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THERMAL BEHAVIOUR OF COPPER(II) COMPLEXES OF HALOASPIRINATES

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Abstract

Complexes of Cu(II) with substituted o-acetoxy benzoic acids (5-haloaspirines, X-asp) with and without pyridine (py), of composition $[Cu_2(X\text{-}asp)_4]$ and $[Cu(X\text{-}asp)_2(py)_2]$ have been synthesized and characterized. Electronic and vibrational spectroscopic data of these complexes are reported. Its thermal behaviour was investigated by thermogravimetry and differential thermal analysis. In all complexes, the haloaspirinate ligands decompose in two or three steps, starting with the break up of the coordinated acetoxy groups. CuO is obtained as the final pyrolysis residue in all cases.

Keywords: Cu(II), electronic spectra, haloaspirinate complexes, IR specra, thermal analysis

Introduction

Aspirin has been widely used as an analgesic agent but it has the disadvantage that it can produce ulcerogenic lesions [1]. The copper(II) complex of aspirin has demonstrated major anti-inflammatory and antiulcer activity with less injurious effects than the free ligand [2–4]. Similar effects have also been obtained with some ternary Cu(II) complexes containing aspirin and a second ligand [5–8].

In this paper we report the thermal behaviour of the complete series of Cu(II) haloaspirinates, prepared by the procedure of Meier *et al*. [9] and of a new series of ternary complexes containing pyridine as the second ligand.

Experimental

Synthesis of the complexes

The copper(II) aspirinate, $[Cu_2(asp)_4]$, was obtained by adding an aqueous solution of copper acetate monohydrate (C. Erba, 1.5 mmol) over a 50% aqueous ethanolic solu-

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tion of aspirine (Sigma, 3.0 mmol).The mixture was shortly heated at 40°C and the precipitated blue solid was filtered off, washed with aqueous ethanol and dried over $CaCl_2$.

The 5-halogen-substituted acetylsalicylic acids were prepared by reacting the appropriate substituted salicylic acid (Aldrich) with acetic anhydride [10]. The copper(II) complexes were prepared by the general procedure described by Meier *et al*. [9]. The ternary complexes derived from fluoro-, chloro- and bromo-aspirinate and pyridine, were crystallized by addition of dried *n*-hexane to concentrated solutions of the respective copper haloaspirinates in pyridine. The corresponding complex with iodo-aspirinate could not be obtained due to the rapid hydrolysis of this halo-aspirinate. All these new complexes have the same composition, $[Cu(X\text{-}asp)_2(py)_2]$.

The results of the chemical analysis of all the prepared complexes are shown in Table 1.

Spectroscopic measurements

UV-visible spectra of methanolic solutions and Nujol mulls of the complexes were recorded on a Perkin Elmer Lambda-2 spectrophotometer. IR spectra were recorded down 400 cm^{-1} with a Nicolet 520 FTIR instrument, using KBr pellets and Nujol mulls.

Thermal analysis

Thermal decomposition studies were carried out on a Rigaku Denki Thermoflex instrument, in flowing air or nitrogen (30 ml min^{-1}), up to a final temperature of 750°C. Heating rates, ranged between 2 and 5°C min^{-1} and sample masses between 7 and 18 mg. Al_2O_3 was used as the DTA reference standard.

Results and discussion

Copper(II) complexes of haloaspirinates

The X-ray diffraction study of Manojlovic-Muir has demonstrated that Cu(II) aspirinate crystallize in dimeric units, $[Cu_2(asp)_4]$, interconnected by acetoxy oxygens from neighbouring units [11]. The stereochemistry of the dimetallic units resembles that found in copper(II) acetate and other copper carboxylate complexes [12, 13]. The same dimetallic units are also present in the haloaspirinate complexes [9].

Selected IR bands of these complexes, related to vibrational modes of the carboxylate and acetoxy groups, are shown in Table 2. In the IR spectra of $[Cu_2(asp)_4]$ and $[Cu_2(F\text{-}asp)_4]$ there are strong bands corresponding to the C=O stretching of two types of acetoxy groups, one of them free of additional interactions, named (I) in Table 2, and the other coordinated to a Cu(II) center of a neighbouring dimeric unit, named as (II). In the chloro-, bromo- and iodo-aspirinates, the vacant sites on the Cu(II) ions are evidently occupied by water or methanol molecules, as becomes evident from the absence of type II bands in the spectra of these complexes.

Table 1 Analytical data of the prepared copper(II) haloaspirinate complexes

Compound	Formula	C/%		H/%		N/%		Cu/%	
		calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
[Cu_2(asp)$_4$]	$C_{36}H_{28}O_{16}Cu_2$	51.25	–	3.35		–	–	15.06	15.88
[Cu_2(F-asp)$_4$]	$Cu_{36}H_{24}F_4O_{16}Cu_2$	47.13	47.03	2.64	2.49	–	–	13.85	13.98
[Cu_2(Cl-asp)$_4$]·4H_2O	$Cu_{36}H_{32}Cl_4O_{20}Cu_2$	41.04	40.17	3.06	2.69	–	–	12.06	11.40
[Cu_2(Br-asp)$_4$]·4H_2O	$Cu_{36}H_{32}Br_4O_{20}Cu_2$	35.06	35.53	2.62	2.22	–	–	10.30	11.20
[Cu_2(I-asp)$_4$]·4CH_3OH	$Cu_{40}H_{40}I_4O_{20}Cu_2$	32.56	31.72	2.73	2.04	–	–	8.61	8.85
[Cu(F-asp)$_2$(py)$_2$]	$Cu_{28}H_{22}F_2N_2O_8Cu$	54.59	54.62	3.60	3.96	4.55	4.64	10.32	10.17
[Cu(Cl-asp)$_2$(py)$_2$]	$Cu_{28}H_{22}Cl_2N_2O_8Cu$	51.82	51.79	3.42	3.37	4.32	4.27	9.79	9.82
[Cu(Br-asp)$_2$(py)$_2$]	$Cu_{28}H_{22}Br_2N_2O_8Cu$	45.74	44.96	3.02	2.53	3.81	3.69	8.64	8.70

Table 2 Selected IR spectral data for the investigated copper(II) haloaspirinates (values in cm^{-1})

Compound	R-CO_2			Acetoxy groups						Pyridine	
	ν_{as}	ν_s	δ	$\nu_{(CO)}$ (I)	$\nu_{(CO)}$ (II)	$\nu_{as(COC)}$ (II)	$\nu_{as(COC)}$ (I)	$\nu_{s(COC)}$ (I)	$\nu_{s(COC)}$ (II)	$\nu_{(CC)}$	$\gamma_{(CH)}$
[Cu_2(asp)$_4$]	1620 vs	1400 vs	1020 m	1760 s	1725 s	1238 vs	1195 vs	1100 s	1036 m	–	–
[Cu_2(F-asp)$_4$]	1629 vs	1389 vs	1014 w	1763 vs	1717 vs	1249 vs	1184 vs	1127 m	1027 w	–	–
[Cu_2(Cl-asp)$_4$]·$4H_2O$	1635 vs	1378 vs	1017 m	1740 vs	–	–	1236 vs	1100 s	–	–	–
[Cu_2(Br-asp)$_4$]·$4H_2O$	1620 vs	1370 m	1013 m	1740 vs	–	–	1200 s	1098 s	–	–	–
[Cu_2(I-asp)$_4$]·$4CH_3OH$	1639 vs	1374 vs	1017 m	1739 vs	–	–	1206 vs	1103 s	–	–	–
[Cu(F-asp)$_2$(py)$_2$]	1608 vs	1368 vs	1018 m	1758 vs	–	–	1185 vs	1127 m	–	1448 s	699 vs
[Cu(Cl-asp)$_2$(py)$_2$]	1605 vs	1360 s	1018 m	1764 vs	–	–	1198 vs	1108 s	–	1448 s	698 vs
[Cu(Br-asp)$_2$(py)$_2$]	1610 vs	1364 vs	1014 m	1765 vs	–	–	1203 vs	1099 s	–	1449 m	700 vs

(X-asp) – haloaspirinate, ν – stretching, δ – in plane deformation, γ – out-of-plane deformation, vs – very strong, s – strong, m: medium, w – weak

The electronic absorption spectra of these complexes present the three band pattern which is characteristic of dimeric Cu–Cu units [9], and which origin has been extensively discussed in the literature [9, 14, 15]. Some data are presented in Table 3.

Table 3 Selected UV-Visible spectral data for copper(II) haloaspirinates

Compound	State	Wavelength/nm				
		Band I	Band II	Bands III		Ref.
$[Cu_2(F\text{-}asp)_4]$	Nujol	675	350	306		9
$[Cu_2(Cl\text{-}asp)_4]\cdot 4H_2O$	Nujol	705	350	305		9
$[Cu(asp)_2(py)_2]$	$HCCl_3$	725 br		285	265	8
$[Cu(F\text{-}asp)_2(py)_2]$	Nujol	792/783 br		342	278	t.w.
	CH_3OH	747		322	276	t.w.
$[Cu(Cl\text{-}asp)_2(py)_2]$	Nujol	818 br		310	270	t.w.
	CH_3OH	765 br		316	277	t.w.
$[Cu(Br\text{-}asp)_2(py)_2]$	Nujol	806 br		312	268	t.w.
	CH_3OH	763 br		315	273	t.w.

asp – aspirinate, br – broad, t.w. – this work

The TG and DTA curves of the five dimeric aspirinate complexes present some common characteristics and peculiarities. As typical examples for the measured TG and DTA traces, those obtained for the fluoro- and chloro-aspirinates under an air flow, are presented in Figs 1 and 2, respectively. The obtained thermal data for the full series of complexes are shown in Tables 4 and 5. The complexes containing water or methanol show an endothermic peak between 40 and 120°C, both under air and nitrogen, corresponding to the removal of these ligands. The IR spectra of residues collected after this first step clearly shows that the sites occupied by water or methanol are immediately occupied by acetoxy groups, in a similar way as in the aspirinate or fluoro-aspirinate compounds.

For all five complexes there is an endothermic process in the range between 145–270°C, named step II in Tables 4 and 5, corresponding to the partial degradation of the aspirinate ligand. These processes appear with almost identical characteristics in the TG and DTA curves obtained under both atmospheres, suggesting a bond breaking without oxygen consumption. The initial decomposition temperature is higher for the fluoro-aspirinate complex, indicating a greater thermal stability, in agreement with some preliminary thermodynamic calculations for the free ligands.

The lost mass fraction in step II was almost the same in all cases (about 100 g mol^{-1} Cu(II)) and the IR spectra of solid residues collected at the end of this

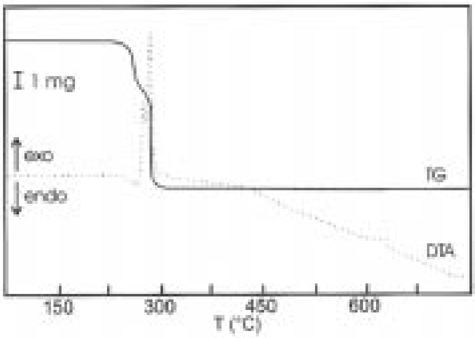

Fig. 1 TG and DTA curves of $[Cu_2(F\text{-}asp)_4]$ in air. Sample mass:10.5 mg; heating rate: 5°C min^{-1}

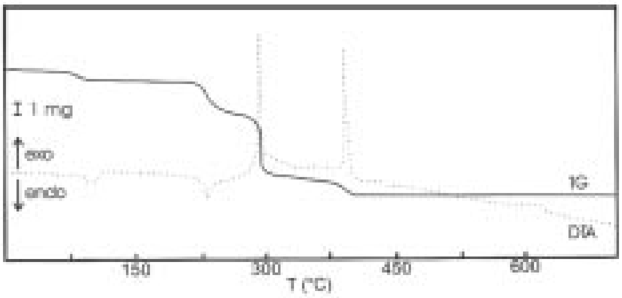

Fig. 2 TG and DTA curves of $[Cu_2(Cl\text{-}asp)_4]4H_2O$ in air. Sample mass: 13.3 mg; heating rate: 3°C min^{-1}

step show important intensity diminution in bands related to vibrations of acetoxy groups coordinated to copper. Besides, several new bands appear in the 1600 cm^{-1} region. On the other hand, the permanency of the uncoordinated acetoxy stretching bands, indicate that these groups decompose at higher temperatures, within the steps named III and IV in Tables 4 and 5.

All these data suggest that, the thermal degradation starts on the acetoxy groups bonded to neighbouring Cu(II) ions, involving these groups and an important part of the aromatic ring.

After step II the final degradation occurs in the temperature range between 260 and 550°C and involves two highly exothermic processes, except for the unsubstituted aspirinate and the fluoro-aspirinate complexes, which decomposes in only one step. For all complexes the final pyrolysis residue was CuO. Calculated and observed percentages of mass loss for step I as well as for the final residues obtained in air, are summarised in Table 6.

It is also interesting to mention that in nitrogen atmosphere the transformations occur at slightly higher temperatures, and eventually with a different degradation mechanism, as suggested by differences in the DTA traces in both atmospheres.

Table 4 Mass loss (in %) and decomposition temperatures from TG and DTA curves (air atmosphere)

Compound	TG			
	Step I	Step II	Step III	Step IV
$[Cu_2(asp)_4]$	–	25.8^a 210–258^b	55.9^c 258–300	
$[Cu_2(F\text{-}asp)_4]$	–	25.1 225–270	57.4^c 270–350	
$[Cu_2(Cl\text{-}asp)_4]\cdot 4H_2O$	6.8 60–120	19.4 145–255	41.8 255–310	16.7 310–500
$[Cu_2(Br\text{-}asp)_4]\cdot 4H_2O$	5.5 40–75	16.5 174–263	25.5 263–360	40.5 360–566
$[Cu_2(I\text{-}asp)_4]\cdot 4CH_3OH$	6.7 45–98	13.3 190–266	23.8 266–320	44.4 320–490
$[Cu(F\text{-}asp)_2(py)_2]$	25.6 65–210	18.7 210–270	42.8^c 270–400	
$[Cu(Cl\text{-}asp)_2(py)_2]$	24.0 75–190	15.6 190–262	23.4 262–368	24.3 368–570
$[Cu(Br\text{-}asp)_2(py)_2]$	20.6 60–190	14.9 190–255	14.8 255–355	38.8 355–600

[a]mass loss/% ; [b]temperature range/°C; [c]only one sharp and continuous step was observed

Compound	DTA				
	Step$^{\#}$ I		Step$^{\#}$ II	Step* III	Step* IV
$[Cu_2(asp)_4]$	–		225–263 (244/251)^d	260–295 (278)	
$[Cu_2(F\text{-}asp)_4]$	–		240–275 (260)	275–320 (274/296)	
$[Cu_2(Cl\text{-}asp)_4]4H_2O$	70–125 (100)		180–237 (227)	255–315 (291)	345–413 (395)
$[Cu_2(Br\text{-}asp)_4]4H_2O$	40–75 (60)		175–255 (244)	260–368 (304/312/334)	368–520 (447)
$[Cu_2(I\text{-}asp)_4]4CH_3OH$	52–95 (64)		213–266 (251)	266–350 (308)	360–500 (424)
$[Cu(F\text{-}asp)_2(py)_2]$	85–155 (143)	155–230 (195)	230–275 (258)	275–370 (298)	
$[Cu(Cl\text{-}asp)_2(py)_2]$	98–158 (128–142)	158–218 (189)	e	240–375 (298–306)	375–570 (400–488)
$[Cu(Br\text{-}asp)_2(py)_2]$	50–143 (120)	143–220 (191)	220–274 (255)	274–398 (304)	398–600 (450)

[#]endothermic peak(s); *exothermic peak(s); [d]peak minimum or maximum; [e]very distorted by step III

Table 5 Mass loss (in %) and decomposition temperatures from TG and DTA curves (nitrogen atmosphere)

Compound	TG				DTA			
	Step I	Step II	Step III	Step IV	Step[#] I	Step[#] II	Step[*] III	Step[*] IV
[Cu$_2$(asp)$_4$]	–	29.5[a] 240–277[b]	53.3 277–400		–	213–286 (258)	286–427 (341–376)[c]	
[Cu$_2$(F-asp)$_4$]	–	26.7 225–270	53.3 270–400		–	243–278 (266)	278–420 (339–377)[c]	
[Cu$_2$(Cl-asp)$_4$]·4H$_2$O	6.4 65–131	15.5 180–248	34.6 248–355	28.3 355–510	70–130 (115)	214–248 (237)	248–371 (315)	371–500 (445)
[Cu$_2$(Br-asp)$_4$]·4H$_2$O	5.6 45–75	16.8 145–260	29.5 260–408	35.1 408–600	45–70 (62)	215–257 (235)	257–355 (315)	415–565 (460)

[a]mass loss/%; [b]temperature/°C; [#]endothermic peak(s); [*] exothermic peak(s); [c]very broad

Table 6 Residue data of complexes and mass loss percentages of step I (air atmosphere)

Coumpound	Step I mass loss/%		Ligand	Residue/% CuO	
	obs.	calc.		obs.	calc.
$[Cu_2(asp)_4]$	–	–	–	18.3	18.9
$[Cu_2(F\text{-}asp)_4]$	–	–	–	17.5	17.4
$[Cu_2(Cl\text{-}asp)_4]\cdot 4H_2O$	6.8	6.8	$-4H_2O$	15.3	15.1
$[Cu_2(Br\text{-}asp)_4]\cdot 4H_2O$	5.5	5.8	$-4H_2O$	13.0	12.9
$[Cu_2(I\text{-}asp)_4]\cdot 4CH_3OH$	6.7	8.7	$-4CH_3OH$	10.7	10.8
$[Cu(F\text{-}asp)_2(py)_2]$	25.6	25.7	–2 pyridine	12.8	12.9
$[Cu(Cl\text{-}asp)_2(py)_2]$	24.0	24.4	–2 pyridine	12.1	12.3
$[Cu(Br\text{-}asp)_2(py)_2]$	20.6	21.4	–2 pyridine	10.6	10.8

Copper(II) complexes of haloaspirinates and pyridine

An X-ray diffraction study of the complex $[Cu(asp)_2(py)_2]$ showed that monomeric units are present in the lattice and that the Cu(II) ion is coordinated by two pyridine N-atoms and two carboxylate O-atoms in a *trans* square planar arrangement whereas the second oxygen atoms from the carboxylate groups are weakly bound to axial positions of the metal center (8). In other ternary aspirinate complexes with imidazole [16] or benzimidazole [17] Cu(II) present also monomeric coordination, as deduced from EPR and electronic spectroscopic data. Therefore, a similar situation may be expected for the present complex compounds.

As shown in Table 2, the IR spectra of the pyridine containing complexes only contains bands corresponding to vibrations of type I acetoxy groups and the carboxylic stretching bands appear at lower frequencies than in the parent dimeric compounds. This spectroscopic behaviour is in agreement with the expected monomeric structure [17, 18].

Data of the UV-visible spectra of the complexes are shown in Table 3. The presence of the broad bands at ca 750 nm in methanolic solution or at ca 800 nm in the solid mulls as well as the absence of the characteristic band II, confirms again a monomeric tetragonal ligand arrangement around the Cu(II) centers [8, 14, 17].

For these complexes the thermal behaviour was investigated only under an air flow. The TG and DTA curves of the three complexes are shown in Figs 3–5. The analysis of data is included in Tables 4 and 6. The three complexes gives up the two pyridine molecules in a two-step process between 60 and 210°C. After this release the behaviour of the fluoro-aspirinate complex is different to that of the other two compounds. For the former complex, the IR spectrum of residues collected at 210°C is identical to the spectrum of $[Cu_2(F\text{-}asp)_4]$. That means, that after the loss of pyridine a structural rearrangement takes place generating again the dinuclear structure characteristic of the parent complex.

The final decomposition of the chloro- and bromo-aspirinate complexes present similar patterns and occur in similar temperature ranges as for the dimeric parent compounds. In the DTA traces, the signal corresponding to step II appears highfy dis-

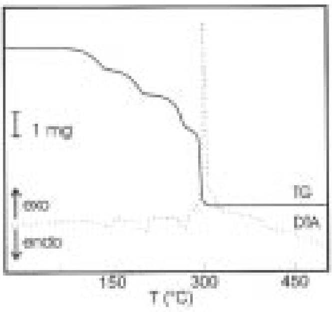

Fig. 3 TG and DTA curves of [Cu(F-asp)$_2$(py)$_2$] in air. Sample mass: 7.8 mg; heating rate: 5°C min^{-1}

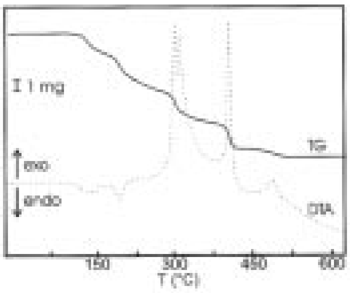

Fig. 4 TG and DTA curves of [Cu(Cl-asp)$_2$(py)$_2$] in air. Sample mass: 13.2 mg; heating rate: 5°C min^{-1}

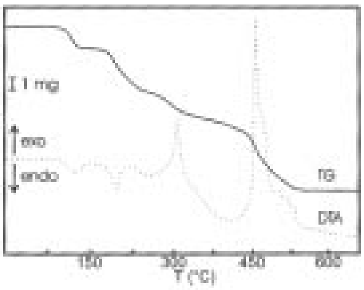

Fig. 5 TG and DTA curves of [Cu(Br-asp)$_2$(py)$_2$] in air. Sample mass: 16.1 mg; heating rate: 5°C min^{-1}

torted by the strong endothermic peak related to step III, especialty for the chloro-aspirinate. On the basis of these results, we consider that after the loss of pyridine, the structures of these two complexes are probably not reorganized to the dimeric arrangement but the structure transformatian involves the coordination of acetoxy groups to the metal center, as suggested by the appearance of type II acetoxy vibration in the IR spectra of products collected after the elimination of pyridine.

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