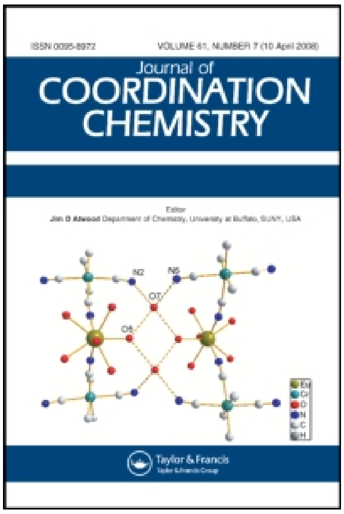

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Complexation and Thermal Studies of Uric Acid with Some Divalent and Trivalent Metal Ions of Biological Interest in the Solid State

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COMPLEXATION AND THERMAL STUDIES OF URIC ACID WITH SOME DIVALENT AND TRIVALENT METAL IONS OF BIOLOGICAL INTEREST IN THE SOLID STATE

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Nine new [metal : uric acid] complexes $[M(Ua)_n]^\circ \cdot XH_2O$ have been synthesized. These complexes have been characterized by elemental analysis, X-ray diffraction (XRD), magnetic susceptibility ($\mu_{eff.}$), FTIR spectra, thermal analysis (TG & DTA), and electronic spectra (UV/visible). Uric acid (HUa) coordinates as a bidentate ligand to Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Cr(III) and Fe(III) through the protonated N-7 within the imidazole ring and O-6 within the pyrimidine ring. Uric acid forms neutral metal urate complexes with all the above metal ions. The quantitative compositions were determined as $[M(Ua)_2 \cdot (H_2O)_2]^\circ \cdot XH_2O$ where M(II) = Mn, Fe, Co, Ni, Cu, Zn and X = 2, 4, 2, 4, 2, 2, respectively. The M(II) complexes exhibit an isostructural octahedral coordination with N-7, O-6 of two uric acid ligand molecules, and O of two water molecules. Compositions were also determined as $[M(Ua)_3]^\circ \cdot YH_2O$ where M(III) = Al, Cr, Fe and Y = 6, 3, 3 respectively. All the M(III) complexes form an isostructural octahedral coordination with N-7 and O-6 of three uric acid ligand molecules. Iron(III) complexes prepared with N_1, N_3 and N_9-methyl uric acid yielded brown complexes with a metal : ligand ratio of 1 : 3, while N_7-methyl uric acid did not yield a complex due to blockage of N-7 with a methyl group.

Keywords: Synthesis; Thermal analysis; Electronic spectra; Solubility of metal urate complexes

INTRODUCTION

Uric acid, uric acid dihydrate and sodium hydrogenurate monohydrates are found as crystalline deposits in the urinary calculi of humans diseased with gouty arthritis [1]. Some chemical information is available about the

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interaction of uric acid with bio-metal ions such as Mg, Ca, Fe, Co, Cu and Zn but no structural investigation has been done. Considerable effort has been devoted to the preparation and structural characterization of metal purine complexes [2, 3], especially in view of their important medical and pharmacological significance. Most of the literature on complexation of metal ions with purines in the recent years deals with guanine and adenine (the major purine bases in DNA and RNA), oxopurines, nucleic acids, and bases derived from nucleic acids [4, 5].

After extensive studies on the interaction of oxopurines with copper(II), Weiss and Venner [6] stated that the chance of isolating metal complexes decreases with the increase of the number of hydroxyl substituents. This statement agrees with the stability constants of the copper(II) complexes with oxopurines where they decrease in the following order: adenine $>$ purine $>$ hypoxanthine $>$ 7-CH_3-hypoxanthine $>$ 9-CH_3-hypoxanthine $>$ xanthine [7]. Thermal analysis, IR and X-ray crystallography characterized different metal(II) complexes of xanthine [8, 9] and hypoxanthine [10].

Uric acid forms mono- and di-substituted metal salts which are sparingly soluble in water and organic solvents [11]. A literature survey shows that many authors have studied the physico-chemical properties of uric acid and its salts, because they are very interesting from the physiological viewpoint. Uric acid salts have been obtained with the following cations: Ba(II), Hg(II), UO_2(II), Ni(II), Cu(II) [12, 13], Li(I), Na(I), Rb(I), Cs(I), Tl(I), NH_4(I), $N(CH_3)_4$(I) [14], Mg(II) [15, 16], Ca(II) [17, 18], Pb(II), Cd(II) [19, 20], Fe(III) [21], Cr(III) [22] and lanthanide [23]. These salts and complexes were first studied from the biochemical viewpoint.

The aim of this work is to synthesize and examine systematically, in the solid state, the urates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Cr(III) and Fe(III). Some physicochemical properties, thermal decomposition, and spectral data were investigated to elucidate the coordination properties of uric acid with these bio-metal ions. This is part of a continuing program to elucidate the coordination properties of some oxopurines and related ligands with some metal ions of biological importance and to study their biological properties as growth substrates and inducers of uricase, as in the mold *Neurospora crassa*.

EXPERIMENTAL

Materials

All chemicals used were of analytical grade (AR) and products of Aldrich (USA); N-methyl uric acids were provided from Sigma Chemical Co. (USA).

Synthesis of the Urate Complexes

Considering preliminary experiments [13, 22, 23], which indicate that more than one metal uric acid complex is formed depending on conditions employed (stoichiometric ratio, pH, heating, time of heating, and type of anion), the following procedures were devised: 10.0 mM uric acid solution, (100 ml, pH = 8.0), was added dropwise with constant stirring to a freshly prepared solution of metal nitrate, (15 ml, 0.20 M adjusted to pH = 4.0 with 0.10 M HNO_3), so that the molar ratio of uric acid to metal ion is 3 : 1 for M(III) and 2 : 1 for M(II). The resulting clear solution (neutralized to pH 6.0 – 6.2 with 0.10 M NaOH) was then heated at $80 \pm 1°C$ for about 60 minutes to incipient turbidity. It was then left to stand at room temperature for 24 hours, filtered off, washed with water to remove the soluble cations and anions, and dried to constant weight. The metal complexes were brought into solution by gentle warming in 0.10 M ammonium formate. Any undissolved free uric acid present was centrifuged off. The solutions were chilled at zero°C thereafter to precipitate each complex which was collected by centrifugation in the cold (5000 rpm, 15 min. zero°C) in a Beckman J2 – 21 centrifuge. Yields of the different pure metal complexes were about 70 – 75% based on uric acid taken. On the other hand, when mixtures of metal salt solutions and uric acid were left at room temperature or chilled under the same condition, only a white precipitate of uric acid was obtained.

Similar procedures were followed to prepare iron(III) complexes with N_1, N_3, N_7 and N_9-methyl uric acid. All N-methyl uric acid ligands, except N_7-methyl uric acid, yielded brown complexes with a metal : ligand ratio of 1 : 3 on prolonged heating with $Fe(NO_3)_3 \cdot 9H_2O$. These complexes were purified by procedures similar to those adopted for the other complexes and their properties were studied.

Analysis of Metal Complexes

The following procedure was developed according to Ramana *et al.* [22] and modified as below to establish the composition of the [metal : uric acid] complexes. Each complex (about 10.0 mg in 5.0 mL of 0.10 M ammonium formate), was heated with (1.0 mL, 1.0 M NaOH), {NH_4OH was used for Al(III) and Zn(II)} in a boiling water bath for exactly 15.0 min., rapidly chilled to zero°C and then the precipitated metal hydroxide was removed by centrifugation. The supernatant was collected. The precipitate was resuspended in water and centrifuged. Uric acid was estimated in the combined supernatants by its absorbance at 290.0 nm in a DK2 spectrophotometer, (Fig. 1b) [18]. The precipitate was then dissolved in 1.0 M

HNO_3 (5.0 mL) and its metal content was estimated using EDTA complexometric titration [24]. The metal oxide content was determined from the TG curve and by ignition of samples of the complexes above 800.0°C and weighing the resulting metal oxide. The contents of C, H and N were determined by elemental analysis using a CHNS analyzer at Microchemical Analysis Center Laboratory, Ain Shams University, Cairo, Egypt.

Careful control of alkali concentration, as well as time of heating was imperative to avoid dissolution of the hydroxide formed in alkali. Replicate analyses of complexes yield values for metal and uric acid, which agreed to within ± 3.0%. The solubility of the prepared urate complexes in water at 25.0°C was examined. Saturated solutions were prepared under isothermal conditions. The results are as follows.

Complex	*Solubility* (10^{-5} *M*)
$Al(Ua)_3$	1.20
$Fe(Ua)_3$	1.45
$Cr(Ua)_3$	1.38
$Mn(Ua)_2$	7.53
$Fe(Ua)_2$	7.26
$Co(Ua)_2$	6.58
$Ni(Ua)_2$	6.04
$Cu(Ua)_2$	5.80
$Zn(Ua)_2$	7.05

The low values of solubility product ($1.20-7.53 \times 10^{-5}$ M) indicates that, these metal urate complexes are non-electrolytic in nature, due to charge neutralization of the metal ion $[M]^{n+}$ with the urate ligand $[Ua]^-$.

APPARATUS

Magnetic moment measurements were carried out at 25.0°C using Gouy's method, where $Hg[Co(SCN)_4]$ was used as a calibrant, and diamagnetic corrections were made by using Pascal's constant.

FTIR spectra were investigated in the range $4000-400\,cm^{-1}$ within sensitivity of $\pm 1.0\,cm^{-1}$ using a MATTSON 1000 FTIR spectrometer and samples were prepared as KBr discs.

Thermal studies of the prepared metal complexes were measured using a TGA-50 derivatograph of Shimadzu Corp. (Japan). Measurements were taken at a sensitivity ± 1% of each range for the ± 20.0 mg sample and the rate output was 1.0 mg/mV when the samples were heated in platinum crucibles in a nitrogen atmosphere to 1000.0°C at a heating rate 10.0°C min^{-1}. The DTA-50 derivatograph of Shimadzu Corp. (Japan) uses a unique Dumbbell-shaped detector which uses a thermocouple of Pt and Pt-10% Rh alloy which provides high sensitivity and good response. The measuring range is ± 0.2 to $\pm 1000\,\mu$V, and the temperature range is 25°C to 1500°C.

X-ray diffraction patterns (XRD) of the prepared solid compounds were recorded using a Philips X-ray diffractometer model PW 1140/90 and Fe-filtered CoK_{α} radiation. The X-ray patterns of powdered samples were recorded automatically with a scanning speed of 2° per minute, and the scanning angular range (2θ) was from $6°-60°$. All the diffraction patterns were measured at room temperature. The -d- (10^{-1}nm) spacing was calculated, together with their relative intensities, compared with the corresponding ASTM data [25].

Electronic Spectra: The UV/visible spectra of freshly made aqueous solutions of uric acid, and urate complexes adjusted to $pH = 7.0$ was recorded in the range $200-800$ nm, on a Beckman DK2 spectrophotometer whereas a Varian spectrophotometer of type Cary 2300 was used for recording polycrystalline samples.

RESULTS AND DISCUSSION

Two complexes, M(II) and M(III) with uric acid ligand [HUa], have been synthesized, two moles of ligand for M^{2+}, and three moles of ligand for M^{3+}. As already mentioned, only 1 : 3 complexes $[FeL_3^*]^\circ$ were synthesizes with N_1, N_3, or N_9-methyl uric acid. No complexes were obtained with N_7-methyl uric acid. This emphasizes that N_7-is one of the mandatory sites of metal-ligand binding since when this site is blocked complexation does not occur.

Elemental analysis data are given in Table I and the metal content as M^{n+}%, and M_XO_Y% for the 1 : 2 $[M(Ua)_2]^\circ$ and 1 : 3 $[M(Ua)_3]^\circ$ metal : uric acid complexes were obtained, respectively.

Magnetic moments of urate complexes show a high spin d^5 configuration for iron(III) having $^6A_1$ as the ground state, the magnetic susceptibility ($\mu_{eff} = 5.95$ B.M), indicates ($t_{2g}^3e_g^2$). The manganese(II) complex shows a high value of magnetic susceptibility ($\mu_{eff} = 5.92$ B.M), which may be due to uric acid being a weak ligand [26]. The iron(II) complex shows a magnetic susceptibility value $\mu_{eff} = 5.35$ B.M that is expected for high spin d^6

TABLE I Analytical data, magnetic moment, and yield % for various [metal(II and III) – urate] complexes

	Elemental		*Analysis*					
	Calcd./Found							
Complex	*C%*	*H%*	*N%*	Mn^{+}% (*EDTA*)	M_XO_Y %(*TG*)	*Color of complex*	μ_{eff} (*B.M.*)	*Yield* %
$[Al(Ua)_3]\cdot 6H_2O$ Mol. wt. = 636	28.30 /27.98	3.30 /3.25	26.42 /26.40	4.25 /4.22	8.02 /8.00	White	–	70
$[Cr(Ua)_3]\cdot 3H_2O$ Mol. wt. = 607	29.65 /29.36	2.47 /2.50	27.68 /27.70	8.57 /8.55	12.52 /13.00	Pale blue -gray	4.25	70
$[Fe(Ua)_3]\cdot 3H_2O$ Mol. wt. = 611	29.46 /29.60	2.45 /2.43	27.50 /27.63	9.16 /9.13	13.10 /13.37	Brown	5.95	70
$[Mn(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$ Mol. wt. = 461	26.03 /25.99	3.04 /2.99	24.30 /24.10	11.93 /11.90	15.40 /15.27	White-yellow	5.92	75
$[Fe(Ua)_2\cdot(H_2O)_2]\cdot 4H_2O$ Mol. wt. = 498	24.10 /24.00	3.61 /3.55	22.49 /22.60	11.24 /11.20	14.46 /14.40	Pale-brown	5.35	72
$[Co(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$ Mol. wt. = 465	25.81 /25.90	3.01 /3.09	24.09 /24.00	12.69 /12.70	15.91 /14.95	Pale-pink	4.40	73
$[Ni(Ua)_2\cdot(H_2O)_2]\cdot 4H_2O$ Mol. wt. = 501	23.95 /24.00	3.59 /3.58	22.36 /22.46	11.77 /11.75	14.97 /14.90	Pale-green	3.10	73
$[Cu(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$ Mol. wt. = 469.5	25.56 /25.38	2.98 /2.90	23.86 /24.00	13.53 /13.50	16.93 /16.90	Yellow brown	2.10	74
$[Zn(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$ Mol. wt. = 471.5	25.45 /25.38	2.97 /2.92	23.75 /23.90	13.89 /13.80	17.29 /17.20	White	–	75

configuration. The other complexes also show high spin magnetic moments as shown in Table I.

Visible spectra obtained from saturated solutions of the complexes Figure 1a shows peaks due to the bound M^{3+} with uric acid at 560 nm for $[Cr(Ua)_3]^\circ$ and at 565 nm for $[Fe(Ua)_3]^\circ$ with $(\varepsilon) = 11.0$ and $12.0 \times 10^3\,M^{-1}\,cm^{-1}$, respectively. These peaks may be attributed to formation of polynuclear structures in solution [22].

Solid-state electronic absorption spectra for Co(II), Ni(II) and Cu(II) urate complexes are given in Figure 1c. In general, it is difficult to relate spectra with the structure of copper(II) compounds, especially in view of the distorted geometry observed for such complexes [27]. Nevertheless, the spectrum of $[Cu(Ua)_2 \cdot (H_2O)_2]^\circ \cdot 2H_2O$ is closely related to those of Cu-N_6 chromophores with approximate octahedral geometry. The absorption spectrum of $[Co(Ua)_2 \cdot (H_2O)_2]^\circ \cdot 2H_2O$ with a band of medium intensity at 1230 nm and a very intense peak at 500 nm including a shoulder at 450 nm is typical for six-coordinate high-spin cobalt(II) complexes. The corresponding bands in the octahedral $[Co(H_2O)_6]^{2+}$ ion have been assigned to $^4T_{1g}$—$^4T_{2g}(F)$, $^4T_{1g}$—$^2A_{1g}(F)$, and $^4T_{1g}$—$^4T_{1g}(P)$ transitions, respectively [27]. The absorption spectrum of $[Ni(Ua)_2 \cdot (H_2O)_2]^\circ \cdot 2H_2O$ is almost identical with that of the octahedral $[Ni(H_2O)_6]^{2+}$ ion.

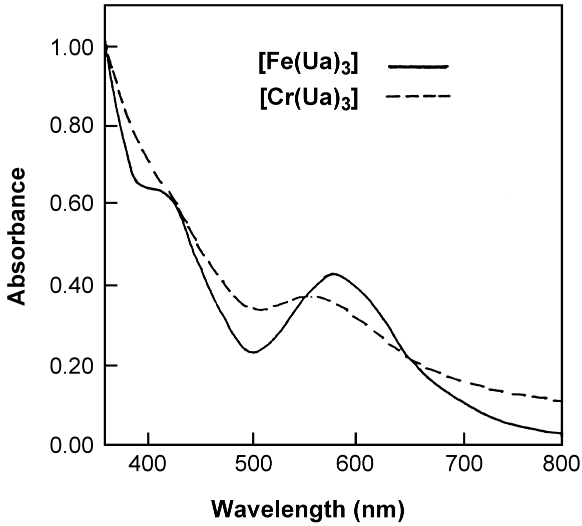

FIGURE 1a Absorption spectra of $[Cr(Ua)_3]$ and $[Fe(Ua)_3]$ complexes in 0.1 M ammonium formate buffer, pH = 7.0.

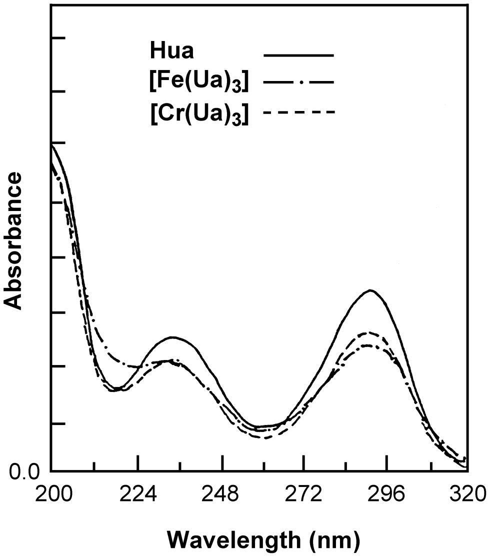

FIGURE 1b Ultraviolet absorption spectra of HUa, $[Cr(Ua)_3]$ and $[Fe(Ua)_3]$ complexes in 0.1 M ammonium formate buffer, pH = 7.0.

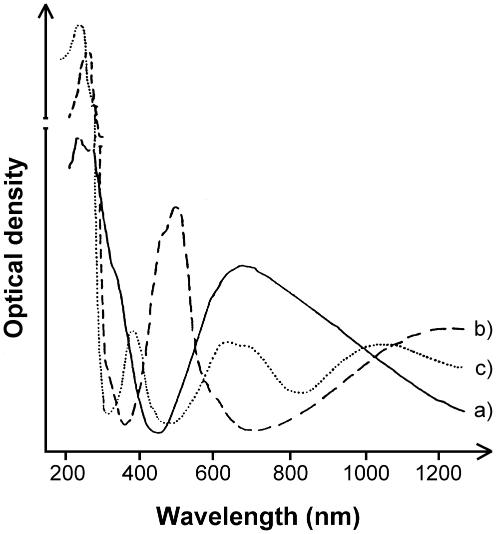

FIGURE 1c Solid-state electronic absorption spectra; (a) $[Cu(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$; (b) $[Co(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$; (c) $[Ni(Ua)_2\cdot(H_2O)_2]\cdot 2H_2O$.

Assignments are 1070 nm $\cong {}^3A_{2g}$—${}^3T_{2g}(F)$, 650 nm $\cong {}^3A_{2g}$—${}^3T_{1g}(F)$, and 380 nm $\cong {}^3A_{2g}$—${}^3T_{1g}(P)$, 710 nm shoulder may correspond to a spin forbidden ${}^3A_{1g}$—${}^1E_g$ transition [27].

The electronic spectral data of all complexes is in full agreement with the respective metal coordination polyhedral derived from crystal structure analysis.

Infrared spectral data and band assignments of different complexes are shown in Table II. Free uric acid [HUa] has major peaks at 3018, 2830, 1676 and $1591\,\text{cm}^{-1}$, respectively. For purines, bands in the region $3000-2000\,\text{cm}^{-1}$ are assigned to the stretching N—H and O—H bands, those in the $1700-1500\,\text{cm}^{-1}$ are assigned to $>$C$=$O groups and those below $1500\,\text{cm}^{-1}$ are due to ring vibrations [28, 29].

One characteristic feature of the trivalent metal complexes of uric acid is that the 3018 and $2830\,\text{cm}^{-1}$ peaks reduce in intensity and appear as a single broad band around $3010\,\text{cm}^{-1}$. A new broad band with a maximum at $3400-3420\,\text{cm}^{-1}$ is due to the vibration ν_{OH} of coordinated water molecules and crystallization water in the hydrated complexes. Likewise, the $1676\,\text{cm}^{-1}$ absorption is diminished by complexation and the $1591\,\text{cm}^{-1}$ peak becomes a shoulder. Within this range the $\delta_{\text{H}_2\text{O}}$ band occurs, causing a change in the spectrum. Within the range $1500-1300\,\text{cm}^{-1}$ there are some weak bands in the spectrum of the acid, which differ in intensity.

In the spectra of the divalent complexes some bands disappear at $878\,\text{cm}^{-1}$ and at $747\,\text{cm}^{-1}$ and two bands with maxima at 1352 and $1310\,\text{cm}^{-1}$ appear as broad single bands. The IR spectrum of the acid displays two strong bands at $1125\,\text{cm}^{-1}$ and $997\,\text{cm}^{-1}$, whereas in the spectra of trivalent metal complexes they reduce in intensity only, while for divalent metal complexes the bands change to higher wavenumbers ($1136\,\text{cm}^{-1}$ and $1005\,\text{cm}^{-1}$). All absorption peaks in the region $1352-477\,\text{cm}^{-1}$ are greatly reduced in intensity, leading to a comparatively muted absorption pattern. The most important changes during the transformation of uric acid into metal complexes take place within the range $650-400\,\text{cm}^{-1}$. In the IR spectrum of the uric acid there are four bands assigned from the ketone groups $>$C$=$O [30] and from purine ring vibrations [31].

The spectra of the synthesized complexes display only three bands of medium intensity at $588-623\,\text{cm}^{-1}$, $500-520\,\text{cm}^{-1}$ and $455-465\,\text{cm}^{-1}$. The frequency of the former two bands decrease with the rise in the atomic number (Z) of the metal where the covalent character of the (M—O) band increases along the series from $455-465\,\text{cm}^{-1}$, which is similar to the view supported by Rosenberg [32].

The complexes show ν_{OH} and δ_{HOH} at $3400-3520\,\text{cm}^{-1}$ and $1661-1703\,\text{cm}^{-1}$ besides rocking mode (r) for water at $770-801\,\text{cm}^{-1}$ this indicates that water molecules are coordinated in these complexes [33]. Also

TABLE IIa Frequencies and band assignments of uric acid and their various metal(II and III) complexes (cm^{-1})

Band assignment	*Uric acid*	*Al*(*Ua*)$_3$	*Fe*(*Ua*)$_3$	*Cr*(*Ua*)$_3$	*Mn*(*Ua*)$_2$	*Fe*(*Ua*)$_2$	*Co*(*Ua*)$_2$	*Ni*(*Ua*)$_2$	*Cu*(*Ua*)$_2$	*Zn*(*Ua*)$_2$
ν_{OH} (**H$_2$O**)	–	3440	3440	3430	3520,	3400	3400	3360	3470	3440
					3440					
ν_{NH}	3015,	3018,	3018,	3018,	3022,	3160	3175	3190	3146	3195
ν_{H-bond}	2830	2830	2830	2830	2860,					
NH.....O					2733					
δ_{H_2O}	1676,	1676,	1676,	1676,	1661	1661,	1703,	1614,	1668	1676,
$\nu_{C{=}O}$	1591	1591	1591	1591	1600	1603	1616	1545	1630	1661
Hetero-	1352,	1352,	1352,	1350,	1410,	1383	1379	1391,	1387	1391,
atomic ring vibr.	1310	1310	1310	1310	1335	1330	1335	1325	1330	1297
ν_{NH}	1125,	1125,	1125,	1125,	1136,	1125,	1128,	1128,	1128,	1125,
ν_{OH}	997,	993,	993,	993,	1005,	1001,	1009,	1009,	993,	1005,
	878,	882,	882,	882,	851,					
	785,	785,	789,	785,	797,	797,	770,	801,	766,	793,
	747,	747,			723					
	708	708,	708,	708,	715	716	720	716	704	708
ν_{M-N}	–	623	623	623	600	588	588	590	604	600
ν_{M-N}	–	520	515,	520,	500,	500,	505,	505,	520,	515,
ν_{M-O}	–	455	455	455	465	460	465	455	460	565

TABLE IIb Frequencies and band assignments of N-methyl uric acid and their various iron(III) complexes $[FeL_3^*]$ (cm^{-1})

Band assignments	N_1MeUa	$Fe(N_1MeUa)_3$	N_3MeUa	$Fe(N_3MeUa)_3$	N_7MeUa	N_9MeUa	$Fe(N_9MeUa)_3$
ν_{OH} **(H_2O)**	–	3455	–	3475	–	–	3450
ν_{NH}			2970,	3100	2975,	3000,	3400,
$\nu_{H\text{–}bond}$	2755	2750	2800,		2800		2905
NH.....O			2700			2700	
$\delta_{H_2O}+$	1670,		1670,	1675,	1650,	1685,	
$\nu_{C{=}O}$	1625,	1620,		1630,	1615,	1600,	1665,
	1575	1570	1560	1520	1575	1580	1585
Hetero-atomic	1480,		1425,	1455,	1440,	1450,	1455,
ring vibr.	1430,	1410	1400,	1405,	1420,	1370,	1385,
	1320,		1345,	1325, 1290,	1390,	1350,	
			1195,	1235,	1330,		
			1160	1180	1160	1170	
ν_{NH}	1020,	1060,	1040,			1040,	1050
ν_{OH}	990,	1000,	1020,	970,	920,		
	955,	920,	950,				
	800,	810,	870, 795,	810,	890,	840,	890, 810
	775,	760,	750,	745,	780,	745, 730,	750, 700,
	715,		725,	615,	680,	665,	600
$\nu_{M\text{–}N}$	–	620, 560	–	595	–	–	615
$\nu_{M\text{–}N}$	–	505	–	500	–	–	495
$\nu_{M\text{–}O}$	–	455	–	450	–	–	445

the (M—N) band increases along the series from 588 – 623 cm^{-1} (in plane ring deformation) [34].

The iron(III) complexes of N_1, N_3, or N_9-methyl uric acid also yield IR spectra with broad similarities to the spectrum of [Fe $(UA)_3$]°, Table II. For the N_1, N_3-methyl uric acid complexes, apart from changes in the 3500 – 2500 cm^{-1} region, considerable is reduction of absorption in the 1670 – 1590 cm^{-1} region is evident. N_9-methyl uric acid is somewhat different as its spectrum has two major peaks at 1660 cm^{-1} and 1480 cm^{-1} in the position of >C=O region.

All these changes are caused by the loss of proton and thus change in the acid structure, as well as by overlapping of the bands of water molecule vibrations. The marked reduction in the intensity of absorption, especially in the carbonyl region and in the other major region of N—H vibrations are explicable by M^{2+} or M^{3+} being bound to carbonyl oxygen(s) and ring nitrogen(s). The inability of N_7-methyl uric acid to form an iron (III) complex strongly suggests that one of the metal binding groups is N-7.

Thermal analysis (TG and DTA) of the urate complexes as well as the results obtained from IR, indicate that water molecules coordinate (lattice) and solvate (crystallize) the complexes. The urate complexes, heated in a nitrogen atmosphere, decompose in different ways in 3 – 5 steps. During heating the hydrated complexes lose some crystallization water molecules in one or two steps followed by the coordinated water molecules, Table III. Dehydration of the aluminum(III) complex occurs at 35 – 457°C and decomposition begins at 457 – 669°C, while for the copper(II) complex the dehydration begins at 50 – 445°C and the decomposition at 445 – 567°C. The decomposition is paralleled by the loss of the last water molecules. The aluminum(III) complex starts to lose water at the lowest temperature (71°C), whereas the cobalt(II) complex at the highest (185°C).

The urate complexes of Al(III), Cr(III), Fe(III) and Mn(III) decompose directly to metal oxides (Al_2O_3, Cr_3O_3, Fe_2O_3 and MnO) on heating, while the decomposition of the complexes of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) proceeds *via* unstable metal oxocarbonates ($MO \cdot CO_3$).

The temperature of oxide formation (T_k) is high for Fe(II), Co(II) and Ni(II), occurring at 692 – 675°C. For Al(III), Cu(II) and Zn(II) they occur at 669 – 654°C. The lowest temperatures are for Fe(III), Cr(III) and Mn(II) at 612 – 542°C. This means that the highest (T_k) is that of Fe(II) complex and the lowest (T_k) is that of the Mn(II) complex.

Dehydration of the complexes suggests that the water molecules bond in various ways. Formation of anhydrous complexes suggests that this outer-sphere water bonds with the urate anion by a hydrogen bond [15]. The

TABLE III Thermal data of the dehydration and decomposition processes of various [metal(II and III) : urate] complexes in nitrogen atmosphere

Complex	*Temp. range of dehydn. °C*	*Loss of wt. % Calcd/ Found*	*No. of H_2O mol.*	*Temp. of endothermic peak°C*	*Temp. range of decomp. °C*	*Loss of wt. (UA) % Calcd. /Found*	*Temp. of exothermic Peak °C*	*Temp. of oxidn. (T_k)°C*	*Final product t*
Uric Acid	–	–	–	–	380 – 516	51.9/51.0	460,	785	
(HUa)						**$C_2H_2N_2O_2$**			
					516 – 785	48.1/47.0	650		–
						$C_3H_2N_2O$			
$Al(Ua)_3\cdot 6H_2O$	35 – 346	2.8/2.7	1	71	457 – 589	52.5/52.0	499,	669	**Al_2O_3**
	346 – 457	11.3/11.5	4	437	589 – 669	26.2/26.0	621		
$Cr(Ua)_3\cdot 3H_2O$	30 – 466	8.9/9.0	3	430	460 – 595	55.0/55.0	477,	595	**Cr_2O_3**
						27.5/27.6	550		
$Fe(Ua)_3\cdot 3H_2O$	57 – 473	5.9/5.9	2	426	498 – 612	82.0/82.1	581	612	**Fe_2O_3**
	473 – 498	2.9/2.9	1	481					
$Mn(Ua)_2\cdot 4H_2O$	35 – 254	3.9/3.8	1	200	264 – 320	36.2/36.1	360,	542	**MnO**
	254 – 264	11.7/12.0	3	250	320 – 542	36.2/36.3	420		
$Fe(Ua)_2\cdot 6H_2O$	55 – 149	7.2/7.1	2	100	340 – 520	33.5/33.3	446,	692	**FeO**
	149 – 217	3.6/3.6	1	230	520 – 692	33.5/33.6	610		
	217 – 340	10.8/10.7	3	320					
$Co(Ua)_2\cdot 4H_2O$	48 – 207	7.8/7.8	2	185	478 – 540	35.9/35.7	488,	675	**CoO**
	207 – 478	7.8/7.8	2	388	540 – 675	35.9/36.0	588		
$Ni(Ua)_2\cdot 6H_2O$	25 – 234	14.4/14.3	4	174	469 – 536	33.3/33.1	496	668	**NiO**
	351 – 469	7.2/7.5	2	399	536 – 668	33.3/33.0	585		
$Cu(Ua)_2\cdot 4H_2O$	50 – 266	7.7/7.6	2	89	445 – 495	35.6/35.4	468,	654	**CuO**
	390 – 445	7.7/7.9	2	427	495 – 567	35.6/35.3	529		
$Zn(Ua)_2\cdot 4H_2O$	65 – 237	11.5/11.3	3	180	371 – 592	35.5/35.8	420,	662	**ZnO**
	237 – 371	3.8/3.7	1	210	592 – 662	35.6/35.4	580		

TABLE IV The three principle *d*-line X-ray pattern results

Uric acid $[HUa]$	$[Al(Ua)_3]$	$[Cr(Ua)_3]$	$[Fe(Ua)_3]$	$[Fe(Ua)_2 \cdot (H_2O)_2]$	$[Co(Ua)_2 \cdot (H_2O)_2]$	$[Ni(Ua)_2 \cdot (H_2O)_2]$	$[Cu(Ua)_2 \cdot (H_2O)_2]$	$[Zn(Ua)_2 \cdot (H_2O)_2]$
3.26_{100}	6.51_{100}	6.51_{100}	6.51_{100}	3.35_{100}	3.35_{100}	3.43_{100}	3.23_{100}	3.35_{100}
6.47_{90}	4.93_{50}	3.12_{90}	3.11_{90}	3.12_{50}	7.40_{90}	7.40_{90}	9.02_{45}	6.35_{90}
4.91_{80}	3.20_{30}	5.07_{80}	4.92_{80}	6.50_{35}	5.72_{80}	5.70_{80}	3.44_{30}	5.36_{70}

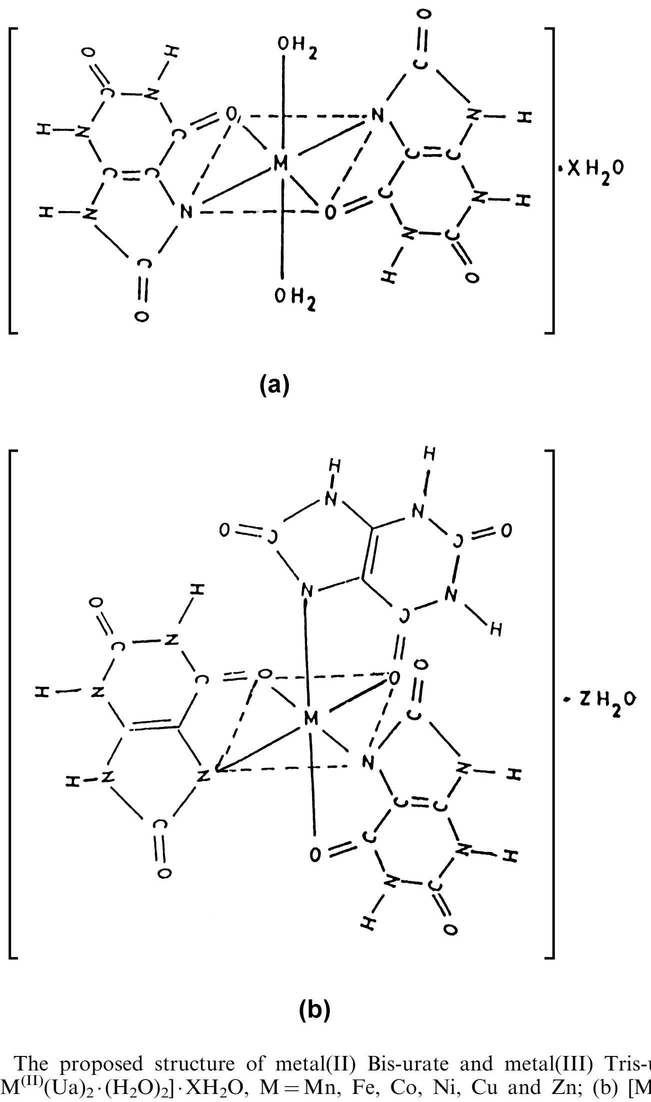

FIGURE 2 The proposed structure of metal(II) Bis-urate and metal(III) Tris-urate complexes: (a) $[M^{(II)}(Ua)_2 \cdot (H_2O)_2] \cdot XH_2O$, M = Mn, Fe, Co, Ni, Cu and Zn; (b) $[M^{(III)}(Ua)_2] \cdot YH_2O$, M = Al, Cr and Fe.

difference in the ionic radius can cause the different water molecule bonding, where some water molecules are coordinated by the metal ion (lattice water) and some are solvated (crystallization water). The dehydration process is accompanied by a strong endothermic effect, whereas the ignition of the decomposition products is associated with an exothermic one [35].

X-ray patterns of the synthesized solid urate complexes were taken over the range of $2\theta = 6-60^\circ$. The three main principle *d*-line X-ray pattern results are represented in Table IV.

Complexes of M(III) are crystalline solids with similar structures (isostructural). The iron(II) urate complex displayed a different structure and a very high degree of crystallinity while the copper(II) complex is characterized by a low degree of crystallinity, the strongest lines in the radiograms assume almost the same position as in the radiograms of other M(II) complexes. Complex of manganese(II) is amorphous (voluminous).

Low symmetry, large size of unit cells and various degrees of crystallinity characterize all crystalline complexes [23].

CONCLUSION

From FTIR spectral data, thermal analysis (DTA and TG), X-ray diffraction (XRD), magnetic susceptibility ($\mu_{\text{eff.}}$), electronic spectra data and elemental analysis one can conclude that:

(A) The synthesized solid urate complexes and the N-methyl uric acid show that the structure of the purine ring retains its planar resonance form. Deprotonation at the N-7 atom causes formation of some hybrid structures in which the negative charge is located around some atoms, N-9, O-8 or O-6. When free acid is transformed into a complex, the character and length of bonds in the imidazole ring are changed [15, 22]. All these changes are reflected by the FTIR spectra. The transformations of the hybrids between themselves lead to a change in the spectra. The spectra of the complexes show that the absorption band ν_{OH} (at $3400-2700\,\text{cm}^{-1}$) and δ_{OH} (at $1630\,\text{cm}^{-1}$) arises from water molecules, also contributing to a change in the spectra.

(B) The Al(III), Cr(III) and Fe(III) complexes differ from the divalent transition metals where the former have only water of crystallization while the others have both water of crystallization and coordination.

(C) High thermal stability and very low solubility ($1.20-7.53 \times 10^{-5}\,\text{M}$) characterize all urate complexes.

(D) When the water molecules are lost, at very high temperatures, a strong endothermic peak appears in the range from 426°C to 437°C for M(III) complexes while for M(II) complexes the endothermic peak is weaker ranging from 210°C to 388°C [35].

(E) All complexes are crystalline precipitates whereas the precipitate of the manganese(II) complex is voluminous and its FTIR spectra exhibit more bands.

(F) All complexes show high spin magnetic moments. Peaks due to the bound M^{3+} at 560 nm for $[Cr(Ua)_3]^\circ$ and at 565 nm for $[Fe(Ua)_3]^\circ$, the bound M^{2+} at 680 nm for $[Cu(Ua)_2 \cdot (H_2O)_2]^\circ \cdot 2H_2O$, at 500 nm for $[Co(Ua)_2 \cdot (H_2O)_2]^\circ \cdot 2H_2O$, and at 650 nm for $[Ni(Ua)_2 \cdot (H_2O)_2]^\circ \cdot 2H_2O$ can be attributed to *d–d* transitions of octahedral geometry [27].

(G) The analytical and spectral data suggest an isostructural octahedral coordination as formulated in Figure 2 The quantitative compositions were determined as $\mathbf{[M(Ua)_2 \cdot (H_2O)_2]^\circ \cdot XH_2O}$, M(II) = Mn, Fe, Co, Ni, Cu, Zn, X = 2, 4, 2, 4, 2, respectively, and $\mathbf{[M(Ua)_3]^\circ \cdot YH_2O}$, M(III) = Al, Cr, Fe, Y = 6, 3, 3, respectively. M(II) and M(III) coordinate with uric acid as a bidentate ligand, two moles of ligand per atom for M^{2+} and three moles of ligand per atom for M^{3+}.

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