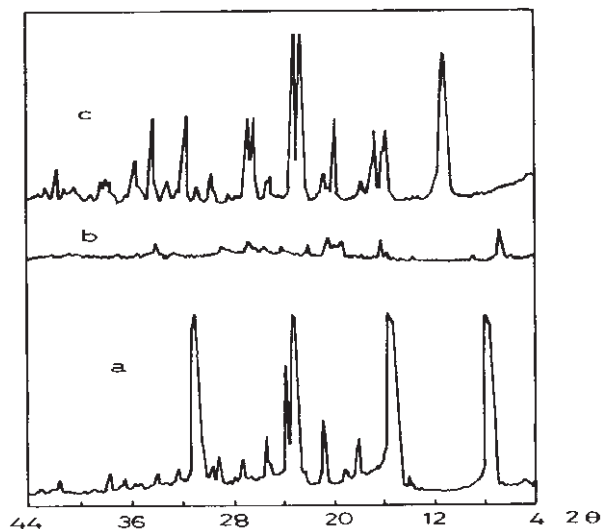


Fig. 4. XRD patterns of *o*-ABAH (a) and its copper (b) and cadmium (c) complexes.

ions *via* the hydrazinic amino group and the oxygen atom of the carbonyl group. This is in a good agreement with the belief that ligands containing different donor atoms of the O–N type form more stable complexes than either O–O or N–N type.¹⁹

To obtain further evidence about the structure of the complexes X-ray diffraction was performed. Representative diffractograms of *o*-ABAH and its complexes with copper and cadmium are shown in Fig. 4. It can be easily seen that the pattern of the free hydrazide differs from those of its complexes, which may be attributed to the formation of a not-well-defined distorted crystalline structure. Probably, this behaviour is due to the incorporation of water molecules into the coordination sphere. The four strongest lines are summarized in Table III. The first and second lines may be ascribed to the interaction of crystalline and coordinated water molecules with the investigated hydrazide, respectively. The change in intensity and the shift in d-spacing observed in the third and fourth lines may be attributed to the formation of M–N and M–O bonds.²⁰

TABLE III. The X-ray data of *o*-ABAH and its copper and zinc complex.

Observation	Ligand		Copper complex		Cadmium complex	
	<i>d</i> /Å	<i>I</i> / <i>I</i> ⁰	<i>d</i> /Å	<i>I</i> / <i>I</i> ⁰	<i>d</i> /Å	<i>I</i> / <i>I</i> ⁰
1st strong line	11.620	0.98	12.98	1.00	7.890	0.85
	5.824	1.00	5.467	0.70	5.401	0.37
2nd strong line	4.267	0.37	4.329	0.65	4.548	0.47
					3.966	1.00
3rd strong line	3.831	0.97	3.349	0.35	3.451	0.50
4th strong line	2.892	0.95	2.635	0.35	2.864	0.52
					2.665	0.50

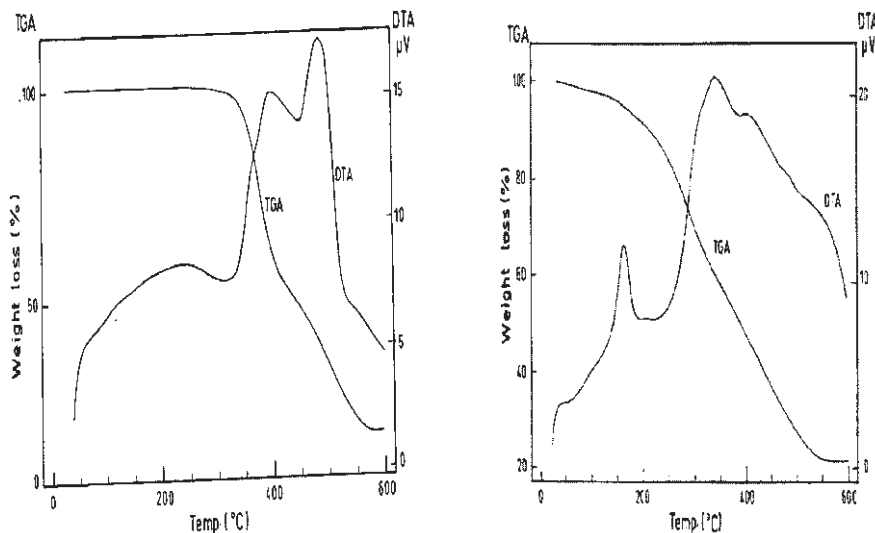


Fig. 5. A: Thermal analysis of Ni-*o*-ABAH complex. B: Thermal analysis of Cu-*o*-ABAH complex.

Thermal analysis plays an important role in studying the properties of metal complexes.²¹ The thermal studies of the nickel and copper complexes with *o*-ABAH as representative examples are illustrated in Fig. 5. It is quite clear that the decomposition of the nickel complex takes place in three steps while that of the copper complex occurs in four steps. The first and second stages at 90.5 °C and 160–200 °C indicate the complete removal of crystalline and coordinated water molecules with a decrease in weight of 23.7 %. The third stage at 341–390 °C shows a loss in weight of 29 % due to the elimination of only one ligand molecule. Finally, the fourth stage at 410–480 °C represents complete oxidation of the remaining organic molecule with the formation of a stable metal oxide as the final product, the weight-loss is 26 %. The thermal decomposition process was followed by employing the relation:

$$Y = (w_t - w_\infty) / (w_0 - w_\infty)$$

where w_0 is the initial weight of the sample, w_t is the weight at temperature, t , and w_∞ is the weight at the end of the thermal decomposition.²² Assuming that the thermal decomposition of the complexes is kinetically a first order reaction, then a plot of $1/Y$ against $1000/T$ should yield a straight line, and the activation energy of the process should be R times the slope of the obtained line. The calculated values of the activation energy are 29.9 and 24.7 kJ mol^{-1} for the nickel and copper complex, respectively.

ИЗВОД

ФИЗИЧКОХЕМИЈСКА ПРОУЧАВАЊА НЕКИХ КОМПЛЕКСА ХИДРАЗИДА
АМИНОБЕНЗОЕВЕ КИСЕЛИНЕ

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Потенциометријски на разним температурама одређене су константе стабилности и одговарајуће термодинамичке функције стварања комплекса двовалентних Ni, Cu, Zn, Cd и Hg, јона са хидразидима *o*- и *p*- аминобензоеве киселине. Стварања ових комплекса су ендотермски процеси. Остварене везе су углавном електростатичке. Кондуктометријском титрацијом одређивана је стехиометрија и стабилност створених комплекса. Структура ових комплекса изведена је на основу IR, ¹H-NMR и ¹³C-NMR спектара и рендгенске дифракције. Процес координације остварује се преко карбонилне групе и терминалне хидразинске амино групе. Термичка стабилност праћена је у температурном опсегу 20 – 600 °C.

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REFERENCES

1. J. Miyazawa, T. Kawabata, N. Ogasawara, *Physiol. Mol. Plant Pathol.* **52** (1998) 115
2. I. Imam, A. Mandour, F. Abd El-Azeem, *Orient. J. Chem.* **8** (1992) 160
3. A. E. Sengupta, A. Bhatnagar, S. K. Khan, *J. Indian Chem. Soc.* **64** (1987) 616
4. B. Singh, R. Srivastava, K. K. Narang, *Synth. React. Inorg. Met.-Org. Chem.* **30** (2000) 1175
5. J. Cymerman-Craig, D. Willis, S. P. Rubbo, S. Edgar, *Nature* **176** (1995) 34
6. R. Malhorta, S. Kumar, K. S. Dhidsa, *Indian J. Chem.* **32A** (1993) 5457
7. K. K. Narang, V. P. Singh, *Synth. React. Inorg. Met.-Org. Chem.* **23** (1993) 971
8. Z. Muhi-Eldeen, K. Al-Obidi, M. Nadir, F. Rochev, *Eur. J. Med. Chem.* **27** (1992) 101
9. J. Martinez, A. Martinez, M. L. Cuenca, A. D. Lopez, *Synth. React. Inorg. Met.-Org. Chem.* **18** (1988) 881
10. M. G. Ebd El Wahed, A. M. Hassan, H. A. Hammad, M. M. El Desoky, *Bull. Korean. Chem. Soc.* **13** (1992) 113
11. R. I. Machkhoshvili, G. V. Tsintsadze, S. A. Lobzhanidez, P. R. Machkhvili, *Zh. Neorg. Khim.* **41** (1996) 1854
12. A. M. Gad, A. El Dissouky, E. M. Mansour, A. El Maghraby, *Polym. Degrad. Stab.* **68** (2000) 153
13. H. Irving, H. S. Rossotti, *J. Chem. Soc.* 2904 (1954)
14. M. G. Abd El Wahed, S. Metwally, K. El Manakhly, H. Hammad, *Cand. J. Anal. Sci. Spectrosc.* **43** (1998) 37
15. S. Murakami, T. Yoshino, *J. Inorg. Nucl. Chem.* **43** (1981) 2065
16. A. E. Martell, *Coordination Chemistry*, Vol. 1, Van Nostrand, New York, 1971, pp. 466
17. M. G. Abd El Wahed, H. M. Katter, *Egypt. J. Anal. Chem.*, accepted for publication (2003)
18. M. G. Abd El Wahed, *J. Serb. Chem. Soc.* **68** (2003) 463
19. K. Sone, Y. Fukuda, *Inorganic Thermochromism, Inorganic Chemistry Concept*, Vol. 10, Springer Verlag, Heidelberg, 1987
20. M. G. Abd El Wahed, A. Brakat, *Afinidad* **50** (1993) 93
21. M. G. Abd El Wahed, E. M. Nour, S. Teleb, S. Fahim, *J. Therm. Anal. Cal.*, accepted for publication (2003)
22. P. G. Mundhe, P. B. Deogonkar, R. A. Bhobe, *J. Indian Chem. Soc.* **75** (1998) 349.