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OROTIC ACID COMPLEXES OF Co(II), Ni(II), Zn(II) AND Cd(II) WITH IMIDAZOLE
Syntheses, spectroscopic and thermal studies

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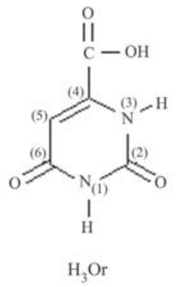
The $[Co(HOr)(H_2O)_2(im)_2]$ (**1**), $[Ni(HOr)(H_2O)_2(im)_2]$ (**2**), $[Zn(H_2O)_2(im)_4](H_2Or)_2$ (**3**) and $[Cd(HOr)(H_2O)(im)_3]$ (**4**) complexes (H_3Or: orotic acid, im: imidazole) were synthesized and characterized by elemental analysis, magnetic and conductance measurements, UV-vis and IR spectra. The thermal behaviour of the complexes was also studied by simultaneous thermal analysis techniques (TG, DTG and DTA). The orotate ligand (HOr^{2-}) coordinated to the Co(II), Ni(II) and Cd(II) ions are chelated to the deprotonated pyrimidine nitrogen ($N_{(3)}$) and the carboxylate oxygen, while do not coordinate to the Zn(II) ion is present as a counter-ion (H_2Or^-). The first thermal decomposition process of all the complexes is endothermic deaquation. This stage is followed by partially (or completely) decomposition of the imidazole and orotate ligands. In the later stage, the remained organic residue exothermically burns. On the basis of the first DTG_{max}, the thermal stability of the complexes follows order: **2**, 176°C>**1**, 162°C>**4**, 155°C>**3**, 117°C in static air atmosphere. The final decomposition products which identified by IR spectroscopy were the corresponding metal oxides.

Keywords: *imidazole complexes, orotic acid complexes, thermal analysis*

Introduction

Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid, vitamin B_{13}, H_3Or, Fig. 1) and its salts and other derivatives play an important role in the metabolism of pyrimidine nucleotides [1, 2] and are found in cell and body fluids of many living organisms. Metal orotates are also widely applied in medicine. Metal orotates have been used e.g. as uricosurica (for enhanced excretion of uric acid) and for electrolyte substitution (in heart and liver protection) [3]. Platinum, palladium and nickel orotates with wide variety of substituents have been screened as therapeutic agents for cancer [4–7]. Besides biologically importance, 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 [8]. The complexes of HOr^{2-} of Mn(II), Co(II), Ni(II), Zn(II), Mg(II) ($[M(HOr)(H_2O)_4]\cdot H_2O$) were reported [4, 5, 9–12]. Synthesis and structural characterization of mixed-ligand transition metal complexes of HOr^{2-} with mono- and bidentate N-donor ligands such as ammine [6, 13, 14], imidazole [15], 1,10-phenanthroline [16, 17], 2,2'-bipyridine [17, 18] and ethylenediamine [12, 19] appear in recent literature. We reported earlier the syntheses and spectrathermal studies of 1,10-phenanthroline complexes of Co(II), Ni(II), Cu(II) and Cd(II) orotates [20], $[Zn(H_2O)_2(phen)_2](H_2Or)_2\cdot 2.125H_2O$ [21], $[Cu(HOr)(tea)]\cdot H_2O$ [22], $[Cu(HOr)(H_2O)(bipy)]$ [18], $[Cu(HOr)(H_2O)(en)]\cdot H_2O$, $[Co(HOr)(en)_2](H_2Or)\cdot 5H_2O$ [12], $[Ni(HOr)(H_2O)(tea)]\cdot H_2O$ [23], $[Co(HOr)(H_2O)_3(na)]\cdot 3H_2O$ [24] and Co(II), Ni(II) and Cu(II) complexes of neutral orotic acid [25] (*phen*=1,10-phenanthroline; *tea*=triethanolamine; *bipy*=2,2'-bipyridine; *en*=ethylenediamine; *na*=nicotinamide).

In the present paper, we describe the syntheses, spectroscopic and thermal behaviour of the new orotic acid complexes of Co(II), Ni(II), Zn(II) and Cd(II) with imidazole.



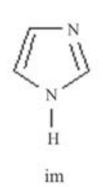


Fig. 1 Structures of the ligands: H_3Or=orotic acid, im=imidazole

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Table 1 Analytical data and conductance values of **1**–**4**

Complexes	F.W./g mol^{-1}	Found (Calc.)/%			Yield/%	Colour	Λ/S cm^2 mol^{-1}
		C	N	H			
[Co(HOr)(H_2O)$_2$(im)$_2$] (**1**) $C_{11}H_{14}N_6O_6Co$	385.20	34.04 (34.30)	3.86 (3.66)	21.99 (21.82)	86	red	24
[Ni(HOr)(H_2O)$_2$(im)$_2$] (**2**) $C_{11}H_{14}N_6O_6Ni$	384.96	33.72 (34.32)	3.75 (3.67)	21.66 (21.83)	84	blue	26
[Zn(H_2O)$_2$(im)$_4$](H_2Or)$_2$ (**3**) $C_{22}H_{26}N_{12}O_{10}Zn$	683.91	39.22 (38.64)	4.03 (3.83)	24.05 (24.58)	60	colourless	103
[Cd(HOr)(H_2O)(im)$_3$] (**4**) $C_{14}H_{16}N_8O_5Cd$	488.74	33.45 (34.41)	3.27 (3.30)	23.45 (22.93)	67	colourless	30

Experimental

Materials and instrumentation

All chemicals used were analytical reagent products.

Synthesis of the complexes

The divalent metal complexes of HOr^{2-}, [M(HOr)(H_2O)$_4$]·H_2O (*M*=Co(II), Ni(II), Zn(II) and Cd(II)), were prepared according to the conventional methods described in [4, 5, 12]. The [M(HOr)(H_2O)$_4$]·H_2O complexes (*M*=Co(II), Ni(II), Zn(II) and Cd(II), 2 mmol, 0.62 g) were dissolved in hot distilled water (20 mL) with stirring at 60°C. The im ligand (8 mmol, 0.55 g), which dissolved in the ethanol (10 mL), was added to the solutions of the [M(HOr)(H_2O)$_4$]·H_2O with continuous stirring for approximately 5 h at 60°C in a temperature-controlled bath. The reaction mixture was then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of water and ethanol and dried in air.

Elemental analyses for C, H and N were carried out at the Tubitak Marmara Research Centre. Magnetic susceptibility measurements at room temperatures 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 900–190 nm. IR spectra were recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FT-IR 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.

Results and discussion

Analytical results, the molar conductivity values and the compositions of the complexes are listed in Table 1. **1**–**4** were synthesized in good yields and with high purity and found to be nonhygroscopic and stable in air. **2** was also structurally characterized [15]. The elemental analyses conformed to their proposed formula (Table 1). The molar ratio M:im:HOr:H_2O in the complexes are 1:2:1:2 for **1** and **2**, 1:4:2:2 for **3** and 1:3:1:1 for **4**. In the complexes, imidazole acts as a monodentate ligand through its nitrogen atom, while dianionic orotate ligand (HOr^{2-}) coordinates to the Co(II), Ni(II) and Cd(II) ions as a bidentate, through carboxylate oxygen and deprotonated nitrogen atom of pyrimidine ring. But, monoanionic orotate (H_2Or^{-}) behaves as a counter ion in **3**. These results were supported by conductivity measurements. The molar conductance values (Λ) of the complexes are 24, 26, 103 and 30 Scm^2 mol^{-1} for **1**, **2**, **3** and **4**, respectively, indicating that **1**, **2** and **4** are a non electrolyte, while **3** is a 1:2 electrolyte in water.

UV-Vis spectra

The λ_{max} values of the intraligand and *d*–*d* transitions displayed, assignment of *d*–*d* transitions and the effective magnetic moment values of the complexes are given in Table 2. **1** and **2** exhibit magnetic moment values of 4.38 and 2.92 BM which correspond to three and two unpaired electrons, respectively, which are consistent with a weak field octahedral geometry as expected. **3** and **4** are diamagnetic.

The intense bands in the 200–300 nm range are assigned to the intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, and the bands with low intensity between 350 and 800 nm are due to *d*–*d* transitions. The assignments of the *d*–*d* transitions corresponded to an octahedral coordination geometry of the metal(II) ions and the values of the Δ_0 parameter were found using Tanabe and Sugano diagrams [26]. **1** displays one peak in the visible region of the electronic spectrum, while **2** shows three maxima in the 350–900 range. **3** and **4** did not display any peak in the visible region, but only exhibit the intraligand transitions. In the spectrum of 1, the λ_{max} value of the absorption band is 493 nm (ε=26 L mol^{-1} cm^{-1}). This value may be assigned to the $^4T_{1g} \rightarrow ^4T_{1g}$ (P) *d*–*d* transition. The $^4T_{1g} \rightarrow ^4A_{2g}$, and

Table 2 Electronic spectra and magnetic moment values of **1–4**

Complexes	λ_{max}/nm	ε/cm^{-1} mol^{-1}	Assignment of *d–d* transitions	Δ_0/cm^{-1}	μ_{eff}/(B.M.)
$[Co(HOr)(H_2O)_2(im)_2]$ (**1**)	493	26	$^4T_{1g}\rightarrow{}^4T_{1g}(P)$	–	4.38
$[Ni(HOr)(H_2O)(im)_2]$ (**2**)	379	26	$^3A_{2g}\rightarrow{}^3T_{1g}(p)$	11.230	2.92
	624	7	$^3A_{2g}\rightarrow{}^3T_{1g}$		
	890	4	$^3A_{2g}\rightarrow{}^3T_{2g}$		
$[Zn(H_2O)_2(im)](H_2O)_2$ (**3**)	–		–	–	Dia.
$[Cd(HOr)(H_2O)(im)_3]$ (**4**)	–		–	–	Dia.

$^4T_{1g}\rightarrow{}^4T_{2g}$ transitions were not observed due to low energy and shift to the IR region [27]. Therefore, the Δ_0 value of **1** could not be calculated. The UV-vis spectrum for **2** exhibits three weak *d–d* absorption bands centered at 379 (ε=26 L mol^{-1} cm^{-1}), 624 (ε=7 L mol^{-1} cm^{-1}) and 890 nm (ε=4 L mol^{-1} cm^{-1}) which support octahedral geometry. These values were assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$,(P), $^3A_{2g}\rightarrow{}^3T_{1g}$ and $^3A_{2g}\rightarrow{}^3T_{2g}$, respectively. The Δ_0 value for **2** was calculated as 11.230 cm^{-1}. The colourless **3** and **4** do not show any *d–d* bands as expected.

IR spectra

The main IR group frequencies of the metal complexes are presented in Table 3. OH stretching bands of aqua ligands appear in the 3475, 3462, 3500 and 3325 cm^{-1} for **1**, **2**, **3** and **4**, respectively. In **1**, **2** and **4**, the disappearance of the $\nu_{N_{(3)}H}$ band at 3160 cm^{-1} which was observed in the free orotic acid [6], was attributed to the deprotonation and coordination of $N_{(3)}$ to the metal ions. However, the $N_{(3)}H$ stretching band was clearly observable as strong at 3144 cm^{-1} in the IR spectrum of **3**. The band in the 3136–3222 region in the complexes can be attributed NH stretching vibration of the imidazole ligand. This data substantiates the suggestion that the imidazole molecules coordinate to the metal ions in their neutral form. The carbonyl groups appear as two main peaks at 1709 [$\nu_{C=O_{(acid)}}+\nu_{C_{(2)}=O}$] and 1671 cm^{-1} [$\nu_{C_{(6)}=O}+\nu_{C=C}$] in the free H_3Or [28]. The carbonyl stretching modes in **3** and **4** were observed at 1674, 1613 cm^{-1} and 1635, 1594 cm^{-1}, while the very broad and strong one band at 1617 and 1618 cm^{-1} in **1** and **2**, respectively, which are prescribed to overlapped C=O and C=C stretching, and bending water and amine modes. The medium-intense band at 1531–1581 cm^{-1} region can be attributed to the imidazole (–C=N–) stretching vibration. The $\nu_{OH_{(acid)}}$ vibration bands which appeared at 2500 cm^{-1} in the free orotic acid have not been observed in all the complexes. The disappearance of the bands was attributed to the deprotonation. The weak bands in the region 400–500 cm^{-1} are due to M–N stretching vibrations [29]. As a result, the IR spectrum of **3** indicates that the orotic acid is monoanionic and counter ion as supported by conductivity measurements, while the IR spectra of **1**, **2** and **4** show that orotic acid is dianionic and coordinated to the metal ions as a bidentate via deprotonated $N_{(3)}$ of pyrimidine and the carboxylate oxygen.

Thermal analyses

The TG-DTG and DTA curves of the complexes are shown in Figs 2–5. The endothermic peak of **1** (DTG_{max}=171°C) in the temperature range of 103–186°C, corresponds to the loss of the two moles aqua ligands (found 10.59, calcd. 9.35%). In the temperature range of 187–380°C, **1** involves the consecutive decompositions of neutral imidazole ligands by giving endothermic effects (DTG_{max}=228 and 301°C). A good agreement between the experimental and calculated values was observed for the mass loss (found 35.10; calcd. 35.35%). The following stage involves

Table 3 IR spectra of **1–4** (cm^{-1})

Complexes	ν_{OH}	$\nu_{N_{(3)}}+\nu_{NH_{im}}$ *	$\nu_{N_{(1)}H}$	$\nu_{C=O_{asit}}+\nu_{C_{(2)}=O}$	$\nu_{C_{(6)}=O}+\nu_{C=C}$	$\nu_{C=N}$	$\delta_{N_{(1)}H}+\delta_{NH_{im}}$ *
$[Co(HOr)(H_2O)_2(im)_2]$ (**1**)	3475m	3222*s	3075w	1617vs,b		1531s	1380*m, 1406w
$[Ni(HOr)(H_2O)_2(im)_2]$ (**2**)	3462m	3220*s	3050w	1618vs,b		1543s	1382*m, 1407w
$[Zn(H_2O)_2(im)](H_2O)_2$ (**3**)	3500s	3144, 3247*m	3053m	1674vs	1613vs	1581s	1384*w, 1425m
$[Cd(HOr)(H_2O)(im)_3]$ (**4**)	3325m	3136*m	3017m	1635vs	1594vs	1534s	1387*s, 1440m

w – weak, m – medium, s – strong, vs – very strong, b – broad

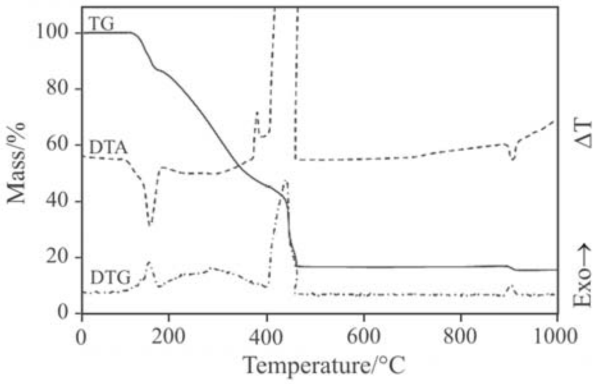

Fig. 2 TG, DTG and DTA curves of [Co(HOr)$(H_2O)_2$$(im)_2$]

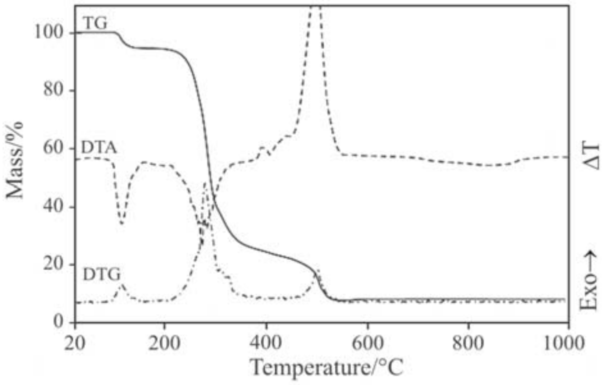

Fig. 4 TG, DTG and DTA curves of [Zn$(H_2O)_2$$(im)_4$]$(H_2Or)_2$

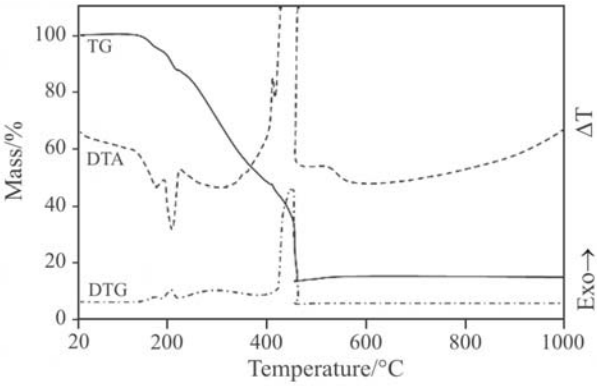

Fig. 3 TG, DTG and DTA curves of [Ni(HOr)$(H_2O)_2$$(im)_2$]

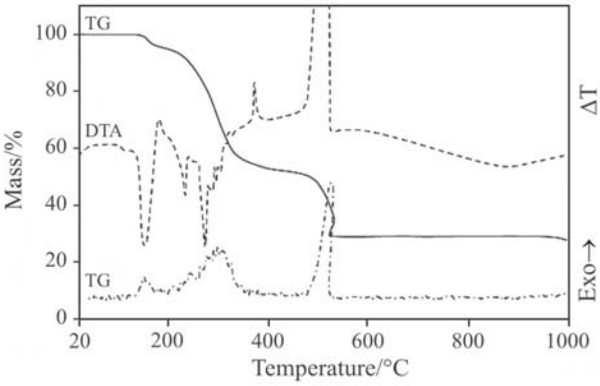

Fig. 5 TG, DTG and DTA curves of [Cd(HOr)$(H_2O)$$(im)_3$]

the decomposition of the orotate ligand by exothermic effect (DTG_{max}=387°C). In the last stage the strong exothermic peak (DTG_{max}=465°C) is associated with the burning of the organic residue, leading finally to the Co_3O_4. The endothermic peak at 901şC (DTG_{max}) is related to the conversion of Co_3O_4 to CoO. The overall mass loss (found 83.45, calcd. 80.60%) agrees with the proposed structure well.

The thermal decomposition of **2** (Fig. 3) is similar with that of the isomorphous **1** [30] (Fig. 2). The first stage of the thermal decomposition of **2** starts at about 120°C with the release of the two moles aqua ligand in two steps (DTG_{max}=184, 204°C, found 10.23, calcd. 9.50%). In the second stage, two moles of imidazole ligand are released, as inferred from the agreement between the theoretical and experimental value for the mass loss (found 36.77, calcd. 35.35%). The following stage involves the extremely exothermic decomposition of orotate ligand and organic residue, leading finally to the NiO.

The thermal behavior of **3** is different from **1**, **2** and **4**, because of **3** has different structure from the complexes. In **3**, the orotates were not coordinated to the Zn(II) ion and act as the counter ions. In the first decomposition stage, endothermic removal of the two aqua ligands occurs at 117°C (DTG_{max}) with a mass loss of 6.19% (calcd. 5.27%). The anhydrous **3** is thermally stable up to about 206°C. In the temperature range of 206–321°C, the endothermic peak of **3** (DTG_{max}=281°C), is related to the release of imidazole ligands and partial decomposition of orotates. This decomposition stage is similar to the other imidazole complexes [31–34]. In the last stage, the strong exothermic mass loss process occurs in a single step. During this stage, the remaining organic part is abruptly burnt (DTG_{max}=504°C). The final decomposition product, ZnO, was identified by IR spectroscopy.

The first decomposition stage of **4**, in the temperature range of 127–189°C, corresponds to mass loss of the aqua ligand (found 4.82, calcd. 3.68%). The following stages between 190–362°C are related to the endothermic decompositions of the three moles of neutral imidazole ligands (DTG_{max}=236, 275 and 307°C, found 41.18, calcd. 41.79%). The exothermic peak at 386°C is associated with the phase transition of the CdHOr compound. In the last stage (363–532°C), the organic residue is abruptly burnt (DTG_{max}=529°C). The final decomposition product is CdO (found 71.90, calcd. 73.73%).

On the basis of the first DTG_{max}, the thermal stability of **1–4** follows order: Ni(II), 176°C>Co(II), 162°C>Cd(II), 155°C>Zn(II), 117°C.

Conclusions

The Co(II), Ni(II), Zn(II) and Cd(II)-orotic acid (H_3Or) complexes with imidazole were synthesized and characterized. The HOr coordinated to the Co(II), Ni(II) and Cd(II) ions are chelated to the deprotonated pyrimidine nitrogen ($N_{(3)}$) and the carboxylate oxygen, while the H_2Or is present as a counter-ion in Zn(II) complex. The thermal decomposition pathway of the complexes has been predicted by the help of thermal analysis (TG, DTG and DTA). The compounds decompose in three thermal stages: (*i*) dehydration (*ii*) release of imidazole ligands and decomposition of orotate (*iii*) remained organic residue burns. The final decomposition products corresponding metal oxides.

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