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SPECTRAL AND THERMAL STUDIES OF SOME BIVALENT METAL CHELATES OF VARIOUS HYDROXY-QUINONES

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ABSTRACT

Spectral studies (^{1}H-NMR and ^{13}C-NMR) on the chelates of hydroxy-quinones (chrysazin, alizarin, jouglone and naphthazarin) with the bivalent metal ions Cu(II), Ni(II), Zn(II), Mn(II), Fe(II), Pd(II) and Pt(II) are reported and discussed. Mass spectral data of metal–chrysazin complexes are also studied.

Thermal investigations by TG, DTG and DTA on the chelate complexes studied were carried out in dynamic atmospheres of air and nitrogen to determine their mode of decomposition. The thermal stability of the ligand is the determining factor in the thermal stability of the complexes which follows the series: naphthazarin < jouglone < alizarin < chrysazin.

INTRODUCTION

The hydroxy-quinones and their coordination compounds have long been known to possess numerous chemically and biologically significant properties [1–3]. It is not surprising then that these compounds have attracted considerable experimental and theoretical interest which has stimulated basic and applied research in several areas. Thus, they have found important applications in electrochemistry, analytical chemistry and coordination chemistry. In fact, in the last few years a number of papers concerning synthesis, characterization and biological function of some metal chelates of hydroxy-quinones have been published [4–8].

In the knowledge of the significant applications of the quinones and their derivatives, a research project [9–11] started several years ago. In this, a large number of hydroxy-quinone chelates with various bivalent metal ions

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have been synthesized and their structures and chemistry have been studied extensively.

Since, in most of the above mentioned applications of quinones, their chelating ability plays an important role [12–14], it was of interest to continue the study of the structure and bonding of mononuclear and homobinuclear chelates of some hydroxy-quinones.

In the present paper we report our results concerning the chelates of 1,8-dihydroxy-9,-10-anthracenedione (1,8-DHAQ) (chrysazin), 1,2-dihydroxy-9,10-anthracenedione (1,2-DHAQ) (alizarin), 5-hydroxy-1,4-naphthalenedione (5-HNQ) (jouglone) and 5,8-dihydroxy-1,4-naphthalenedione (5,8-DHNQ) (naphthazarin) with some bivalent metal ions such as Cu(II) Zn(II), Ni(II), Mn(II), Fe(II) Pd(II) and Pt(II). The investigated homobinuclear chelates of naphthazarin were of the general formula $[M_2(C_{10}H_4O_4)(C_{10}H_8N_2)_2](PF_6)_2$where M = Cu, Ni, Zn, $C_{10}H_4O_4$ = anion of naphthazarin and $C_{10}H_8N_2$ = 2,2′-bipyridyl). The 2,2′-bipyridyl ligand was selected as the nonbridging ligand because it prevents the formation of polynuclear chelates (polymers).

We describe here the spectral data (proton and carbon-13 nuclear magnetic resonance, as well as the mass spectra of metal–chrysazin complexes) and the thermal studies of the above metal chelates of hydroxy-quinones. In particular, a thermal investigation has been done on these complexes using the TG/DTG and TG/DTA techniques in dynamic atmospheres of nitrogen and air atmosphere, respectively. A literature survey covering the past decade reveals that little work has been done on thermal studies of hydroxy-quinone chelates [15–18], and contains especially the thermal stability of the polymer complexes of naphthazarin.

Recently, Bhatia et al. [19–24] reported results on the non-isothermal decomposition of various metal complexes of lapachol, jouglone and lawsone. They found that the anhydrous complexes dissociated to metal oxides with an intermediate corresponding to $ML_{1.78}$.

EXPERIMENTAL

All complexes were prepared by known methods [9–11]. ^{1}H-NMR spectra were obtained on a Varian FT-80A (80 MHz) spectrometer in $CDCl_3$ or DMSO solutions, using TMS as an internal standard. ^{13}C-NMR spectra were recorded on a Varian CFT spectrometer operating in the Fourier transform mode at 20 MHz using 10 mm diameter sample tubes. An internal deuterium lock ($CDCl_3$ or DMSO) was employed with broad-band proton noise decoupling.

Mass spectra were recorded on a R.M.V.-GL-Hitachi–Perkin-Elmer mass spectrometer.

The thermograms (TG/DTG) were scanned on a Du-Pont Instruments

Series 99, thermal analyser with combined apparatus Du-Pont Instruments Series 951, thermogravimetric analyser. The thermograms (TG/DTA) were obtained on a Rigaku Model 8076-D-1 thermal analyser.

The measurements were performed in dynamic atmospheres of air and nitrogen at a flow rate 60 ml $\min^{-1}$ up to to 1000°C, using a chromel/alumel thermocouple. The heating rate was 20 K $\min^{-1}$ and the weight of sample was approximately 15 mg with a Al_2O_3 as reference.

RESULTS AND DISCUSSION

Spectral studies

Nuclear magnetic resonance

In this paper, we report our ^{1}H-NMR and ^{13}C-NMR measurements on some hydroxy-quinones (chrysazin, alizarin and naphthazarin) metal chelates with the metal ions Pd^{2+} and Zn^{2+}. The aim is to fill the gap in this research field of hydroxy-quinones and to study the ligand's chelating ability on the structure of the investigated compounds.

^{1}H-NMR. The signals observed in the proton NMR spectra (in τ values) for the investigated mononuclear chelate complexes appeared to be shifted to lower frequencies ($\Delta = 0$–0.65 τ values) than the corresponding protons of the free hydroxy-quinones (Table 1). This could be attributed to the expected electron density transfer from the ligands to the central atom due to the enhanced positive charge on the metal atoms and to the bidentate character of the hydroxy-quinone group. For the homobinuclear chelates, however, the signals appeared to be slightly shifted to higher frequencies ($\Delta = 0$–$0{,}2$ τ values) than the corresponding protons of the free hydroxy-quinones.

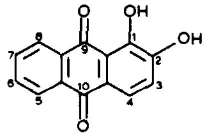
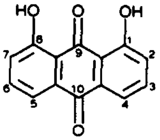
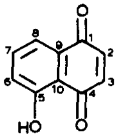
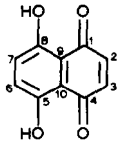
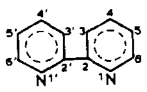
The proton signals of the hydroxyl group of the free ligands are not detectable in the spectrum of alizarin while they appeared at negative τ values in the spectra of chrysazin and naphthazarin. These signals, however, disappeared in the spectra of the corresponding metal–quinone chelates.

^{13}C-NMR. In Table 2 are listed the chemical shifts (δ, ppm), the intensities, and the assignments of the ^{13}C-NMR signals of some metal–quinone chelates. Chemical shift assignments were made by noting ranges of resonances for analogue compounds [25]. The ^{13}C resonances of the sp^2 carbon atoms of the alkene bonds appear, as one would expect, in the region of 120–160 ppm downfield from TMS. Because of the non-existence of symmetry in the molecule of alizarin, there are more signals in this spectrum than in the spectrum of the symmetrical molecule of chrysazin.

The most interesting feature on these spectra is that the quinoid carbon carbonyls resonance of the ligands is absent at 175 ppm as it has to be. Also, the hydroxyl-bonded carbon signal at about 160 ppm does not exist or

TABLE 1

Proton NMR spectra (τ values) for some metal chelates of hydroxy-quinones and their free ligands [a]

Ligand	Protons	τ Free ligand	τ $|Pd(C_{14}H_7O_4)_2|\cdot 2H_2O$	τ $|Zn(C_{14}H_7O_4)_2\cdot 2H_2O$
	(3)	2.80(d)	3.45(d)	2.80(d)
	(4)	2.37(d)	2.70(d)	2.37(d)
	(5, 6, 7, 8)	2.03(m)	2.10(m)	2.03(m)
	OH	–	–	–
($C_{14}H_8O_4$ = Alizarin)				
	(2,7)	2.75(m)	2.65(m)	2.85(m)
	(3, 4, 5, 6)	2.32(m)	2.32(m)	2.45(m)
	OH	–		–
($C_{14}H_8O_4$ = Chrysazin)				
	(2,3)	3.06(s)		
	(6)	2.78(m)		
	(7,8)	2.42(m)		
	OH	−1.88(s)		
($C_{10}H_6O_3$ = Jouglone)				
			$|Zn_2(C_{10}H_4O_4)(C_{10}H_8N_2)_2|(PF_6)_2$	
	(2,3)	3.50(s)		3.10(s)
	(6,7)	2.78(m)		2.82(m)
	OH	−2.43		–
($C_{10}H_4O_4$ = Naphthazarin)				
	(6,6′)	1.30(d)		1.40(m)
	(3,3′)	1.65(d)		
	(4,4′)	2.08(m)		1.85(m)
	(5,5′)	2.57(m)		2.37(m)
$C_{10}H_8N_2$ = Bipyridyl)				

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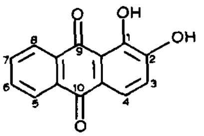
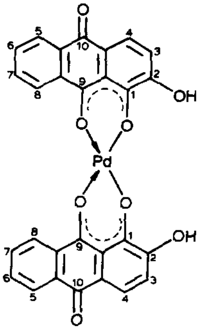
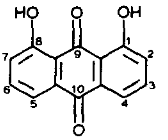
[a] s = singlet; d = doublet; m = multiplet.

appears with very low intensity. The latter may be due to the absence of neighbouring carbon which contains protons.

The fact that the carbonyl carbon ^{13}C signals are present in the metal chelates of hydroxy-quinones means that the nature of the metal affects the CO carbon assignment. It is notable that this signal is shifted to higher frequencies and this is more evident in the case of palladium binuclear complexes.

TABLE 2

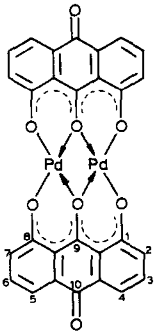
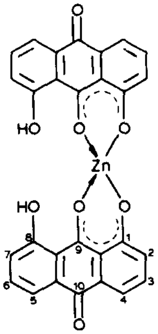
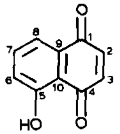
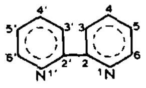
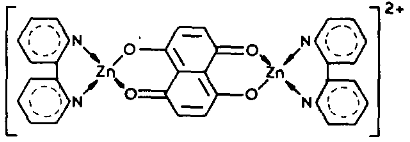
Carbon-13 chemical shifts (δ, ppm downfield from TMS) and assignments for some metal chelates of hydroxy-quinones

Compound	No.	Int.	ppm	Assignments
	not shown			CO
	1	7.54	153.47	C_1-OH
	2	26.48	135.91	C_5, C_7
	3	22.63	134.85	C_2-OH
	4	7.32	133.75	C_6
	5	36.37	127.56	C_4, C_8
	6	19.38	127.34	C_3
	7	27.15	121.94	C_{12}, C_{14}
($C_{14}H_8O_4$ = Alizarin)	8	24.96	121.73	C_{11}, C_{13}
$\|Pd(C_{14}H_7O_4)_2\| \cdot 2H_2O$	1	6.64	189.46	C_{10}-CO
	2	10.64	135.89	C_5
	3	9.57	134.82	C_2-OH
	4	6.19	133.81	C_7
	5	5.66	133.44	$C_{1,9}$-O
	6	11.09	127.56	C_4
	7	6.96	127.31	C_3
	8	7.51	126.87	C_6
	9	6.30	126.62	C_8
	10	11.28	121.94	C_{14}
	11	10.15	121.75	C_{13}
	12	6.50	121.16	C_{12}
	13	6.30	118.91	C_{11}
$\|Zn(C_{14}H_7O_4)_2\| \cdot 2H_2O$	not shown			C_{10}-CO
($C_{14}H_8O_4$ = Alizarin)	1	12.39	135.91	C_5, C_6, C_7
	2	13.24	134.84	C_2-OH
	3	12.71	127.56	C_4, C_8
	4	11.61	127.35	C_3, C_{13}
	5	12.35	121.94	C_{11}, C_{12}, C_{14}
	not shown			C-OH
	1	54.09	137.24	C_2, C_4, C_5, C_7
	2	55.79	124.63	C_3, C_6, C_{12}, C_{14}
	3	53.80	120.04	C_{11}, C_{13}
($C_{14}H_8O_4$ = Chrysazin)				

Mass spectra

The mass spectrum of the simple 1,8-dihydroxy-anthraquinone, chrysazin, and its fragmentation pattern are reported elsewhere [26]. Here, we studied the mass spectral data of ten complexes of chrysazin with the bivalent metals Cu, Ni, Zn, Mn, Fe, Pd and Pt, as mentioned previously, and also three adducts with pyridine, of the general formulae $Cu_xL_2(Py)(OH_2)$ ($x = 1$ or 2, L = chrysazin) and $[Ni_2L_2(Py)_2(OH_2)_2(OH_2)_2] \cdot 2H_2O$.

TABLE 2 (continued)

Compound	No.	Int.	ppm	Assignments
$\vert Pd_2(C_{14}H_7O_4)_2\vert \cdot H_2O$	1	5.16	192.82	C_{10}-CO
	2	6.88	179.50	C–O
	3	6.10	139.46	C_2, C_4, C_5, C_7
	4	8.31	139.25	C_3, C_6
	5	7.90	125.25	C_{12}, C_{14}
	6	7.25	120.16	C_{11}, C_{13}
$Zn(C_{14}H_7O_4)_2$	1	5.87	177.46	C_{10}-CO
	2	5.04	159.58	C_8-OH
	3	8.20	137.12	C_2, C_4, C_5, C_7
	4	5.44	134.58	$C_3, C_6, C_{11}, C_{14}, C_{12}, C_{13}$
	not shown			C–CO
	not shown			C–OH
	1	109.09	139.63	C_6, C_8
	2	73.46	138.67	C_7
	3	79.13	136.56	C_9
	4	82.12	124.50	C_{10}
	5	107.83	119.17	C_2, C_3
	1	8.24	156.12	C_2, C_2'
	2	74.10	150.01	C_6, C_6'
	3	108.83	137.95	C_4, C_4'
	4	129.98	124.86	C_5, C_5'
($C_{10}H_8N_2$-bipyridyl)	5	109.02	121.25	C_3, C_3'
$\vert Zn_2(C_{10}H_4O_4)(C_{10}H_8N_2)_2\vert_2^{2+}$	1	8.38	149.56	bipyridyl C_6, C_6'
($C_{10}H_4O_4$ = Naphthazarin)	2	4.85	139.70	bipyridyl C_4, C_4' + naphthazarin
	3	4.78	127.20	bipyridyl C_5, C_5' + naphthazarin
	4	5.12	122.53	bipyridyl C_3, C_3'

The mass spectral study of all complexes under investigation reveals that the fragmentation pattern agrees with that proposed for the ligand, the characteristic being the absence of the peak corresponding to the molecular ion M^{7+} or to the ion $M-L^{7+}$, which can be formed by removal of one hydroxy-quinone group from the parent compounds.

The molecular ion of chrysazin ($m/e = 240$) was the base peak in the spectrum in each case with the exception of the complexes of platinum(II) and palladium(II), where the base peak was at much lower m/e values. This may be attributed to the different behaviour of the complexes of Pt and Pd due to the π-back donation of these metals which leads to the strength of the metal–ligand bond.

As far as the complexes of chrysazin with adduct pyridine are concerned, in the mass spectrum of these the base peak was that corresponding to the ion of pyridine ($m/e = 75$) and to its pyrolytic daughter ion at m/e 52, while the ionic fragments of chrysanin and its pyrolytic products were found at very low intensities.

Thermal studies

The thermal analysis curves (TG/DTG and TG/DTA) of some representative complexes under study are depicted in Figs. 1–8. It can be seen that, in all cases, the decomposition process in nitrogen or air atmosphere, over the temperature range 20–1000°C, includes various thermal effects.

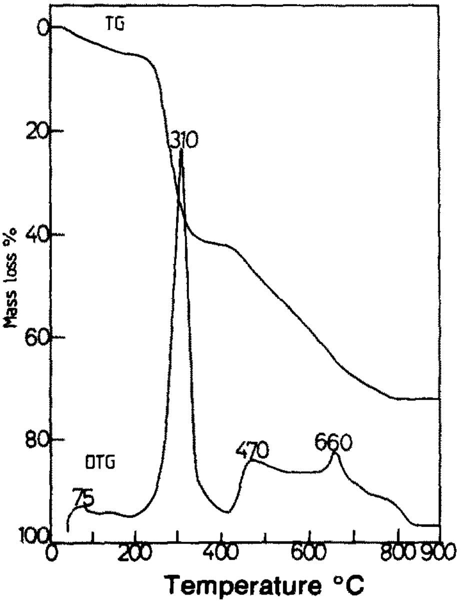


Fig. 1. Thermal curves (TG/DTG) for $Mn(C_{14}H_7O_4)_2 \cdot (H_2O)_2$, $C_{14}H_7O_4$ = alizarin, in nitrogen.

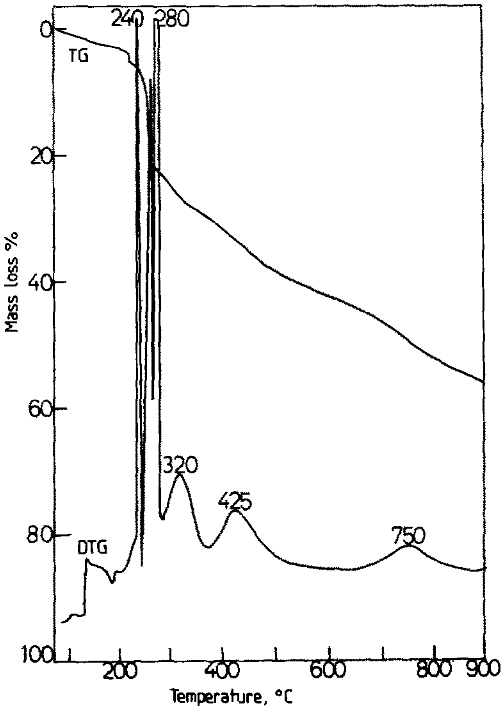


Fig. 2. Thermal curves (TG/DTG) for $[Pd(C_{14}H_7O_4)_2]\cdot 2H_2O$, $C_{14}H_7O_4$ = alizarin, in nitrogen.

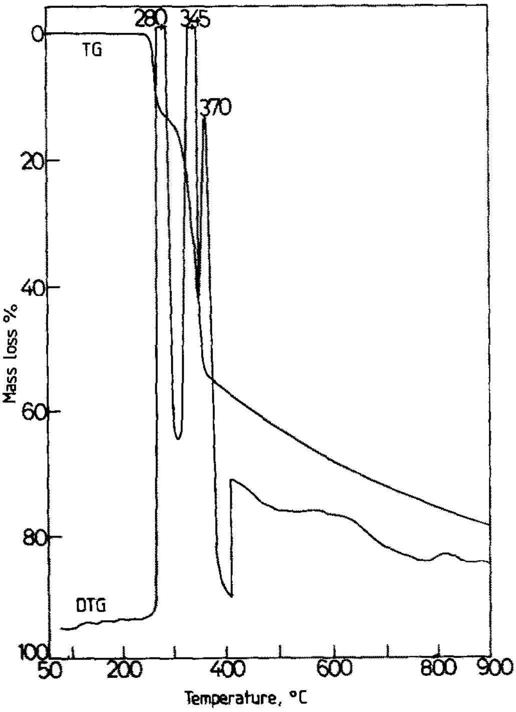


Fig. 3. Thermal curves (TG/DTG) for $Cu(C_{10}H_5O_3)_2$, $C_{10}H_5O_3$ = jouglone, in nitrogen.

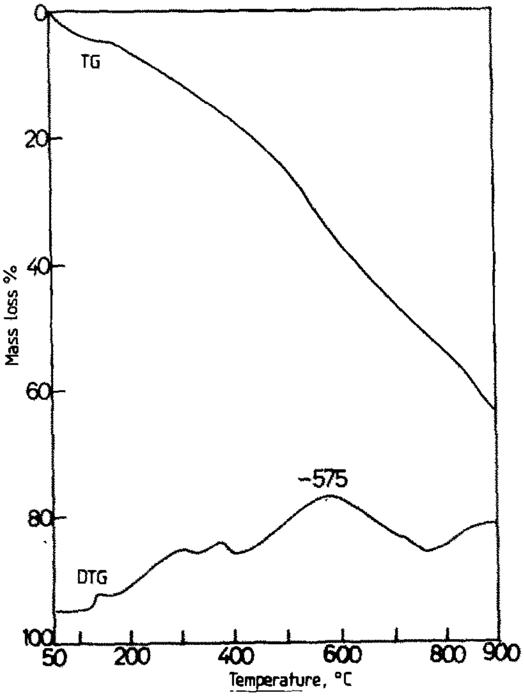


Fig. 4. Thermal curves (TG/DTG) for $Pt(C_{10}H_5O_3)_2$, $C_{10}H_5O_3$ = jouglone, in nitrogen.

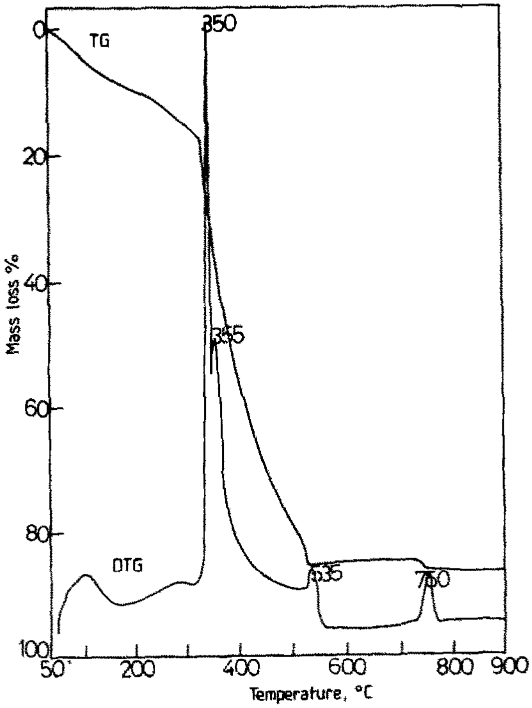


Fig. 5. Thermal curves (TG/DTG) for $Pd(C_{10}H_5O_3)_2(NH_3)_2$, $C_{10}H_5O_3$ = jouglone, in nitrogen.

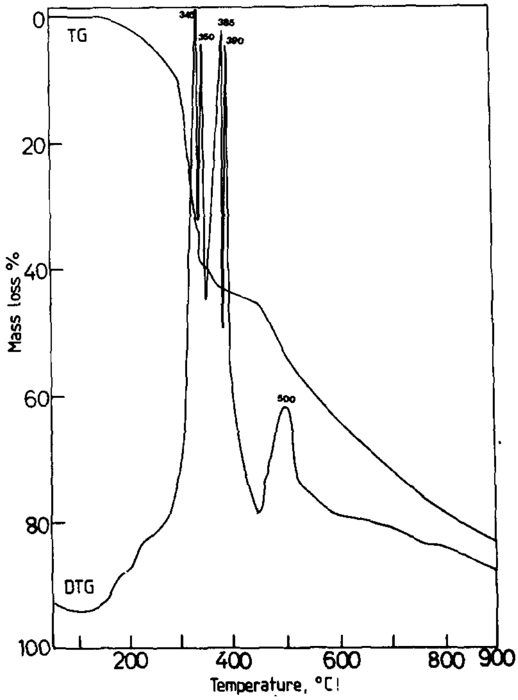


Fig. 6. Thermal curves (TG/DTG) for $[Cu(C_{10}H_4O_4)(C_{10}H_8N_2)_2]^{2+}(PF_6^-)_2$, $C_{10}H_4O_4$ = napthazarin, $C_{10}H_8N_2$ = bipyridyl, in nitrogen.

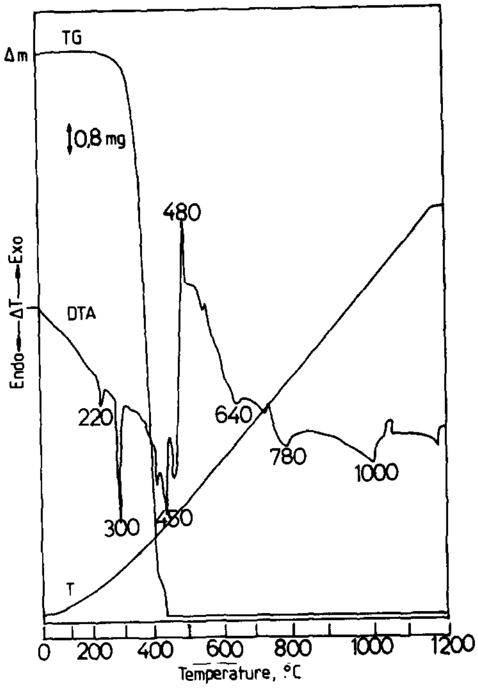


Fig. 7. Thermal curves (TG/DTA) for chrysazin in air.

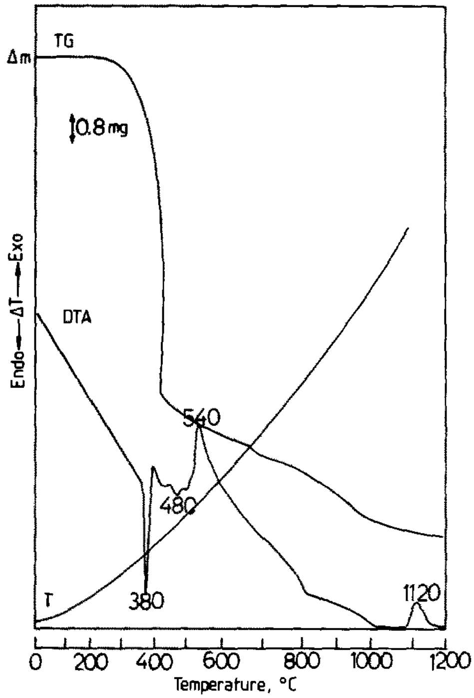


Fig. 8. Thermal curves (TG/DTA) for alizarin in air.

The temperature ranges and percentage mass losses of the decomposition are given in Tables 3–8. The temperatures of the greatest rate of decomposition (DTG_{max}), the theoretical percentage mass losses, and the DTA data are also given.

In particular, the thermal analysis results (TG/DTG) for chrysazin and metal–chrysazin complexes, in nitrogen atmosphere, are depicted in Table 3. It can be seen that hydrated chelates lose water in the temperature range 50–180°C. The chrysazin TG curve showed no loss up to 180°C. From 180 to 280°C a rapid mass loss was observed (95.6%), which was the main decomposition stage. From the DTG curve, however, it is clear that this stage is a combination of two consecutive processes with maximum rate of decomposition at 225 and 270°C. From 280 to 420°C a gradual mass loss occurred (4.4%).

The thermal decomposition of anhydrous metal–chrysazin complexes occurred between 180 and 600°C in one or two stages, the mass losses corresponding either to two ligand molecules or to one L–O group and one molecule of the ligand chrysazin. This means that the metal–oxygen coordinated bond in these complexes, is equivalent in strength to the bond carbon–oxygen (attached to metal), due to the high chelating ability of chrysazin.

TABLE 3

Thermal analysis results (TG/DTG) on metal–chrysazin chelates in nitrogen atmosphere

Compound	Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss (%)	Evolved formula	Moiety mass calc. (%)
$C_{14}H_8O_4$	1	180–280	225, 270	95.6	$C_{14}H_8O_4$	100.00
	2	280–420	–	4.4	–	–
	residue	> 420		0.0	–	–
$Cu(C_{14}H_7O_4)_2$	1	250–320	260	40.2	$C_{14}H_7O_3$	41.18
	2	320–480	410	43.9	$C_{14}H_7O_4$	44.14
	residue	> 1000		13.8	CuO	14.67
$Cu(C_{14}H_7O_4)_2(Py)(OH_2)_2$	1	50–165	165	2.5	H_2O	2.81
	2	165–200	170	11.5	Py	12.30
	3	200–410	270	33.4	$C_{14}H_7O_3$	34.93
	4	410–500	440	37.2	$C_{14}H_7O_4$	37.40
	residue	> 1000		13.2	CuO	12.50
$Zn(C_{14}H_7O_4)_2$	1	250–300	260	38.5	$C_{14}H_7O_3$	41.05
	2	300–420	330	45.5	$C_{14}H_7O_4$	44.00
	residue	> 1000		15.0	ZnO	14.90
$[Ni_2(C_{14}H_7O_4)_2(OH_2)_4] \cdot 2H_2O$	1	50–130	120	5.0	$2\ H_2O$	5.13
	2	130–320	300	11.5	$4\ H_2O$	10.26
	3	320–580	500	61.4	$2\ (C_{14}H_7O_3)$	63.22
	residue	> 1000		21.0	2 NiO	21.20
$[Pd_2(C_{14}H_7O_4)_2] \cdot H_2O$	1	50–170	150	2.3	H_2O	2.50
	2	170–230	210	26.0 } 70.0	$2(C_{14}H_7O_4)$	67.60
	3	230–470	420	44.0		
	residue	> 1000		19.7	2 Pd	30.00
$[Pt(C_{14}H_7O_4)_2] \cdot 2H_2O$	1	50–150	140	4.9	$2\ H_2O$	5.07
	2	150–500	390	67.0	$2\ (C_{14}H_7O_4)$	67.40
	residue	> 1000		28.0	Pt	27.51

TABLE 4

Thermal analysis results (TG/DTG) on metal–alizarin chelates in nitrogen atmosphere

Compound	Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss (%)	Evolved formula	Moiety mass calc. (%)
$Ni(C_{14}H_7O_4)_2(OH_2)_2$	1	50–170	145	6.8	2 H_2O	6.20
	2	170–500	–	3.2	–	–
	3	500–900	630	34.0	$C_{14}H_7O_3$ or $C_{13}H_7O_3$	38.90 or 36.82
	residue	> 900		54.0	NiO + $C_{14}H_7O_4$	13.0 + 41.70
$Mn(C_{14}H_7O_4)(OH_2)_2$	1	50–170	75	6.0	2 H_2O	6.32
	2	170–420	310	37.5	$C_{13}H_7O_3$	37.08
	3	420–800	470, 660	30.5	$C_{13}H_7O_2$	31.45
	residue	> 900		26.0	MnO_2	16.28
$|Pd(C_{14}H_7O_4)_2|\cdot 2H_2O$	1	50–225	–	5.2	2 H_2O	5.80
	2	225–265	240	16.0	C_6H_4CO	15.78
	3(a)	265–375	280, 320	8.8 } 19.2	CO + CHO	9.19 } 19.35
	3(b)	375–550	425	10.4	C_5H_3	10.16
	4	550–900	750	16.0	C_6H_4CO	16.78
	residue	> 900		43.6	Pd + unknown	17.05 + –

TABLE 5

Thermal analysis results (TG/DTG) on some metal chelates of hydroxy-quinones in air atmosphere

Compound	Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss (%)	Evolved formula	Moiety mass calc. (%)
$[Pd(C_{14}H_7O_4)_2] \cdot 2H_2O$	1	50–250	125	6.0	2 H_2O	5.80
	2	250–275	275	15.2	C_6H_4CO	16.78
$C_{14}H_7O_4$ = alizarin)	3	275–400	315	16.0	C_6H_4CO	16.78
	4(a)	400–675	–	11.2 } 21.6	C_5H_3	10.16 } 19.35
	4(b)	675–900	750	10.4	CO + CHO	9.19
	residue	> 900		41.2	Pd + unknown	17.05 + –
$Fe(C_{10}H_5O_3)_2$	1	50–180	–	4.0 } 22.8	$C_4H_2O_2$	20.39
	2	180–400	265	18.8		
($C_{10}H_5O_3$ = jouglone)	3	400–900	–	24.8	C_6H_3O	22.63
	residue	> 900		52.0	FeO + $C_{10}H_5O_2$	17.90 + 39.05

TABLE 6

Thermal analysis results (TG/DTG) on metal–jouglone chelate in nitrogen atmosphere

Compound	Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss (%)	Evolved formula	Moiety mass calc. (%)
$Mn(C_{10}H_5O_3)_2(OH_2)_2$	1	50–160	75	8.0	2 H_2O	8.24
	2	160–540	440	42.0	$C_{10}H_5O_2$	35.92
	3	540–900	–	45.0	$C_{10}H_5O_3$	39.58
	residue	> 900		5.0	MnO	16.24
$Cu(C_{10}H_5O_3)_2$	1	250–300	280	14.0	2 CO	13.67
	2	300–375	345, 370	40.8	$C_{10}H_5O_3$	42.25
	3	375–900	–	24.4	C_8H_5	24.90
	residue	> 900		20.8	CuO	19.42
$Fe(C_{10}H_5O_3)_2$	1	100–340	270	20.0	$C_4H_4O_2$	20.39
	2	340–600	~ 430	22.0	C_6H_3O	22.63
	3	600–900	–	18.0	$C_4H_4O_2$	20.39
	residue	> 900		40.0	$FeO+C_6H_6$	17.90 + 19.40
$Pd(C_{10}H_5O_3)_2 \cdot (NH_3)_2$	1	50–150	100	7.2	2 NH_3	7.00
	2	150–325	–	$\left.\begin{array}{r}8.8\\64.4\end{array}\right\}73.2$	2 $C_{10}H_5O_3$	71.24
	3	325–510	350, 355			
	residue	510		19.6	Pd	21.76
	4	510–550	535	4.0	partial dec. of Pd	
		550–720	plateau		Pd	
	5	720–780	750	2.0	–	
	residue	> 900		13.6	< Pd	
$Pt(C_{10}H_5O_3)_2$	1	100–400	–	13.2	$C_4H_2O_2$	15.16
	2	400–740	575	32.8	$C_{10}H_5O_3$	31.97
	3	740–900	–	14.0	C_6H_4	14.05
	residue	> 900		38.0	Pt	36.08

TABLE 7

Thermal analysis results (TG/DTG) on metal–naphthazarin chelates in nitrogen atmosphere

Compound	Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss (%)	Evolved formula	Moiety mass calc. (%)
$\|Cu_2(C_{10}H_4O_4)(Py)_2\|^{2+}(PF_6^-)_2$	1	150–350	340, 350	36.8	2 bipyridyl	34.02
	2	350–450	390, 405	6.8	–	–
	3	450–580	500	16.4	$C_{10}H_4O_2$	17.01
	4	580–850	–	22.0	2 (PF_6)	31.62
	residue	> 900		18.0	2 CuO	17.34
$\|Zn_2(C_{10}H_4O_4)(Py)_2\|^{2+}(PF_6^-)_2$	1	100–350	275	18.4	bipyridyl	16.94
	2	350–475	375	16.0	bipyridyl	16.94
	3	475–850	~ 680	16.8	$C_{10}H_4O_3$ or $C_{10}H_4O_2$	18.68 or 16.94
	residue	> 900		48.0	$Zn(PF_6)_2$ ZnO	38.59 8.84 } 47.43
$\|Ni_2(C_{10}H_4O_4)(Py)_2\|^{2+}(PF_6^-)_2$	1	50–160	150	10.4	unknown	–
	2	160–590	450, 560	36.0	2 bipyridyl	34.40
	3	590–850	–	22.4	$C_{14}H_4O_3$	18.95
	residue	> 900		31.2	2 NiO + (PF_6)	16.46 + 15.98

TABLE 8

Thermal analysis results (TG/DTA) on metal–alizarin chelates in air atmosphere

Compound	DTA		TG				
	endo(−)	*exo*(+)	Stage	Temperature range (°)	Mass loss (%)	Evolved formula	Moiety mass calc. (%)
$C_{14}H_8O_4$ = chrysazin	220, 300		1	260– 440	92.2 }	$C_{14}H_8O_4$	100.00
	450	480	2	440– 480	7.8 }		
	640, 780,						
	1000, 1140						
			residue	>1200	0	–	
$C_{14}H_8O_4$ = alizarin	380		1	180–420	76.8	$C_{12}H_8O_2$	76.66
	480	540	2	420–1000	23.8	2 CO	23.33
	1120						
			residue	>1200	0	–	
$Cu(C_{14}H_7O_4)_2(OH_2)_2$	130 br [a]		1	50– 320	5.8	2 H_2O	6.23
	350 br	420	2	320– 530	32.6 } 77.9	$C_{14}H_7O_3$	38.64 } 80.04
	540, 1050		3	530–1100	45.3 }	$C_{14}H_7O_4$	41.40 }
			residue	>1200	16.3	CuO	13.75
$Ni(C_{14}H_7O_4)_2(OH_2)_2$			1	50– 130	5.9	2 H_2O	6.28
	180 br, 300		2	130– 310	5.9	CO	4.88
		360	3	310– 780	59.2	$C_{12}H_7O_2$ }	31.90 } 61.04
						$C_{12}H_7O$ }	29.14 }
	800, 960,	820	4	780–1000	9.5	2 CO	9.76
	1080		residue	>1200	19.5	NiO	12.96
$[Zn(C_{14}H_7O_4)_2]\cdot 2H_2O$	150		1	50– 200	6.2	2 H_2O	6.21
	360 br		2	200– 410		anhydrous complex	
	510, 640	480	3	410– 660	28.0	$C_{14}H_7O_4-X$	41.26−X
			4	660–1000	36.0	$C_{14}H_7O_3$ or	38.47 or
						$C_{13}H_7O_3$	36.39
			residue	>1200	29.8	ZnO+X	14.03+X
$Mn(C_{14}H_7O_4)_2(OH_2)_2$	150		1	50– 250	5.8	2 H_2O	6.32
		420	2	250– 590	18.0	$C_{14}H_7O_4-X$	42.15−X
	590, 660,		3	590–1000	38.2	$C_{14}H_7O_3$	39.91
	1050						
			residue	>1200	38.0	Mn_3O_4+X	13.39+X

[a] br = broad; X = a part of the ligand alizarin decomposed.

At 1000°C, the residue was the corresponding metal oxide for the complexes of Cu, Zn and Ni, while in the case of Pd and Pt complexes this corresponds to the metal instead of the oxide. May be the PdO and PtO are formed but they are stable up to 830°C and decompose at higher temperatures (even in air atmosphere) to metallic palladium and platinum, respectively, [27].

The thermal stability of the anhydrous metal–chrysazin complexes, that result from the procedural decomposition temperature, follows the series: Ni > Cu ~ Zn > Pd > Pt.

The thermal analysis results (TG/DTG) for metal–alizarin complexes, in nitrogen atmosphere, are given in Table 4. The hydrated chelates of Ni and Mn lose water in the temperature range 50–170°C. Above this temperature, the NiL_2 decomposed very slowly, with only 3.2% mass loss, after which the rapid decomposition, loss being 34% from 500 to 900°C (DTG_{max} 630°C) was noticed. The whole decomposition was not completed until 900°C and the residue found (54%) corresponds to the metal oxide NiO (13.0% c) plus one molecule of alizarin (41.7% c).

The decomposition reaction of MnL_2 was carried out in two separate stages between 170–420 and 420–800°C, the mass losses being 37.5 and 30.5%, respectively. These are due to the rupture (26.0%) assumed to be MnO_2 (15.28% c), the difference being due, possibly, to elemental carbon. As far as the $PdL_2 \cdot 2H_2O$ (L = alizarin) complex is concerned, the TG curve showed gradual loss of two molecules of crystallization water in the temperature range 50–225°C. The decomposition reaction of the anhydrous complex of palladium is more complicated and involved the partial decomposition of the ligand alizarin in many stages, as postulated from the DTG curve. The residue found at 900°C (43.6%) corresponds to the metallic palladium (17.05% c) plus the remaining organic portion of the ligand.

The thermal decomposition (TG/DTG) in air atmosphere for the Pd–alizarin dihydrated complex resembles that in nitrogen atmosphere and is given in Table 5. The characteristic is the dissociation of the ligand in many stages as is manifested in the DTG curve.

The 5-hydroxy naphthoquinone (jouglone) [17] decomposes between 180 and 400°C and 400 and 520°C, the losses being 75 and 25%, respectively, due to the partial decomposition of the ligand. In the same paper, the authors reported the thermal decomposition of the complex CuL_2 (L = jouglone) in one stage, from 320 to 360°C, assuming the residue to be the metal oxide, CuO.

Table 6 presents the thermal analysis results (TG/DTG) for metal–jouglone complexes in nitrogen atmosphere. The decomposition of $MnL_2(H_2O)_2$, after the loss of water in the temperature range 50–160 (DTG_{max} 75°C), was carried out in two consecutive stages, unresolved (the greatest rate of decomposition being attained at 440°C) which correspond to the elimination of two jouglone molecules. The residue experimentally found (5.0%) was much lower than the calculated one (16.24%) if it is considered to be MnO. The analogous anhydrous metal jouglone complexes of Cu, Fe and Pt, however, decomposed in three different stages assuming the rupture of bonds in the chelate ring, the first removal being the carbonyl group. The residues (from the calculated and found mass losses) are assumed to be CuO, FeO + L_x and Pt, respectively.

The thermal decomposition (TG/DTG) of Fe–jouglone in air (Table 5) is not complete and resembles the decomposition of the complex in nitrogen atmosphere. The residue (52% f) is assumed to be the metal oxide FeO or Fe_2O_3 (17.90% or 19.90% c, respectively) plus a part of the remaining ligand.

As the thermal decomposition of the complex $PdL_2 \cdot (NH_3)_2$ (L = jouglone) is concerned, after the loss of ammonia in the temperature range 50 to 150°C (DTG_{max} 100°C), the organic part of the complex decomposed in two stages (150–335 and 335–510°C) by removal of the carbonyl group first. At 510°C the remaining weight (19.6% f) corresponds to the metallic palladium (21.76% c) which, furthermore, partially decomposed, so that at 900°C the residue found (13.6%) is much less than one molecule of Pd.

Naphthazarin decomposes, in nitrogen atmosphere, in the temperature range 194 to 250°C with considerable sublimation, and between 250 and 270°C [15]. The thermal analysis results (TG/DTG) for metal–naphthazarin

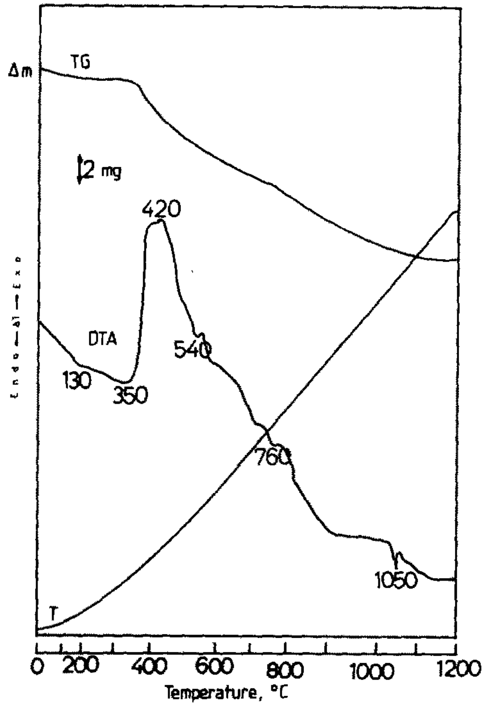


Fig. 9. Thermal curves (TG/DTA) for $Cu(C_{14}H_7O_4)_2(H_2O)_2$, $C_{14}H_7O_4$ = alizarin, in air.

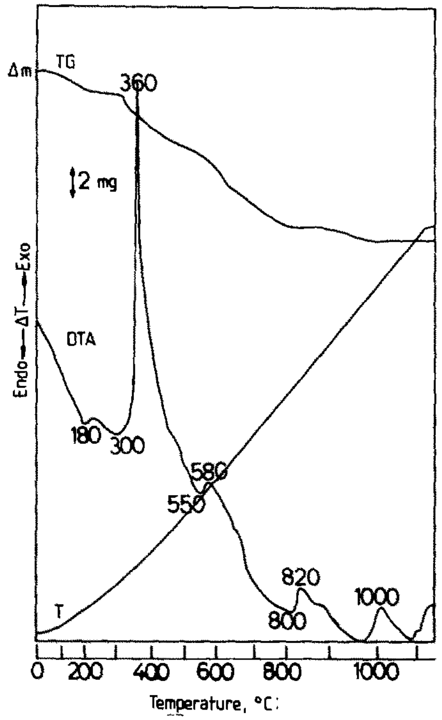


Fig. 10. Thermal curves (TG/DTA) for $Ni(C_{14}H_7O_4)(H_2O)_2$, $C_{14}H_7O_4$ = alizarin, in air.

complexes where M = Ni, Cu, Zn, in nitrogen atmosphere, are given in Table 7. The decomposition took place in three or four different stages. The first stage involved the elimination of two molecules of bipyridyl which followed the separation of the L-20 group. The salts M^{II} $(PF_6^{-1})_2$, (M = Ni, Cu, Zn) are the possible intermediates which, on further heating, decompose by the elimination of one or two PF_6 moieties. The residues at 850°C corresponded to metal oxide, e.g., CuO or to metal oxide plus the above mentioned salt, e.g., ZnO + Zn $(PF_6)_2$, due to the high stability of this salt.

Representative thermal analysis curves (TG/DTA), in air atmosphere, over the temperature range 20–1200°C, for the dihydroxy-quinones chrysazin and alizarin and for the metal–alizarin complexes are shown in Figs. 6–10. It can be seen that, in all cases, the decomposition process in air, includes various thermal effects. The temperatures and percentage mass losses of the decompositions and also the DTA data are given in Table 8.

The chrysazin TG curve showed no loss up to 260°C. From 260 to 440°C a sudden and almost total mass loss occurred, amounted to 92.2%. A slow decomposition region, from 440 to 480°C, loss being 7.8% was also detected. The DTA trace pointed in three endotherms with peak heights at 220, 300 and 450°C which are attributed to the partial decomposition and sublimation of the ligand. An exotherm was noticed at 480°C which may be attributed to further decomposition and combustion of the remaining ligand. Small and broad endotherms centered at about 640, 780, 1000 and 1140°C were also observed.

Alizarin is less stable than chrysazin, as can be seen from TG curve, the decomposition occurring from 180 to 420°C with mass loss 76.8%. After 420°C the decompostion slowed down and 23.8% loss from 420 to 1000°C was observed. The DTA trace pointed to endotherms at 380, 480 and 1120°C while an exotherm at 540°C was also noticed.

The hydrated metal–alizarin complexes, in air atmosphere, lose water mainly in the temperature range 50–250°C. The vaporization of coordinated or crystallization water is manifested by the broad endotherm centered at about 150°C, in the DTA curve. The thermal decomposition of the anhydrous complexes of alizarin occurred between 250 and 1000°C in two or three successive stages which correspond to the rupture of the coordinated M–ligand bond and also to the rupture of the carbon–oxygen bond (the oxygen attached to the metal) or to the elimination of a carbonyl group as indicated in Table 8. The decompositions are mostly endothermic while a high exotherm at about 420°C is noticed in each case.

The residues found above 1200°C correspond to the metal oxides CuO, NiO as far as the corresponding complexes of Cu and Ni are concerned, while for the analogous complexes of Zn and Mn the decompositions are not complete and the residues found correspond to the metal oxides ZnO and Mn_3O_4 plus an uncombusted moiety of the ligand. The thermal stability of the anhydrous metal–alizarin complexes increases in the order Ni < Zn < Mn < Cu.

In conclusion, we can say that the whole procedure of the thermal decomposition of the studied complexes with the same ligand depends on the nature of the metal and resembles the thermal decomposition reaction of the type $A(s) \rightarrow B(s) + C(g)$. The complexes of Pd and Pt show different behaviour upon heating, as was expected, due to their different position in the periodic table of the elements.

It is also noticed, that the thermal stability of the complexes depends on the bond broken first which can be either the M–O bond or one of the several bonds within the ligand. Hence, the thermal stability of the ligand is an important determining factor in the thermal stability of the complexes. The increased order of thermal stability for the investigated metal–chelate complexes, with the exception of Cu–alizarin, which is the most stable, is: naphthazarin < jouglone < alizarin < chrysarin.

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