

## Copper(II) Complexes of 4-Aminobenzoic and 4-Aminosalicylic Acids

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### Abstract

Copper(II) complexes of 4-aminobenzoic (HAB) and 4-aminosalicylic (HAS) acids were prepared and characterized by means of thermal analysis, magnetic measurements, ESR, IR and electronic spectroscopy. Both ligands behave as monodentate (carboxylate bonded) or bridging bidentate (amino and carboxylate bonded) donors yielding two types of complexes having essentially planar  $\text{CuO}_4$  and  $\text{CuN}_2\text{O}_2$  chromophores, respectively.

### Introduction

4-Aminobenzoic acid is well-known as an inhibitor of the bacteriostatic action of sulfonamide [1] and has been shown to be a growth factor in certain micro-organisms [2], particularly *Enterococci* and *Lactobacilli*. It also seems that 4-aminobenzoic acid is involved in the biosynthesis of folic acid, which is a constituent of the vitamin B complex and is found in animal and plant tissues.

The interaction of 4-aminobenzoic acid with metal ions was previously studied and several metal complexes were synthesized [3–9]. X-ray diffraction studies showed that the ligand coordinates the metal ions via the carboxylate group. However, depending on the metal ion, the amino group can also be involved in complex formation and polymeric species are formed.

It is known that 4-aminobenzoate adopts simple carboxylate coordination in  $[\text{Mn}(\text{AB})_2(\text{H}_2\text{O})_4]$  and  $[\text{Co}(\text{AB})_2(\text{H}_2\text{O})_4]$  [3, 4].

In contrast,  $[\text{Ni}(\text{AB})_2(\text{H}_2\text{O})_2]$  (5),  $[\text{Cd}(\text{AB})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  [6] and  $[\text{Zn}(\text{AB})_2] \cdot 1.5\text{H}_2\text{O}$  [7] are polymeric complexes where 4-aminobenzoate acts as a bridging ligand coordinating through both the car-

boxylate and amino groups. Both types of structures were observed for lead(II) complexes [8, 9].

Due to our interest in the metal complexes of growth factors and metabolic inhibitors [10–12], we have examined the copper(II) 4-aminobenzoate complexes for which relatively limited information is available [13–14]. This paper reports on the synthesis and the characterization of two copper(II) 4-aminobenzoate complexes which, based on the spectral and analytical results, have been formulated as  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}(\text{AB})_2]$ , respectively.

Being interested also in the interaction of metal ions with salicylic-like ligands [15, 16], we have extended the investigation to the copper complexes of 4-aminosalicylate. Also in this case two compounds with different physical properties were obtained, which were identified as  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$ .

All spectral results reported in this study indicate that 4-aminobenzoate and 4-aminosalicylate behave in a similar way and adopt either carboxylate or carboxylate and amino coordination toward copper(II), acting as bridging ligands in the latter case.

It is noteworthy that recently two copper(II) complexes of 4-aminosalicylic acid have been reported and described as *cis* and *trans* isomers of bis-(4-aminosalicylato)copper(II), where the ligand was suggested to bind the metal *via* bidentate carboxylate groups [17].

### Experimental

#### Materials

All chemicals were of reagent grade. The acids were recrystallized from water.

### Preparation of Complexes

#### *Bis(4-aminobenzoato)copper(II), [Cu(AB)<sub>2</sub>]*

4-Aminobenzoic acid (4 mmol) or its potassium salt (4 mmol), dissolved in hot water (25 ml), was added to a solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (2 mmol) in the same solvent (10 ml). After stirring at 65 °C a green precipitate separated after a few minutes. Calc. for C<sub>14</sub>H<sub>12</sub>CuN<sub>2</sub>O<sub>4</sub>: C, 50.07; H, 3.60; N, 8.34. Found: C, 50.20; H, 3.70; N, 8.16. M.p. 298 °C dec.  $\mu_{\text{eff}}$ : 1.95 B.M.

#### *Bis(4-aminobenzoato)diaquocopper(II), [Cu(AB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]*

4-Aminobenzoic acid (4 mmol) or its potassium salt (4 mmol) was dissolved in hot water and, after cooling, added drop by drop to 10 ml of water containing CuCl<sub>2</sub>·2H<sub>2</sub>O (2 mmol). By stirring at room temperature an olive-green compound separated. Calc. for C<sub>14</sub>H<sub>16</sub>CuN<sub>2</sub>O<sub>6</sub>: C, 45.22; H, 4.34; N, 7.53; H<sub>2</sub>O, 9.69. Found: C, 45.30; H, 4.30; N, 7.63; H<sub>2</sub>O, 9.7. M.p. 225 °C dec.  $\mu_{\text{eff}}$ : 1.97 B.M.

#### *Bis(4-aminosalicylato)copper(II) monohydrate, [Cu(AS)<sub>2</sub>·H<sub>2</sub>O] and Bis(4-aminosalicylato)diaquocopper(II) dihydrate, [Cu(AS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O]*

In preparing the complexes, synthetic procedures similar to those described by Moore and Vigeo [17] were followed, except that the precipitates were air-dried in order to avoid removal of coordinated water. In this way compounds were obtained exhibiting the same colours as those described by Moore and Vigeo. However, whereas the dark green complex which separated at reactant concentrations below 0.075 M was analysed as Cu(AS)<sub>2</sub>·H<sub>2</sub>O, the bright green compound showed the molecular formula Cu(AS)<sub>2</sub>·4H<sub>2</sub>O.

[Cu(AS)<sub>2</sub>·H<sub>2</sub>O]: Calc. for C<sub>14</sub>H<sub>14</sub>CuN<sub>2</sub>O<sub>7</sub>: C, 43.58; H, 3.66; N, 7.26; H<sub>2</sub>O, 4.67. Found: C, 43.25; H, 3.40; N, 7.54; H<sub>2</sub>O, 4.5. M.p. 223 °C dec.  $\mu_{\text{eff}}$ : 1.92 B.M.

[Cu(AS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O]: Calc. for C<sub>14</sub>H<sub>20</sub>CuN<sub>2</sub>O<sub>10</sub>: C, 38.23; H, 4.58; N, 6.37; H<sub>2</sub>O, 16.38. Found: C, 38.44; H, 4.60; N, 6.58; H<sub>2</sub>O, 16.0. M.p. 198 °C dec.  $\mu_{\text{eff}}$ : 1.82 B.M.

### Analytical and Spectroscopic Measurements

C, H and N were determined using a Perkin-Elmer 240 B elemental analyser. Thermal studies were performed on a Perkin-Elmer thermogravimetric apparatus in nitrogen atmosphere at a scanning rate of 5 °C min<sup>-1</sup>. IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer as KBr pellets in the range 4000–300 cm<sup>-1</sup>, and a Perkin-Elmer 180 spectrophotometer as Nujol mulls on polythene as support in the range 500–200 cm<sup>-1</sup>. Electronic spectra were taken on a Beckman Acta M IV

TABLE I. ESR and Absorption Data for the Complexes.

Complex	$\nu_{\text{max}}$ (10 <sup>3</sup> cm <sup>-1</sup> )	$g_{\parallel}$	$g_{\perp}$
[Cu(AB) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	14.93	2.306	2.058
[Cu(AB) <sub>2</sub> ]	16.26	2.058	2.145
[Cu(AS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·2H <sub>2</sub> O]	14.60	2.319	2.059
[Cu(AS) <sub>2</sub> ·H <sub>2</sub> O]	15.58	2.055	2.144

spectrophotometer using BaSO<sub>4</sub> as the reference sample. Powder ESR spectra were recorded on a Varian E 9 spectrometer with DPPH as standard field marker. The magnetic moments were measured at room temperature by the Faraday method with Hg[Co(NCS)<sub>4</sub>] as a calibrant.

### Results

#### *Magnetic and Thermal Data*

The magnetic moments exclude strong exchange interaction between the metal ions.

Thermal studies performed on the hydrate complexes show that the water molecules of [Cu(AB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] are simultaneously released over the range 125–180 °C. The water molecule of [Cu(AS)<sub>2</sub>·H<sub>2</sub>O] is lost between 35 and 85 °C. Dehydration of [Cu(AS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O] occurs in two partially overlapping steps at temperatures below 100 °C, as expected for a complex where the water molecules (either coordinated or not) are hydrogen-bonded to each other [18].

#### *Electronic and ESR Spectra*

The solid-state electronic absorption and ESR data for the complexes are listed in Table I. The energy of the *d*-*d* maximum of [Cu(AB)<sub>2</sub>] (Fig. 1) is indicative of a planar or strongly tetragonally elongated complex with nitrogen and oxygen as donor atoms [19]. This substantiates the involvement of both the amino and carboxylate groups in metal coordination to give a CuN<sub>2</sub>O<sub>2</sub>-based chromophore. However, the ESR features of the complex (Fig. 2), which do not show any appreciable temperature dependence down to 110 K, are anomalous for a tetragonally elongated copper(II) complex. Indeed, the spectrum is of the 'reversed' type with  $g_{\parallel}$  greater than  $g_{\perp}$ , suggesting the ground state to be  $d_{z^2}$ . Based on the electronic spectrum it is far more likely that the ground state for [Cu(AB)<sub>2</sub>] is largely  $d_{x^2-y^2}$  and thus the shape of the ESR spectrum must be due to inequivalent sites within the unit cell and misalignment of the tetragonal axes [20]. In addition, the unusually rather narrow resonances could indicate magnetic exchange transmitted *via* 4-aminobenzoate bridges in polymeric chains.

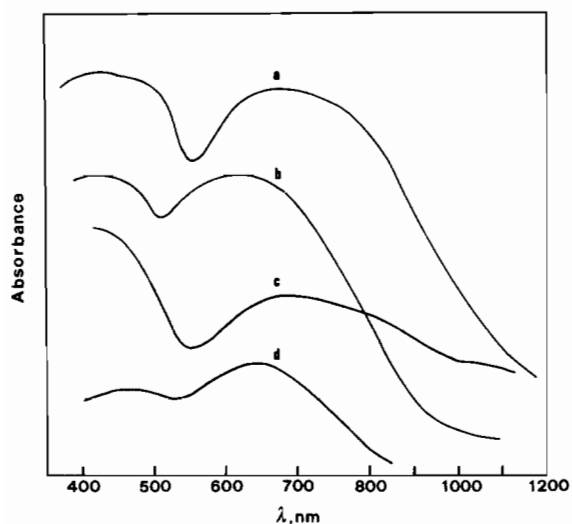


Fig. 1. Solid-state electronic spectra of:  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  (a),  $[\text{Cu}(\text{AB})_2]$  (b),  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (c) and  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$  (d).

On the other hand, the energy of the absorption maximum for  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  is too low for a nitrogen-containing chromophore of the  $\text{CuN}_2\text{O}_2$  or  $\text{CuN}_2\text{O}_4$  type. Indeed, the  $d-d$  absorption band (Fig. 1) resembles those of almost planar  $\text{CuO}_4$  complexes (e.g., bis(salicylato)diaquocopper(II)) in which the metal ion is coordinated to monodentate carboxylate groups and water molecules [15, 21, 22]. Accordingly, the ESR spectrum (Fig. 2), which is of the axial type, exhibits  $g$  values typical of copper-oxygen complexes strongly distorted toward planar geometry [15, 21–24]. Besides, the width of the powder ESR resonances is typical of magnetically dilute copper(II) complexes, suggesting the absence of conducting bridges between the copper centres.

The ESR and absorption spectra of  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$ , (Figs. 1 and 2) show a striking resemblance to those of  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}(\text{AB})_2]$ , respectively. In effect, the  $g_{\parallel}$  value is higher and the energy of the absorption maximum is lower for  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  than for  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$ , as expected for increased axial interaction or decreased in-plane field strength. Analogously, the absorption maximum of  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$ , while still consistent with  $\text{CuN}_2\text{O}_2$ -based chromophores, exhibits a lower energy value than that of  $[\text{Cu}(\text{AB})_2]$ . In addition, the ESR resonances of  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$  are broader than those of  $[\text{Cu}(\text{AB})_2]$ , indicating diminished exchange interaction between the metal ions.

Dehydration has no effect on the ESR and absorption spectra of  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$ , confirming the absence of coordinated water. Instead, after dehydration  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  display spectral features similar to those of  $[\text{Cu}(\text{AB})_2]$  and  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$ , respectively, suggesting

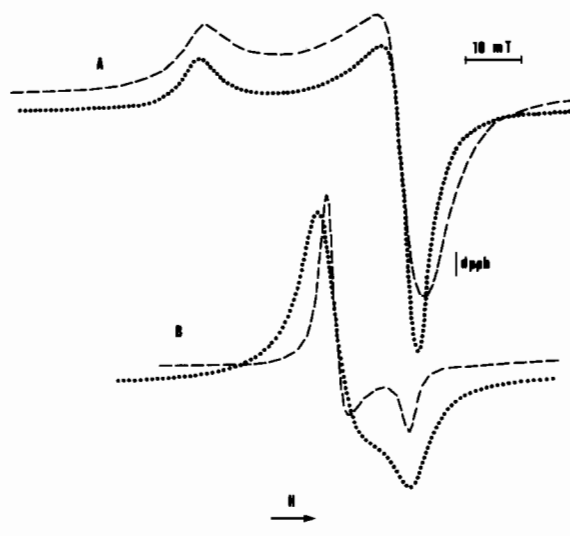


Fig. 2. Room-temperature ESR spectra of: (A)  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  (---),  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (.....) and (B)  $[\text{Cu}(\text{AB})_2]$  (---),  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$  (.....).

the formation of  $\text{CuN}_2\text{O}_2$  complexes. For the intermediate dehydration compounds, which are probably mixtures of hydrate and anhydrous complexes, broad ESR absorptions were observed resembling those described by Moore and Vigee [17].

#### Infrared Spectra

The more relevant IR bands for the copper(II) complexes are listed in Table II. It is worth pointing out that markedly different spectra are observed within both the series of 4-aminobenzoate and 4-aminosalicylate compounds. However, in each case the IR features of  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  are more similar to those of the corresponding alkali salts.

Of particular interest is examination of the absorption bands relative to the amino and carboxylate groups. The  $\nu(\text{NH}_2)$  stretching frequencies for the complexes show a negative shift of 135–185  $\text{cm}^{-1}$  with respect to those of the alkali salts, indicating that the amino group is involved in metal coordination and/or hydrogen bonding. Different trends are observed for the  $\delta(\text{NH}_2)$  absorptions which were assigned after examination of N-deuterated analogues. In fact, whereas the frequency values for  $[\text{Cu}(\text{AB})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}(\text{AS})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  compare well with those of the corresponding alkali salts, significant shifts to higher frequency occur in  $[\text{Cu}(\text{AB})_2]$  and  $[\text{Cu}(\text{AS})_2] \cdot \text{H}_2\text{O}$ , supporting coordination through the amino nitrogen atoms [25].

For the carboxylate stretching bands, whereas  $\nu_s(\text{CO}_2)$  is more easily assigned, some difficulties arise with the identification of  $\nu_{\text{as}}(\text{CO}_2)$  which is recognized by comparing the spectra of the acids,

TABLE II. More Relevant IR Bands for the Complexes in the 4000–200 cm<sup>-1</sup> Region.<sup>a</sup>

[Cu(AB) <sub>2</sub> ]	[Cu(AB) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[Cu(AS) <sub>2</sub> ] <sub>2</sub> ·H <sub>2</sub> O	[Cu(AS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	Assignment
3275s	3280m,br	3275s	3280m,br	ν <sub>as</sub> (NH <sub>2</sub> )
3170s	3150m,br	3175s	3175m,br	ν <sub>s</sub> (NH <sub>2</sub> )
–	3450s,br			ν(OH) <sup>b</sup>
–		3600–3400m,br	3560–3460vs,br	ν(OH) <sup>c</sup>
–	1680m	1645w	1645w	δ(H <sub>2</sub> O)
1638s	d	1625s	1620s	δ(NH <sub>2</sub> )
1587vs	1620s	1580s	1575s	ν <sub>as</sub> (CO <sub>2</sub> )
1410s	1399s	1405s	1400s	ν <sub>s</sub> (CO <sub>2</sub> )
445m,s	446m,br	462m,br	462m,br; 446sh	ν(Cu–O)
388m,br; 297s	–	360m,br; 296s	–	ν(Cu–N)

<sup>a</sup>s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. <sup>b</sup>Water. <sup>c</sup>Water and phenolic group. <sup>d</sup>Absorption band probably obscured by ν<sub>as</sub>(CO<sub>2</sub>) and observed at 1620 cm<sup>-1</sup> for the K-salt.

their alkali salts, the complexes and the deuterated analogues.

As to the low frequency region, the bands at 446 and 445 cm<sup>-1</sup> for the 4-aminobenzoate complexes can be recognized as arising from Cu–O (water or carboxylate) stretching modes. The major ν(Cu–N) contribution in the spectrum of [Cu(AB)<sub>2</sub>] is ascribed to the 388 and 297 cm<sup>-1</sup> absorption bands. A simpler trend is observed for the Cu-4-aminosalicylates, as an absorption at 462 cm<sup>-1</sup> is common to both complexes and is probably assignable to ν(Cu–O (carboxylate)). Also bands at 446 cm<sup>-1</sup>, attributable to ν(Cu–O (water)), and at 360 and 293 cm<sup>-1</sup>, identified as ν(Cu–N), are detected for [Cu(AS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O and [Cu(AS)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O, respectively.

## Conclusion

All physical measurements carried out in this study suggest that 4-aminobenzoate and 4-aminosalicylate can adopt two types of coordination modes, giving rise to complexes with markedly different chromophores and structural arrangements. In fact [Cu(AB)<sub>2</sub>] and [Cu(AS)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O exhibit properties which are fully consistent with N<sub>2</sub>O<sub>2</sub> metal surroundings arising from the coordination of the amino and carboxylate groups. Polymeric complexes are thus formed and the metal environment is planar (or very nearly).

On the other hand, [Cu(AB)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and [Cu(AS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O have monomeric arrangements involving two ligand molecules coordinating through essentially monodentate carboxylate groups and two water molecules, so that the metal coordination is almost planar in this case also.

The slight differences observed between the 4-aminobenzoate and 4-aminosalicylate complexes are interpreted as arising either from greater axial inter-

action or smaller in-plane covalency in the latter compounds. Oxygen atoms from carboxylate groups acting in a strongly asymmetrical bidentate mode could be the axial donors.

The thermal desorption of the water molecules from the hydrate complexes leads to irreversible thermochromism connected with the change from CuO<sub>4</sub>- to CuN<sub>2</sub>O<sub>2</sub>- based coordination.

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