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THERMAL DECOMPOSITION OF SOME METAL CHELATES OF SUBSTITUTED HYDRAZOPYRAZOLONES

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Abstract

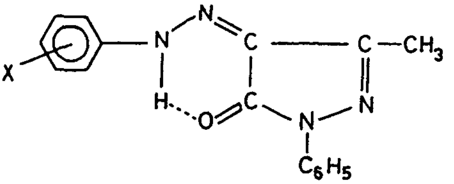
The thermal dissociation of 1-phenyl-3-methyl-4-(X-phenylhydrazo)-5-pyrazolone metal chelates [M(XPhHyPy)](*X* = *m*-OH (I), *m*-OCH_3 (II), *m*-COOH (III), *p*-CH_3 (IV), *p*-OCH_3 (V) or *p*-$COCH_3$ (VI) was studied by TG, DTG and differential thermal analysis (DTA). A rough sequence of thermal stability, obtained from the peak maximum temperatures, for the various metal chelates was Hg(II) < Cu(II) < Fe(III) < UO_2(II). The bonding of the ligands to metal ions was investigated by elemental analysis and infrared spectroscopy. The number and relative energies of nitrate combination frequencies are discussed in terms of the complexation of para-substituted hydrazopyrazolone with Th(IV) and UO_2(II) metal ions.

Keywords: metal chelates, TG-DTG-DTA

Introduction

One of the less frequently studied aspects of analytical and coordination chemistry is the thermal behaviour of metal complexes with organic chelating agents. We have recently carried out stability, conductometric and polarographic studies [1–5] of the coordination selectivity of some lanthanides, actinides and transition metals with hydrazopyrazolone derivatives. The present study deals with the preparation, characterization and thermal behaviour of metal complexes of Fe(III), Cu(II), Hg(II), Th(IV) and UO_2(II) with hydrazopyrazolone ligands I–VI. A literature review suggested that such a study has not been attempted so far.

The hydrazo structure of the ligands I–VI is depicted in Formula 1.



Formula 1 1-Phenyl-3-methyl-4-(X-phenylhydrazo)-5-pyrazolone

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X = m-OH (3-OH-PhHyPy) [I]
X = m-OCH$_3$ (3-OCH$_3$-PhHyPy) [II]
X = m-COOH (3-COOH-PhHyPy) [III]
X = p-CH$_3$ (4-CH$_3$-PhHyPy) [IV]
X = p-OCH$_3$ (4-OCH$_3$-PhHyPy) [V]
X = p-COCH$_3$ (4-COCH$_3$-PhHyPy) [VI]

Experimental

All reagents used in this work were of A. R. grade or equivalent. Solutions of Hg(II), Cu(II) and Fe(III) were prepared from their chloride salts. Solutions of Th(IV) and UO$_2$(II) were prepared from the nitrates. The solid complexes were prepared by mixing equimolar amounts of aqueous solutions of the metal salts and the respective ligands [4] [dissolved in 75% dioxane-water (v/v)] in the *pH* range 5–7. The reaction of ligand I with Hg(II) was an exception, where the mixing was performed at a ligand : metal molar ratio of 2:1. Each mixture was heated to 60°C with stirring for about 2 h, and was left to stand overnight. The solid complexes were collected, washed with double distilled water followed by alcohol, then dried in air and stored in a vacuum desiccator. The results of elemental analyses are given in Table 1.

The thermal stabilities of the solid complexes were studied by using TG, DTG and DTA techniques. The measurements were made with an OD-102 Paulik-Paulik-Erdey derivatograph (MOM, Hungary). The samples were heated in platinum crucibles in static air atmosphere at a heating rate of 5 deg·min^{-1} up to 600°C, using α-Al$_2$O$_3$ as a reference compound.

The infrared spectra were obtained from 4000 to 200 cm^{-1} on a PERKIN-ELMER IR spectrophotometer, with samples dispersed in KBr discs.

Results and discussion

Thermal Analysis

The determined temperature ranges, % losses in mass and thermal effects accompanying the changes in the solid complexes on heating are given in Table 2, which revealed the following findings:

(i) The observed loss in mass within the temperature range 50–130°C could be correlated with the loss of water of hydration. At higher temperatures (130–210°C), the coordinated water could be eliminated from all complexes.

(ii) Coordinated Cl could be removed within the temperature range 180–280°C, and coordinated NO$_3$ could be eliminated within the range 210–310°C [5].

Table 1 Elemental Analysis data for UO_2(II), Cu(II), Hg(II), Fe(III) and Th(IV) complexes with hydrazolo ligands derived from 1-phenyl-3-methyl-5-pyrazolone

Complex	Colour	%C[a]	%H[a]	%N[a]	%Cl[a]	%M[a,b]
Ligand I						
$[UO_2LNO_3{\cdot}4H_2O]$	red	26.90 (27.54)	3.30 (3.01)	10.28 (10.04)	–	33.77 (34.15)
$[CuLCl]{\cdot}2H_2O$	dark-red	46.18 (46.83)	3.87 (3.66)	13.25 (13.66)	8.41 (8.66)	15.83 (15.49)
$[FeLCl_2{\cdot}H_2O]$	greenish-red	44.40 (43.95)	3.71 (3.43)	13.10 (12.81)	15.80 (16.02)	13.01 (12.78)
$[HgL_2{\cdot}4H_2O]$	light-red	44.31 (44.72)	4.21 (3.95)	13.21 (13.04)	–	23.25 (23.36)
Ligand II						
$[UO_2LNO_3]{\cdot}2H_2O$	orange	29.71 (30.22)	3.23 (2.81)	9.98 (10.27)	–	34.78 (35.26)
$[CuLCl]{\cdot}3H_2O$	red	45.03 (44.35)	4.74 (4.56)	12.50 (12.17)	7.70 (7.72)	13.31 (13.80)
$[FeLCl_2]{\cdot}H_2O$	green-yellow	45.81 (45.25)	4.01 (3.77)	12.20 (12.42)	15.29 (15.53)	11.96 (12.39)
$[HgLCl]{\cdot}4H_2O$	orange	36.87 (36.49)	3.25 (3.04)	10.46 (10.02)	6.52 (6.35)	35.20 (35.88)
Ligand III						
$[UO_2LNO_3]{\cdot}H_2O$	orange	30.95 (30.40)	2.60 (2.23)	10.85 (10.43)	–	33.22 (33.68)
$[CuLCl{\cdot}H_2O]$	red	46.15 (46.57)	3.16 (3.42)	12.24 (12.78)	7.85 (8.10)	14.80 (14.49)
$[FeLCl_2{\cdot}H_2O]$	orange	44.20 (43.88)	3.50 (3.23)	11.90 (12.05)	14.77 (15.06)	12.21 (12.01)
$[HgLCl{\cdot}2H_2O]$	orange	34.90 (34.39)	3.04 (2.86)	10.81 (9.44)	6.13 (5.98)	34.47 (33.82)
Ligand IV						
$[UO_2LNO_3]{\cdot}4H_2O$	brownish-red	29.63 (29.35)	3.66 (3.30)	9.91 (10.07)	–	34.60 (34.24)
$[ThL{\cdot}2H_2O](NO_3)_3{\cdot}2H_2O$	brown	26.51 (26.12)	3.20 (2.94)	12.21 (12.54)	–	30.05 (29.70)
Ligand V						
$[UO_2LNO_3]{\cdot}4H_2O$	brownish-red	29.01 (28.69)	3.65 (3.23)	9.50 (9.84)	–	33.89 (33.47)
$[ThL{\cdot}2H_2O](NO_3)_3$	light-brown	27.40 (26.80)	3.21 (2.49)	13.06 (12.87)	–	30.80 (30.49)
Ligand VI						
$[UO_2LNO_3]{\cdot}3H_2O$	yellowish-red	31.10 (30.64)	3.01 (2.79)	9.78 (9.92)	–	33.21 (33.76)
$[ThLH_2O]{\cdot}(NO_3)_3$	bright-red	29.13 (28.61)	2.59 (2.25)	12.45 (12.98)	–	31.09 (30.72)

[a] % Found (% Calculated); [b] M = metal ion; [c] molar ratio 2:1 (ligand:metal)

(iii) Exotherms due to oxidation, decomposition of the complexes and the formation of metal oxides were present in all curves except those for compounds containing Hg(II).

(iv) From complexes containing Hg(II) (Fig. 1a), mercury began to sublime within the temperature range 210–240°C [6]. The organic part of the chelate gradually burned away and the crucible became empty within the temperature range 410–550°C. The degradation of the organic part of the chelate was an endothermic reaction, which resulted in carbon as residue. The combustion of carbon to carbon dioxide was an exothermic reaction [7].

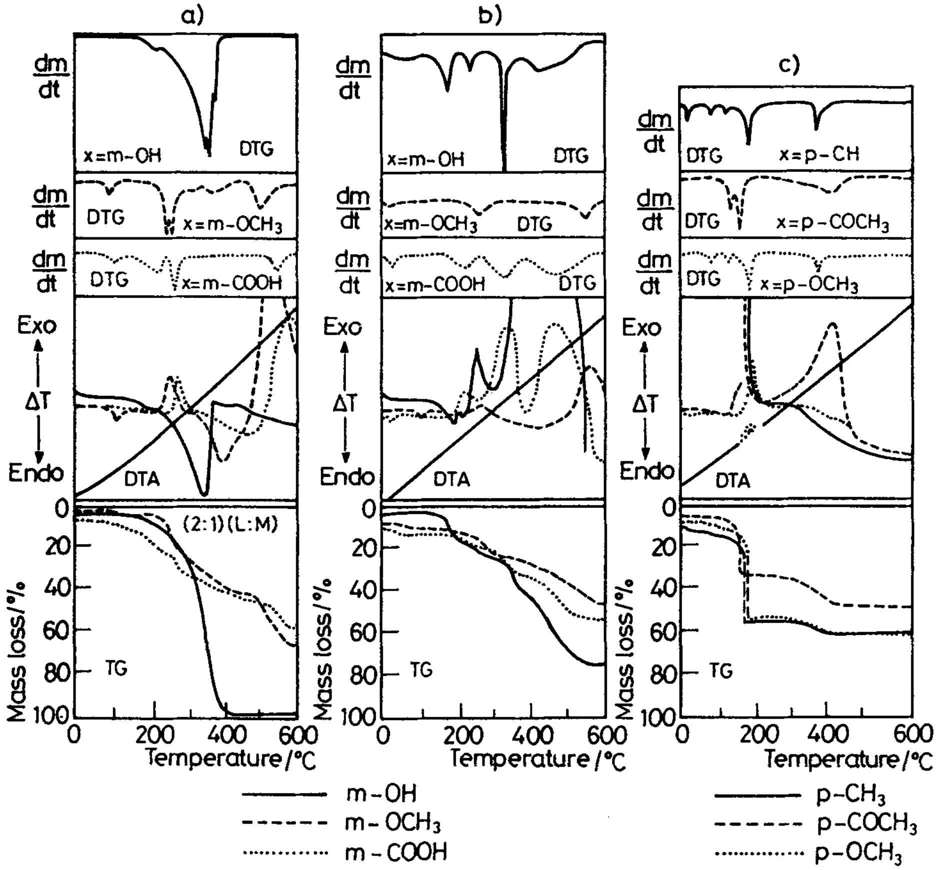


Fig. 1 TG, DTA and DTG curves of a) Hg(II) complexes of 1-phenyl-3-methyl-4(X-phenylhydrazo)-5-pyrazolone ligands; b) UO_2(II) complexes of 1-phenyl-3-methyl-4(X-phenylhydrazo)-5-pyrazolone ligands; c) Th(IV) complexes of 1-phenyl-3-methyl-4(X-phenylhydrazo)-5-pyrazolone ligands

Table 2 Thermogravimetric analysis of some solid complexes of 1-phenyl-3-methyl-4-(X-phenylhydrazo)-5-pyrazolone ligands

X	Complex	Temp. range /°C	Mass loss / % Calc.	Mass loss / % Found	Effect type	Assignment
3-OH	$[UO_2(C_{16}H_{13}N_4O_2)(NO_3)\cdot 4H_2O]$	170–210	10.33	10.84	Endo	Loss of 4 coordinated H_2O molecules
		235–260	19.23	19.87	Exo	Loss of NO_3 group
		330–340	36.59	37.42	Exo	Loss of organic part ($HO–C_6H_4–N_2–$)
		350–500	61.27	62.92	Exo	Loss of rest of ligand (phenylpyrazolone) and formation of metal oxide (UO_2)
3-COOH	$[UO_2(C_{17}H_{13}N_4O_3)(NO_3)]\cdot H_2O$	100–110	2.68	2.80	Endo	Loss of $1H_2O$ molecule
		260–310	11.92	12.00	Exo	Loss of NO_3 group
		330–430	34.13	34.79	Exo	Loss of organic part ($COOH–C_6H_4–N_2–$)
		450–560	59.76	61.18	Exo	Loss of rest of ligand (phenylpyrazolone) and formation of metal oxide (UO_2)
$3-OCH_3$	$[UO_2(C_{17}H_{15}N_4O_2)(NO_3)]\cdot 2H_2O$	105–130	5.33	4.82	Endo	Loss of $2H_2O$ molecules
		210–260	14.52	14.14	Exo	Loss of NO_3 group
		280–470	59.99	57.98	Exo	Decomposition of complex and formation of metal oxide (UO_3)
$4-CH_3$	$[UO_2(C_{17}H_{15}N_4O)(NO_3)]\cdot 4H_2O$	100–120	10.36	10.55	Endo	Loss of $4H_2O$ molecules
		230–290	19.28	19.34	Exo	Loss of NO_3 group
		470–540	61.15	59.42	Exo	Decomposition of complex and formation of metal oxide (UO_3)
$4-OCH_3$	$[UO_2(C_{17}H_{15}N_4O_2)(NO_3)]\cdot 4H_2O$	50–120	10.13	10.37	Endo	Loss of $4H_2O$ molecules
		210–280	18.85	19.16	Exo	Loss of NO_3 group
		420–530	62.03	60.62	Exo	Decomposition of complex and formation of metal oxide (UO_3)
$4-COCH_3$	$[UO_2(C_{18}H_{15}N_4O_2)(NO_3)]\cdot 3H_2O$	70–120	7.66	7.63	Endo	Loss of $3H_2O$ molecules
		250–290	16.45	16.53	Exo	Loss of NO_3 group
		470–580	61.70	59.76	Exo	Decomposition of complex and formation of metal oxide (UO_3)

Table 2 Continued

X	Complex	Temp. range /°C	Mass loss / %		Effect type	Assignment
			Calc.	Found		
4-CH_3	$[Th(C_{17}H_{15}N_4O)\cdot H_2O](NO_3)_3\cdot 3H_2O$	70–95	4.61	4.57	Endo	Loss of $2H_2O$ molecules
		115–125	6.91	6.85	Endo	Loss of $1H_2O$ molecule
		150–165	9.21	9.13	Endo	Loss of 1 coordinated H_2O molecule
		190–260	60.55	60.25	Exo	Elimination of $3NO_3$ groups, decomposition of complex and formation of $ThOCO_3$
		270–460	66.18	65.83	Exo	Decomposition of carbonate and formation of metal oxide (ThO_2)
4-OCH_3	$[Th(C_{17}H_{15}N_4O_2)\cdot H_2O](NO_3)\cdot 3H_2O$	120–130	2.37	2.36	Endo	Loss of $1H_2O$ molecule
		150–170	4.73	4.72	Endo	Loss of 1 coordinated H_2O molecule
		210–260	59.53	59.28	Exo	Elimination of $3NO_3$ groups, decomposition of complex and formation of $ThOCO_3$
		300–470	65.31	65.00	Exo	Decomposition of carbonate and formation of metal oxide (ThO_2)
4-$COCH_3$	$[Th(C_{18}H_{15}N_4O_2)\cdot H_2O](NO_3)_3$	150–160	2.38	2.28	Endo	Loss of 1 coordinated H_2O molecule
		170–210	41.72	41.43	Exo	Elimination of $3NO_3$ groups, decomposition of complex and formation of $ThOCO_3+Th(CO_3)_2$
		300–460	65.03	64.67	Exo	Decomposition of carbonate and formation of metal oxide (ThO_2)
3-OH	$[Hg(C_{16}H_{13}N_4O_2)\cdot 4H_2O]$	190–210	8.38	8.41	Endo	Loss of 4 coordinated H_2O molecules
		230–360	91.61	91.53		Sublimation of Hg
					Endo	Decomposition of organic matter, leaving carbon as residue
		410–460	99.99	99.94	Exo	Formation of volatile CO_2
3-COOH	$[Hg(C_{17}H_{13}N_4O_2)Cl\cdot 2H_2O]$	130–150	6.07	5.95	Endo	Loss of 2 coordinated H_2O molecules
		180–230	45.87	46.29	Exo	Elimination of Cl atom
		240–300			Endo	Sublimation of Hg
		300–500	65.60	66.46	Endo	Decomposition of organic matter, leaving carbon as residue
		500–540	99.99	101.13	Exo	Formation of volatile CO_2

Table 2 Continued

X	Complex	Temp.	Mass loss / %		Effect	Assignment
		range /°C	Calc.	Found	type	
3-OCH$_3$	[Hg(C$_{17}$H$_{15}$N$_4$O$_2$)Cl]·H$_2$O	115–130	3.22	3.20	Endo	Loss of 1H$_2$O molecule
		185–200	45.45	44.93	Exo	Elimination of Cl atom
		210–290			Endo	Sublimation of Hg
		290–400	63.87	63.38	Endo	Decomposition of organic matter, leaving carbon as a residue
		–550	9.99	100.11	Exo	Formation of volatile CO$_2$
3-OH	[Cu(C$_{16}$H$_{13}$N$_4$O$_2$)Cl]·H$_2$O	80–110	4.39	4.32	Endo	Loss of 1H$_2$O molecule
		180–205	13.05	12.52	Exo	Elimination of Cl atom
		205–310	42.56	41.00	Exo	Loss of organic part (HO–C$_6$H$_4$–N$_2$–)
		460–520	84.51	80.84	Exo	Loss of rest of ligand (phenylpyrazolone, and formation of CuO through CuCO$_3$
3-COOH	[Cu(C$_{17}$H$_{13}$N$_4$O$_3$)Cl·H$_2$O]	160–180	4.11	4.14	Endo	Loss of 1 coordinated H$_2$O molecule
		200–220	12.22	12.10	Exo	Loss of 1 coordinated Cl molecule
		230–360	46.24	46.19	Exo	Loss of organic part (COOH–C$_6$H$_4$–N$_2$–)
		400–540	85.51	83.42	Exo	Loss of rest of the ligand (phenylpyrazolone), and formation of CuO through CuCO$_3$
3-OCH$_3$	[Cu(C$_{17}$H$_{15}$N$_4$O$_2$)Cl]·3H$_2$O	100–120	11.74	11.36	Endo	Loss of 3H$_2$O molecules
		180–230	19.46	19.07	Exo	Loss of 1 coordinated Cl molecule
		230–460	86.20	84.77	Exo	Decomposition of complex and formation of metal oxide (CuO)
3-OH	[Fe(C$_{16}$H$_{13}$N$_4$O$_2$)Cl$_2$·H$_2$O]	150–210	4.12	4.18	Endo	Loss of 1 coordinated H$_2$O molecule
		210–420	87.21	81.45	Exo	Elimination of Cl atoms, decomposition of complex and formation of metal oxide (Fe$_2$O$_3$)
3-COOH	[Fe(C$_{17}$H$_{13}$N$_4$O$_3$)Cl$_2$·H$_2$O]	170–210	3.87	3.69	Endo	Loss of 1 coordinated H$_2$O molecule
		220–280	18.93	18.46	Exo	Loss of 2 coordinated Cl molecules
		310–480	87.98	83.32	Exo	Decomposition of complex and formation of Fe$_2$O$_3$
3-OCH$_3$	[Fe(C$_{17}$H$_{15}$N$_4$O$_2$)Cl$_2$]·H$_2$O	85–110	3.99	3.92	Endo	Loss of 1H$_2$O molecule
		210–270	19.52	19.22	Exo	Loss of 2 coordinated Cl molecules
		350–540	87.61	83.55	Exo	Decomposition of complex and formation of Fe$_2$O$_3$

(v) The thermal behaviour of the uranyl complexes (Fig. 1b) shows that, in the cases of ligands I and III, two close exotherms (in addition to that for the coordinated NO_3 at 235–310°C) are observed (Table 2). One is related to the X-phenylhydrazo moiety (X = 3-OH or 3-COOH) and the other to the release of the rest of the ligand itself [8], the final pyrolysis product being UO_2. In the other derivatives, one strong exotherm (in addition to that of the coordinated NO_3 at 210–290°C) is observed (Table 2) and is related to the decomposition of the complex, with the formation of UO_3 as final pyrolysis product [9, 10].

(vi) The Th(IV) chelates undergo almost explosive decomposition (exothermic explosion) in the temperature range 215–250°C (Fig. 1c). The results suggest the following general decomposition processes:

$$ThL(NO_3)_3 \cdot nH_2O \xrightarrow{70 - 170^\circ C} ThL(NO_3)_3 \xrightarrow{210 - 260^\circ C}$$

$$ThOCO_3 \xrightarrow{300 - 470^\circ C} ThO_2$$

where $n = 4$, L = (p-CH_3PhHyPy) and $n = 2$, L = (p-OCH_3PhHyPy); and

$$ThL(NO_3)_3 \cdot H_2O \xrightarrow{150 - 160^\circ C} ThL(NO_3)_3 \xrightarrow{170 - 210^\circ C}$$

$$ThOCO_3 + Th(CO_3)_2 + C \xrightarrow{300 - 460^\circ C} ThO_2$$

where L = (p-$COCH_3$PhHyPy).

It is possible that the intermediate is not pure $ThOCO_3$, but a mixture [11] of

$$ThOCO_3 + Th(CO_3)_2 + C$$

or

$$ThOCO_3 + Th(CO_3)_2 + ThO_2 + C$$

The explosive decomposition of Th(IV) hydrazopyrazolone complexes indicates that the nitrate groups do not participate in the chelation [12].

The results show that the thermal decompositions of the thorium(IV) chelates are similar to those of Th(IV) isophthalate and Th(IV) terephthalate [12].

(vii) A rough sequence of thermal stability for the complexes, obtained from the peak maximum temperatures, is Hg(II) < Cu(II) < Fe(III) < UO_2(II)

The results for the metal contents [%M], calculated from the masses of the residual oxides, support the stoichiometry obtained from the elemental analyses.

Infrared spectroscopy

The bonding of the ligands to different metal ions was investigated by comparing the IR spectra of the free ligands [13] with those of their solid complexes (Fig. 2, Table 3). The following conclusions can be drawn:

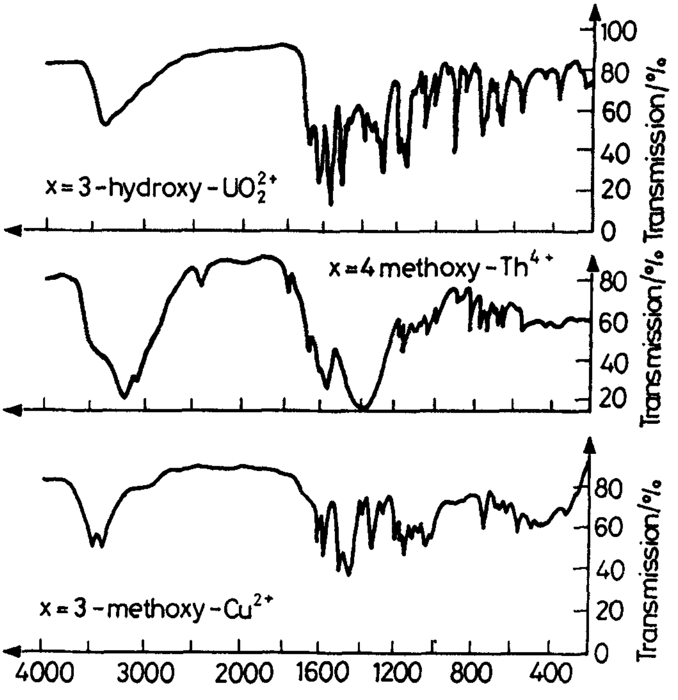
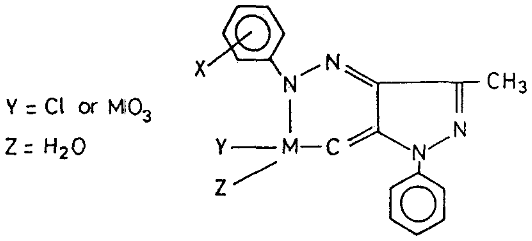


Fig. 2 IR spectra of some solid complexes of 1-phenyl-3-methyl-4-(X-phenylhydrazo)-5-pyrazolone ligands

(i) The spectra of the solid complexes exhibited a broad band at 3500–3400 cm^{-1}, which could be attributed to $\nu_{(OH)}$ of the associated water molecules, while the band observed at approximately 760 cm^{-1} was assigned to coordinated water molecules [2], this being supported by results of TG and dehydration methods [14].

(ii) The carbonyl absorption band $\nu_{(CO)}$ (of the pyrazolone ring), at 1632, 1642, 1650, 1645, 1635 and 1650 cm^{-1} [15] for ligands I, III, II, IV, V and VI, respectively, was shifted to frequencies higher by 30–15 cm^{-1} for all complexes. The changes in the carbonyl band position [16] in the IR spectra of the metal complexes indicate that the carbonyl group in the hydrazopyrazolone compounds is coordinated to the metal ions.

Table 3 Solid-state infrared frequencies (cm^{-1}) of some solid complexes of 1-phenyl-3-methyl-4-(X-phenylhydrazo)-5-pyrazolone ligands



X	Complex	ν_{OH} lattice	ν_{NO_3} (ionic)	ν_{CO}	ν_{NO_3} (coordinated)	$\nu_{M\text{-}O}$	$\nu_{M\text{-}N}$	$\nu_{M\text{-}Cl}$
3-OH	[UO_2(X-PhHyPy)(NO_3)·4H_2O]^{a,b}		–	1650	1500, 1274, 1028	610, 445	560, 375	–
3-COOH	[UO_2(X-PhHyPy)(NO_3)]·H_2O	3500–3400		1664	1503, 1270, 1030	617, 422	564, 380	–
3-OCH$_3$	[UO_2(X-PhHyPy)(NO_3)]·2H_2O	3500–3400	–	1665	1505, 1283, 1030	610, 468	578, 365	–
4-CH$_3$	[UO_2(X-PhHyPy)(NO_3)]·4H_2O	3500–3400	–	1667	1506, 1271, 1029	610, 455	563, 370	–
4-OCH$_3$	[UO_2(X-PhHyPy)(NO_3)]·4H_2O	3500–3400	–	1655	1500, 1281, 1030	605, 465	574, 360	–
4-COCH$_3$	[UO_2(X-PhHyPy)(NO_3)]·3H_2O	3500–3400	–	1675	1502, 1271, 1030	608, 455	572, 375	–
4-CH$_3$	[Th(X-PhHyPy)·2H_2O](NO_3)$_3$·2H_2O]^{b,c}	3400, 3150, 3040	2405, 1773	1669	–	610, 435	540, 380	–
4-OCH$_3$	[Th(X-PhHyPy)·H_2O](NO_3)$_3$·H_2O	3400, 3150, 3039	2410, 1772	1665	–	611, 445	565, 385	–
4-COCH$_3$	[Th(X-PhHyPy)·H_2O]·H_2O(NO_3)$_3$	3400, 3155, 3038	2398, 1771	1680	–	613, 446	570, 387	–

Table 3 Continued

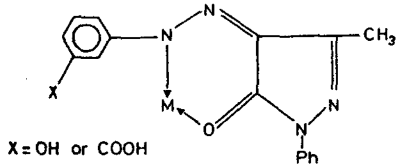
X	Complex	ν_{OH} lattice	ν_{NO_3} (ionic)	ν_{CO}	ν_{NO_3} (coordinated)	ν_{M-O}	ν_{M-N}	ν_{M-Cl}
3-OH	$[Cu(X\text{-}PhHyPy)Cl]\cdot H_2O^{a,c}$	3500–3400	–	1661	–	630, 500	574, 370	315
3-COOH	$[Cu(X\text{-}PhHyPy)Cl\cdot H_2O]^{b,c}$	–	–	1664	–	629, 503	579, 375	315
3-OCH$_3$	$[Cu(X\text{-}PhHyPy)Cl]\cdot 3H_2O^{c}$	3480, 3330	–	1666	–	630, 500	575, 370	317
3-OH	$[Fe(X\text{-}PhHyPy)Cl_2\cdot H_2O]^{a,b}$	–	–	1655	–	613, 500	567, 380	320
3-COOH	$[Fe(X\text{-}PhHyPy)Cl_2\cdot H_2O]^{b}$	–	–	1665	–	615, 500	567, 386	320
3-OCH$_3$	$[Fe(X\text{-}PhHyPy)Cl_2]\cdot H_2O$	3500–3400	–	1668	–	612, 500	570, 382	320
3-OH	$[Hg(X\text{-}PhHyPy)_2\cdot 4H_2O]^{a,b}$	–	–	1658	–	615, 500	564, 375	–
3-COOH	$[Hg(X\text{-}PhHyPy)Cl\cdot 2H_2O]^{b}$	–	–	1665	–	618, 501	566, 379	340
3-OCH$_3$	$[Hg(X\text{-}PhHyPy)Cl]\cdot H_2O$	3500–3400	–	1666	–	614, 500	568, 380	340

[a] ν_{OH} phenolic at 3400–3300 cm^{-1}; [b] coordinated water molecule at 770–750 cm^{-1}; [c] ν_{CO} has disappeared

(iii) Additionally, the band of the free ligands located at 1592–1570 cm^{-1}, due to ν(>C=N) (attached to the hydrazo group), was shifted to frequencies lower by 10–35 cm^{-1}, due to chelation with the metal ions [16].

(iv) The disappearance of the ν(>NH) stretching frequency (located at 2090–2030 cm^{-1} for the free ligands) on chelate formation may be caused by coordination of the hydrazo-nitrogen to the metal ion upon complexation.

(v) The IR spectra of the solid complexes of ligands I and III show that the ν(OH) phenolic and ν(>C=O) (of the COOH group) bands are still at the same frequencies as for the free ligands. This indicates that *m*-hydroxy and *m*-carboxylate groups do not participate [4] in chelate formation leading to a bidentate ligand, as shown in the following Formula:



(vi) For UO_2(II) complexes with *m*- and *p*-hydrazopyrazolone derivatives, the spectra show ν(NO) stretchings at 1506–1500, 1270–1283 and 1028–1030 cm^{-1}. This indicates the coordinated nature of the nitrate group, which acts as a bidentate ligand [17].

(vii) The IR spectra of Th(IV)-hydrazopyrazolone complexes exhibit bands near 1770 and 2400 cm^{-1}. That near 1770 cm^{-1} is relatively strong (very sharp) and could be assigned to a combination of the ν_1 symmetric stretch and the doubly degenerate in-plane bending mode ν_4. The band near 2400 cm^{-1} is weaker and more or less broad. The above two bands indicate that the nitrato group does not participate in chelation [18].

(viii) The spectra of the solid complexes of Fe(III), Cu(II) and Hg(II) exhibit a band in the range 315–360 cm^{-1} that could be attributed to M–Cl [19, 20].

(ix) The new bands appearing in the ranges 647–605 and 503–422 cm^{-1} are assigned to ν(M–O), while those at 579–540 and 387–360 cm^{-1} are assigned to ν(M–N) [21].

(x) A sharp, intense band near 900 cm^{-1} in the spectra of all uranyl complexes is assigned to the asymmetric uranyl stretching frequency ν(U=O) [22–24].

(xi) Bands corresponding to those at 605–617 and 422–468 cm^{-1} in the uranyl complexes were present in nearly all spectra and were the principal bands in the far IR region, exhibiting appreciable substituent sensitivity. Their assignment to $\nu_{(U\text{-}O)}$ was therefore preferred. Moreover, the corresponding bands at 630 and 500 cm^{-1} in the spectra of copper complexes were reliably assigned [25] to $\nu_{(Cu\text{-}O)}$ on the basis of normal coordinate [26, 27] and ^{18}O labelling [28] studies. The finding that $\nu_{(U\text{-}O)}$ is at lower frequency than $\nu_{(Cu\text{-}O)}$ is expected in view of the greater mass and higher coordination number of the uranium atom.

(xii) The ligand orbitals of hydrazopyrazolones are group theoretically, energetically and occupationally suitable for participation in both donor (U→L) and acceptor (L→U) π-interactions with the uranyl ion [29–31]. Convincing evidence [29] has been adduced that U→L π-bonding makes a significant contribution to the bonding in uranyl complexes, whereas in copper(II)-hydrazopyrazolone, Cu→O π-bonding is generally considered to be relatively weak [32, 33]. This idea is supported by our thermal stability measurements.

(xiii) Electron-withdrawing substituents appear to decrease the donor capacity of the carbonyl groups. This is evident from the $\nu_{(C-O)}$ values of our complexes and is a general feature of all transition and non-transition metal β-ketoenolates, with electron-withdrawing substituents [25]. At the same time, U→O π-bonding will be facilitated by such substituents, leading to a positive contribution to $\nu_{(U-O)}$.

* * *

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Zusammenfassung — Mittels TG, DTG und DTA wurde die thermische Dissoziation der 1-Phenyl-3-methyl-4(x-phenylhydrazo)-5-pyrazolon-Metallchelate [M(x-PhHyPy)](*x*=*m*-OH(I), *m*-OCH_3(II), *m*-COOH(III), *p*-CH_3(IV), *p*-OCH_3(V) und *p*-$COCH_3$(VI) untersucht. Die anhand der Peakmaxima-Temperaturen erhaltene ungefähre Reihenfolge für die thermische Stabilität lautete: Hg(II) Cu(II) Fe(III) UO_2(II). Die Bindung der Liganden an den Metallionen wurde mittels Elementaranalyse und IR-Spektraldaten untersucht. Außerdem wurde die Anzahl und die relativen Energien von Nitrat-Kombinationsfrequenzen bei der Komplexierung von para-substituiertem Hydrapyrazolon mit Th(IV)- und UO_2(II) Metallionen diskutiert.