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THERMAL DEAMINATION-ANATION IN COBALT(III) THIOCYANATE COMPLEXES

Novel decarbonylation of the equatorial amide ligand

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Abstract

The solid state thermal behavior of *trans*-[Co(bpb)(amine)₂]NCS·H₂O complexes where (bpb)=[N,N'-bis(2-pyridinecarboxamido-N)-1,2-benzene], and amine=pyrrolidine (*prldn*) (1), and benzylamine (*bzlan*) (2), and *trans*-[Co(bpb)(piperidine)₂]ClO₄·H₂O (3) (mixed with KSCN), has been studied using thermoanalytical techniques, infrared spectroscopy, and pyrolysis coupled to both infrared and mass spectrometry, PY/FTIR and PY/MS. The deamination-anation reaction is clearly observed for all three complexes. The estimated values of E_a for the deamination-anation are: $E_a(1)=246.8 \text{ kJ mol}^{-1}$, $E_a(2)=255.7 \text{ kJ mol}^{-1}$, $E_a(3)=234.7 \text{ kJ mol}^{-1}$. The trend in E_a values is rationalized based on the ligand field strength of the amines and the structural effects. A novel decarbonylation of the amide CO group from the equatorial ligand is observed after the release of one amine molecule. This process has been monitored for complex (1) by FTIR in the carbonyl region and by mass spectrometry for the detection of CO₂ at 280°C. The activation energy of this process is estimated for complex (1) ($662.5 \text{ kJ mol}^{-1}$). The reaction scheme for the observed reactions is proposed.

Keywords: amide decarbonylation, cobalt(III) complexes, deamination-anation, kinetics, NCS counterion

Introduction

Thiocyanate has a special place among small anionic ligands. Its role in thermal deamination-anation reactions of many transition metal complexes in solid state has been studied [1–5] and the kinetics of these reactions has been reviewed [6]. We have recently

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synthesized a series of *trans*-[Co(acacen)(amine)₂]NCS complexes (*acacen*=N,N'-ethylenebis(acetylacetonate) dianion) [7], and studied the kinetics of their deamination-anation reactions by thermogravimetric techniques and IR spectroscopy [8].

The electronic and structural effects of different equatorial ligands on the kinetics of deamination-anation reactions are quite interesting [9]. As an extension of our earlier studies on Schiff-base cobalt(III) complexes [7, 10], we have synthesized and determined the structure of *trans*-[Co(bpb)(amine)₂]X·H₂O complexes (1), (2) and (3) [11]. The electronic and structural properties of these complexes are different from those of the acacen analogues, therefore influencing the thermal properties of these complexes. Here we report the results of our thermoanalytical studies of these complexes in dynamic air atmosphere. The thermal behavior under nitrogen is limited to the deamination-anation followed by the overlapping decomposition of all organic fragments. The kinetic parameters of deamination-anation of (1), (2) and (3) (mixed homogeneously with KNCS) and the decarbonylation of the amide ligand for (1) in air are estimated. The effect of the intermolecular hydrogen bonding (Fig. 1) on the decarbonylation of the equatorial ligand is also discussed.

Experimental

The cobalt complexes were prepared as reported elsewhere [11]. Infrared spectra were recorded as KBr pellets with a Perkin Elmer Paragon 1000 FTIR instrument. TG and DSC were performed using Mettler TA 4000 and Rheometric Scientific STA 1000 thermal analyzers. TG experiments were carried out in a dynamic atmosphere (20 mL min⁻¹) of air or nitrogen with a heating rate of 1–10°C min⁻¹. TG and DSC curves were recorded by heating the samples ca 2.5–10 mg of the complex up to about 550°C. Indium was used as reference to calibrate the temperature and heat flow. PY/MS experiment was performed using a Pyroprobe 2000 (CDS Instruments)

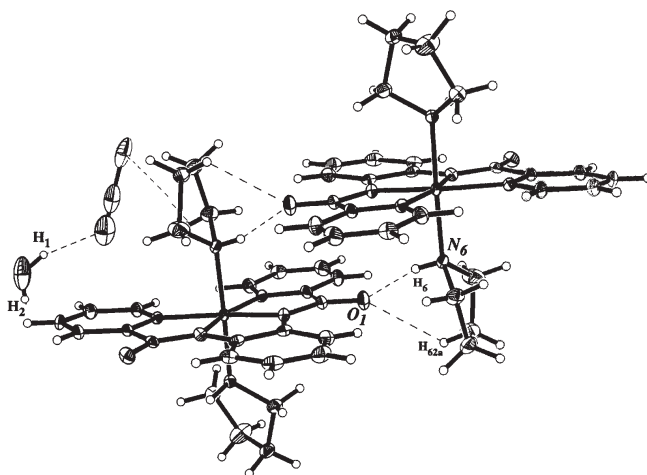


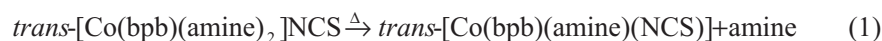
Fig. 1 X-ray crystal structure of *trans*-[Co(bpb)(prldn)₂]NCS·H₂O complex, showing NH···O=C intermolecular hydrogen bonding

pyrolizer coupled to a quadrupole mass filter (Thermolab, TA Instruments) via a heated silica capillary interface. PY/FTIR experiments used the Pyroprobe 2000 pyrolizer coupled to a home-made infrared gas cell of 65 mm pathlength equipped with KBr windows.

Results and discussion

Thermal behavior of complex (1)

The thermoanalytical data for complex (1) are given in Table 1. The combined TG, DTG, and DSC curves of (1) in dynamic air atmosphere, with heating rate of $5^{\circ}\text{C min}^{-1}$, are shown in Fig. 2. Four well defined steps can clearly be observed, in the TG and DTG curves. The first between $30\text{--}110^{\circ}\text{C}$ is associated with the endothermic loss of water accompanied by 2.96% mass loss ($\text{H}_2\text{O}=3.03\%$). This step is common to all three complexes and is similar to the dehydration of many other complexes with water of crystallization [5]. The second step between 120 and 220°C belongs to the endothermic deamination-anation reaction represented by Eq. (1).



The mass loss in this step is 11.86% (pyrrolidine=11.97%) and during this endothermic process, one of the axial pyrrolidine ligands is replaced by NCS.

The substitution of the amine by NCS in this step is accompanied by characteristic changes in the intensity of the N–H stretching band at 3165 cm^{-1} and a considerable shift in the position of the thiocyanate stretching band in the IR spectra from 2048 for the thiocyanate counterion to 2114 cm^{-1} for the coordinated NCS, Fig. 3. As the deamination–anation reaction proceeds, the intensity of the peak at 2114 increases on the expense of the decrease in the intensity of the peak at 2048 cm^{-1} . This new band is assigned to a coordinated NCS group [12] and clearly indicates that the

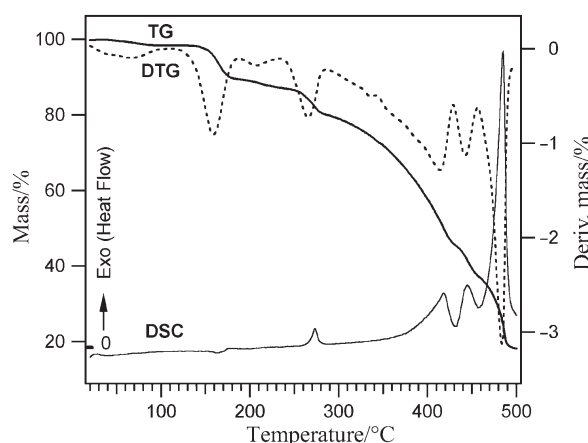


Fig. 2 TG, DTG, and DSC curves of (1) in a dynamic air atmosphere (20 mL min^{-1})

NCS ligand is coordinated to the metal center in the deamination-anation reaction. The IR spectrum of complex (1) after prolonged heating at 150°C is similar to that of *trans*-[Co(bpb)(prldn)(NCS)] complex produced by direct synthesis [11].

Table 1 Thermoanalytical data for the thermal behavior of complexes (1)–(3) in dynamic air atmosphere at 5°C min⁻¹ heating rate^a

Temperature range/°C	DTG $T_{\max}/^{\circ}\text{C}$	DSC	$\Delta m/\%$		Remarks: release of
			exp.	theor.	
[R(prldn) ₂]NCS·H ₂ O (1)					
30–110	90	endo	2.96	3.03	1 mol H ₂ O
120–220	170	endo	11.86	11.97	1 mol C ₄ H ₈ NH
240–290	270	exo	4.32	4.70	1 mol CO
290–420	410	exo	44.40	43.14	1 mol C ₄ H ₈ NH+1 mol CO+2 mol py
430–500	–	exo	–	–	decomp.
[R(bzlan) ₂]NCS·H ₂ O (2)					
30–120	80	endo	2.75	2.70	1 mol H ₂ O
180–260	205	endo	16.01	16.10	1 mol C ₆ H ₅ CH ₂ NH ₂
260–400	320	exo	44.70	48.30	2 mol CO+1 mol C ₆ H ₅ CH ₂ NH ₂
	340	endo			+2 mol py
440–550	–	exo	–	–	decomp.
[R(pprdn) ₂]ClO ₄ ·H ₂ O (3)+ KSCN					
30–110	–	endo	2.50	2.37	dehydration
110–200	150	exo	11.60	11.33	1 mol C ₅ H ₁₀ NH+oxidation
230–320	300	exo	4.00	3.68	1 mol CO
420–530	–	exo	–	–	decomp.

^aR=Co^{III}(bpb)

An interesting observation in the thermal behavior of (1) is the loss of one of the amide C=O groups from the equatorial ligand between 240–290°C. This exothermic reaction takes place in the third step when the intermolecular N–H···O=C hydrogen bonding breaks apart in the deamination process and one of the two amide C=O groups per complex molecule is no longer engaged in hydrogen bonding. It is evident from the DSC curve (Fig. 2) that, no detectable structural transformation associated with further N–H···O=C hydrogen bond rupture occurs prior to decarbonylation. The endothermic dissociation of such relatively strong H-bonds (H···O=2.319 Å) will probably show endothermic peaks in the DSC curve. The mass loss in this step is 4.32% (CO=4.70%) and during this exothermic process only one CO group, free from hydrogen bonding, is oxidized to CO₂ according to Scheme 1. The conversion of CO to CO₂, is confirmed by monitoring the evolution of CO₂ in this temperature range using temperature programmed mass spectrometry, and the decrease in the relative intensity of C=O stretching

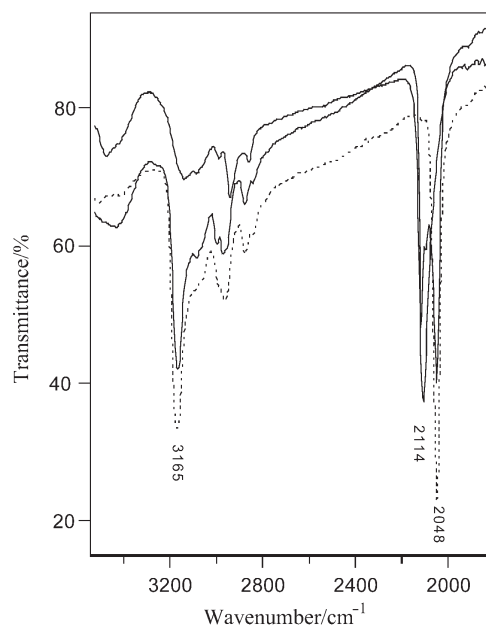


Fig. 3 Infrared spectra of (1) before heating ---, after 3 h —, and after prolonged —, heating at 150°C

band at 1623 cm^{-1} by PY/FTIR technique. The second CO group of the equatorial ligand, which remains engaged in hydrogen bonding with the second axial amine, is oxidized after the release of the second amine ligand, overlapping with the loss of the two pyridine residues. The total observed mass loss for these overlapping steps are 44.4 as compared to the calculated values of 43.14% for (pyrrolidine+CO+2py). The release of the rest of the ligands is accompanied by total decomposition of the sample as shown by an expressive exothermic peak on DSC curve at 480°C .

Thermal behavior of complex (2)

The thermoanalytical data for complex (2) are listed in Table 1. The combined TG, DTG, and DSC curves of complex (2) in a dynamic air atmosphere are shown in Fig. 4. Similar to complex (1), the first and the second steps, which take place in the temperature ranges $40\text{--}120$ and $180\text{--}260^\circ\text{C}$, belong to the dehydration and deamination-anation processes, respectively. The observed mass loss in the first step is 2.75 as against the calculated value of 2.70% for the release of H_2O . In the second step, one of the axial benzylamine molecules splits off with a mass loss of 16.01 as against the calculated value of 16.10%. The third step, which by analogy to complex (1), is the decarbonylation of one CO group from the equatorial ligand, begins at 270°C . This step is immediately followed by several overlapping steps including the release of the second benzylamine molecule, the decarbonylation of the remaining equatorial ligand, and the release of the two pyridine residues. The observed mass

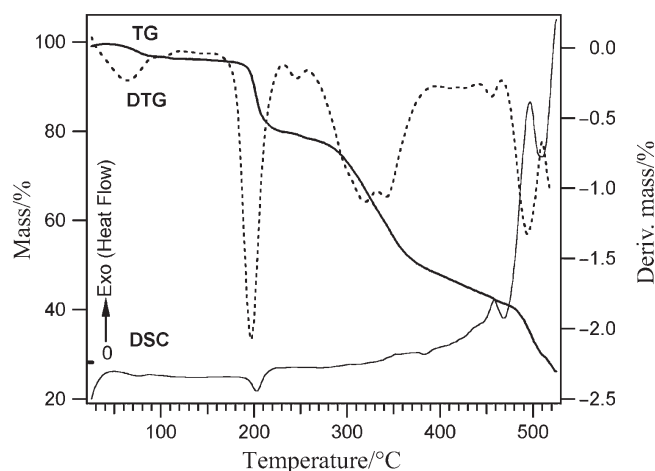


Fig. 4 TG, DTG, and DSC curves of (2) in a dynamic air atmosphere (20 mL min^{-1})

loss between 260–400°C is 44.7 as against the calculated value of 48.30% for (benzylamine+2CO+2py). The rest of the ligands are exothermically decomposed along with the total decomposition of the sample at above 450°C.

Thermal behavior of complex (3)

To study the thermal behavior of a bis(piperidine) complex similar to (1) and (2), it was desired to synthesize the *trans*-[Co(bpb)(pprdn)₂]NCS compound. However, our attempts led to a mixture containing a high percentage of the thermal anation product, *trans*-[Co(bpb)(pprdn)NCS]. Therefore, a homogeneous mixture of the perchlorate salt, *trans*-[Co(bpb)(pprdn)₂]ClO₄·H₂O, and KSCN was used for thermal deamination-anation studies. The thermoanalytical data for complex (3)+KSCN are listed in Table 1 and the combined TG, DTG, and DSC curves of this mixture in a dynamic air atmosphere are presented in Fig. 5. The thermal behavior of complex (3)+KSCN mixture in air atmosphere, is very close to the other two complexes (1) and (2). However the dehydration process consists of two very close steps associated with successive release of the adsorbed and crystallization water between 30 and 110°C. In the second step between 110 and 200°C, piperidine molecule is replaced by NCS. The observed mass loss in this step is ca 11.60 as compared to the calculated value of 11.20% for piperidine. It is worth noting that, since the organic molecules are readily oxidized in air in the presence of perchlorate at elevated temperatures, the endothermic release of piperidine is probably counterbalanced by the exothermic oxidation of this amine, resulting in an exothermic peak in the DSC curve, Fig. 5. The decarbonylation of (3) occurs between 230 and 310°C with the observed mass loss of ca. 4.0 as compared to the theoretical value of 3.68% for the release of CO. Other processes at higher temperatures are complicated by the oxidative nature of the perchlorate anion. However it is noteworthy that the qualitative thermal behavior of (3) mixed

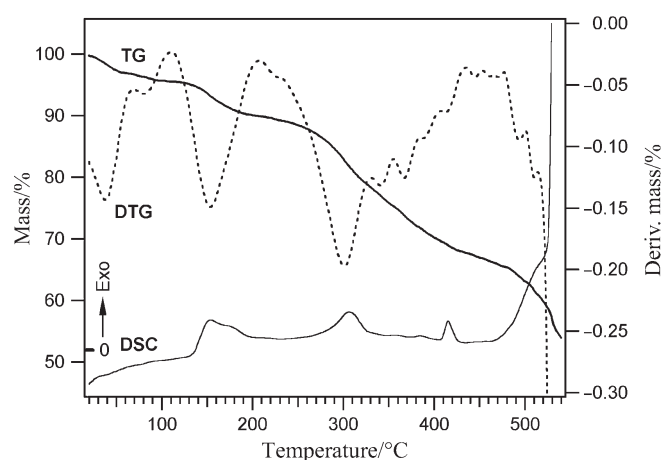


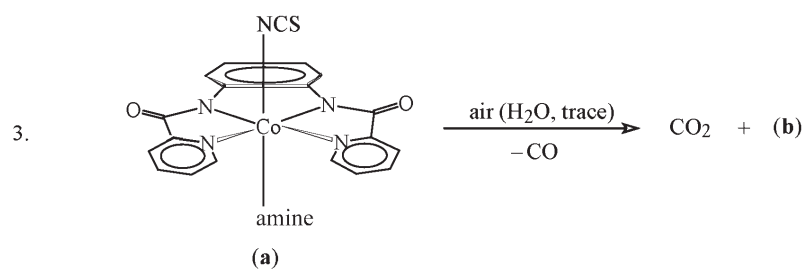
Fig. 5 TG, DTG, and DSC curves of (3)+KSCN in a dynamic air atmosphere (20 mL min^{-1})

with KSCN resembles that of (1), though the presence of the perchlorate anion results in the exothermic oxidation of all organic fragments released at high temperatures, and rough estimation of the mass loss.

Kinetic and mechanism of the reactions

The thermal behavior of the cobalt complexes can be expressed briefly as shown in Scheme 1. The steps outlined in Scheme 1 are more clearly observed in the thermal decomposition of complex (1). In the case of (2) and (3) however, it seems that some successive steps overlap to a great extent or occur all at once.

1. $\text{trans-[Co(bpb)(amine)}_2\text{]NCS}\cdot\text{H}_2\text{O} \longrightarrow \text{trans-[Co(bpb)(amine)}_2\text{](NCS)} + \text{H}_2\text{O}$
2. $\text{trans-[Co(bpb)(amine)}_2\text{]NCS} \longrightarrow \text{trans-[Co(bpb)(amine)(NCS)] (a)} + \text{amine}$



4. (b) - (amine+CO+2py) \longrightarrow (c)
5. (c) (decomp.) \longrightarrow decomposition products

Scheme 1

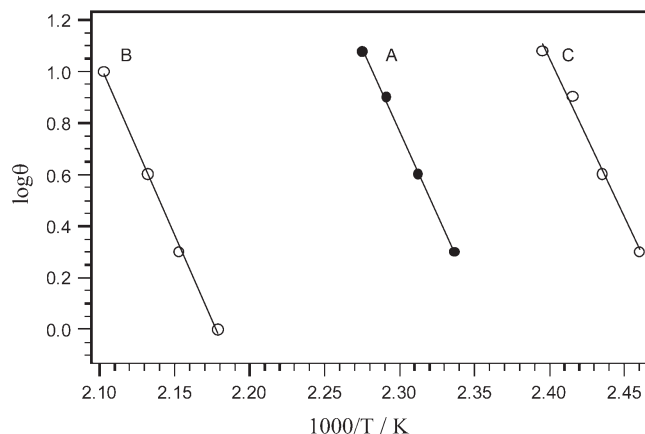


Fig. 6 Log θ vs. $1000/T(K)$ plot for deamination-anation of (1) (A), (2) (B), and (3) (C)

TG, DTG, and DSC curves provide comprehensive information about the reaction stoichiometry and the temperatures at which different reactions take place. It is evident from these curves that the deamination-anation reaction occurs at a higher temperature for the complex in which the axial amine has a higher ligand field strength. A higher activation energy is also expected for the substitution of the more strongly coordinated amine. In order to estimate the activation energy of the deamination reaction, the temperature (T_m) at maximum mass loss (DTG) in the deamination process for each complex was determined as a function of heating rate (θ) applied, from the thermoanalytical curves. The activation energies were directly estimated [13] from the slope of the graph $\log\theta$ vs. $1/T_m$ (Fig. 6) according to the Eq. (2).

$$E_a = -2.303R[d(\log\theta)/d(1/T)] \quad (2)$$

The estimated values of $E_a(1)=246.8 \text{ kJ mol}^{-1}$, $E_a(2)=255.7 \text{ kJ mol}^{-1}$, and $E_a(3)=234.7 \text{ kJ mol}^{-1}$, show a trend similar to that observed in the energy of the first ligand field (LF_1) transition (ca 10 Dq) of these hexacoordinate complexes. The $E(LF_1)=15.823 \text{ kK}$ ($\lambda_{\max}=632 \text{ nm}$) for (1), 16.565 kK ($\lambda_{\max}=604 \text{ nm}$) for (2), and 14.815 kK ($\lambda_{\max}=675 \text{ nm}$) for (3), have been determined from the UV-Vis spectral measurements [11]. These observations are in accordance with the expectation considering a dissociative activation process for ligand substitution in the low spin d^6 Co(III) complexes [14–16].

It is interesting to note that the activation energies of deamination-anation of (1)–(3) are, in general, higher by about 100 kJ mol^{-1} than those of the corresponding *trans*-[Co(acacen)(amine)₂]NCS complexes [8]. A comparison between the electronic spectra and the structure of these complexes would make it possible to rationalize these observations. It is evident from the electronic absorption spectra of (1)–(3) that bpb is a tetradentate ligand with a lower ligand field strength compared to acacen, due to its lower electron donating character. The decreased bonding interaction between the equatorial ligand and Co(III) promotes the affinity for axial ligands.

A stronger interaction between Co(III) metal center and the axial amines, and a relatively strong intermolecular N–H···O=C hydrogen bonding (Fig. 1) may well account for the higher E_a of deamination-anation of (1)–(3) relative to the acacen analogues.

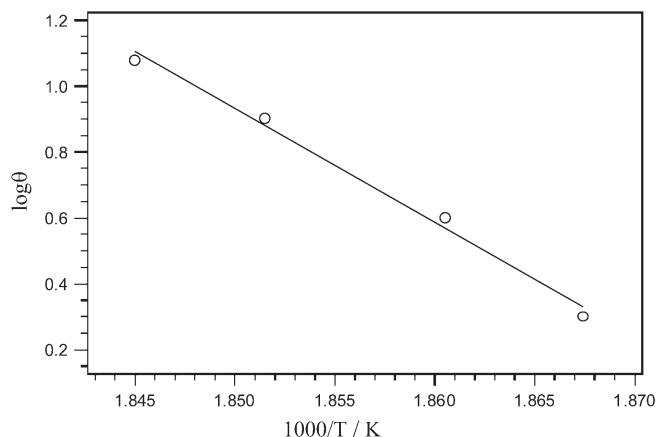


Fig. 7 Log θ vs. 1000/T(K) plot for the decarbonylation of (1)

The decarbonylation of the coordinated equatorial ligand contrasts the thermal behavior observed for the free ligand and the O-bonded amide complexes reported in the literature [17]. While the free ligand undergoes endothermic melting at 175°C followed by the endothermic evaporation at 275°C, the overall thermal stability of the coordinated ligand is increased due to the chelate effect. However, the amide linkage is weakened to some extent and undergoes pyrolysis at elevated temperatures in air to give CO₂. The exothermic release of CO₂, accompanied by the production of isocyanates (R–N=C=O), is also reported in the thermal decomposition of cyclic amides in air [18]. The mechanism of the reaction may include an intramolecular rearrangement followed by oxidative conversion of CO to CO₂. The decarboxylation of the carboxylic groups attached to strongly coordinated ligands is a normal process to occur at high temperatures [19, 20]. The decarbonylation temperature in complex (1) (270°C) is close to those for the coordinated carboxylic acid derivatives [20, 21]. In addition, the energy of activation for this process in complex (1), $E_a=662.5$ kJ mol⁻¹ estimated from Fig. 7, is close to that reported for the hexacoordinate tris(mandelato)-thallium(III) complex [21]. The concomitant rearrangement and decarboxylation processes may well account for this relatively high activation energy. Supporting evidence for the loss of one CO group comes from the mass loss (TG), the heat flow (DSC) in this exothermic step, Table 1, and the detection of CO₂ by mass spectrometry at 280°C for complex (1).

Conclusions

Thermoanalytical investigation of the title complexes shows that the deamination-anation reaction takes place in a dissociative process resulting in the replacement of one of the axial amines by NCS. The trend in the activation energy for this process follows the ligand field strength of the coordinated amines: bzlan > prldn > pprdn [11]. This is consistent with a dissociative activation process. In addition, the observed higher activation energy relative to similar cobalt(III) acacen complexes [8] is explained by the stronger interaction of the axial amine ligands with Co(III) and a relatively strong intermolecular hydrogen bonding between the amine and the CO group of the equatorial ligand, bpb, in these complexes.

The most interesting aspect of this study is the exothermic decarbonylation of the coordinated equatorial amide ligand as compared to the endothermic melting and evaporation processes of the free ligand. This is presumably due to the fact that the bonding between the CO group and the pyridine and phenylenediamine moieties are weakened to some extent upon coordination of the ligand to Co(III). This speculation remains to be tested by further theoretical studies.

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References

- 1 J. Zsakó, M. Várhelyi and Cs. Várhelyi, *Thermochim. Acta*, 51 (1981) 277.
- 2 J. A. Real, M. C. Munzo and J. Borrás, *Thermochim. Acta*, 101 (1986) 83.
- 3 Z. Liming, D. Lide and X. Xinquan, *Thermochim. Acta*, 196 (1992) 437.
- 4 E. Jóna, M. Kubranova, P. Simon and J. Morzinski, *J. Thermal Anal.*, 46 (1996) 1325.
- 5 D. Czakis-Sulikowska and J. Kałuzna, *J. Thermal Anal.*, 47 (1996) 1763.
- 6 J. E. House Jr., *Coord. Chem. Rev.*, 128 (1993) 175.
- 7 M. Amirnasr and R. Vafazadeh, *Scientia Iranica*, 4 (1997) 35.
- 8 M. Amirnasr and R. Vafazadeh, *Scientia Iranica*, 4 (1997) 46.
- 9 M. Corbella and J. Ribas, *Inorg. Chem.*, 25 (1986) 4390.
- 10 M. Amirnasr, K. J. Schenk, A. Gorji and R. Vafazadeh, *Polyhedron*, 20 (2001) 695.
- 11 M. Amirnasr, K. J. Schenk and S. Meghdadi, submitted to *Inorg. Chim. Acta*.
- 12 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds' 4th ed.; John Wiley & Sons, New York 1986, p. 285.
- 13 T. Ozawa, *J. Thermal Anal.*, 7 (1975) 601.
- 14 R. G. Wilkins, 'Kinetics and Mechanism of Reactions of Transition Metal Complexes' 2nd ed., VCH Weinheim, New York 1991, p. 94.

- 15 A. Haim, *Inorg. Chem.*, 9 (1970) 426.
- 16 N. J. Curtis, *Inorg. Chem.*, 25 (1986) 1033.
- 17 A. N. Nelwamondo, D. J. Eve, G. M. Watkins and M. E. Brown, *Thermochim. Acta*, 318 (1998) 165.
- 18 C. Shimasaki, H. Nakayama, A. Iwaki, E. Tsukurimichi, T. Yoshimura and K. Hasegawa, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1993.
- 19 J. C. Bezial, M. Besson, P. Gallezot and S. Durecu, *J. Catal.* 182 (1999) 129.
- 20 M. Amirnasr, Md. K. Nazeeruddin and M. Graetzel, *Thermochim. Acta*, 348 (2000) 105.
- 21 P. V. Khadikar, *Thermochim. Acta*, 116 (1987) 171.