

Thermal Behaviour of Some Yttrium (III)- Violurate Complexes and Crystal Structure of $[Y(C_4H_2N_3O_4)_2 \cdot 4H_2O]Cl$ Complex

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The title compounds were prepared by mixing either aqueous and / or ethanolic solutions of $YCl_3 \cdot 6H_2O$ and violuric acid monohydrate in mole ratio (1:2). The prepared crystalline complex belongs to orthorhombic system, with unit cell constants: $a = 8.6925(4)$, $b = 17.0421(9)$, $c = 5.5285(3)$ Å, $V = 818.98(7)$ Å³, $Z = 2$, space group $P2_1 2_1 2$ (half the molecule occupies the asymmetric unit cell). The structure was solved by direct method using SIR 92 software and then refined by full matrix least square using anisotropic temperature factors. The hydrogen atoms were located and their positions and isotropic temperature factors were refined giving R-factor 0.061 and wR 0.134. The thermogravimetric analyses for the prepared complexes were studied under nitrogen gas and the activation energies of decomposition steps were determined.

1. Introduction:

Yttrium(III) chloride violurate complexes (1:2) were prepared in a previous work [1] and were studied together with Sc(III) and La(III) – violurate complexes as powders using IR, electronic spectra and X-ray powder diffraction techniques. The study revealed that bonding takes place through coordination bond between the central metal ions and the oxygen atom of the oximino C-N=O group and covalent bond between the central metal ions and oxygen atom of the phenolic C-OH group in the case of 1:2 complexes. The aim of this work is to prepare new complexes of Y(III) – violurate (1:2) and to characterize them structurally by single crystal X-ray diffraction technique and by thermogravimetric analysis.

2. Experimental:

All the chemicals used were purchased from BDH, Aldrich or Sigma (99.9% quality). The solid complexes were prepared by mixing either aqueous and / or ethanolic solutions of $YCl_3 \cdot 6H_2O$ and violuric acid monohydrate $V.A \cdot H_2O$ in mole ratio metal : ligand (1:2). The hot yttrium solutions were added with stirring to the hot solutions of violuric acid. The mixtures were heated for few hours on a water bath then left in the dark for about 3 to 7 days where yellow precipitates separated (the yield is > 90%). Crystalline complex I ($[Y(C_4H_2N_3O_4)_2 \cdot 4H_2O]Cl$), was obtained by dissolving the metal salt in bidistilled water and violuric acid in ethanol, but on dissolving both in ethanol, complex II ($[Y(C_4H_2N_3O_4)_2 \cdot 4H_2O]Cl \cdot 2H_2O \cdot H_3O^+ Cl^-$) was obtained. They were filtered, washed by ethanol-water mixture and ethanol respectively, and then dried in a desiccator over calcium chloride. Complex III ($[Y(C_4H_2N_3O_4)_2 \cdot 4H_2O]Cl \cdot 2H_2O$), was prepared by dissolving complex II in bidistilled water, which dissolves freely, then heated for few hours, left for about 3 days. Fine crystals (powder-like precipitate) were obtained, filtered, washed with ethanol-water mixture and dried as before.

The yttrium percentage was determined by complexometrical titration [2]. Elemental (C, H, N & Cl) and thermogravimetric analyses were assayed in the Microanalytical Center, Cairo University. Thermogravimetric analyses were carried out by Shimadzu TGA-50H apparatus with heating rate of 10 °C/min. up to 800°C, under nitrogen gas.

X-ray crystallographic study was done in the National Research Center, Cairo, Egypt. A yellow crystal of $[Y(V.A)_2 \cdot 4H_2O]Cl$ complex having approximate dimensions of 0.3 x 0.2 x 0.25 mm³ was mounted on a glass fiber in a random orientation. The data collection were performed with Mo k_{α} -radiation of wavelength 0.71073 Å, on a Bruker – Nonius, Holland, computer controlled kappa axis diffractometer CCD, with computing data reduction of Denzo and Scalepack [3]. All diagrams and calculations recorded, the computing structure refinement and publication material were done by Maxus [4], and the computing molecular graphics by Ortep [5]. Cell measurement reflections used is 1103 and the computing cell refinement by hkl Scalepack [3]. The reflection threshold expression is $I > 3.00 \text{ Sigma (I)}$. The crystal data and structure refinements are shown in Table(1).

Table(1): Crystal data and structure refinements for $[Y(V.A)_2.4H_2O]Cl$ complex

Crystal data:	
$Y(C_4H_6N_3O_6)_2 Cl$	$D_x = 2.062 \text{ gm cm}^{-3}$
$M_r = 508.572$	Mo k_α radiation
Orthorhombic P21212	Cell parameters from reflections 1103
$a = 8.6925(4) \text{ \AA}$	$\theta = 2.91 - 27.485^\circ$
$b = 17.0421(9) \text{ \AA}$	$\mu = 0.380 \text{ mm}^{-1}$
$c = 5.5285(3) \text{ \AA}$	Prism, Yellow
$v = 818.98(7) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.25 \text{ mm}^3$
$z = 2$	
Data collection:	
Kappa CCD diffractometer	1103 independent reflections
ϕ s and ω scans	999 reflections with $I > 3 \sigma(I)$
with kappa offset scans	$R_{int} = 0.063$
Absorption correction	$h = 0 \text{ --- } 11$
not provided	$k = 0 \text{ --- } 22$
1155 measured reflections	$l = 0 \text{ --- } 7$
Refinements:	
Refinement on F^2	H – atom parameters constrained
$R [F^2 > 3\sigma(F^2)] 0.061$	$w = 1 / [s^2(F_o^2) + 0.1 F_o^2]$
$wR(F^2) = 0.134$	$(\Delta\rho)_{max} = 0.21 \text{ e \AA}^{-3}$
$S = 2.792$	$\Delta\rho_{max} = 1.13 \text{ e \AA}^{-3}$
999 reflections	$\Delta\rho_{min} = -1.51 \text{ e \AA}^{-3}$
122 parameters	

Activation energies of the pyrolyzed compounds were obtained from the slopes of the straight lines of the relation $\ln \ln 1/C_s$ versus $\theta (T-T_s)$, according to the equation:

$$\ln \ln 1/C_s = (W_o - W_t^f) / (W - W_t^f) = E^* \theta / RT_s^2$$

where W is the weight remaining at a given temperature T , W_o and W_t^f are the initial and final weights, respectively, C_s is the weight pyrolyzed after being converted to mole fraction, E^* is the energy of activation, and $\theta = T - T_s$, where T_s is the intermediate temperature of degradation [6].

3. Results and Discussion:

The analytical data of the complexes are presented in Table (2). The proposed chemical formulae of complexes I, II and III are $[Y(V.A)_2.4H_2O]Cl$, $[Y(V.A)_2.4H_2O]Cl.3H_2O.HCl$ and $[Y(V.A)_2.4H_2O]Cl.2H_2O$, respectively. They are yellowish orange (the colours of violuric acid compounds with a variety of metals were interpreted) [7], easily dissolve in hot water and do not melt up to $300^\circ C$. Complex II dissolves freely in cold water and shows slight acidity towards $NaHCO_3$.

The final positional and thermal parameters of complex I are given in Table (3). A selection of the molecular geometry data is collected in Table (4). A view of the complex showing the geometry of Table (4) is given in Figure (1) with the numbering of atoms.

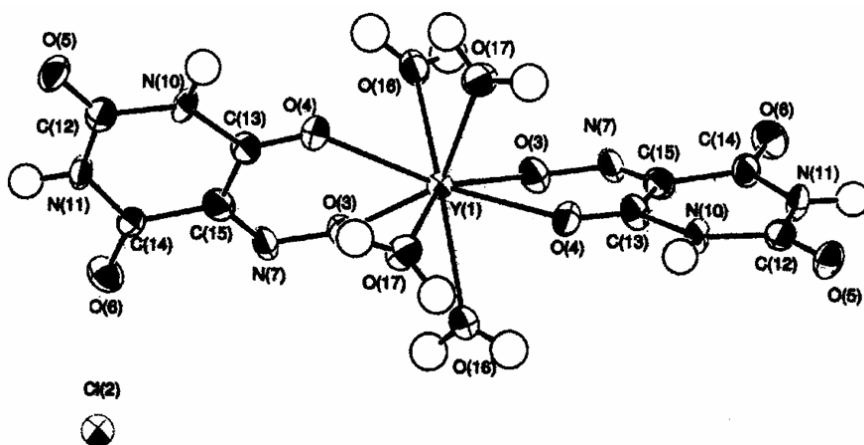
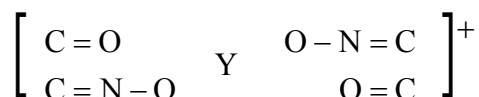
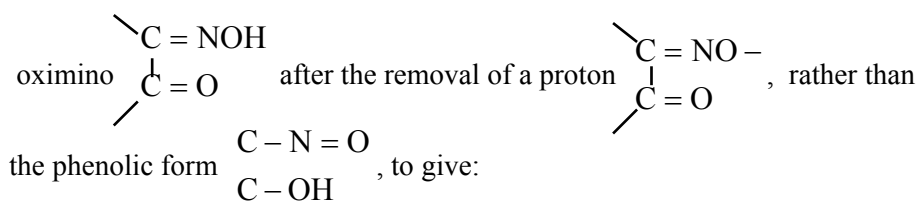


Fig. (1) The molecular geometry with numbering of atoms.

The structure shows that Cl^- ions are situated in the cavities between the molecules, and are supported by Van der Waals contacts as is assured from the intermolecular non-bonded distances of Y_1-Cl_2 [4.7380(9), 5.6714(5) Å]. The violurate ligand behaves in the structure as a bidentate ligand, because it is coordinated to the Y ion through its O₃ and O₄ atoms forming a metallocyclic six-membered ring (Y, O₃, N₇, C₁₅, C₁₃, and O₄). On the other hand, two water molecules are coordinated also to the Y ion via their O₁₆ and O₁₇ atoms. The Y ion occupies a special position (2a) of the space group $P2_12_12$, this means that it occurs at the 2-fold axis in the unit cell. This situation will create symmetrical two bidentate violurate ligands and four water molecules, giving rise to a 8-coordination number for Y ion, as is shown in Fig. (1). This will lead to two

identical chelate rings and eight identical Y-O bond lengths around the Y ion, forming cubic coordination geometry. The eight coordinate bonds are directed to the corners of a dodecahedron so that the coordination system can be described as a dodecahedral polyhedron. The bond distances between Y and O atoms range between $Y_1-O_3 = 2.295 \text{ \AA}$ to $Y_1-O_4 = 2.363 \text{ \AA}$, with an average value equals 2.329 and e.s.d. of about 0.005 \AA ; the difference between the two extreme values is therefore not significant, taking into consideration that, the Y_1-O bond distances are nearly equal to the sum of the covalent radii of both yttrium and oxygen atoms (1.62 and 0.74 \AA , respectively) [8]. It is worth mentioning that, all the bond lengths equal to the sum of the two covalent radii of all the atoms in the molecule, taking into account their relative electronegativities. The short bond distances of $C_{12}-O_5$ (1.203 \AA), $C_{13}-O_4$ (1.212 \AA) and $C_{14}-O_6$ (1.238 \AA) indicate that they are double bonds (C=O). From this sense, it can be estimated that the shortest bonds between Y_1-O_3 of V.A are covalent in nature, whereas, bonds of Y_1-O_4 and those between Y_1 and oxygen atoms of water molecules are coordinate ones, which contradicts with the results suggested in the previous work [1]. Thus, it is concluded that violuric acid reacted in the form of ketonic



Table(2): Elemental analyses and molecular formulae of Y(III)-violurate complexes

Complex	wt% Found (Calculated)					Molecular Weight
	C	H	N	Cl	Y	
$[\text{Y}(\text{V.A})_2 \cdot 4\text{H}_2\text{O}]\text{Cl}$ (I)	18.8 (19.0)	2.37 (2.5)	16.52 (16.50)	6.98 (6.90)	17.48 (17.20)	508.572
$[\text{Y}(\text{V.A})_2 \cdot 4\text{H}_2\text{O}]\text{Cl} \cdot 3\text{H}_2\text{O} \cdot \text{HCl}$ (II)	16.06 (16.10)	3.03 (3.40)	14.05 (14.50)	11.87 (11.3)	14.86 (14.70)	599.128
$[\text{Y}(\text{V.A})_2 \cdot 4\text{H}_2\text{O}]\text{Cl} \cdot 2\text{H}_2\text{O}$ (III)	17.64 (17.60)	2.96 (2.90)	15.43 (15.50)	6.52 (6.60)	16.32 (16.50)	544.604

GEOMETRY TABLES OF COMPLEX I

Table (3): Fractional Atomic Coordinates & U(Iso) Of Complex I

Atom	x/a	y/b	z/c	U(iso)
Y(1)	0.500(13)	0.500(9)	0.29(3)	0.020400
Cl(2)	0.500(13)	0.000(9)	0.06(3)	0.030310
O(3)	0.400(13)	0.416(9)	0.00(3)	0.031947
O(4)	0.265(13)	0.449(9)	0.43(3)	0.032620
O(5)	-0.172(13)	0.316(9)	0.58(3)	0.035313
O(6)	0.115(13)	0.233(9)	-0.05(3)	0.037713
N(7)	0.304(13)	0.358(9)	-0.01(3)	0.029760
N(10)	0.050(13)	0.381(9)	0.51(3)	0.029950
N(11)	-0.029(13)	0.277(9)	0.26(3)	0.028773
C(12)	-0.061(13)	0.322(9)	0.45(3)	0.029147
C(13)	0.181(13)	0.396(9)	0.37(3)	0.026783
C(14)	0.096(13)	0.279(9)	0.11(3)	0.029743
C(15)	0.200(13)	0.348(9)	0.15(3)	0.028667
H(11)	-0.100(13)	0.236(9)	0.21(3)	0.033070
O(16)	0.701(13)	0.422(9)	0.13(3)	0.035793
O(17)	0.442(13)	0.589(9)	0.58(3)	0.035240
H(10)	0.037(13)	0.414(9)	0.65(3)	0.034630
H(16A)	0.804(13)	0.429(9)	0.19(3)	0.039980
H(16B)	0.679(13)	0.383(9)	0.01(3)	0.039980
H(17A)	0.523440	0.614620	0.671960	0.039360
H(17B)	0.336720	0.600600	0.623080	0.039360

Table (4): Intramolecular Bond Lengths

Bond length limits use covalent radii + 0.20A

Y(1) - O(3)	2.295(5)	Y(1) - O(4)	2.363(5)
Y(1) - O(4)	2.363(4)	Y(1) - N(7)	3.396(6)
Y(1) - C(13)	3.328(6)	Y(1) - C(15)	3.753(7)
Y(1) - O(16)	2.362(5)	Y(1) - O(17)	2.301(5)
Cl(2) - O(4)	3.652(6)	Cl(2) - O(4)	3.752(5)
Cl(2) - O(4)	3.652(6)	Cl(2) - O(4)	3.752(5)
Cl(2) - N(7)	3.594(6)	Cl(2) - N(10)	3.751(7)
Cl(2) - N(10)	3.183(7)	Cl(2) - N(10)	3.751(7)
Cl(2) - N(10)	3.183(7)	Cl(2) - C(13)	3.344(8)
Cl(2) - C(15)	3.329(7)	Cl(2) - O(16)	3.091(5)
O(3) - O(3)	3.338(9)	O(3) - O(4)	3.401(8)
O(3) - O(4)	2.718(8)	O(3) - O(6)	3.164(7)
O(3) - N(7)	1.306(7)	O(3) - N(11)	3.649(8)
O(3) - C(13)	2.822(8)	O(3) - C(14)	3.586(8)
O(3) - C(15)	2.256(9)	O(3) - O(16)	2.709(7)
O(3) - O(16)	2.976(7)	O(3) - O(17)	3.752(8)
O(4) - N(7)	2.938(9)	O(4) - N(7)	3.450(9)
O(4) - N(10)	2.242(7)	O(4) - C(12)	3.572(8)
O(4) - C(13)	1.212(8)	O(4) - C(14)	3.690(9)
O(4) - C(15)	2.391(9)	O(5) - O(6)	3.498(7)

O(5) - O(6)	3.562(8)	O(5) - O(6)	3.301(8)
O(5) - N(10)	2.263(7)	O(5) - N(11)	2.269(8)
O(5) - N(11)	3.587(7)	O(5) - C(12)	1.203(9)
O(5) - C(13)	3.555(8)	O(5) - C(14)	3.537(9)
O(5) - C(14)	3.082(9)	O(5) - C(15)	3.337(9)
O(5) - O(16)	3.292(8)	O(5) - O(16)	3.682(8)
O(5) - O(17)	2.853(7)	O(6) - N(7)	2.702(7)
O(6) - N(7)	3.131(7)	O(6) - N(10)	3.537(9)
O(6) - N(11)	2.275(8)	O(6) - N(11)	3.306(7)
O(6) - C(12)	3.472(9)	O(6) - C(12)	3.543(10)
O(6) - C(12)	3.700(9)	O(6) - C(13)	3.690(8)
O(6) - C(14)	1.238(9)	O(6) - C(15)	2.385(9)
N(7) - N(10)	3.461(9)	N(7) - N(10)	3.658(9)
N(7) - N(11)	3.552(8)	N(7) - N(11)	3.037(8)
N(7) - C(13)	3.621(10)	N(7) - C(13)	2.475(9)
N(10) - N(11)	2.341(8)	N(10) - C(12)	1.425(9)
N(10) - C(13)	1.390(8)	N(10) - C(14)	2.807(10)
N(10) - C(15)	2.432(10)	N(11) - C(12)	1.344(10)
N(11) - C(13)	2.798(9)	N(11) - C(14)	1.356(8)
N(11) - C(15)	2.410(9)	N(11) - O(16)	3.489(8)
N(11) - O(17)	3.395(8)	C(12) - C(13)	2.496(9)
C(12) - C(14)	2.431(11)	C(12) - C(15)	2.856(11)
C(12) - O(16)	3.229(9)	C(12) - O(17)	3.710(9)
C(13) - C(14)	2.553(11)	C(13) - C(15)	1.479(11)
C(14) - C(15)	1.490(10)	C(14) - O(17)	3.658(10)
Y(1) - H(16A)	2.96334(14)	O(3) - H(11)	2.860(5)
O(5) - H(11)	2.531(5)	N(10) - H(11)	3.227(6)
N(11) - H(11)	0.960(6)	C(12) - H(11)	2.002(8)
C(12) - H(10)	2.080(7)	C(12) - H(16A)	2.620(7)
C(14) - H(11)	1.930(7)	C(14) - H(11)	3.222(7)
C(15) - H(11)	3.243(7)	H(11) - O(16)	3.638(5)

The three charges of Y(III) ion are, thus, partly satisfied by two negative charges of two violurato molecules, while the third charge is satisfied ionically by the chloride ion incorporated in the lattice system. This renders the complex ionic in character which is responsible for its rather thermal stability and the ease of its dissolution in water and polar solvents.

The angles formed between yttrium and oxygen atoms ensure the dodecahedral stereochemistry. A dodecahedron is produced by an appropriate concerted motion of the ligands such that a cubic arrangement can be converted into a dodecahedron (D_{2d}). The interconversion takes place by imagining that two encountered atoms in the square projection of the cube become more distant from one another, while the other two encountered atoms become nearer to each other such that, some of the nearly 110° angles would be increased to about $124.0 - 142.3^\circ$, while some others are decreased to about $70 - 90^\circ$. Other angles remain nearly constant at 99° which correspond to the situation of the atoms on the edges of the cube (Figure 2). Thus, the angles $O_3-Y_1-O_3$ are $93.3^\circ(3)$; $O_3-Y_1-O_4$ are $71.4^\circ(2)$ & $142.3^\circ(2)$; $O_3-Y_1-O_{16}$ are $71.1^\circ(2)$ & $79.4^\circ(2)$; $O_3-Y_1-O_{17}$ are $99.6^\circ(2)$ & $145.1^\circ(2)$; $O_4-Y_1-O_4$ are $139.8^\circ(2)$; $O_{17}-Y_1-O_{17}$ are $88.0^\circ(3)$; $O_4-Y_1-O_{16}$ are $72.2^\circ(2)$ and $124.0^\circ(2)$ and $O_4-Y_1-O_{17}$ are $72.5^\circ(2)$ & $78.8^\circ(2)$ degrees.

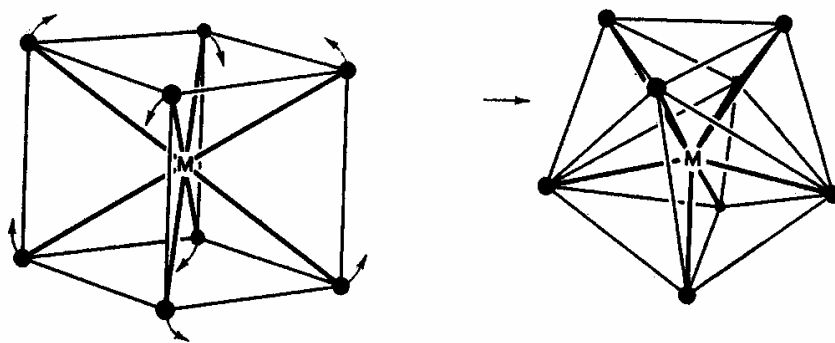


Fig. (2): The interconversion of the cube to dodecahedron.

Sigma bonding with symmetries of ligand orbitals for a D_{2d} point group are of the types $2a_1+2b_2+2e$, while the corresponding symmetries of metal orbitals are: $s + dz^2 = 2a_1$, $p_z + d_{xy} = 2b_2$ and $p_x, p_y + d_{yz}, d_{zx} = 2e$ [9].

The TG and DTG thermograms of V.A.H₂O and Y-violurate complexes are shown in Fig. (3). The thermal decomposition of these compounds occurs in three to five consecutive steps between 30°C to 800°C. The patterns of TG and DTG curves of complexes I, II and III show a great similarity in the temperature ranges 200-400°C and 400-800°C due to the decomposition of V.A in the molecules. Complex II shows two inflections more than complex I at the beginning of the curve (50-70° & 105-130°C) which agree with losses of adsorbed Cl and water of crystallization, respectively. In complex III, there is only one degradation step more than complex I at 100-137°C which arise due to loss of 1.5 H₂O of crystallization. At temperatures 215.25, 326.83; 209.90, 329.23 and 210.60, 318.01°C for complexes I, II and III, respectively, two degradations occur which correspond to the evolution of coordinated water and decomposition of V.A molecules as volatile gases such as HCN, N₂, CO and CO₂. The last decomposition step appears at about 400 to 800°C where the remained stable product is YClO₃, as suggested due to calculations. The activation energies (E^*) of the pyrolyzed compounds could be calculated from the slopes of $\ln 1/C_s$ vs. $T-T_s$ (Fig. 4) by applying the method of Horowitz and Metzger. The values of E^* in kilo joules per mole, for each step are shown in Table (5), and declare that the largest activation energies occur at the temperature range 200-360°C, i.e. it means that this step of pyrolysis at which complexes decompose, is the rate - determining step.

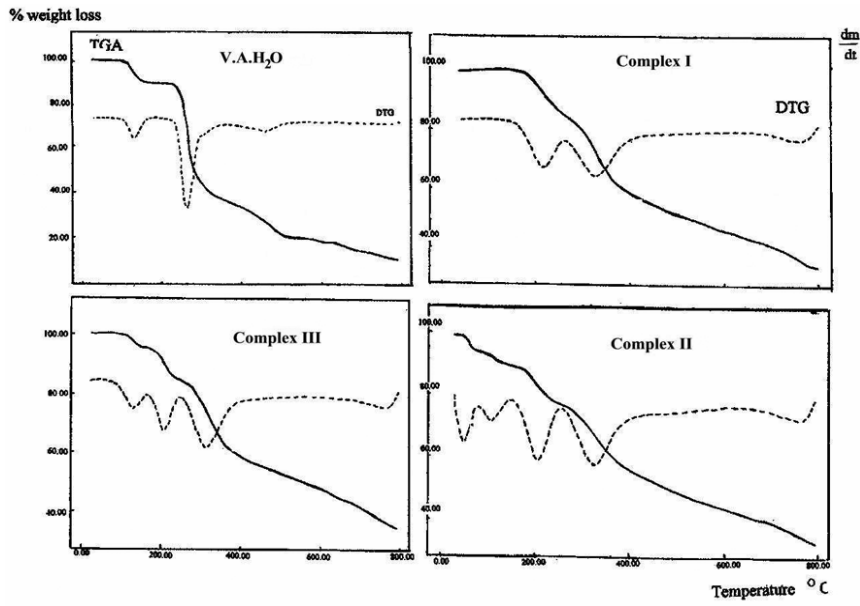


Fig. (3): TGA & DTG Thermograms of V.A. H₂O and Complexes I, II and III.

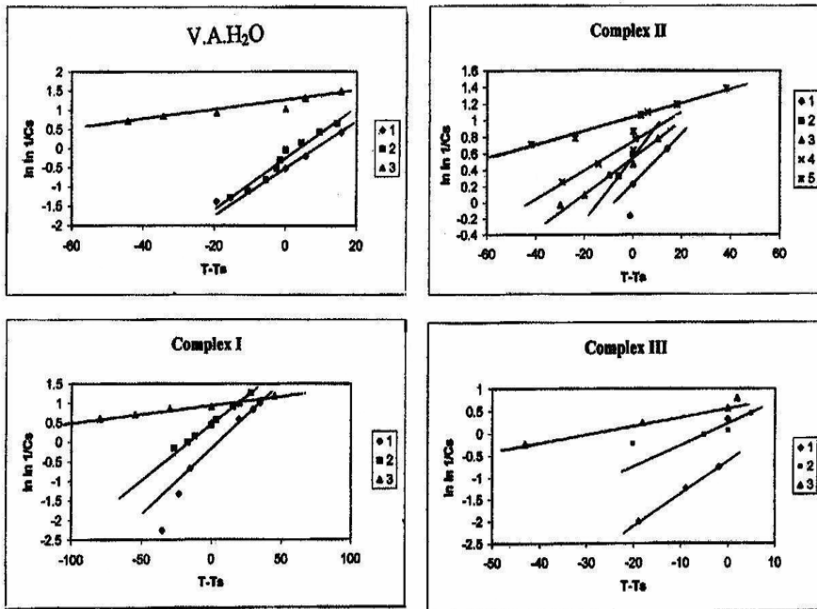


Fig. (4): Weight – temperature plots.

Table (5): Thermal parameters of V.A.H₂O and Y- violurate complexes

Compound	Mass loss % Calcd. (found)	Temperature range °C	Weight of sample mg	Slope	T _s °C	E* kJ/mole
V.A.1H ₂ O	10.28(10.035)	100 - 150	5.225	0.05971	129.3	8.3002
	57.74(57.562)	250 - 295		0.056305	265.54	33.008(r. d.s.)
	18.298(18.295)	415 - 500		0.012735	459.4	22.345
Complex I	11.816(11.919)	180 - 260	2.900	0.02800	215.25	10.786
	16.925(16.924)	300 - 360		0.02333	326.83	20.718(r. d.s.)
	20.656(20.389)	400 - 575		0.00456	505.00	9.679
	17.212(17.741)	600 - 800				
Complex II	5.925(5.532)	50 - 70	4.986	0.03188	51.08	0.6915
	4.518(4.222)	105 - 130		0.03960	111.00	4.0646
	12.048(12.098)	180 - 230		0.02330	209.90	8.5494
	26.27(26.065)	300 - 350		0.01705	329.23	16.365 (r.d.s.)
	11.707(11.540)	420 - 550		0.00909	462.00	15.1362
Complex III	4.96(4.577)	100 - 137	3.367	0.06694	128.82	9.2355
	11.57(11.206)	190 - 225		0.07303	210.06	6.791 (r. d. s.)
	35.09(35.041)	275 - 330		0.01874	318.01	15.759

References

1. A.A.M. Gad, I.S. Ahmed Farag & R.M. Awadallah, *Cryst. Res. Technol.*, **27**, (2),201, (1992).
2. Ionashiro, M.; Graner, C.A.F., *Zuanon Netto, J. Ecl. Quim.*, (29), (1983).
3. Z. Otwinowski, and Minor, W., In *Methods in Enzymology*, 276, Edit. by C.W. Carter, Jr. and R.M. Sweet, pp. 307-326, New York: Academic Press, (1976).
4. S., Mackay, C. J., Gilmore, Edwards, C., N. Stewart, and Shankland, K. Maxus, "*Computer Program for the solution and Refinement of Crystal Structures*", B uker Nonius, The Netherlands, MacScience, Japan & The University of Glasgow, (1999).
5. Johnson, C.K., "*ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program*", Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.,(1976).
6. H.H. Horowitz and G. Metzger, *Anal. Chem.*, **55**, 1464 (1963).
7. R.M. Awadallah, A.A.M. Belal, R.M. Issa and Robert D. Peacock, *Spectrochimica Acta*, **47A**, (11), 1541 (1991).
8. J.D. Lee, "*Concise Inorganic Chemistry*" 5th Edition, Dep. Of Chem. at Loughborough Univ. Of Technology, U.K. (1999).
9. S.F.A. Kettle, "*Physical Inorganic Chemistry*", Oxford Univ. Press. A Coordination Chemistry Approach, (1996).