Journal of Thermal Analysis, Vol. 18 (1980) 263—270

COMPLEXES FORMED BETWEEN NICKEL(II), COPPER(II), ZINC(II) AND ASPIRIN

J. R. ALLAN and J. GAVIN

Chemistry Department, Napier College of Commerce and Technology, Edinburgh, U.K.

(Received August 22, 1979)

Complexes of nickel(II), copper(II) and zinc(II) with aspirin have been prepared. Examination of the complexes of nickel(II) and zinc(II) indicates that they are salicylato complexes in which the aspirin has been de-ethanoylated.

Chemical, spectral and magnetic properties show that the nickel(II) and copper(II) complexes have dimeric, octahedral structures while the zinc(II) complex has a tetrahedral structure. The decomposition of the complexes was studied by thermogravimetry and differential thermal analysis. Thermal decomposition products were obtained for the nickel(II) and zinc(II) complexes. Their structures are octahedral with the exception of *bis*-salicyclic acid-zinc(II) which is tetrahedral.

Aspirin (acetylsalicylic acid) was introduced into medical practice in 1896. It is used most commonly as an antipyretic and analgesic agent for the relief of headaches and minor ailments.

Aspirin suffers from one great disadvantage: it irritates the gastric mucosa, producing slight haemorrhaging and ulcerogenic lesions. This effect is limited in time, as the aspirin decomposes to ethanoic acid and salicyclic acid in the body. Some derivatives of aspirin which have less of an irritating effect are used where aspirin cannot be used: furthermore, the copper-aspirin complex whose preparation is described below has the analgesic and antipyretic properties of aspirin, without the disadvantage of causing gastric lesions [7]. A number of complexes of salicyclic acid and its derivatives have been reported in the literature [1–8]. The present paper describes the preparation of complexes formed between aspirin and nickel (II), copper (II), zinc (II) ions, together with the results of thermal analysis, visible spectra, infrared spectra, and magnetic measurements.

Experimental

Two methods of preparation were used:

(A) The complexes were prepared by dissolving (18g, 0.1 mole) aspirin in 150 ml water, bringing this solution to boiling, and gradually adding (6g, 0.05 mole) of the appropriate metal carbonate. The resulting solution was reduced in volume and the complex which formed, was filtered, washed with ether and dried.

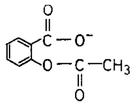
(B) The complex prepared by method (A) was heated on a thermobalance at a fixed temperature until constant weight was obtained.

Table 1

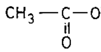
Analysis of compounds

Compound	Method of preparation	Colour	Experimental			Theory		
			%C	%H	% Metal	%C	%H	% Metal
Ni(SAL)(Ac)H_2O	A	Green	39.56	3.66	21.62	39.61	3.69	21.64
Ni(SAL)(Ac)	B	Yellow	42.38	3.10	23.02	42.41	3.16	23.03
Ni(SAL)	B	Brown	42.64	2.52	29.92	42.93	2.57	29.98
$Cu(ASA)_2$	A	Blue-green	51.20	3.30	15.02	51.23	3.35	15.06
$Zn(SAL)_2 \cdot 3\ H_2O$	A	White	42.68	3.02	16.60	42.72	3.07	16.60
$Zn(SAL)_2$	B	White	49.46	2.94	19.23	49.51	2.97	19.25
Zn(SAL)	B	White	41.48	2.44	31.24	41.52	2.49	32.28

ASA Acetylsalicylate anion

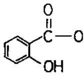


Ac Ethanoate



$CH_3-C(=O)-O^-$

SAL Salicylate anion



The complexes prepared by these methods are listed in Table 1.

Thermal decomposition studies were carried out in air on a Stanton Redcroft Model TR-01 Thermobalance working at chart speed of 6 in/hr with DTA attachment. Electronic spectra were obtained on a Beckman ACTA M-IV spectrophotometer.

Infrared absorption spectra (KBr discs) were obtained with a Perkin–Elmer Infrared Spectrophotometer, Model 257. Far infrared spectra were obtained on a Beckman IR 720M interferometer using a polythene matrix to support the complexes. Magnetic susceptibility measurements were made by the Gouy method using a Newport balance and the calibrant $Hg[Co(SCN)_4]$.

Results

The green complex formed between aspirin and nickel (II) ions has stoichiometry Ni(SAL) (Ac) $\cdot$ H_2O. Thermal decomposition studies of the complex (Fig. 1) show that this compound undergoes an endothermic reaction at 407K with loss of the water molecule. Further endothermic reactions take place with mass loss corresponding to ethanoate at 477K and the salicylic acid at 588K and the formation of NiO (Residue: found 20.02%; theory 19.92%). Figure 1 shows these points as discontinuities in the smooth curve (A), the points being marked to show the formula of the compound at the temperature quoted. The visible reflectance spectra of the compounds (Table 3) resemble that normally found for octahedrally coordinated nickel (II) although the true environment will be of lower symmetry than O_h. The observed transitions are $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^1E_g(G)$. The broadening of the band for the transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ reflects the lowering of the symmetry in the compound and is probably due to spin-orbit coupling. A study of the magnetic moment for the compounds Ni(SAL)(Ac) (H_2O) and Ni(SAL) (Ac) further supports an octahedral environment for the nickel atom

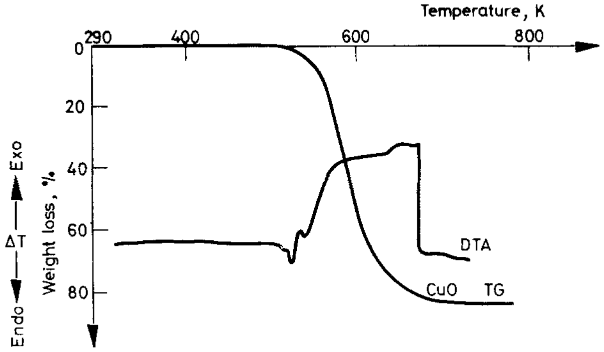


Fig. 1. TG and DTA curves of Ni(SAL)Ac · H_2O. Sample weight: 74.6 mg, heating rate: 4°/min, atmosphere: static air

(Table 2). The magnetic moments are found to be in the range 3.2 – 3.8 B.M. [9]. The far infrared spectra (Table 4) support an essentially octahedral environment round the nickel atom [10].

The blue-green complex formed between aspirin and copper (II) ions has stoichiometry $Cu(ASA)_2$. Thermal decomposition studies of the complex (Fig. 2) show that no intermediate compounds are formed and that the compound undergoes an exothermic reaction at 521K with loss of two molecules of aspirin and the formation of CuO (Residue: found 24.02%; theory 24.42%). The magnetic moment of 1.39BM for the compound (Table 2) would suggest an octahedral or square planar

Table 2

Magnetic data

Compound	Temp, K	$\chi_m/10^{-6}$	$\chi_m^{corr}/10^{-6}$	μ(B. M)
Ni(SAL)(Ac)H_2O	297	5975	6041	3.80
Ni(SAL)(Ac)	300	5349	5402	3.62
$Cu(ASA)_2$	297	737	800	1.39

environment for the copper (II). Thus the evidence for the structural assignment is from spectral data (Table 3).

The compound shows one broad absorption band at 15.385 cm^{-1}. This suggests an octahedral environment for the copper atom since square planar copper (II) complexes show two bands of near equal intensity at about 15.000 cm^{-1} and 18000 cm^{-1} [12–14]. The band at 15.385 cm^{-1} is due to the transition $^2E_g \to {}^2T_{2g}$. The broadness of the band is due to Jahn-Teller distortion involving the ^2E_g ground state. The far infrared spectrum (Table 4) would also agree with an octahedral structure [10].

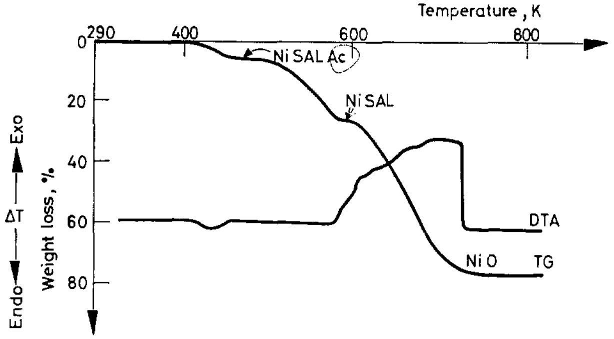


Fig. 2. TG and DTA curves of $Cu(ASA)_2$. Sample weight: 61.8 mg, heating rate: 4°/min, atmosphere: static air

The white complex formed between aspirin and zinc (II) ions has stoichiometry $Zn(SAL)_2 \cdot 3\,H_2O$ indicating that the aspirin molecule has once again lost the ethanoate group. Thermal decomposition studies of the complex (Fig. 3) show that the compound undergoes an endothermic reaction at 356K with loss of three water

Table 3

Nickel compounds

Octahedral environment, ground state $^3A_{2g}(F)$

Electronic spectra, cm^{-1}

Compound	$^3A_{2g}(F) \to {}^3T_{2g}(F)$	$^3A_{2g}(F) \to {}^3T_{1g}(F)$	$^3A_{2g}(F) \to {}^1E_g(G)$
$Ni(SAL)(Ac)H_2O$	11.380	18.720	34.200
Ni(SAL)(Ac)	11.440	18.840	34.400
Ni(SAL)	11.510	—	34.640

Copper compounds

Octahedral environment, ground state ^2E_g

Compound	$^2E_g \to {}^2T_{2g}$
$Cu(ASA)_2$	15.385

molecules followed by further endothermic reactions at 516K and 616K corresponding to the loss of each of the salicylic acid molecules and the formation of ZnO (Residue: found 21.06%; theory 21.32%). Figure 3 shows these points as discontinuities in the smooth curve (A), the points again being marked to show the formula of the compound at the temperature. The zinc (II) ion has a d^{10} configuration so that evidence for structural assigment is from the far-infrared spectra (Table 4). The zinc complexes $Zn(SAL)_2 3\ H_2O$ and $Zn(SAL)_2$ with metal-oxygen bands at 394 and 392, respectively have tetrahedral structures [15].

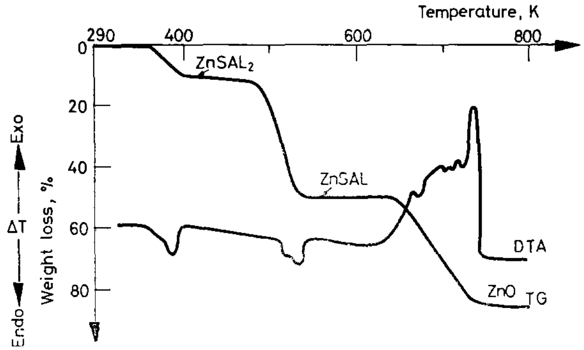


Fig. 3. TG and DTA curves of $Zn(SAL)_2 \cdot 3\ H_2O$. Sample weight: 86.9 mg, heating rate: 4°/min, atmosphere: static air

Table 4

Infrared spectra, 3.500 – 50 cm^{-1}

Compound	$\nu_{C=O}$	ν_{O-H}	ν_{M-O}
Aspirin	1750, 1685	3100–2540	
Salicylic acid	1650	3240	
$Ni(SAL)(Ac)H_2O$	1620	3507	292; $\nu(Ni-OH_2)$ 316
$Ni(SAL)(Ac)_2$	1620	3507	291
$Cu(ASA)_2$	1725, 1620	–	286
$Zn(SAL)_2 3\ H_2O$	1590	3500–2800	394
$Zn(SAL)_2$	1585	3220	392

Discussion

The analytical data reported in Table 1 shows that for the reaction of nickel (II) and zinc (II) ions with aspirin in aqueous solution the aspirin undergoes decomposition to salicylic acid and the ethanoate ion whereas for the reaction with copper (II) ions a copper – aspirin complex is formed. The copper complex is anhydrous whereas the nickel and zinc complexes are hydrated. The presence of a band at 316 cm^{-1} in the nickel complex. suggests that the water is coordinated to the nickel atom [16].

Table 5

TG data of complexes

Compound	Stage	Ligand removed	Expected loss	
			Calc. %	Actual %
Ni(SAL)(Ac)H_2O				
↓	(1)	H_2O	6.03	6.60
Ni(SAL)(Ac)				
↓	(2)	Ac	22.11	21.64
Ni(SAL)				
↓	(3)	SAL	49.32	50.25
NiO				
$Cu(ASA)_2$				
↓	(1)	2 ASA	83.01	84.94
CuO				
$Zn(SAL)_2 \cdot 3\ H_2O$				
↓	(1)	3 H_2O	13.72	11.51
$Zn(SAL)_2$				
↓	(2)	SAL	37.74	33.84
Zn(SAL)				
↓	(3)	SAL	35.10	33.84
ZnO				

For the compound $Zn(SAL)_2 3\ H_2O$ the absorption bands which occur in the range 3500–3200 cm^{-1} ν(OH) and 1630–1590 cm^{-1} S(HOH) confirm the presence of water of crystallization [10]. The presence of water as water of crystallization and as coordinated water in the nickel compound is further borne out by the thermal decomposition data (Figs 1 & 3). The mass losses observed in the TG curves of the nickel and zinc complexes are separated by a period of constant mass, indicating that the products are stable over an approximate temperature range of 20–100K. The sequence of decomposition reactions as deduced from the TG studies (Table 5) are summarized below:

$$\begin{aligned}
&\mathrm{Ni(SAL)\,(Ac)H_2O} &&\longrightarrow \mathrm{Ni(SAL)\,(Ac) + H_2O}\\
&\mathrm{Ni(SAL)\,(Ac)} &&\longrightarrow \mathrm{Ni(SAL) + Ac}\\
&\mathrm{Ni(SAL)} &&\longrightarrow \mathrm{NiO + SAL}\\
&\mathrm{Cu(ASA)_2} &&\longrightarrow \mathrm{CuO + 2\ ASA}\\
&\mathrm{Zn(SAL)_2 3\ H_2O} &&\longrightarrow \mathrm{Zn(SAL)_2 + 3\ H_2O}\\
&\mathrm{Zn(SAL)_2} &&\longrightarrow \mathrm{Zn(SAL) + SAL}\\
&\mathrm{Zn(SAL)} &&\longrightarrow \mathrm{ZnO + SAL}
\end{aligned}$$

Without X-ray analysis, no definite structures can be described for the different components. However, spectroscopic and magnetic data available enable us to predict structures and we can also use chemical analysis to help us. The infrared spectra of the solid free ligands are almost identical to those of their complexes in the region 2000–625 cm^{-1}. The frequencies of most interest with regard to structure are the C–O and O–H vibrations. The $\nu(C=O)$ band at 1658 cm^{-1} is shifted to a lower frequency in all of the complexes showing that complexation has taken place through the carboxyl group [17]. The infrared spectrum of the compound $Ni(SAL)(Ac) \cdot H_2O$ shows that the $\nu(O-H)$ band has shifted from 3240 cm^{-1} in salicylic acid to 3507 cm^{-1} in the compound indicating the absence of hydrogen bonding [18]. For the compound $Zn(SAL)_2 \cdot 3\,H_2O$ this band is not observed due to the broad band produced by the absorption of the water molecules. The $\nu(O-H)$ band in $Zn(SAL)_2$ is observed at 3220 cm^{-1} suggesting the presence of hydrogen bonding in the compound [18].

The nickel complexes are sparingly soluble in water and it is suggested that they have dimeric structures with the nickel atoms in an octahedral environment. The thermal decomposition would appear to be consistent with this type of structure and would suggest that the water and ethanoate are directly bonded to the nickel, with two salicylate molecules bridging between two nickel atoms to give a coordination number of six for each of the nickel (II) ions.

The method of preparation used in the present investigation for the copper complex is different from that reported in the literature [7]. The compound is insoluble in water and common organic solvents. It has been suggested [7] that the structure includes four units of acetylsalicylate and two copper ions, each copper ion in an octahedral environment with five Cu–O bonds and one Cu–Cu linkage. The presence of the Cu–Cu linkage is further borne out by the abnormally low magnetic moment of 1.38 BM found for the compound in the present investigation.

The zinc complexes, $Zn(SAL)_2 3\,H_2O$ and $Zn(SAL)_2$ have tetrahedral structures.

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ZUSAMMENFASSUNG — Komplexe von Nickel (II), Kupfer (II) und Zink (II) mit Aspirin wurden hergestellt. Die Untersuchung der Koordinationsverbindungen von Nickel (II) und Zink (II) zeigt, daß dies Salycylatkomplexe sind, in welchen das Aspirin de-äthanoliert wurde.

Die chemischen, spektralen- und magnetischen Eigenschaften zeigen, daß die Nickel (II)- und Kupfer (II)-Komplexe dimere Oktaederstrukturen besitzen, während der Zink (II)-Komplex eine Tetraederstruktur besitzt. Die Zersetzung der Komplexe wurde durch Thermogravimetrie und Differentialthermoanalyse untersucht. Thermische Zersetzungsprodukte der Nickel (II)- und Zink (II)-Komplexe wurden erhalten. Ihre Strukturen sind oktaedrich, mit Ausnahme von *Bis*-Salicyclosäure-Zink (II), dessen Struktur tetraedrisch ist.

Резюме — Получены комплексы никеля(II), меди(II) и цинка(II) с аспирином. Исследование комплексов никеля(II) и цинка(II) показало, что в действительности они являются салицилатокомплексами, т. е. произошло деацетилирование аспирина. Химические, спектральные и магнитные свойства этих комплексов показали, что комплексы никеля и меди обладают димерной, октаэдрической структурой, а комплекс с цинком имеет тетраэдрическое строение. Разложение комплексов было изучено с помощью термогравиметрии и дифференциального термического анализа. В случае комплексов никеля и цинка были получены продукты термического разложения. Структура этих продуктов окраэдрическая, за исключением бис-салицилата цинка, для которого характерно тетраэдрическое строение.