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# SPECTROTHERMAL STUDIES OF 1,10-PHENANTHROLINE COMPLEXES OF Co(II), Ni(II), Cu(II) AND Cd(II) OROTATES

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The 1,10-phenanthroline (phen) complexes of Co(II), Ni(II), Cu(II) and Cd(II) orotates were synthesized and characterized by elemental analysis, magnetic susceptibility, spectral methods (UV-vis and FTIR) and thermal analysis techniques (TG, DTG and DTA). The Co(II), Ni(II), Cu(II) and Cd(II) ions in diaquabis(1,10-phenanthroline)metal(II) diorotate octahedral complexes $[M(H_2O)_2(phen)_2](H_2Or)_2 \cdot nH_2O$ ($M$=Co(II), $n$=2.25; Ni(II), $n$=3; Cu(II) and Cd(II), $n$=2) are coordinated by two aqua ligands and two moles of phen molecules as chelating ligands through their two nitrogen atoms. The monoanionic orotate behaves as a counter ion in the complexes. On the basis of the first $DTG_{max}$, the thermal stability of the hydrated complexes follows the order: Cd(II), 68°C<Ni(II), 74°C<Cu(II), 135°C<Co(II), 166°C in static air atmosphere.

***Keywords:*** *orotic acid complexes, 1,10-phenanthroline complexes, spectrothermal analysis*

## Introduction

Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid, vitamin $B_{13}$, $H_3Or$, Fig. 1) occupies a unique position biologically by being the only effective precursor in the biosynthesis of the pyrimidine based of nucleic acids [1–3]. Metal orotates are also widely applied in medicine. Recent interest has focused on the proposed biological carrier function of orotic acid and the corresponding anionic species for metal ions, which is held responsible for the obviously successful application of metal orotates in curing syndromes associated with a deficiency of a variety of metals such as calcium, magnesium, zinc or iron [4, 5]. Besides biologically important, orotic acid is also an interesting ligand in coordination chemistry. It may coordinate through the two nitrogen atoms of the pyrimidine ring, the two carbonyl oxygens and the carboxyl group. Although, the most potential coordination sites are the deprotonated carboxyl group and its adjacent nitrogen, when they coordinate to metal ion, the complexation ability of the exocylic carbonyl oxygen is greatly enhanced [6]. Owing to the biological interest in orotic acid complexes, several investigators have focused their attention on the coordinating properties of the acid. It was found that, in neutral or slightly acidic environment, it coordinates through the carboxylate group while in basic surroundings it coordinates through the carboxylate and the adjacent $N_{(3)}$ [7–11]. The crystal structure determination of the complexes confirms the bidentate coordination of orotic acid through $N_{(3)}$ and the carboxylate group [12–18]. In the $[Ni(HOr)(H_2O)_3]$, $[M(HOr)bipy(H_2O)]$ ($M$=Mn(II), Co(II)) [19], $[Co(HOr)(OH)(H_2O)(NH_3)]_n$ and $[Ni(HOr)(OH)(H_2O)_2(NH_3)]_n$ complexes [20] the orotate anion acts as a bridge between the metal ions forming one-dimensional polymeric chains, its coordination sites being the carboxylate and the $N_{(3)}$ and $O_{(4)}$ atoms. In the polymeric copper(II)-orotato complexes, $[Cu(HOr)(H_2O)_2]_n$, the molecules form chains in a way that the carboxylate group acts as a bridge between the metal ions and the orotato-group being tridentate [21].

In the present paper, the synthesis, spectroscopic properties and thermal decomposition of the Co(II), Ni(II), Cu(II) and Cd(II) complexes with orotic acid and 1,10-phenanthroline (Fig. 1) are reported.

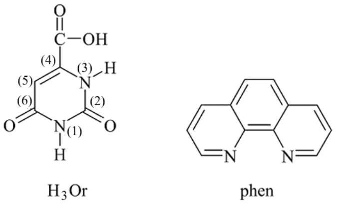

**Fig. 1** Structures of the ligands: $H_3Or$=orotic acid; phen=1,10-phenanthroline

## Experimental

### *Materials and instrumentation*

All chemicals used were analytical reagent products. Elemental analyses for C, H and N were carried out at

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**Table 1** Analytical data and conductance values of the metal complexes

| Complex | F.W./g mol$^{-1}$ | Found (calc.)/% | | | Yield/ % | Colour | Λ/S cm$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | C | N | H | | | |
| $[Co(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2.25H_2O$<br>$C_{34}H_{30.5}N_8O_{12.25}Co$ | 806.09 | 50.79<br>(50.66) | 4.01<br>(3.81) | 13.56<br>(13.90) | 73 | orange | 106 |
| $[Ni(H_2O)_2(phen)_2](H_2Or)_2{\cdot}3H_2O$<br>$C_{34}H_{32}N_8O_{13}Ni$ | 819.36 | 49.50<br>(49.84) | 3.79<br>(3.94) | 13.61<br>(13.68) | 88 | pink | 105 |
| $[Cu(H_2O)_2(phen)_2](H_2Or)_2.2H_2O$<br>$C_{34}H_{30}N_8O_{12}Cu$ | 806.20 | 50.59<br>(50.65) | 3.60<br>(3.75) | 13.63<br>(13.90) | 87 | green-blue | 98 |
| $[Cd(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2H_2O$<br>$C_{34}H_{30}N_8O_{12}Cd$ | 855.07 | 48.04<br>(47.76) | 3.95<br>(3.54) | 12.87<br>(13.10) | 66 | colourless | 117 |

the Tübitak Marmara Research Centre. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. UV-vis spectra were obtained for the aqueous solutions ($10^{-3}$ M) of the complexes with a Unicam UV2 spectrometer in the range of 900–190 nm. IR spectra were recorded in the 4000–500 cm$^{-1}$ region with a Mattson 1000 FTIR spectrometer using KBr pellets. Thermal analysis curves (TG, DTG and DTA) were recorded simultaneously in a static air atmosphere with a Rigaku TG8110 thermal analyser. The heating rate was 10°C min$^{-1}$ and the DTG sensitivity was 0.05 mg s$^{-1}$. Conductance values were measured on 522 CRISON conductimeter.

### *Synthesis of $[M(HOr)(H_2O)_4]{\cdot}H_2O$ complexes*

A solution of sodium orotate (0.890 g, 5 mmol) in distilled water (20 mL) was added dropwise with stirring at 60°C to a solution of $MCl_2{\cdot}xH_2O$ (5 mmol; $M$=Co(II), 1.185 g; Ni(II), 1.185 g; Cu(II), 0.850 g, Cd(II), 0.917; $x$=7, 7, 2 and 0, respectively) in distilled water (20 mL). The mixture was stirred for 4 h at 60°C and then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of cold distilled water and dried in air.

### *Synthesis of $[M(H_2O)_2(phen)_2](H_2Or)_2{\cdot}nH_2O$ (M=Co(II), n=2.25; Ni(II), n=3; Cu(II) and Cd(II), n=2)*

A solution of phen (0.792 g, 4 mmol) in ethanol (10 mL) was added dropwise with stirring to a solution of $[M(HOr)(H_2O)_4]{\cdot}H_2O$ (2.0 mmol; $M$=Co(II), 0.605 g; Ni(II), 0.605 g; Cu(II), 0.615 g and Cd(II), 0.697 g) in hot distilled water (30 mL). The solutions were heated to 60°C in a temperature-controlled bath and stirred for 4 h. The reaction mixtures were then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of cold distilled water and ethanol and dried in air.

## Results and discussion

### *Structures of the complexes*

Analytical results and the molar conductivity values of the complexes are listed in Table 1. The complexes were synthesized in good yields and with high purity. All complexes were found to be nonhygroscopic and stable in air. The results of elemental analyses show that two phen and two aqua ligands have been incorporated into the M(II) orotates ($M$=Co(II), Ni(II), Cu(II) and Cd(II)). The complexes have pseudooctahedral geometries with two phen molecules coordinated to the metal ions as chelating ligands through their two N atoms and two aqua ligands in the *cis* positions. Also the monoanionic orotate behaves as a counter ion in the complexes. This result was supported by conductivity measurements. The molar conductance values (Λ) of the Co(II), Ni(II), Cu(II) and Cd(II) complexes are 106, 105, 98 and 117 S cm$^2$ mol$^{-1}$, respectively, indicating that the complexes are electrolyte in 1:2 ratio in water and the orotate behaves as a counter ion.

### *UV-vis spectra and magnetic moments of the complexes*

The $\lambda_{max}$ and ε values of the various absorption bands, $\Delta_0$ (10 Dq) values of *d–d* transitions displayed by the complexes, assignments of *d–d* transitions and the effective magnetic moment values of the complexes are given in Table 2. The Co(II), Ni(II) and Cu(II) complexes exhibit magnetic moment values of 4.27, 2.41 and 1.64 BM which corresponds to three, two and one unpaired electrons, respectively, which are consistent with a weak field octahedral geometry as expected. The Cd(II) complex is diamagnetic.

All the complexes comprise broad composite bands in the UV region. These bands exhibit mainly three maxima at about 206, 233 and 278 nm, being due to π→π* and *n*→π* intraligand transitions of $H_2Or$ and phen. The assignments of *d–d* transitions corresponded to an octahedral coordination geometry of the metal ions and the values of $\Delta_0$ parameter, Racah parameter (*B*') and nephelauxetic ratio

**Table 2** Electronic spectra and magnetic moments of the metal complexes

| Complex | $\lambda_{max}$/cm$^{-1}$ | $\varepsilon$/L cm$^{-1}$ mol$^{-1}$ | Assignment of *d–d* transitions | $\Delta_0$/cm$^{-1}$ | $\mu_{eff}$/BM |
|---|---|---|---|---|---|
| $[Co(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2.25H_2O$ | (23717)*<br>21142<br>11236 | –<br>42<br>18 | $^4T_{1g} \rightarrow {}^4A_{2g}$<br>$^4T_{1g} \rightarrow {}^4T_{1g}(P)$<br>$^4T_{1g} \rightarrow {}^4T_{2g}$ | 12481 | 4.27 |
| $[Ni(H_2O)_2(phen)_2](H_2Or)_2 \cdot 3H_2O$ | (29771)*<br>19157<br>12853 | –<br>15<br>10 | $^3A_{2g} \rightarrow {}^3T_{1g}(P)$<br>$^3A_{2g} \rightarrow {}^3T_{1g}$<br>$^3A_{2g} \rightarrow {}^3T_{2g}$ | 12853 | 2.41 |
| $[Cu(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2H_2O$ | 14570 | 48 | $^2E_g \rightarrow {}^2T_{2g}$ | 14570 | 1.64 |
| $[Cd(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2H_2O$ | – | – | – | – | Dia. |

*calculated

($B'/B=\beta$) values for the Co(II) and Ni(II) complexes were found using Tanabe–Sugano diagrams [22]. The $\lambda_{max}$ values of the first two absorption bands in the spectra of $[Co(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2.25H_2O$ are 11236 ($\varepsilon$=18 L mol$^{-1}$ cm$^{-1}$) and 21142 cm$^{-1}$ ($\varepsilon$=42 L mol$^{-1}$cm$^{-1}$). These values were assigned to the following *d–d* transitions, $\nu_1$: $^4T_{1g} \rightarrow {}^4T_{2g}$ and $\nu_2$: $^4T_{1g} \rightarrow {}^4T_{1g}(P)$, respectively. $\nu_3$: $^4T_{1g} \rightarrow {}^4A_{2g}$ transition was not observed which is of high energy and shifts to the UV region and hidden under the intraligand transitions in the spectrum. The $B'$, $\nu_3$ and $\Delta_0$ values for the cobalt complex were found as 744, 23717 and 12481 cm$^{-1}$, respectively. The nephelauxetic ratio ($B'/B=\beta$) was calculated as 0.77 by using 971 cm$^{-1}$ for the free Co(II) ion.

The UV-vis spectrum for $[Ni(H_2O)_2(phen)_2](H_2Or)_2 \cdot 3H_2O$ exhibits two weak *d–d* absorption transitions centred at 12853 ($\varepsilon$=10 L mol$^{-1}$ cm$^{-1}$) and 19157 cm$^{-1}$ ($\varepsilon$=15 L mol$^{-1}$ cm$^{-1}$) which support the octahedral geometry. These values were assigned to $\nu_1$: $^3A_{2g} \rightarrow {}^3T_{2g}$, and $\nu_2$: $^3A_{2g} \rightarrow {}^3T_{1g}$, respectively. The $\nu_3$: $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition was not observed, which is of high energy and shifts to the UV region and overlapped by the intraligand transitions in the spectrum. The $B'$, $\nu_3$ and $\Delta_0$ values for the nickel complex were found as 691, 29771 and 12853 cm$^{-1}$, respectively. The nephelauxetic ratio ($B'/B=\beta$) was calculated as 0.67 by using 1030 cm$^{-1}$ for the free Ni(II) ion.

The UV-vis spectrum for the complex $[Cu(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2H_2O$ exhibits a very broad *d–d* absorption transition centred at 14570 cm$^{-1}$ ($\varepsilon$=48 L mol$^{-1}$ cm$^{-1}$). This value was assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition, thereby suggesting octahedral geometry around Cu(II). The $\Delta_0$ value for the Cu(II) complex was obtained as 14570 cm$^{-1}$.

The colourless Cd(II) complex does not show the *d–d* bands as expected.

## *IR spectra*

The main IR group frequencies of the metal complexes are presented in Table 3. $\nu_{OH}$ stretching of the coordinated and crystal water molecules appears in the range of 3371–3603 cm$^{-1}$. The coordinated water appears at frequencies lower than those of the crystal water [23]. The $N_{(3)}H$ stretching band at 3160 cm$^{-1}$ of orotic acid [7] was clearly observable as strong at 3151, 3155, 3149 and 3161 cm$^{-1}$ in the IR spectrum of the Co(II), Ni(II), Cu(II), Cd(II) complexes, respectively.

The IR spectra of the all complexes resemble each other and show the characteristic $\nu_{C=O_{acid}}+\nu_{C_{(2)}=O}$ and $\nu_{C_{(6)}O}+\nu_{C=C}$ absorption bands of the $H_2O_r$ moiety. The stretching modes of the carbonyl groups are used most frequently for structural studies of various orotates [7, 17, 18]. Strong absorption bands in the range of 1620–1705 cm$^{-1}$ characterize the C=O group of the $H_2Or$ moiety in the complexes. The carbonyl groups appear as two main peaks at 1709 cm$^{-1}$

**Table 3** IR spectra of the metal complexes

| Complex | $\nu_{OH}$ | $\nu_{N_{(3)}H}$ | $\nu_{N_{(1)}H}$ | $\nu_{OH_{acid}}$ | $\nu_{C=O_{acid}}+\nu_{C_{(2)}=O}$ | $\nu_{C_{(6)}=O}+\nu_{C=C}$ |
|---|---|---|---|---|---|---|
| Orotic acid | 3524 s | 3160 s | 3020 m<br>2835 m | 2500 w,b | 1709 vs | 1671 vs |
| $[Co(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2.25H_2O$ | 3603 m<br>3396 s | 3151 s | 3090 m | – | 1707 vs | 1640 s |
| $[Ni(H_2O)_2(phen)_2](H_2Or)_2 \cdot 3H_2O$ | 3380 s | 3155 s | 3088 m | – | 1703 vs | 1622 s |
| $[Cu(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2H_2O$ | 3371 s | 3149 s | 3050 m | – | 1703 vs | 1625 s |
| $[Cd(H_2O)_2(phen)_2](H_2Or)_2 \cdot 2H_2O$ | 3598 m<br>3394 s | 3161 s | 3060 m | – | 1705 vs | 1639 vs |

[a] Abbreviations: m – medium, w – weak, s – strong, vs – very strong, b – broad

$[\nu_{C=O_{acid}} + \nu_{C_{(2)}=O}]$ and 1671 $cm^{-1}$ $[\nu_{C_{(6)}O} + \nu_{C=C}]$ in the free $H_3Or$ [7]. The carbonyl stretching modes in the Co(II), Ni(II), Cu(II) and Cd(II) complexes were observed at 1704, 1620 $cm^{-1}$; 1703, 1625 $cm^{-1}$; 1703, 1625 $cm^{-1}$ and 1705, 1639 $cm^{-1}$, respectively. The $\nu_{OH(acid)}$ vibration bands which appeared at 2500 $cm^{-1}$ in the free orotic acid have not been observed in the all complexes. The disappearance of the bands was attributed to the deprotonation.

The $\nu_{C_{(4)}-C_{(5)}}$ was observed at 1312 $cm^{-1}$, which appears as a main peak at 1295 $cm^{-1}$ in the free $H_3Or$ [7], in the $[Co(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2.25H_2O$ complex whose crystal structure has been determined [24]. In this complex, monoanionic orotate behaves as a counter ion. The $\nu_{C_{(4)}-C_{(5)}}$ of the Ni(II), Cu(II) and Cd(II) complexes, appeared at 1310, 1337 and 1335 $cm^{-1}$, respectively. As a result, the IR spectrum of the complexes indicates that the orotic acid is monoanionic and counter ion as supported by X-ray [24, 25] and conductivity measurements.

### *Thermal analysis*

The thermal analysis curves of the studied complexes are shown in Figs 2–5.

Thermal decomposition of $[Co(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2.25H_2O$ proceeds in four stages (Fig. 2). The broad endothermic peak ($DTG_{max}$=166°C), in the temperature range of 37–188°C, corresponds to the loss of 2 moles of coordinated water and 2.25 moles of crystallization water (found 10.43, calcd. 9.49%). The anhydrous Co(II) complex is stable up to 235°C. The second and third stages, in the temperature range of 235–410°C, are related to the consecutive decomposition of phen and the decarboxylate of orotate, respectively. During these stages, the Co(II) complex releases one phen and two $CO_2$ molecules (found 32.91, calcd. 33.27%). This type of behaviour of neutral ligands in the saccharinato [26, 27], salicylato [28], isoorotato and 2-thioisoorotato [29] complexes has been reported earlier. The exothermic and endothermic effects at about 264 and 377°C, respectively, are likely due to the release of phen and $CO_2$. The IR spectra of the Co(II) complex heated just to the end of this mass loss show no evidence of $CO_2$ bands. In the last stage, the strong exothermic peak ($DTG_{max}$: 452°C) is associated with the burning of organic residue, leading finally to the $Co_3O_4$. The endothermic peak at 905°C is related to the conversion of $Co_3O_4$ to CoO. The over-

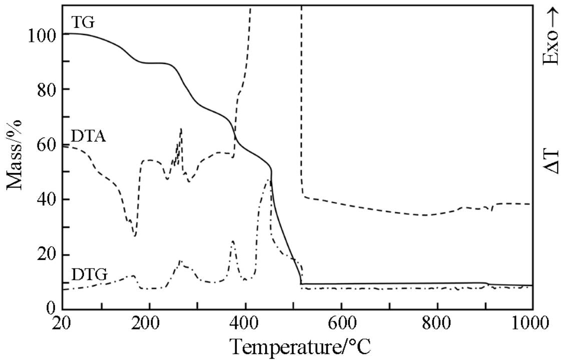

**Fig. 2** TG, DTG and DTA curves of $[Co(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2.25H_2O$

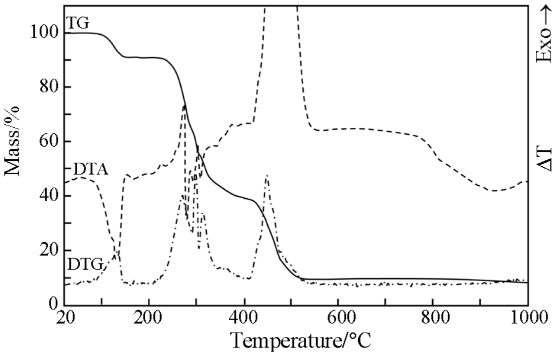

**Fig. 4** TG, DTG and DTA curves of $[Cu(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2H_2O$

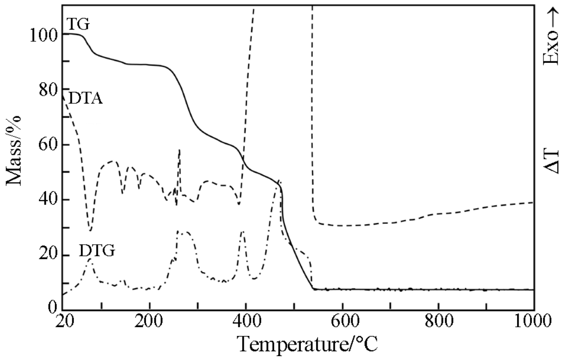

**Fig. 3** TG, DTG and DTA curves of $[Ni(H_2O)_2(phen)_2](H_2Or)_2{\cdot}3H_2O$

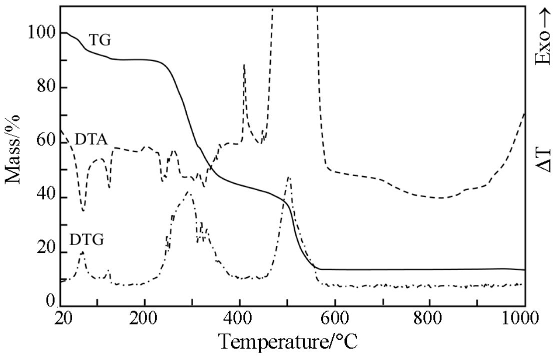

**Fig. 5** TG, DTG and DTA curves of $[Cd(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2H_2O$

all mass loss (found 91.87, calcd. 90.71%) agrees with the proposed structure well.

The thermal analysis curves of the $[Ni(H_2O)_2(phen)_2](H_2Or)_2{\cdot}3H_2O$ complex (Fig. 3) is similar with the Co(II) compound (Fig. 2). The complex mainly exhibits four stages of decomposition. In the stage of range 43–184°C, involves endothermic decomposition at 74, 145 and 179°C (DTG) corresponding to the loss of five moles of water molecules as indicated by TG mass loss (found 11.09, calcd. 10.93%). In the second and third stages, the successive decomposition process is initially exothermic, an endothermic contribution is also observed in the DTA curve of the complex. In these stages of the complex, one mole of phen and two moles of $CO_2$ are released ($DTG_{max}$: 262, 397°C). In the fourth stage, remaining organic part is abruptly burnt ($DTG_{max}$: 473°C), leading finally to the NiO (found 92.12, calcd. 90.84%).

The thermal decomposition pathway of the complex $[Cu(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2H_2O$, presented in Fig. 4, is well-defined, consisting of four stages. The first stage is related to the dehydration in the temperature interval of 53–177°C, the four moles of water molecules are released by giving endothermic effect at 135°C ($DTG_{max}$). A good agreement between the experimental and the calculated values was observed for the mass loss (found 8.55; calcd. 8.94%). The anhydrous complex is stable in air up to 218°C. In the second stage, in the temperature range of 218–340°C, the Cu(II) complex undergoes the decomposition of the two moles of phen ligand giving exothermic effect ($DTG_{max}$=270°C, found 43.06, calcd. 44.71%). The third stage is related to the release of $CO_2$ from the orotate (found 9.89, calcd. 10.92%). The isoorotic acid and 2-thioisoorotic acid-metal complexes and their ammonium, sodium and barium salts decompose by releasing of $CO_2$ [29, 30]. The last strong exothermic stage can be assigned to the combustion of the residual organic matter. The final solid product of thermal decomposition was identified as CuO (found 89.07, calcd. 90.13%).

The $[Cd(H_2O)_2(phen)_2](H_2Or)_2{\cdot}2H_2O$ complex is decomposed at three stages (Fig. 5). The thermal dehydration of the complex occurs by giving endothermic effects at 68 and 124°C ($DTG_{max}$). The TG curve of the complex shows a mass loss in the range of 56–143°C corresponding to the loss of two moles of coordinated water and two moles of crystal water (found 9.54, calcd. 8.43%). The second stage is related to the decomposition of neutral two moles of phen ligand and two moles of $CO_2$. The Cd(II) compound shows an exothermic effect at about 445°C that can be assigned to the phase transition. The strong exothermic peak is associated with the burning of the organic residue in the range of 478–576°C. The final decomposition product, namely CdO was identified by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides. The total mass loss is found as 86.18% (calcd. 84.18%).

Based on the initial $DTG_{max}$ temperatures, the thermal stabilities of the complexes follow the sequence: Cd(II), 68°C<Ni(II), 74°C<Cu(II), 135°C<Co(II), 166°C.

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