

RELATED THERMOGRAVIMETRIC AND SPECTROPHOTOMETRIC STUDIES ON LANTHANIDE(III) COMPLEXES WITH THE 3-ACETILPYRIDINE *N*-OXIDE LIGAND

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ABSTRACT

Some lanthanide complexes of 3-acetylpyridine *N*-oxide have been isolated and characterized. These complexes were subjected to elemental analysis, molar conductivity measurements, thermogravimetric analysis, UV and IR spectral studies. Based on these physicochemical studies, the suggested general formula for the obtained complexes is $ML_n(H_2O)_x(ClO_4)_3 \cdot Y \cdot H_2O$, where L = 3-acetylpyridine *N*-oxide; M = Pr, Nd, Sm, Eu, Gd, and Y; $n = 6-8$; $x = 0, 1$ or 2; and $Y = 1-3$.

Thermogravimetric analysis for some isolated complexes has already indicated different modes of interaction between various types of ligand including water, and central metal ions. UV and IR spectral studies have indicated that the coordination of the ligand to the central metal ion is via oxygen atoms of the N–O group, and also elucidates the presence of some water molecules in the identity of these complexes. The ionic nature of all perchlorate groups has been established by molar conductivity measurements, and confirmed by the related IR spectral studies.

INTRODUCTION

Lanthanides usually exhibit high coordination numbers in their complex formation. The coordination numbers depend primarily on the size of the lanthanide ion as well as the nature of the ligand. In general, the coordination number decreases with decrease in size [1,2] of the lanthanide(III) ions (La to Lu). Furthermore, some recent investigations [3,4] have indicated that

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the separation and characterization of lanthanide(III) ion complexes, with a relatively small coordination number, becomes easier when they are coordinated with bulky and side-branched ligands. However, the lanthanide ions in their complexes of substituted pyridine *N*-oxide [5,6] show high coordination numbers, on average about 7 or 8.

The complexes of 4-acetylpyridine with some lanthanide(III) ions were thoroughly investigated and characterized in a more recent study by Khater et al. [7]. As a continuation, the lanthanide(III) complexes of 3-acetylpyridine *N*-oxide complexes are presented, based on some UV and IR spectral studies, chemical analysis, electrical conductivity measurements, as well as thermogravimetric analysis. The present investigation deals mainly with the coordination chemistry of tripositive lanthanide ion complexes of the pyridine *N*-oxide ligand.

EXPERIMENTAL

The 3-acetylpyridine *N*-oxide (3-AcPyO) ligand was prepared from the corresponding reagent grade 3-acetylpyridine (Merk) by a method reported previously by Kanno [8].

Preparation of the hydrated perchlorates has been described in detail elsewhere [9]. Briefly, the lanthanide oxides (Koch Light) were dissolved in 70% perchloric acid followed by heating and continuous stirring. The filtrate so obtained was evaporated to dryness, and the resulting solids were preserved in a vacuum desiccator containing anhydrous calcium chloride.

Preparation of the 3-AcPyO: lanthanide(III) complexes involved mixing of solutions of 3-AcPyO (1 g in 10 ml ethanol) and lanthanide(III) perchlorate (0.25 g in 10 ml ethanol), which had been separately brought to the boil and thoroughly stirred before mixing, then left over night until a semi-solid product was formed. The slimy precipitate so obtained was filtered off, treated with 40 ml petroleum ether, 40–60°C, and solidified by addition of 10 ml cold ethanol using stirring and scratching. The precipitate formed was finally washed several times with diethyl ether and preserved in a vacuum desiccator. The solid complexes so obtained are yellow (except those of Nd and Y), hygroscopic, slightly soluble in organic solvents but completely soluble in dimethylformamide (DMF).

Chemical analyses of C, H and N were kindly performed by microanalysts at Cairo University (cf. Table 1). Analysis of the metal content in the given complexes was made spectrophotometrically [10]. The perchlorate content in the moiety of these complexes was determined using cation exchange technique [11] by titration of the obtained perchloric acid in the effluent.

Thermogravimetric analyses (TG) of Sm, Eu, Gd and Y complexes were recorded on a Shimadzu TG system (Shimadzu 30 Series) thermal analyzer. The weight losses in 2.5–6.0 mg samples were measured in the temperature

TABLE 1

Elemental analysis of some lanthanide complexes of 3-acetylpyridine *N*-oxide

Complex ^a	Found (%)					Calcd. (%)				
	M ^b	ClO ₄	C	H	N	M ^b	ClO ₄	C	H	N
PrL ₈ (ClO ₄) ₃ ·H ₂ O	8.65	18.65	43.8	3.8	7.5	9.07	19.2	43.26	3.7	7.2
NdL ₈ (ClO ₄) ₃ ·H ₂ O	8.80	18.65	43.8	3.7	7.0	9.07	19.17	43.17	3.7	7.2
SmL ₇ H ₂ O(ClO ₄) ₃ ·3 H ₂ O	9.75	19.71	39.2	4.3	6.9	10.16	20.17	39.72	3.9	6.6
EuL ₇ H ₂ O(ClO ₄) ₃ ·2 H ₂ O	9.90	21.00	40.2	4.2	6.3	10.38	20.27	40.18	3.8	6.7
GdL ₇ H ₂ O(ClO ₄) ₃ ·2 H ₂ O	10.25	20.85	39.9	4.1	6.3	10.71	20.32	40.03	3.7	6.6
YL ₆ (H ₂ O) ₂ (ClO ₄) ₃ ·3 H ₂ O	6.80	22.40	38.6	4.3	6.8	6.94	22.97	38.79	4.0	6.5

^a L = 3-AcPyO.^b M = Lanthanide(III) metal ion.

range 20–400°C, with a heating rate of 10°C min⁻¹.

The IR spectra were recorded as KBr discs on a Pye Unicam SP 1100 IR spectrophotometer for a range of wave numbers (400–4000 cm⁻¹). The UV spectra of the ligand and its lanthanide complexes were measured in water, DMF, methanol, and ethanol as polar solvents, and 1,4-dioxan and cyclohexane as non-polar solvents using a Pye Unicam SP 1750 recording spectrophotometer. In addition, UV spectra of these complexes and the ligand were also measured by nujol mulls technique, as recently reported elsewhere [6,12].

The electrical conductivity measurements were carried out for 1 mM solutions in water and DMF using a D 812 conductivity meter Model LBR (cell constant = 0.741) at 25 ± 0.1°C.

RESULTS AND DISCUSSION

Based on chemical analysis of the separated solid complexes for the elements C, H, N and M (the metal), the suggested formula is ML_{*n*}(H₂O)_{*x*}(ClO₄)₃·*Y* H₂O, where L = 3-AcPyO, M = Pr, Nd, Sm, Eu, Gd, Y; *n* = 6–8; *x* = 0, 1 or 2; and *Y* = 1–3. Obviously, all the solid complexes are isolated with solvent water molecules in outer and/or inner spheres and are considerably hygroscopic.

In order to study the effect of solvent on the stability of these complexes, it is important to study spectrophotometrically the effect of different solvents on both the ligand and the complexes. The polar solvents used are water, DMF, ethanol and methanol as well as the non-polar solvents 1,4-dioxan, cyclohexane and nujol.

The presence of two bands at 210–240 and 270–300 nm is established in a study of the effect of polar solvents on the 3-AcPyO ligand. The first band is assigned to the π–π* transition within the pyridine rings [13], while the

second band is assigned to the $\pi-\pi^*$ transition in acetyl groups influenced by intramolecular charge transfer interaction. This is supported by the presence of only one band at 257–265 nm obtained in the case of pyridine and pyridine *N*-oxide [13]. It is worth mentioning that the polar and non-polar solvents mostly exhibit the same effect (or behaviour) on both 3- and 4-AcPyO ligands. A detailed study of the effect of different solvents on 3- and 4-AcPyO ligands as compared with pyridine has been reported elsewhere [14].

The weak band obtained at 340 nm taken using nujol as a nonpolar solvent, was attributed to an $n-\pi^*$ transition. Therefore, where a polar solvent was used instead of a non-polar solvent, the two main bands were blue shifted to 270 and 300 nm, and subsequently the $n-\pi^*$ transition completely disappeared. This behaviour is attributed to the fact that the oxygen 2p non-bonding orbital in the N–O group is energetically stabilized by hydrogen bond formation with the polar solvent molecules (cf. Fig. 1).

Comparing the UV spectra of the 3-AcPyO in polar solvents with that of its lanthanide(III) complexes, a great similarity between their behaviour in such solvents is observed, and hence the ligand shows less tendency to form these complexes. Eventually, this behaviour is attributed to the competition between polar solvents, which actually forms a hydrogen bond with the N–O group and the metal ion which forms the N–O \cdots M bond. Therefore, to avoid these competitive forces, the UV spectra of this type of complex were studied in different non-polar solvents, such as nujol, 1,4-dioxan and cyclohexane.

Using nujol as solvent (see Fig. 2), the ligand shows the first band at 290 nm and the other band at 276 nm. The first band becomes sharp as an individual peak, and is still located in the same position as in the case of complex formation. This is attributed to the steady mode of acetyl group interactions during the process of complex formation.

The second band of the ligand becomes broader, and is in the range 280–330 nm during complex formation. The intensity of this broad band increases measurably on going from Nd to Gd, following the order of decreasing ionic size. In fact, this is attributed to the perturbation of the π electron system of the ligand during the complex formation process. However, in the case of Y, the band previously appearing at 280 nm completely

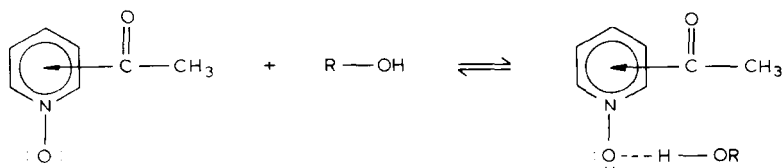


Fig. 1. Hydrogen bond formation of acetylpyridine *N*-oxide ligand with polar solvents.

disappears, as result of great perturbation of the ligand π electron system in the case of forming Y complex formation. Consequently, this directly indicates that the Y: 3-AcPyO complex is measurably more stable than the

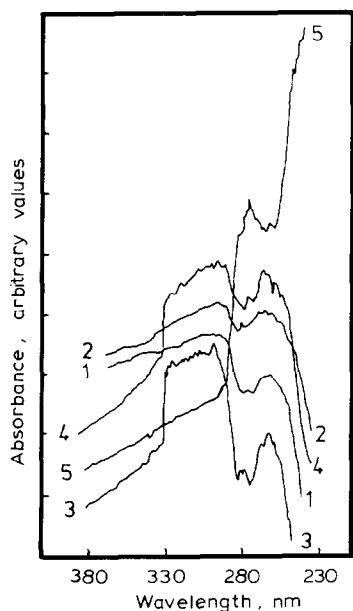


Fig. 2. UV spectra of (1) 3-acetylpyridine *N*-oxide and its complexes with: (2) Nd, (3) Eu, (4) Gd, and (5) Y ions in nujol mulls.

other lanthanide complexes of the same ligand. The finite band of the ligand at 340 nm which is attributed to $n-\pi^*$ transition in the N–O group completely disappears during the complex formation process. This can be inferred because of the formation of the N–O \cdots M bond between the ligand and central metal ion. Analogous behaviour was observed in the other non-polar solvents.

Molar conductivity measurements

The molar conductivity values of 1 mM solutions in water and DMF of the given lanthanide(III) complexes are listed in Table 2. The values obtained are 200–203 and 370–394 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ in water and DMF, respectively, which are in good agreement with those reported earlier [15,16] for 1:3 electrolytes in the same solvents. These anomalous values are attributed to ionic association rather than the coordination of perchlorate groups to the lanthanide(III) cations during complex formation. This directly supports the fact that all perchlorate groups in these complexes are ionic in nature.

TABLE 2

Molar conductance data of the rare earth complexes with 3-acetylpyridine *N*-oxide at 25°C

Complex	Concentration (in water) (mM)	Λ (ohm ⁻¹ cm ² mole ⁻¹)	Concentration (in DMF) (mM)	Λ (ohm ⁻¹ cm ² mole ⁻¹)	No. of dissociated charged species
PrL ₈ (ClO ₄) ₃ ·H ₂ O	0.95	394	1.12	203	1:3
NdL ₈ (ClO ₄) ₃ ·H ₂ O	0.61	376	1.12	201	1:3
SmL ₇ H ₂ O(ClO ₄) ₃ ·3 H ₂ O	1.12	374	1.15	202	1:3
EuL ₇ H ₂ O(ClO ₄) ₃ ·2 H ₂ O	1.11	370	1.10	200	1:3
GdL ₇ H ₂ O(ClO ₄) ₃ ·2 H ₂ O	1.13	372	1.04	202	1:3
YL ₆ (H ₂ O) ₂ (ClO ₄) ₃ ·3 H ₂ O	0.96	371	1.04	200	1:3

Thermogravimetric analysis

Thermogravimetric analysis is one very useful method for the study of the thermal decomposition of solid substances involving simple metal salts [17], as well as for complex compounds [5]. The thermogram follows the decrease in sample weight with the linear increase in heat treatment temperature. Therefore, in cases of constant heating rate, e.g. 4–6°C min⁻¹ and using a constant chart drive of the printer as a time base, comparisons may be indicative for the nature (or the mode) of the thermal decomposition, and the temperature range of this decomposition stage may also be denoted.

In the present investigation, heating rates were suitably controlled at 10°C min⁻¹ and the chart drive of the printer was kept at 1 in./5 min as a time response of the instrument. Depending on the extent of total mass lost at 400°C, sample weights were monitored in the range 2.5–6.0 mg during the experimental runs. Further details about the use of thermogravimetric analysis have been reported elsewhere [18], and skilful manipulation of this technique was recently presented by Khalil and Kolboe [19,20].

Sm, Eu, Gd and Y complexes of the 3-acetylpyridine *N*-oxide ligand were subjected to this technique; the stage of decomposition, the temperature range concerned, the thermal decomposition products, and the estimated and calculated mass losses are listed in Table 3. The estimated mass loss calculations were based on thermogravimetric analysis and the calculated mass losses were calculated using the results of microchemical analysis for these solid complexes (cf. Table 1).

As indicated in Table 3 (column 2), for the Sm complex the first stage of decomposition in the range 50–180°C indicates a loss of three molecules of water of hydration; both estimated and calculated mass losses were in reasonable agreement and amounted to 4%. In the range 200–400°C (second decomposition stage) about 20% mass loss occurs, which quantitatively interprets the loss of two ligand molecules and a coordinated water molecule

TABLE 3

Mass loss of 3-acetylpyridine *N*-oxide (L) complexes in different temperature ranges

Decomp. stage	Complex ^a	Temp. range (°C)	Decomposition products lost	Wt. loss (%) ^b	
				Found	Calcd.
First	I	50–180	3 H ₂ O hyd.	4.0	4.0
	II	30–140	2 H ₂ O hyd. + L + H ₂ O coordn.	12.0	12.94
	III	65–270	2 H ₂ O hyd. + H ₂ O coordn.	4.0	4.0
	IV	30–110	3 H ₂ O hyd.	5.0	5.98
Second	I	200–400	2 L + H ₂ O coordn.	20.0	19.26
	II	150–200	2 CO	4.0	4.14
	III	290–400	3 CO	6.0	6.0
	IV	130–200	2 H ₂ O coordn.	2.91	2.65
Third	II	200–325	4 L	36.0	35.8
Fourth	II	350–400	L + CO	11.0	11.02

^a I = SmL₇H₂O(ClO₄)₃·3 H₂O; II = EuL₇H₂O(ClO₄)₃·2 H₂O; III = GdL₇H₂O(ClO₄)₃·2 H₂O; IV = YL₆(H₂O)₂(ClO₄)₃·3 H₂O.

^b Mass losses were calculated based on the residual weights.

(calculated mass loss ≈ 19.26%). As indicated, the coordination number of Sm was significantly reduced to 5.

However, in the case of the Eu complex, the initial mass loss in the temperature range 30–140°C is attributed to the loss of two molecules of water of hydration together with the loss of one coordinated water molecule, and finally the dissociation of one ligand molecule of 3-AcPyO, which subsequently escapes from the lattice matrix of the complex. Both the estimated and the calculated mass losses are in satisfactory agreement (12.0 and 12.94%, respectively). As indicated, this step comprises breakage of the N–O···M bond with the consequent release of one molecule of pyridine *N*-oxide derivative.

In the second decomposition stage (cf. column 3, Table 3) heating at 150–200°C results in nearly 4% mass loss, which corresponds to the loss of two carbonyl (CO) groups from the moiety of the acetyl groups (i.e. from the ligands) in this complex. The calculated mass loss of 4.14% significantly agrees with that estimated by TG method (~ 4.0%).

An increased mass loss (~ 36%) due to the loss of four ligand molecules (calculated gram% ~ 35.81) occurs in the temperature range 200–325°C. The third decomposition stage (330–400°C), as well as the fourth decomposition stage (350–400°C), are responsible for a loss of 11%, which is due to the loss of two ligand molecules accompanying the loss of two carbonyl groups in

each step (both losses are in good agreement with the calculated loss of $\sim 11.02\%$). This final decomposition stage of the Eu complex at 400°C leads to the formation of $\text{Eu}(\text{ClO}_4)_3$.

As shown in column 4 of Table 3, for the Gd complex the initial loss of 4% at $65\text{--}270^\circ\text{C}$ is due to the loss of two molecules of water of hydration together with a coordinated water molecule. In the second stage of decomposition, the mass loss of 6% at $290\text{--}400^\circ\text{C}$ is reasonably attributed to the loss of three carbonyl groups from the acetyl groups in the pyridine *N*-oxide derivative which was attached to the central metal ion (calculated g% ≈ 6.0).

In the case of the Y complex (cf. column 5 of Table 3), the first decomposition stage of 5.0% weight loss at $30\text{--}110^\circ\text{C}$ is due to the loss of three molecules of water of hydration (calculated mass loss $\approx 5.98\%$). In the second decomposition stage ($130\text{--}200^\circ\text{C}$) a fractional loss of 2.91% is mainly attributed to the loss of two coordinated water molecules (calculated mass loss $\approx 2.65\%$). The final high mass loss of 28.3% in the temperature range $215\text{--}400^\circ\text{C}$ is due to the loss of three molecules of 3-AcPyO ligand, together

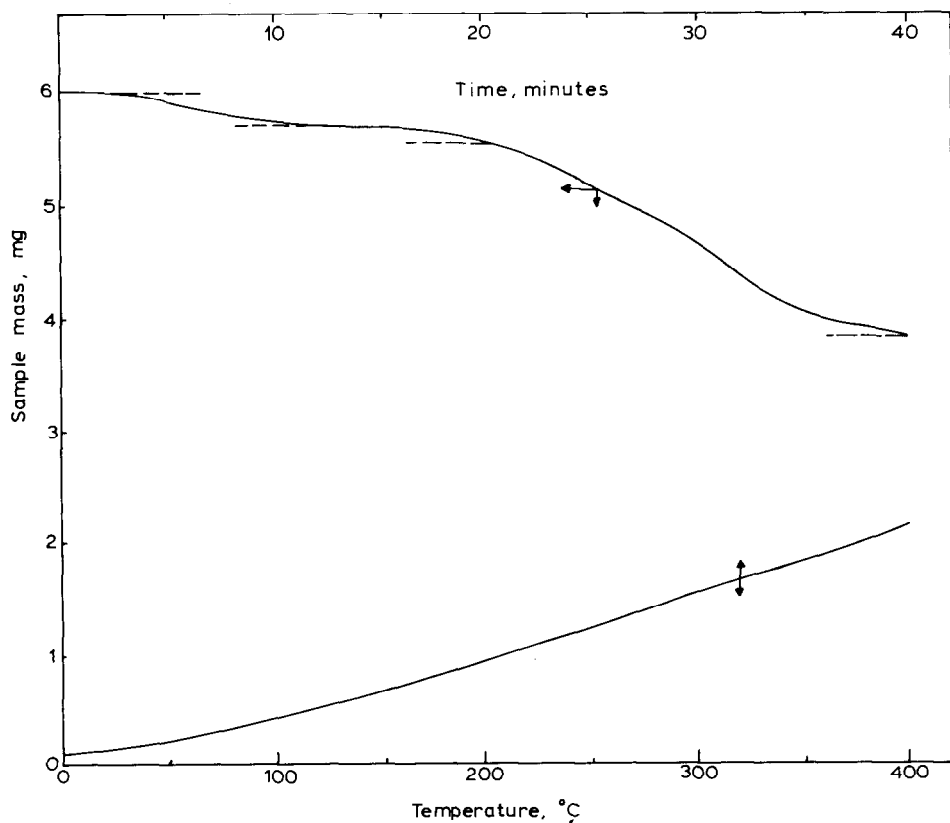


Fig. 3. Thermogravimetric analysis for Y: 3-AcPyO complex.

with two carbonyl groups from the other three remaining molecules in the complex (calculated mass loss 28.76%). The thermogram of the Y : 3-AcPyO complex is shown in Fig. 3.

It was finally concluded that the gradual mass losses in 3-AcPyO: lanthanide(III) complexes involve the loss of hydrated water molecules in the temperature ranges 30–110°C, 30–140°C, 50–180°C and 65–270°C for the complexes of Y, Eu, Sm, and Gd, respectively. This indicates that the binding energy of the hydrated water molecules [to the central lanthanide(III) ions] increases in the same order as the atomic size of these elements increases [21]. On the other hand, coordinated water molecules were lost in the same order in the temperature ranges 130–200°C, 30°–140°C, and 200–400°C in the case of Y, Eu and Sm complexes, respectively. Exceptionally for Gd complex, the coordinated water molecules are stable even at the highest temperature treatment (400°C).

Furthermore, the loss of carbonyl groups from the ligand molecules attached to central metal ions and/or dissociated from the complex elucidates the fact that the acetyl groups do not share in complex formation. The loss of carbonyl (CO) groups from the complexes finds support in another recent report [5] concerning the thermal treatment of pyridine *N*-oxide complexes for similar lanthanide(III) elements.

It is worth mentioning that the decomposition of the ligand molecules from the lattice matrix of these complexes occurs at higher temperatures ($\geq 200^\circ\text{C}$), followed by stepwise loss of the other ligand molecules of this complex. As an exception, in the case of the Eu complex, one ligand molecule is thus lost at nearly 140°C. This indicates that the Eu: 3-AcPyO complex is less stable, since it possesses the largest atomic size. On the other hand, the Gd complex exhibits no loss of ligand molecules, which means that it is the most thermally stable complex, and hence it has the lowest atomic size. These findings are in good agreement with similar trends presented elsewhere [5] for Sm, Eu and Er: 2-AcPyO complexes.

The three perchlorate groups in these complexes are ionically attached even at relatively high treatment temperatures. This result confirms the previously conclusions deduced from the respective UV and electrical conductivity measurements.

IR spectral studies

Assignment of the selected IR bands for the ligand and complexes is presented in Table 4. A study of IR spectra seems necessary for a better understanding of the nature of bonding in these complexes.

The strong broad band at 3400 cm^{-1} is assigned to OH stretching mode, and indicates the presence of hydrated and/or coordinated water molecules. This band does not appear in the case of the ligand only.

The bands appearing in the region $450\text{--}415\text{ cm}^{-1}$ have been assigned to

TABLE 4

Functional group and perchlorate vibrations of 3-acetylpyridine *N*-oxide (L) and its lanthanide complexes (cm^{-1}).

Mode ^a	Ligand ^b	Pr ^b	Nd ^b	Sm ^b	Eu ^b	Gd ^b	Y ^b
ν_{OH}	—	3380b	3440b	3430b	3380b	3460b	3380b
ν_{CO}	1678vs	1688vs	1687vs	1692vs	1685vs	1680vs	1694vs
$\nu_{\text{ring stret.}}$	1550s	1560m	1560m	1567m	1558m	1555m	1566m
$\nu_{\text{NO stret.}}$	1293vs	1275vs	1280vs	1277vs	1277vs	1273vs	1277vs
ν_3	—	1084s	1083s	1090s	1080s	1085s	1090s
$\nu_{\text{NO bend.}}$	805vs	812vs	808vs	803vs	802vs	803vs	805vs
ν_4	—	620s	620s	617s	618s	615s	620s
$\nu_{\text{M}\cdots\text{ON stret.}}$	—	432m	433m	434m	434m	436m	438m

^a ν_3 and ν_4 are the modes of vibrations of perchlorate group.

^b s = strong, m = medium, w = weak, v = very, b = broad; — not observed.

metal–ligand bond stretching frequencies and considered indicative for the connection of the central metal ion to the ligand molecules via oxygen atoms of the N–O group.

The bands at 1293 and 805 cm^{-1} in the spectrum of the ligand, which were assigned to N–O stretching and bending vibrations [16], were slightly shifted to 1277 and 812 cm^{-1} , indicating coordination of the N–O group through oxygen atoms to the central lanthanide(III) ions. Indeed, the formation of the $\text{O}\cdots\text{M}$ bond increases the electron demand of the oxygen donor atom, thereby decreasing the N=O double bond character; this subsequently diminishes the contribution of resonating structures II (cf. Fig. 4) and increases the contribution of structures III to the overall state of the ligand.

The withdrawing effect of the acetyl group increases the contribution of structures II (cf. Fig. 4), thereby opposing the effect of the $\text{M}\cdots\text{O}$ bond, and thus decreasing the strength of this bond. The occurrence of these two opposing factors leads to a decrease in the stability of the complexes.

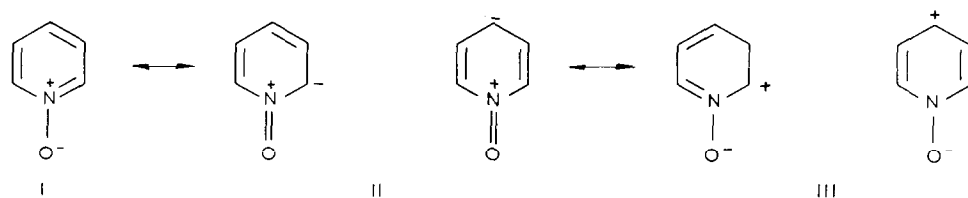


Fig. 4. Resonating structures of pyridine *N*-oxide molecules.

Therefore, this coordination results in a small shift of ν_{NO} ($\sim 20 \text{ cm}^{-1}$), which is considered merely as a qualitative measure for the strength of the $\text{M} \cdots \text{O}$ bond. This shift ($\sim 20 \text{ cm}^{-1}$) was measurably less than those occurring in the complexes of trivalent transition metal ions, amounting to $40\text{--}60 \text{ cm}^{-1}$ [22].

The ν_{CO} stretching vibration appears at 1678 cm^{-1} in the spectrum of the ligand only, and was infinitesimally shifted to $1680\text{--}1694 \text{ cm}^{-1}$ in the state of complexation. This directly indicates that the carbonyl CO group is not entirely involved in complex formation.

The band at 620 cm^{-1} and the partially resolved triplet band at $1080\text{--}1150 \text{ cm}^{-1}$ were assigned to ν_4 and ν_3 of the perchlorate groups in the given complexes. The forbidden ν_1 and ν_2 bands were not observed in the spectra of these complexes. Splitting of the ν_3 band is attributed to the extreme high pressure used in formulating the KBr discs, which significantly distorts the tetrahedral symmetry of the pure perchlorate group rather than the sharing in complex formation.

The effect of compaction may induce not only a change in the chemistry of the perchlorate group, by distortion, but also reflects the change in surface and/or pore structure of the discs. Similar behaviour was recently studied by Khalil [23], as well as previously established by Dubinin [24].

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