

Spectral and Magnetic Characterization of Copper(II) 5-Bromosalicylates

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The compounds of copper(II) 5-bromosalicylate with pyridine, 3-picoline, ethylenediamine and dioxane, have been prepared and studied by magnetic susceptibility measurements between 77 and 294 K, by infrared, electronic and EPR spectroscopy and by thermal analyses. All the compounds here reported are magnetically dilute, except $\text{Cu}(\text{5Brsal})_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{H}_2\text{O}$. For copper(II) 5-bromosalicylate trihydrate and its anhydrous form we propose a pseudo-octahedral coordination of Cu(II), and for the dioxane adduct a binuclear structure. For the pyridine, 3-picoline and ethylenediamine compounds, octahedral stereochemistry with different tetragonal distortions around Cu(II) is proposed.

The donor properties of substituted salicylic acids have not been studied so extensively as those of unsubstituted salicylic acid. Ernst and Menashi¹ have studied the thermodynamic stability constants of some ferric substituted salicylates using the spectrophotometric method. They found that the stabilities depend on the nature of the substituent. The π -contribution in ferric salicylates was also investigated,¹ with the conclusion that the Fe(III) ion behaves as a π -donor in the ground state and π -electron acceptor in the excited state. The various complexes formed between Fe(III) ion and substituted salicylic acids in aqueous medium in the wider pH range 2–8 have been investigated by Jahagirdar.² The interactions of uranyl ion with some salicylates have been studied by potentiometric titrations.³ We have previously studied the spectral and magnetic properties of solid copper(II) 5-chlorosalicylates.⁴ Practically no work has been done on copper(II) compounds with 5-bromosalicylic acid

in the solid state. The present work deals with some copper(II) 5-bromosalicylates: the trihydrate of copper(II) 5-bromosalicylate, its anhydrous form, and pyridine, 3-picoline, ethylenediamine and dioxane adducts have been prepared and the compounds characterized by elemental analyses and thermal, spectral and magnetic properties.

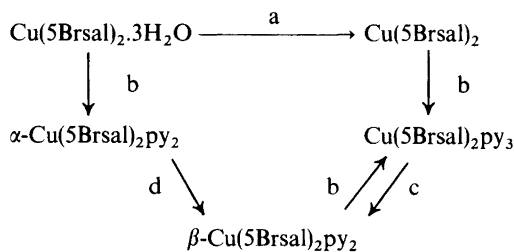
EXPERIMENTAL

Preparative study. The trihydrate of copper(II) 5-bromosalicylate was prepared by reaction of a solution of the sodium salt of 5-bromosalicylic acid (pH adjusted to 4.5–5.0 with free acid) and an aqueous solution of copper(II) sulfate in the molar ratio 2:1. The green product that precipitated after a few minutes was isolated, washed with water and dried at room temperature. The anhydrous copper(II) 5-bromosalicylate was obtained by drying over phosphorus pentoxide for about 8 h at 105 °C. The brown $\text{Cu}(\text{5Brsal})_2$, ($\text{5Brsal} = 5\text{-BrC}_6\text{H}_3\text{-OHCOO}^-$) was found to be non-hygroscopic.

The two isomeric forms of $\text{Cu}(\text{5Brsal})_2\text{py}_2$, (py = pyridine), as well as tris(pyridine)copper(II) 5-bromosalicylate were prepared as described previously⁵ (Scheme 1).

The grey-blue $\text{Cu}(\text{5Brsal})_2(3\text{-pic})_2$, (3-pic = 3-picoline), was prepared by a heterogeneous reaction between trihydrate of copper(II) 5-bromosalicylate and 3-picoline. The powdered sample of $\text{Cu}(\text{5Brsal})_2 \cdot 3\text{H}_2\text{O}$ was left in an evacuated desiccator over 3-picoline for a few hours. The final compounds were dried at room temperature.

The violet-blue $\text{Cu}(\text{5Brsal})_2(\text{en})_{2.5}$, (en = ethylenediamine), was formed by a heterogeneous reaction between $\text{Cu}(\text{5Brsal})_2 \cdot 3\text{H}_2\text{O}$ and ethylenediamine; the procedure was the same as for $\text{Cu}(\text{5Brsal})_2(3\text{-pic})_2$.



Scheme 1. a, at 105 °C; b, over pyridine; c, at 60 °C; d, at 80 °C.

Green $\text{Cu(5BrSal)}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{H}_2\text{O}$ was observed after trihydrate of copper(II) 5-bromosalicylate was kept over 1,4-dioxane in an evacuated desiccator for 48 h.

Analytical data of the compounds are given in Table 1.

Thermal studies. The thermal decomposition was studied by means of a derivatograph (MOM Budapest). The measurements were made as previously described,⁶ in air atmosphere.

Spectral studies. IR spectra were measured in the region $400\text{--}3600\text{ cm}^{-1}$ with a UR 10 spectrophotometer and electronic spectra in the region $10\text{--}28\text{ kK}$ with a Perkin-Elmer 450 spectrophotometer. The Nujol suspension technique was used in both cases. EPR spectra of the powdered samples were run on a Varian Model E 4 spectrometer at room and liquid nitrogen temperatures.

Magnetic susceptibility measurements. Magnetic susceptibility measurements for the compounds were obtained over the temperature range $77\text{--}294\text{ K}$ by the Gouy method with mercury tetrathiocyanatocobaltate(II) as calibrant.⁷ Samples were finely ground powders. The effective absence of ferromagnetic impurities was indicated by the invariance of the observed susceptibilities to the

field strength of the electromagnet (2000–10000 G). Diamagnetic corrections were calculated from Pascal's constants.⁸ The effective magnetic moments were calculated from the expression $\mu_{\text{eff}} = 2.83 (\chi_M \times T)^{1/2}$.

RESULTS AND DISCUSSION

The thermal analyses of the copper(II) 5-bromosalicylate trihydrate indicate the presence of two types of differently bonded H_2O molecules. In the temperature range $90\text{--}125\text{ °C}$ the first two water molecules were liberated in one step (experimental 6.5%, theoretical 6.54%), which gave an endothermic peak in the DTA curve at that temperature. The third water molecule is given off at 140 °C . Above this temperature the oxidation of the volatile organic product takes place, heat being emitted in the strong exothermic peak at 340 °C with a shoulder at about 420 °C . The final level obtained at 660 °C corresponds to formation of CuO .

The $\text{Cu(5BrSal)}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{H}_2\text{O}$ is stable until 60 °C , appearing on the TG curve as a plateau. Above this temperature, the elimination of the neutral ligand begins. At 170 °C the TG curve shows a break corresponding to the loss of H_2O and the dioxane molecule (theoretical weight loss 17.7%, experimental $\sim 18.5\%$). Above 170 °C the decomposition accelerates rapidly to give at 660 °C copper oxide. On the DTA curve there are three endothermic peaks whose maxima are, respectively, at 100 , 170 and 250 °C . A strongly exothermic double peak at about 360 °C represents an oxidation-reduction reaction.

The initial temperature of decomposition is 70 °C for $\text{Cu(5BrSal)}_2\text{py}_3$. In the temperature range $70\text{--}105\text{ °C}$ the compound loses one molecule pyridine in one step (experimental $\sim 10\%$; theo-

Table 1. Elemental analyses of copper(II) 5-bromosalicylates.

Compound	Calc. (%)				Found (%)			
	Cu	C	H	N	Cu	C	H	N
$\text{Cu(5BrSal)}_2 \cdot 3\text{H}_2\text{O}$	11.59	30.58	2.30		11.66	30.84	1.95	
Cu(5BrSal)_2	12.89	33.49	1.24		12.96	32.80	1.25	
$\alpha\text{-Cu(5BrSal)}_2\text{py}_2$	9.71	44.09	2.78	4.28	9.62	43.46	2.72	4.09
$\beta\text{-Cu(5BrSal)}_2\text{py}_2$					9.70	43.87	2.74	4.12
$\text{Cu(5BrSal)}_2\text{py}_3$	8.67	47.53	3.16	5.73	8.71	47.67	3.14	5.66
$\text{Cu(5BrSal)}_2(3\text{-pic})_2$	9.31	45.80	3.25	4.11	9.36	45.69	3.23	4.7
$\text{Cu(5BrSal)}_2(\text{en})_{2.5}$	9.83	35.34	4.37	10.84	9.76	34.92	4.18	11.0
$\text{Cu(5BrSal)}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{H}_2\text{O}$	10.56	35.93	3.02		10.45	36.3	3.2	

retical 10.8%), displayed as an endothermic peak in the DTA curve at that temperature. At 180 °C the TG curve shows a pseudo pause corresponding to the loss of the half molecule of pyridine. There is an endothermic peak in the DTA curve at that temperature. The DTA curve also shows exothermic peaks at 260 and 470 °C with a shoulder at about 570 °C. It is not possible to isolate Cu(5BrSal)₂ because it decomposes before complete elimination of the pyridine molecules.

Further information about the ligand coordination was obtained from IR data.

The IR spectrum of Cu(5BrSal)₂·3H₂O shows a wide absorption band at ~3300 cm⁻¹ which can be attributed to the antisymmetric and symmetric OH stretching modes of the water molecules. The width of the band shows that lattice-held water is present in the compound. The absorption bands at 1630 cm⁻¹ and especially at 825 cm⁻¹, on the other hand are probably due to bonded water molecules. No bands in these regions were found in the case of the anhydrous form. In the IR spectrum of the free 5-bromosalicylic acid there is an intense band due to the carboxyl group: ν_a at 1668 cm⁻¹ and ν_s at 1300 cm⁻¹. The anhydrous form has a splitting band at about 1680 and 1635 cm⁻¹, which can be assigned to ν_aCOO⁻. The antisymmetric COO⁻ stretch absorbs at 1645 cm⁻¹ in the case of trihydrate copper(II) 5-bromosalicylate. Locating the symmetric COO⁻ stretch is very difficult because there is a wide band in the region ~1400 cm⁻¹ where the bands are expected. The IR spectrum of Cu(5BrSal)₂·C₄H₈O₂·H₂O shows absorption bands at 3360, 3210, 1625 and 820 cm⁻¹ which can be attributed to the H₂O molecule. The ν_aCOO⁻ was found at 1650 cm⁻¹ and ν_sCOO⁻ at 1420 cm⁻¹. Malherbe and Bernstein⁹ assigned the rocking and wagging modes of A_g vibrations of pure 1,4-dioxane at 827 and 1127 cm⁻¹, respectively. In the case of the dioxane adduct we found the bands at 880 cm⁻¹ and at 1105 cm⁻¹ and conclude that the dioxane is bonded to the Cu(II) ion.

The stretching vibration of C=N in the pyridine ring¹⁰ appears at 1582 cm⁻¹. In the pyridine and 3-picoline adducts of copper(II) 5-bromosalicylate the peak shifts to higher frequencies ~1590 cm⁻¹. This may suggest a bond formation between the Cu(II) and the ring nitrogen, as the dipolar contribution of C=N⁺ in the pyridine ring increases.¹⁰ The ν_aCOO⁻ of Cu(5BrSal)₂L₂ (L=pyridine or 3-picoline) absorbs at about ~1630 cm⁻¹ and that

Table 2. Electronic spectral data (ν_{max}(kK)).

Compound	Band I	Band II
Cu(5BrSal) ₂ ·3 H ₂ O	14.3	24
Cu(5BrSal) ₂	13.6	22
α-Cu(5BrSal) ₂ py ₂	17.0, 14.1	—
β-Cu(5BrSal) ₂ py ₂	17.2, 14.2	23
Cu(5BrSal) ₂ py ₃	15.6	—
Cu(5BrSal) ₂ (3-pic) ₂	17.0, 14.3	22.5
Cu(5BrSal) ₂ en _{2.5}	17.6	28.5
Cu(5BrSal) ₂ C ₄ H ₈ O ₂ ·H ₂ O	13.6	24

Table 3. EPR data.

Compound	g ₁	g ₂	g _{av}
Cu(5BrSal) ₂ ·3 H ₂ O	2.06 ₆ (2.06 ₃)	2.34 ₉ 2.33 ₉	2.17 ₀ 2.15 ₈ ^a
Cu(5BrSal) ₂	2.04 ₁	2.38 ₄	2.16 ₀ (2.06 ₃) ^a
α-Cu(5BrSal) ₂ py ₂	2.05 ₅	2.27 ₃	2.13 ₀
β-Cu(5BrSal) ₂ py ₂	2.04 ₆	2.25 ₂	2.11 ₇
Cu(5BrSal) ₂ py ₃	2.02 ₈	2.24 ₈	2.10 ₃
Cu(5BrSal) ₂ (3-pic) ₂	2.05 ₉	2.24 ₃	2.12 ₂
Cu(5BrSal) ₂ en _{2.5}			2.10 ₂

^a At liquid nitrogen temperature.

of the tri(pyridine) adduct at 1665 and 1620 cm⁻¹.

The IR spectrum of ethylenediamine¹¹ shows two absorption peaks in the amino region, one at about 3510 cm⁻¹ and the other at about 1595 cm⁻¹; both represent free amino groups. In the spectrum of Cu(5BrSal)₂en_{2.5} these peaks are located at about 3295, 3130 and 1575 cm⁻¹, and are probably due to bonded amino groups.¹² The ν_aCOO⁻ absorbs at about 1660 cm⁻¹ and ν_sCOO⁻ at 1440 cm⁻¹ as a splitting band.

Electronic absorption spectra (Table 2) of copper(II) 5-bromosalicylate trihydrate and its anhydrous form exhibit a broad band with a maximum at ~14 kK (band I) and a shoulder at ~23 kK (band II). Band I can be assigned to *d-d* transitions and band II to a charge-transfer. Similar spectra were observed for Cu(5BrSal)₂py₃ and Cu(5BrSal)₂en_{2.5}. In the compounds of composition Cu(5BrSal)₂L₂ (L=pyridine or 3-picoline), a pair of bands were observed instead of a single *d-d* band. This splitting in the band may be considered to result from distortion of octahedral structure. Similar splitting has been observed by Kettle and Pioli.¹³

Table 4. Magnetic data.

<i>T</i> , K	$\chi_g \times 10^6$	$\chi'_M \times 10^6$	μ_{eff} , B.M.	<i>T</i> , K	$\chi_g \times 10^6$	$\chi'_M \times 10^6$	μ_{eff} , B.M.
Cu(5Brsal)₂·3 H₂O ($-\Delta \times 10^6 = 255$)				Cu(5Brsal)₂ ($-\Delta \times 10^6 = 216$)			
77	12.33	7030	2.08	77	9.53	4938	1.74
100	9.55	5503	2.09	100	8.88	4616	1.89
112	8.32	4827	2.07	121	7.04	3704	1.89
125	7.45	4349	2.08	133	6.20	3288	1.87
138	6.70	3937	2.08	146	5.76	3070	1.89
151	6.11	3612	2.08	159	5.35	2867	1.91
164	5.47	3261	2.07	178	5.02	2703	1.95
177	5.01	3008	2.06	192	4.55	2470	1.95
190	4.69	2832	2.06	205	4.36	2376	1.97
203	4.38	2662	2.06	218	4.15	2272	1.98
216	4.14	2530	2.08	231	3.93	2163	1.99
229	3.92	2409	2.09	245	3.75	2074	2.00
245	3.64	2255	2.09	260	3.56	1980	2.02
259	3.34	2090	2.08	275	3.39	1885	2.03
272	3.09	1953	2.07	285	3.25	1826	2.04
285	2.94	1870	2.07	294	3.19	1796	2.05
294	2.85	1821	2.07				
α-Cu(5Brsal)₂py₂ ($-\Delta \times 10^6 = 326$)				Cu(5Brsal)₂py₃ ($-\Delta \times 10^6 = 381$)			
93	7.23	5051	1.94		5.74	4591	1.85
113	5.80	4117	1.93		4.65	3788	1.85
133	4.88	3510	1.93		3.81	3178	1.84
153	4.14	3036	1.93		3.33	2822	1.86
173	3.62	2691	1.93		2.88	2489	1.86
193	2.96	2260	1.87		2.55	2244	1.86
213	2.64	2050	1.87		2.25	2030	1.86
233	2.36	1872	1.87		2.01	1854	1.86
253	2.13	1725	1.87		1.78	1689	1.85
273	1.95	1600	1.87		1.62	1568	1.86
293	1.75	1472	1.86		1.49	1476	1.86
Cu(5Bral)₂(3-pic)₂ ($-\Delta \times 10^6 = 350$)				Cu(5Brsal)₂en_{2,5} ($-\Delta \times 10^6 = 332$)			
93	6.99	4678	1.87		6.36	4444	1.82
113	5.67	3858	1.87		5.15	3656	1.82
133	4.79	3318	1.88		4.26	3082	1.81
153	4.14	2914	1.89		3.77	2766	1.84
173	3.64	2605	1.90		3.26	2440	1.84
193	3.22	2344	1.90		2.88	2190	1.84
213	2.85	2116	1.90		2.41	1982	1.84
233	2.52	1912	1.89		2.29	1815	1.84
253	2.09	1780	1.90		2.38	1675	1.84
273	1.91	1650	1.90		1.89	1557	1.84
293	1.72	1521	1.89		1.72	1442	1.84

The well-resolved EPR spectra obtained for the polycrystalline samples at room temperature show absorption bands of axial type,¹⁴ except Cu(5BrSal)₂en_{2.5} which has an isotropic spectrum (Table 3). At liquid nitrogen temperature, copper(II) 5-bromosalicylate trihydrate has a clearly anisotropic spectrum, but the anhydrous form exhibits an isotropic spectrum (Table 3). In the case of Cu(5BrSal)₂py₃, the resonance of g_{\parallel} is split into hyperfine lines with a value of $A_{\parallel} = 118$ Oe. The EPR spectra of all the compounds are typical of an effective spin $S = 1/2$.

Study of the magnetic properties of the compounds showed all except Cu(5BrSal)₂.C₄H₈O₂.H₂O to be magnetically diluted copper(II) compounds (Table 4). Variable-temperature magnetic susceptibility data obey the Curie-Weiss law, $\chi_M = C/(T - \theta)$. The best parameter values of the Curie (C) and Weiss constant (θ) are given in Table 5. From the value of θ , it is evident that in Cu(5BrSal)₂ there is an antiferromagnetic super-exchange interaction between the Cu(II) atoms in the polynuclear structure, weaker than in the case⁴ of Cu(5ClSal)₂, how-

Table 5. The values of the C and θ constants.

Compound	C, c.g.s.u.kmol ⁻¹ (± 0.003)	θ K (± 0.2)
Cu(5BrSal) ₂ .3H ₂ O	0.534	2.2
Cu(5BrSal) ₂	0.582	-37
α -Cu(5BrSal) ₂ py ₂	0.412	14.3
Cu(5BrSal) ₂ py ₃	0.432	-0.1
Cu(5BrSal) ₂ (3-pic) ₂	0.450	-1.5
Cu(5BrSal) ₂ en _{2.5}	0.430	-1.6

Table 6. Magnetic data of Cu(5BrSal)₂.C₄H₈O₂.H₂O, ($-\Delta \times 10^6 = 273$).

T, K	$\chi_g \times 10^6$	$\chi'_M \times 10^6$	μ_{eff} , B.M.
93	0.60	634	0.69
113	0.69	690	0.79
133	0.70	695	0.86
153	0.83	770	0.97
173	0.90	815	1.06
193	0.96	853	1.15
213	0.93	866	1.23
233	1.02	887	1.28
253	1.06	910	1.36
273	1.12	946	1.44
293	1.13	953	1.50

ever. There is a small ferromagnetic interaction in α -Cu(5BrSal)₂py₂, on the other hand. The increase in magnetic moment with decrease in temperature for α -Cu(5BrSal)₂py₂ is small but significant and probably, as in Cu(5ClSal)₂py₂, indicates that the singlet level lies appreciably above the ground state.⁴ In other cases, (Table 5), the Weiss constant is less than 5 K, the interaction is very small and does not seriously affect the ground state.⁸

In summary, tetragonal coordination of Cu(II) may be proposed for trihydrate copper(II) 5-bromosalicylate and its anhydrous form. The pseudo-octahedral coordination is proposed for copper(II) 5-bromosalicylates with 3-picoline or ethylenediamine. The two isomers of Cu(5BrSal)₂py₂ were assumed⁵ to possess octahedral stereochemistry with different tetragonal distortions around the Cu(II).

The magnetic properties of Cu(5BrSal)₂.C₄H₈O₂.H₂O are surprisingly similar to those observed for copper(II) acetate monohydrate¹⁵ (Table 6). The temperature variation of the molar susceptibility may be described by the Van Vleck equation for exchange-coupled dimers.¹⁶ A Fortran V program was written and used to interpret the data with a Univac 1108 computer. The TIP term was set equal to 60×10^{-6} cgs units. The best fit parameters were found to be $g = 2.20$ (± 0.03); $-2J = 333$ cm⁻¹ (± 30).

At room temperature the EPR spectrum of the dioxan adduct showed well-resolved absorption bands belonging to the triplet state.¹⁷ The spin-Hamiltonian for triplet state dimeric copper(II) compounds is given by

$$H = g\beta HS + D(S_z^2 - 1/3S(S+1))$$

where $S = 1$ and D , the zero-field parameter, and other symbols have their usual meanings.¹⁷ The observed values of $g_{\parallel} = 2.09_6$, $g_{\perp} = 2.38_6$ and $|D| = 0.355$ cm⁻¹ are very close to those reported for copper(II) acetate monohydrate. On the basis of spectral and magnetic properties a binuclear structure may be proposed for Cu(5BrSal)₂.C₄H₈O₂.H₂O.

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