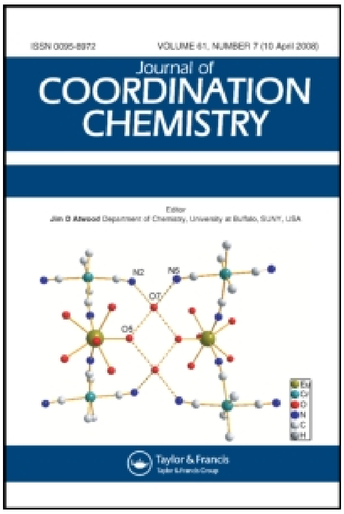

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# Synthesis, characterization and thermal (tg-dsc) study of yttrium methanesulfonate coordination compounds with pyridine *N*-oxide and 2-,3- and 4-picoline *N*-oxides

Maria De F. V. De Moura[a]; Jivaldo Do R. Matos[b]; Robson F. De Farias[c]
[a] Departamento de Química, Universidade Federal do Rio Grande do Norte, 59078-970 Natal, Rio Grande do Norte, Brazil [b] Instituto de Química, Universidade de São Paulo, 05508-900 São Paulo, São Paulo, Brazil [c] Departamento de Química, Universidade Federal de Roraima, 69310-270 Boa Vista, Roraima, Brazil

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# SYNTHESIS, CHARACTERIZATION AND THERMAL (TG-DSC) STUDY OF YTTRIUM METHANESULFONATE COORDINATION COMPOUNDS WITH PYRIDINE *N*-OXIDE AND 2-,3- AND 4-PICOLINE *N*-OXIDES

MARIA DE F.V. DE MOURA[a], JIVALDO DO R. MATOS[b]
and ROBSON F. DE FARIAS[c,*]

[a]*Departamento de Química, Universidade Federal do Rio Grande do Norte, CP 1662, 59078-970 Natal, Rio Grande do Norte, Brazil;* [b]*Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05508-900 São Paulo, São Paulo, Brazil;* [c]*Departamento de Química, Universidade Federal de Roraima, 69310-270 Boa Vista, Roraima, Brazil*

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The synthesis, characterization and thermal (TG and DSC) study of the coordination compounds $Y(MS)_3\cdot(py\text{-}NO)_2\cdot H_2O$, $Y(MS)_3\cdot(2\text{-}picNO)_3$, $Y(MS)_3\cdot(3\text{-}picNO)_2$ and $La(MS)_3\cdot(4\text{-}picNO)_2$ are reported (MS = methanesulfonate, py-NO = pyridine *N*-oxide, and 2-picNO, 3-picNO and 4-picNO are 2-, 3- and 4-picoline *N*-oxides, respectively). The observed thermal stability trend is: 2-picNO $\approx$ 4-picNO $<$ 3-picNO $<$ py-NO. Release of ligand molecules (endothermic) is followed by thermal degradation of the ligands (exothermic) with an increase in the exothermic values from 2-picNO to 4-picNO.

*Keywords:* Yttrium; Coordination compounds; Thermogravimetry

## INTRODUCTION

Thermal techniques were recently suggested to have a prominent role in the study and understanding of the physico-chemical behavior and properties of coordination compounds [1], with the existence of very close correlations between thermal and spectroscopic parameters.

Some coordination compounds involving lanthanide methanesulfonates and picoline *N*-oxides have been prepared [2–4], but investigation of their spectroscopic properties (luminescence) was the main purpose, and a complete thermal study of such compounds is still lacking. The aim of this publication is therefore to report the synthesis, characterization and thermal (TG and DSC) study of the coordination compounds $Y(MS)_3\cdot(py\text{-}NO)_2\cdot H_2O$, $Y(MS)_3\cdot(2\text{-}picNO)_3$, $Y(MS)_3\cdot(3\text{-}picNO)_2$ and

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*Corresponding author. E-mail: robsonfarias@aol.com

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$Y(MS)_3A(4\text{-picNO})_2$, where MS = methanesulfonate, py-NO = pyridine *N*-oxide, and 2-picNO, 3-picNO and 4-picNO are 2-, 3- and 4-picoline *N*-oxides, respectively.

## EXPERIMENTAL

All reagents were of analytical grade and used without further purification.

The yttrium methanesulfonate was prepared from the respective hydroxycarbonate, which was prepared as follows: 10.0 g of $Y_2O_3$ was suspended in 10.0 $cm^3$ of deionized water. A 10% HCl solution was added dropwise, under heating, until complete dissolution of the oxide. The solution was evaporated to dryness, and then diluted with deionized water to a 50 $cm^3$ volume, and filtered. More deionized water was then added until a 800 $cm^3$ volume was reached. The pH of the solution was in the range 3–4, and the solution was heated to boiling. To this solution was added a 1.0 mol $dm^{-3}$ urea solution until complete precipitation of the hydroxycarbonate occurred. The hydroxycarbonate was then exhaustively washed with deionized water and dried at room temperature for 12 h, and then at 350 K for another 24 h.

The Y(III) methanesulfonate was synthesized as follows: 2.0 g of the hydroxycarbonate was suspended in 20.0 $cm^3$ of deionized water. Then, to the boiling suspension was added, dropwise, methanesulfonic acid. The solution was filtered, leaving a residue of unreacted hydroxycarbonates, and the solution was then evaporated in a water bath. The solid obtained was dried at room temperature and stored under vacuum in a desiccator.

Yttrium methanesulfonate coordination compounds were prepared as follows: the solutions of pyridine *N*-oxide, 2-, 3- and 4-picoline *N*-oxide were mixed with lanthanum methanesulfonate previously dissolved in methanol. In a first synthetic attempt, the lanthanum methanesulfonate and the respective aromatic aminoxides were mixed in a 1 : 3 (mol : mol) stoichiometric ratio, with the aminoxides previously dissolved in acetone. By using this synthetic approach, the compounds with pyridine *N*-oxide and 2- and 3-picoline *N*-oxide were prepared. The synthesis of the 4-picoline *N*-oxide was achieved by using triethyl orthoformiate as solvent for the aminoxide. The compounds obtained were then filtered off and washed with acetone or triethyl orthoformiate. The white solids obtained (all of them white) were then dried at room temperature and stored under vacuum.

The CHN elemental analyses were performed in an elemental analyzer, Perkin-Elmer model 2400. The infrared spectra were obtained in KBr disks on a 1750 Perkin-Elmer spectrophotometer. The metal content was obtained by EDTA titration, and the volumetric method of Schöniger [5] was used for sulfur.

The thermogravimetric curves were obtained in a Shimadzu TGA-50 instrument, under a nitrogen atmosphere at four heating rates: 2.5, 5, 10 and 20 K $min^{-1}$.

The DSC curves were obtained by using a Shimadzu DSC-50 instrument, under a nitrogen atmosphere and at a heating rate of 10 K $min^{-1}$.

## RESULTS AND DISCUSSION

The elemental analyses for the compounds synthesized are summarized in Table I. The experimental values are in good agreement with the proposed formulas.

TABLE I Elemental analysis results for yttrium methanesulfonate coordination compounds with py-NO, 2-, 3- and 4-picNO. Calculated values are in parentheses

| *Compound* | *M*/% | *C*/% | *H*/% | *S*/% | *N*/% |
|---|---|---|---|---|---|
| Y(MS)$_3$A(py-NO)$_2$AH$_2$O | 14.9 (15.3) | 27.0 (26.8) | 3.5 (3.5) | 16.0 (16.5) | 4.7 (4.8) |
| Y(MS)$_3$A(2-picNO)$_3$ | 12.3 (12.7) | 36.6 (36.0) | 4.4 (4.3) | 12.7 (13.7) | 5.4 (6.0) |
| Y(MS)$_3$A(3-picNO)$_2$ | 14.1 (15.0) | 30.3 (30.4) | 4.1 (3.9) | 14.7 (16.2) | 4.8 (4.7) |
| Y(MS)$_3$A(4-picNO)$_2$ | 14.6 (15.0) | 30.3 (30.4) | 3.8 (3.9) | 13.3 (16.2) | 4.5 (4.7) |

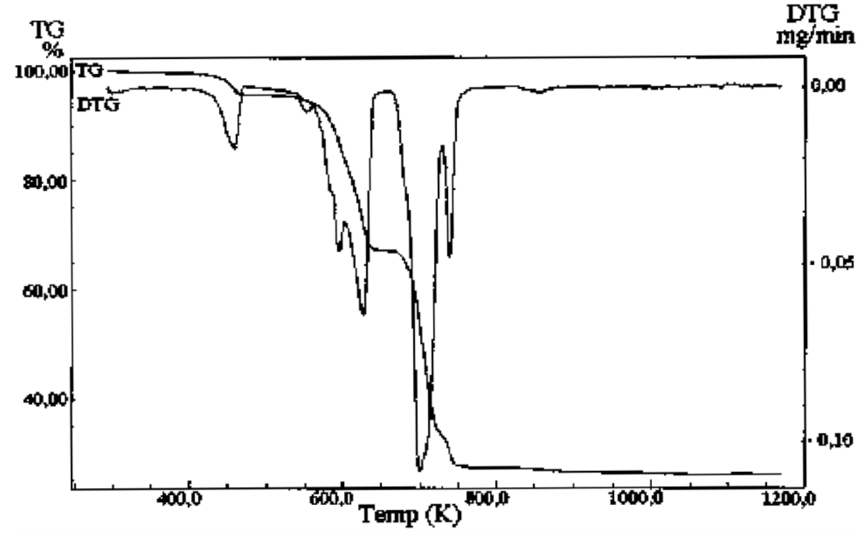

FIGURE 1 Thermogravimetric and derivative curves for Y(MS)$_3$A(py-NO)$_2$AH$_2$O.

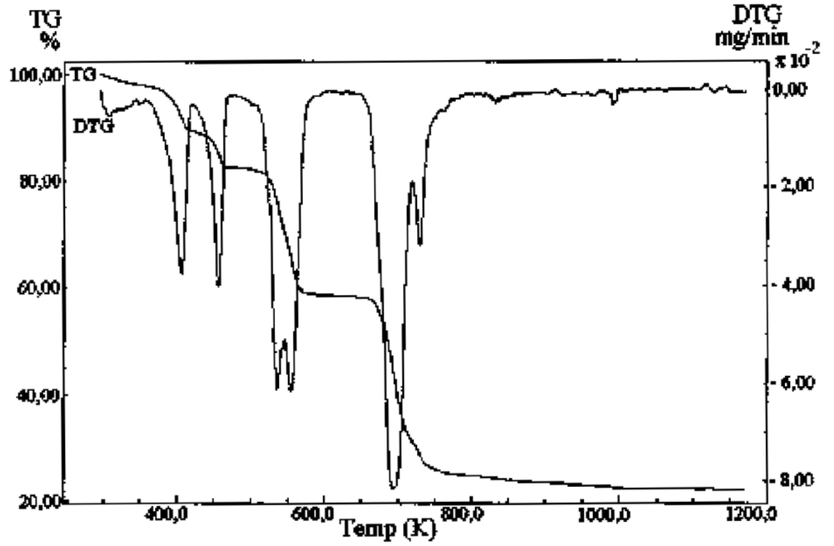

FIGURE 2 Thermogravimetric and derivative curves for Y(MS)$_3$A(2-picNO)$_3$.

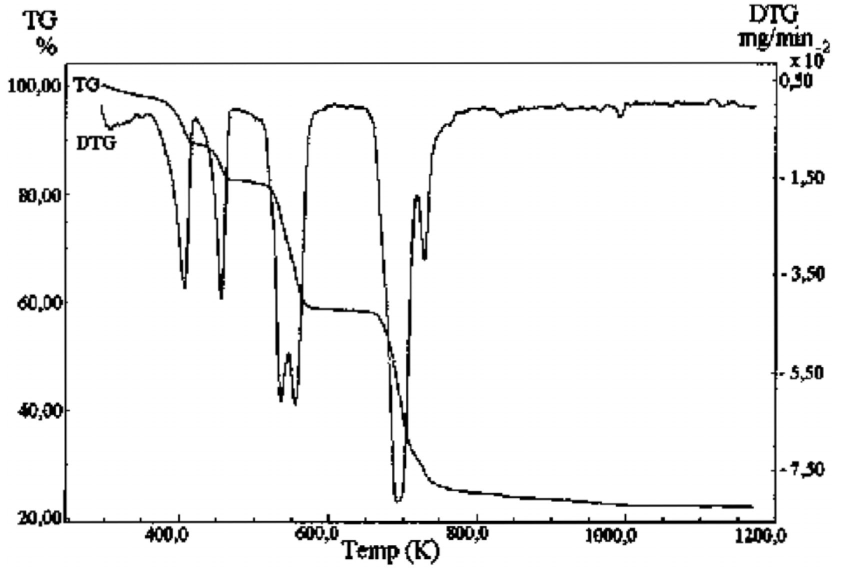

FIGURE 3 Thermogravimetric and derivative curves for $Y(MS)_3A(3\text{-picNO})_2$.

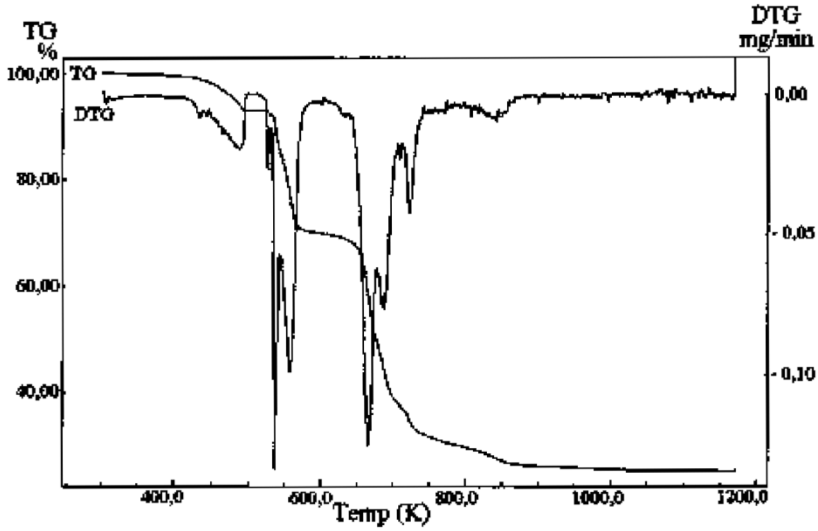

FIGURE 4 Thermogravimetric and derivative curves for $Y(MS)_3A(4\text{-picNO})_2$.

The infrared data are in agreement with those previously obtained for similar compounds [2–4] and confirm the identity of the synthesized adducts.

The thermogravimetric and derivative curves for the compounds synthesized at a heating rate of $2.5\,K\,min^{-1}$ are shown in Figs. 1–4. The mass loss steps observed for the compounds at the four heating rates of 2.5, 5, 10 and $20\,K\,min^{-1}$ are summarized in Table II. These data show that lower heating rates provide experimental mass loss steps in better agreement with the calculated values. For all compounds the ligand

TABLE II Thermogravimetric results for the compounds studied. $\beta$ is the heating rate, $\Delta T$ is the temperature range for the considered mass loss step, $\Delta m$ is the percentage mass loss associated with the temperature range and $\Delta m_t$ is the calculated mass for the total release of the ligands

| *Compound* | $\beta/K\,\text{min}^{-1}$ | $\Delta T/K$ | $\Delta m/\%$ | $\Delta m_t/\%$ |
|---|---|---|---|---|
| Y(MS)$_3$A(py-NO)$_2$AH$_2$O | 2.5 | 438–466 | 3.8 | |
| | | 563–634 | 28.7 | 32.5 |
| | 5 | 441–473 | 3.4 | |
| | | 578–653 | 29.1 | 32.5 |
| | 10 | 442–491 | 3.2 | |
| | | 594–676 | 29.5 | 32.5 |
| | 20 | 466–502 | 3.4 | |
| | | 585–664 | 27.9 | 32.5 |
| Y(MS)$_3$A(2-picNO)$_3$ | 2.5 | 383–412 | 8.9 | |
| | | 445–462 | 6.9 | |
| | | 519–569 | 24.6 | 40.3 |
| | 5 | 384–421 | 5.9 | |
| | | 444–458 | 4.0 | |
| | | 546–590 | 28.7 | 40.3 |
| | 10 | 374–419 | 4.3 | |
| | | 450–478 | 4.9 | |
| | | 542–588 | 29.8 | 40.3 |
| | 20 | 376–423 | 4.4 | |
| | | 454–496 | 6.3 | |
| | | 549–597 | 29.2 | 40.3 |
| Y(MS)$_3$A(3-picNO)$_2$ | 2.5 | 448–487 | 12.6 | |
| | | 545–584 | 20.9 | 33.5 |
| | 5 | 458–504 | 11.4 | |
| | | 563–611 | 23.2 | 33.5 |
| | 10 | 451–517 | 8.8 | |
| | | 560–615 | 24.9 | 33.5 |
| | 20 | 465–541 | 9.0 | |
| | | 585–634 | 25.1 | 33.5 |
| Y(MS)$_3$A(4-picNO)$_2$ | 2.5 | 428–494 | 6.6 | |
| | | 530–567 | 23.2 | 29.8 |
| | 5 | 445–517 | 7.9 | |
| | | 533–581 | 21.7 | 29.8 |
| | 10 | 457–519 | 5.5 | |
| | | 558–594 | 22.3 | 29.8 |
| | 20 | 466–608 | 29.4 | 29.8 |

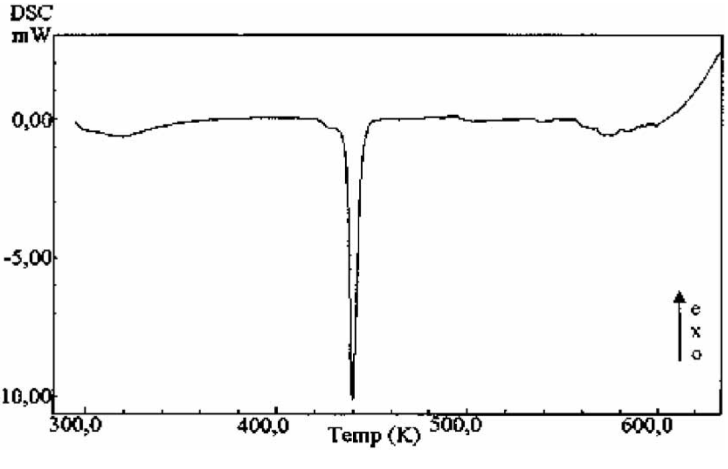

FIGURE 5 DSC curve for Y(MS)$_3$A(py-NO)$_2$AH$_2$O.

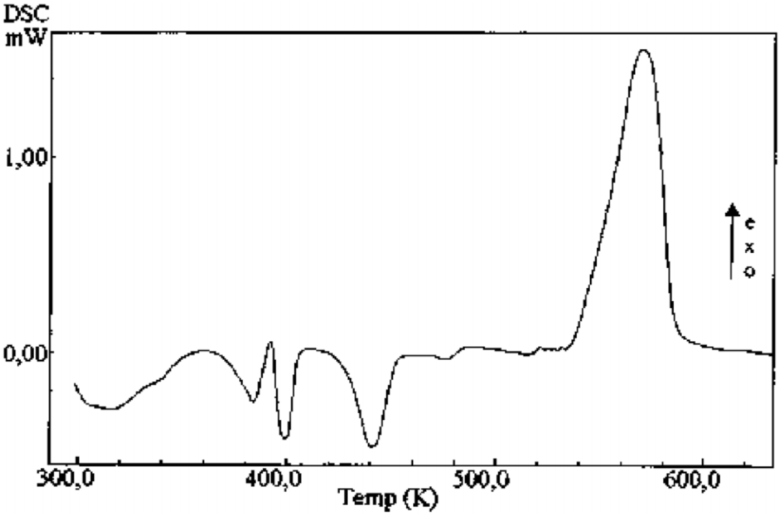

FIGURE 6 DSC curve for $Y(MS)_3A(2\text{-picNO})_3$.

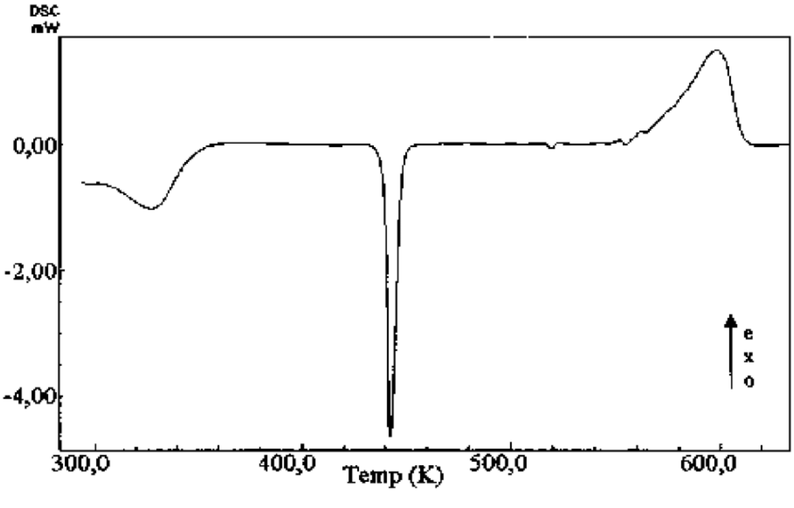

FIGURE 7 DSC curve for $Y(MS)_3A(3\text{-picNO})_2$.

release occurs in more than one step, suggesting that the ligand molecules are not in equivalent (from an energetic point of view) coordination sites.

The observed thermal stability trend is: 2-picNO $\approx$ 4-picNO < 3-picNO < py-NO. The lower thermal stability of the 2-picNO compound is probably due to the higher steric hindrance caused by the presence of the methyl group in the ortho position of the aromatic ring; that is, for this ligand, the metal–ligand bond is probably longer and weaker than for the other three ligands. The compound with py-NO is the most stable, probably due to formation of stronger Y–ligand bonds.

The DSC curves obtained are shown in Figs. 5–8. The main information extracted from the DSC curves is summarized in Table III. The sharp endothermic peaks

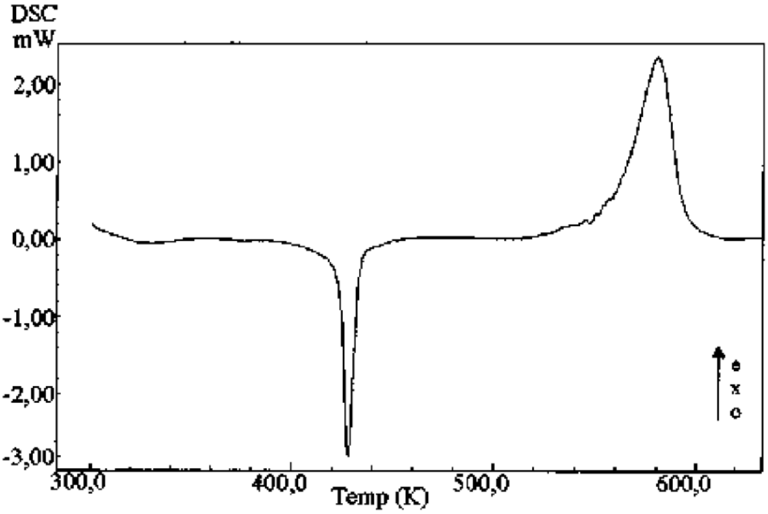

FIGURE 8 DSC curve for $Y(MS)_3A(4\text{-}picNO)_2$.

TABLE III DSC results for the compounds studied. $\Delta T$ is the temperature range for the considered enthalpy variation, $\Delta H$

| *Compound* | $\Delta T$/K | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|
| $Y(MS)_3A(py\text{-}NO)_2AH_2O$ | 416–457 | 108.0 |
| | 637– | – |
| $Y(MS)_3A(2\text{-}picNO)_3$ | 367–392 | 13.9 |
| | 395–405 | 15.2 |
| | 423–452 | 28.9 |
| | 537–587 | −160.3 |
| $Y(MS)_3A(3\text{-}picNO)_2$ | 438–449 | 112.8 |
| | 559–612 | −183.2 |
| $Y(MS)_3A(4\text{-}picNO)_2$ | 418–437 | 109.3 |
| | 543–597 | −265.4 |

observed for the compounds with py-NO, 3- and 4-picNO are associated with the melting of the compounds/release of ligand molecules. The well-defined exothermic peak observed for the compounds with picolines is associated with the thermal decomposition of the ligand molecules. Table III data also show that such endothermic peaks exhibits an increase from 2-picNO to 4-picNO.

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