Complex Compounds of SCHIFF's bases of 3-aldehydo-salicylic acid

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Summary

The present paper describes the preparation and properties of SCHIFF's bases derived from 3-aldehydo-salicylic acid and aniline, ethylenediamine, orthophenylenediamine, glycine, anthranilic acid, sulfanilic acid or sulfanilamide, as well as the metallic complexes of them. The SCHIFF's bases with mono-amines or amino-acids behave as tridentate ligands with acidic group of the amino-component remaining free, while those with diamines behave as quadridentate ligands with both the carboxyl groups of the 3-aldehydo acid remaining unattached. The magnetic moment values of the metal complexes reveal that all of them, with the exception of the two nickel compounds of the SCHIFF's bases of ethylenediamine-3aldehydosalicylic acid and ortho-phenylenediamine-3-aldehydo salicylic acid, are of ionic or outer-level covalent type. The two nickel compounds, just mentioned, are diamagnetic and orangeyellow in colour and should, therefore, be represented as penetration or innerlevel complexes with planar dsp² hybrid bonds.

Inhaltsübersicht

Darstellung und Eigenschaften SCHIFFscher Basen aus 3-Aldehydosalicylsäure und verschiedenen Aminen bzw. Aminosäuren sowie von Metallchelaten dieser SCHIFFschen Basen werden beschrieben. Die Basen aus Monaminen und Aminosäuren wirken gegenüber Cu^{2+} , Ni²⁺, Co²⁺ und UO_2^{2+} als dreizähnige, diejenigen aus Diaminen als vierzähnige Liganden. Die Messung der magnetischen Momente der Metallkomplexe ergab, daß diese – mit Ausnahme zweier Durchdringungskomplexe des Nickels mit wahrscheinlich planarer dsp²-Konfiguration – Normalkomplexe sind.

SCHIFF's bases of 3-aldehydo-salicylic acid(salicylaldehyde-3-carboxylic acid) with aniline, ethylenediamine, ortho-phenylenediamine, glycine, anthranilic acid, sulphanilic acid and sulphanilamide were prepared. The metal-chelates of these SCHIFF's bases were then prepared by the interaction of the latter with the corresponding metal acetates in aqueous alcohol medium.

The composition of the various metallic complexes formed by the above-mentioned SCHIFF's bases may be represented as follows:

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- $\begin{array}{ll} M(\mathrm{SB}) \cdot H_2\mathrm{O}, & \mathrm{where} \ \mathrm{SB}H_2 = 1 \ \mathrm{mol. \ of \ SCHIFF's \ base \ derived \ from \ aniline, \ anthra-nilic \ acid, \ sulphanilic \ acid, \ sulphanilamide \ or \ glycine \ and \ contains \ 1 \ \mathrm{mol. \ of \ the \ 3-aldehydo \ acid. } \end{array}$
- $\begin{array}{ll} \mathbf{M}(\mathbf{SB'})^{=}, & \text{where } \mathbf{SB'H}_4 = 1 \text{ mol. of } \mathbf{SCHIFF}\text{'s base derived from ethylenediamine} \\ \mathbf{(II)} & \text{or orthophenylenediamine and contains two mols. of the 3-aldehydo} \\ & \text{acid. } \mathbf{M} = \mathbf{Cu^{II}}, \ \mathbf{Ni^{II}}, \ \mathbf{Co^{II}} \text{ and } \mathbf{UO_{i}^{II}}. \end{array}$

Structurally:



The chemical properties of these complexes are in accord with the structures shown. Their magnetic moment values show that all the metal complexes, with the exception of the two nickel compounds of the SCHIFF's bases of ethylenediamine 3-aldehydo-salicylic acid and of ortho-phenylenediamine 3-aldehydo-salicylic acid, belong to the ionic or outer-level covalent type. Their magnetic moment values are more or less identical with those for the corresponding free metal ions. The two orange-yellow nickel compounds, just mentioned, are diamagnetic and hence should be represented as penetration or inner-level complexes with planar dsp² hybrid bonds.

The SCHIFF's bases of 5-aldehydo-salicylic acid with amine and aminoacids mentioned above, unlike those of the 3-aldehydo acid, do not, however, give any metallic complexes as might usually be expected. Thus, for instance, when the SCHIFF's base of the 5-aldehydo acid with ethylenediamine, is treated with copper acetate in aqueous alcoholic solution and the mixture allowed to evaporate in air, a dark-brown glassy residue is obtained. The product, on analysis, gives no definite composition. It appears that some sort of polymerisation is responsible for this phenomenon.

The SCHIFF's base of 5-aldehydo-salicylic acid with ethylenediamine has been found to react with acids and alkalis, giving sharp colour changes, from yellow at $5.9 \,\mathrm{pH}$ (acid) to orange at 7.06 pH (neutral) and then to red at 9.6 pH (alkali). But as the salt effect is very high, amounting to $+1.4 \,\mathrm{pH}$ units for 0.5 N KCl, the compound is unsuitable, for use as acid-base indicator.

Experimental

3-aldehydo-salicylic acid was prepared following the method of DUFF and BILLS¹). SCHIFF's bases of 3-aldehydo-salicylic acid with bases like aniline, anthranilic acid, sulphanilic acid, sulphanilamide, glycine, ethylenediamine and ortho-phenylene-diamine were prepared by refluxing 1 mol. of the acid and 1 mol. of the base (2 mols. of the acid and 1 mol. of the base in case of ethylenediamine and ortho-phenylenediamine) in alcoholic medium for about 2 hours.

The SCHIFF's bases, thus prepared are all more or less strongly coloured, insoluble in water, but (with the exception of ethylenediamine compound) soluble in alcohol and other organic solvents. They are decomposed by acids, but are soluble in ammonia and alkalis. The SCHIFF's base with ethylenediamine is insoluble in alcohol as well.

Analysis

The nitrogen content of the SCHIFF's bases was determined by DUMAS method. The amount of 3-aldchydo-salicylic acid was estimated by weighing the copper salt of 3-oximino methyl salicylic acid ($R\hat{a}x$ and $R\hat{a}x^2$)) after decomposing the SCHIFF's base by warming with dilute sulphuric acid and then adding a slight excess of hydroxylamine hydrogenchloride and copper sulphate solution.

1. With aniline: Yellow needles, m. p. 192 °C. Found: N 5.92; C₆H₃(COOH)(OH)CHO 69.0; Calculated for C₆H₃(COOH)(OH)CH = N \cdot C₆H₅, N 5.8; C₆H₃(COOH)(OH)CHO 68.8 per cent.

2. With anthranilic acid: Orange-yellow crystals, m. p. 182 °C. Found: N 4.85; C₆H₃(COOH)(OH)CHO 57.9; Calculated for C₆H₃(COOH)(OH)CH = N-C₆H₄ · COOH, N 4.91; (CH₃(COOH)(OH)CHO 58.2 per cent.

3. With sulphanilic acid: Light orange-yellow crystals, m. p. 178 °C. Found: N 4.29; C₆H₃(COOH)(OH)CHO 51.9; Calculated for C₆H₃(COOH)(OH)CH = N-C₆H₄ · SO₃H, N 4.36; C₆H₃(COOH)(OH)CHO 51.7 per cent.

4. With sulphanilamide: Deep orange-yellow crystals, m. p. 186 °C. Found: N 8.43; $C_6H_3(COOH)(OH)CHO$, 52.01; Calculated for $C_6H_3(COOH)(OH)CH = N-C_6H_4 \cdot SO_2NH_2$,

N 8.75; C₆H₃(COOH)(OH)CHO 51.9 per cent.

5. With glycine: Light yellow needles, m. p. 165 °C.

Found: N 6.3; C₆H₃(COOH)(OH)CHO 74.3;

Calculated for $C_6H_3(COOH)(OH)CH = N-CH_2 \cdot COOH$,

N 6.28; C₆H₃(COOH)(OH)CHO 74.4 per cent.

6. With ethylenediamine: Bright yellow precipitate, m. p. 290 °C (with decomposition). Found: N 7.28; $C_6H_3(COOH)(OH)CHO 84.3$; $H_2O 9.3$;

Calculated for $C_6H_3(COOH)(OH)CH = N-(CH_2)_2N = CH(OH)(COOH)C_6H_3$, 2 H₂O, N 7.14; $C_6H_3(COOH)(OH)CHO$ 84,7; H₂O 0.18 per cent.

¹) J. DUFF and E. BILLS, J. chem. Soc. [London] 1932, 1987.

²) P. Rây and A. Rây, Sei. and Cult. 21, 547 (1956).

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7. With ortho-phenylenediamine: Orange-yellow crystals, m. p. 200 °C. Found: N 6.82; $C_6H_3(COOH)(OH)CHO$ 82.05; Calculated for $C_6H_3(COOH)(OH)CH = N-C_6H_4 \cdot N = CH(OH)COOH)C_6H_3$. N 6.95; $C_6H_3(COOH)(OH)CHO$ 82.18 per cent.

Copper 3-aldehydo-salicylic acid-aniline

1,2 g. of the SCHIFF's base was dissolved by warming in 30 ml. of rectified alcohol, and 0.8 g. of copper acctate dissolved in 50 ml. of 50% ethanol was added to it. The mixture was refluxed on water-bath for about an hour. The precipitated compound was filtered, washed with hot alcohol and dried in air.

The substance forms green crystals insoluble in water and alcohol, but soluble in acctone and pyridine. It is decomposed by warm mineral acids with the separation of free 3-aldehydo-salicylic acid, but is not dissolved or decomposed by alkalis even on warming. The substance is paramagnetic ($\mu_{\rm B} = 1.82$).

Found: Cu 20.0; N 4.50; C₆H₃(COOH)(OH)CHO 51.6;

Calculated for Cu C₁₄H₉O₃N, H₂O,

Cu 19.8; N 4.36; C₆H₃(COOH)(OH)CHO 51.8 per cent.

Nickel 3-aldehydo-salicylic acid-aniline

A solution of 1.2 g. of the SCHIFF's base and 1.3 g. of nickel acetate in 100 ml. of 50% ethanol was refluxed for 2 hours on the water-bath. The mixture was then allowed to cool. A greenish yellow coloured silky needle-shaped crystalline precipitate separated out; this was filtered, washed with cold 50% ethanol and then dried in air.

The substance was insoluble in water but soluble in alcohol and other organic solvents. It resembles the corresponding copper compound in properties. The substance is paramagnetic ($\mu_{\rm B} = 2.86$).

Found: Ni 18.48; N 4.51; C₆H₃(COOH(OH)CHO, 52.70;

Calculated for Ni C14H9O3N, H2O,

Ni 18.6; N 4.43; C₆H₃(COOH(OH)CHO 52.58 per cent.

Cobaltous 3-aldehydo-salicylic acid-aniline

The cobaltous complex was instantaneously precipitated as a light rose-red compound on refluxing a mixture of alcoholic solutions of the SCHIFF's base (1.2 g.) and cobalt acetate (1.3 g.). The precipitate was washed and dried as before.

The substance was insoluble in water and alcohol but soluble in pyridine, ammonia and alkali solutions. It was decomposed on warming with mineral acids. The substance is paramagnetic ($\mu_{\rm B} = 4.4$).

Found: Co 18.60; N 4.52; C₆H₃(COOH)(OH)CHO 52.32;

Calculated for Co C₁₄H₉O₃N, H₂O,

Co 18.64; N 4.43; C₆H₃(COOH)(OH)CHO 52.54 per cent.

Uranyl 3-aldehydo-salicylic acid-aniline

The uranyl complex of the SCHIFF's base was obtained as a yellow precipitate on refluxing together the alcoholic solutions of uranyl acetate (2.1 g.) and the SCHIFF's base (1.2 g.).

The substance is insoluble in water and alcohol. On heating with alkalis, the compound decomposes with the formation of uranates. On warming with mineral acids, the free 3-aldehydo-salicylic acid separates out. The substance is diamagnetic.

22 Z. anorg. allg. Chemie. Bd. 322.

Found: U 45.22; N 2.58; $C_6H_8(COOH)(OH)CHO$ 31.30; Calculated for UO₂ $C_{14}H_9O_3N$, H_2O , U 45.16; N 2.65; $C_6H_3(COOH)(OH)CHO$ 31.5 per cent.

Copper 3-aldehydo-salicylic acid-anthranilic acid

A solution of 1.4 g. of the SCHIFF's base in 30 ml. alcohol was refluxed with a solution of 0.8 g. of copper acetate in 50 ml. of 50% ethanol on the water-bath for about 2 hours. A dark green solution resulted which, on cooling, gave olive-green silky needles.

The copper complex is insoluble in water but soluble in alcohol and other organic solvents. It is decomposed by hot mineral acids. The compound is soluble in ammonia and dilute alkali solutions. With strong alkalis, copper hydroxide is precipitated. The substance is paramagnetic ($\mu_{\rm B} = 1.83$).

Found: Cu 17.38; N 3.90; $C_6H_3(COOH)(OH)CHO$ 45.62; Calculated for Cu $C_{15}H_9O_5N$, H_2O , Cu 17.42; N 3.84; $C_6H_3(COOH)(OH)CHO$ 45.54 per cent.

Nickel 3-aldehydo-salicylic acid-anthranilic acid

The nickel complex was prepared in a way similar to that of the copper complex, by refluxing the alcoholic solutions of the SCHIFF's base (1.4 g.) and nickel acetate (1.3 g.). The yellow-coloured solution after reflux was allowed to stand overnight when the crystals of the nickel compound separated out. These were washed with 50% cthanol and dricd in air.

The substance forms fine yellow needles, insoluble in water, but soluble in alcohol and other organic solvents. It resembles the copper compound in properties. The substance is paramagnetic ($\mu_{\rm B} = 2.91$).

Found: Ni 16.40; N 3,94; C₆H₃(COOH)(OH)CHO 46.22;

Calculated for Ni C₁₅H₉O₅N, H₂O,

Ni 16.32; N 3,89; C₆H₃(COOH)(OH)CHO 46.15 per cent.

Cobaltous 3-aldehydo-salicylic acid-anthranilic acid

The cobaltous complex was obtained as a yellowish-red precipitate on refluxing alcoholic solutions of the SCHIFF's base (1.4 g.) and cobalt acetate (1.3 g.).

The compound is insoluble in water and alcohol, but soluble in pyridine, ammonia and alkalis giving a dark brown solution. It is decomposed by mineral acids like all other compounds. The substance is paramagnetic ($\mu_{\rm B} = 4.54$).

Found: Co 16.42; N 3.90; C₆H₃(COOH)(OH)CHO 46.3;

Calculated for Co C₁₅H₉O₅N, H₂O,

Co 16.36; N 3.89; C₆H₃(COOH)(OH)CHO 46.12 per cent.

Uranyl 3-aldehydo-salicylic acid-anthranilic acid

It was obtained as a bright yellow product on refluxing alcoholic solutions of the SCHIFF's base (1.4 g.) and uranyl acetate (2.1 g.) on the water-bath for about an hour.

The uranium compound is insoluble in water and alcohol, but soluble in pyridine. The substance is diamagnetic.

Found: U 41.72; N 2.60; C₆H₃(COOH)(OH)CHO 29.18;

Calculated for UO₂ C₁₅H₉O₅N, H₂O,

U 41.68; N 2.45; C₆H₃(COOH)(OH)CHO 29.07 per cent.

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Copper 3-aldehydo-salicylic acid-sulphanilic acid

An alcoholic solution of copper acetate (0.8 g.) was mixed with an alcoholic solution of the SCHIFF's base (1.6 g.) and the mixture was refluxed on water-bath for about 2 hours. This was then cooled and allowed to stand in a desiccator over conc. H_2SO_4 for about 2 days. Brilliant green crystals gradually separated out, which were collected on a filter, washed with a little cold aqueous alcohol and then dried in air.

The copper compound was slightly soluble in water and more so in alcohol and other organic solvents. It resembles the previous compounds in properties. The substance is paramagnetic ($\mu_{\rm B} = 1.84$).

Found: Cu 15.88; N 3.52; C₆H₃(COOH)(OH)CHO 41.22;

Calculated for Cu C₁₄H₉O₆NS, H₂O,

Cu 15.85; N 3.49; C₆H₃(COOH)(OH)CHO 41.19 per cent.

Nickel 3-aldehydo-salicylic acid-sulphanilic acid

The nickel compound was prepared in a manner exactly similar to that of the corresponding copper compound by using alcoholic solution of nickel acetate in place of copper acetate. It formed green needles which were slightly suluble in water and easily so in alcohol and other organic solvents. The substance is paramagnetic ($\mu_{\rm B} = 3.12$).

Found: Ni 14.85; N 3.60; C₆H₃(COOH)(OH)CHO 42.0;

Calculated for Ni C₁₄H₉O₆NS, H₂O,

Ni 14.83; N 3.53; C₆H₃(COOH)(OH)CHO 41.95 per cent.

Cobaltous 3-aldehydo-salicylic acid-sulphanilic acid

The cobaltous complex was obtained as reddish-yellow crystals as in the previous cases by using an alcoholic solution of cobalt acetate. The substance is paramagnetic ($\mu_{\rm B} = 4.3$). Found: Co 14.80; N 3.56; C₆H₃(COOH)(OH)CHO 42.0;

Calculated for Co C₁₄H₉O₆NS, H₂O,

Co 14.87; N 3.53; C₆H₃(COOH)(OH)CHO 41.93 per cent.

Uranyl 3-aldehydo-salicylic acid-sulphanilic acid

The uranyl compound separated out as deep yellow crystals on refluxing and cooling a mixture of alcoholic solutions of the SCHIFF's base (1.6 g.) and uranyl acetate (2.1 g.).

The substance is sparingly soluble in water, but readily in alcohol and other organic solvents on warming. The substance is diamagnetic.

Found: U 39.3; N 2.35; C₆H₃(COOH)(OH)CHO 27.42;

Calculated for UO₂ C₁₄H₉O₆NS, H₂O,

U 39.21; N 2.30; C₆H₃(COOH)(OH)CHO 27.34 per cent.

Copper 3-aldehydo-salicylic acid-sulphanilamide

A mixture of 50 ml. alcoholic solution of the SCHIFF's base (1.6 g.) and 50 ml. alcoholic solution of copper acetate (0.8 g.) was refluxed on water-bath for an hour. A green product separated after a time, which was filtered hot, washed with alcohol and dried in air.

The copper compound is insoluble in water and alcohol and is paramagnetic ($\mu_B = 1.86$). Found: Cu 15.92; N 7.12; C₆H₃(COOH)(OH)CHO 41.63;

Calculated for Cu C₁₄H₁₀O₅N₂S, H₂O,

Cu 15.89; N 7.0; C₆H₃(COOH)(OH)CHO 41.55 per cent.

Nickel 3-aldehydo-salicylic acid-sulphanilamide

A mixture of alcoholic solutions of the SCHIFF's base (1.6 g.) and nickel acetate (1.3 g.) was refluxed on a water-bath for about 2 hours. This was then cooled and allowed to stand overnight when greenish-yellow crystals separated out.

The nickel compound is insoluble in water, but soluble in alcohol and other organic solvents. The substance is paramagnetic ($\mu_{\rm B} = 2.99$).

Found: Ni 14.9; N 7.13; C₆H₃(COOH)(OH)CHO 42.11;

Calculated for Ni C₁₄H₁₀O₅N₂S, H₂O,

Ni 14.87; N 7.09; C₆H₃(COOH)(OH)CHO 42.05 per cent.

Cobaltous 3-aldehydo-salicylic acid-sulphanilamide

The cobaltous complex was obtained as a light rose-red substance on refluxing a mixture of alcoholic solutions of the SCHIFF's base and cobalt acctate. It was insoluble in water and alcohol, but soluble in pyridine, ammonia and alkalis producing deep brown solutions. The substance is paramagnetic ($\mu_{\rm B} = 4.56$).

Found: Co 15.0; N 7.15; $C_6H_3(COOH)(OH)CHO$ 41.93; Calculated for Co $C_{14}H_{10}O_5N_2S$, H_2O ,

Co 14.91; N 7.09; $C_6H_3(COOH)(OH)CHO$ 42.03 per cent.

Uranyl 3-aldehydo-salicylic acid-sulphanilamide

The uranyl complex was prepared in a way similar to that of the corresponding cobaltous salt described above, using uranyl acetate solution in place of cobalt acetate. The deep yellow product is insoluble in water and alcohol, but soluble in pyridine. The substance is diamagnetic.

Found: U 39.5; N 4.71; $C_6H_3(COOH)(OH)CHO$ 27.6; Calculated for UO₂ $C_{14}H_{10}O_5N_2S$, H_2O , U 39.27; N 4.62; $C_6H_3(COOH)(OH)CHO$ 27.39 per cent.

Copper 3-aldehydo-salicylic acid-glycine

Solutions of 1.1 g. of the SCHIFF's base in 30 ml. alcohol and 0.8 g. of copper acetate in 40 ml. alcohol were mixed tohether and the mixture refluxed on the water-bath for 2 hours. It was then cooled and allowed to stand in a desiccator over conc. H_2SO_4 for 2 days, when shining green crystals separated out. These were collected on a filter, washed with a little cold 50% aqueous ethanol and dried in air.

The substance is insoluble in water but highly soluble in alcohol and other organic solvents. The substance is paramagnetic ($\mu_{\rm R} = 1.90$).

Found: Cu 21.08; N 4.7; C₆H₃(COOH)(OH)CHO 55.0;

Calculated for Cu C₁₀H₇O₅N, H₂O,

Cu 20.99; N 4.62; C₆H₃(COOH)(OH)CHO 54.87 per cent.

Nickel 3-aldehydo-salicylic acid-glycine

The nickel compound was prepared like the copper compound, using nickel acetate solution in place of copper acetate. It forms green crystals and resembles the corresponding copper compound in properties. The substance is paramagnetic ($\mu_{\beta} = 3.13$).

Found: Ni 19.82; N 4.75; C₆H₃(COOH)(OH)CHO 55.82;

Calculated for Ni C₁₀H₇O₅N, H₂O,

Ni 19.71; N 4.70; C₆H₃(COOH)(OH)CHO 55.76 per cent.

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Cobaltous 3-aldehydo-salicylic acid-glycine

The cobaltous compound was obtained as a rose-red crystalline substance on refluxing the alcoholic solutions of the SCHIFF's base (1 mol.) and cobalt acetate (1 mol.) together on the water-bath for about an hour.

The cobaltous complex is insoluble in water and alcohol, but soluble in pyridine as well as in ammonia and alkali solutions. The substance is paramagnetic ($\mu_B = 4.28$).

Found: Co 19.85; N 4.75; C₆H₃(COOH)(OH)CHO 55.86;

Calculated for Co C₁₀H₂O₅N, H₂O,

Co 19.77; N 4.69; C₆H₃(COOH)(OH)CHO 55.71 per cent.

Uranyl 3-aldehydo-salicylic acid-glycine

This was obtained as a light orange-yellow product in a way similar to that of the corresponding cobaltous compound, using uranyl acetate in place of cobalt acetate. The substance is insoluble in water and alcohol, as well as in ammonia and pyridine. The substance is diamagnetic.

Found: U 46.87; N 2.82; $C_{6}H_{3}(COOH)(OH)CHO$ 32.7; Calculated for UO₂ $C_{10}H_{7}O_{5}N$, H₂O, U 46.76; N 2.75; $C_{6}H_{3}(COOH)(OH)CHO$ 32.61 per cent.

Copper 3-aldehydo-salicylic acid-ethylenediamine-disodium salt

2 g. of the SCHIFF's base was dissolved in 50 ml. of caustic soda solution containing 0.4 g. of NaOH. The solution was heated on the water-bath and to the hot solution 0.8 g. of copper acetate dissolved in 50 ml. alcohol was added with stirring. The solution turned violet. This was heated on the water-bath for about $\frac{1}{2}$ hours, then filtered hot and allowed to cool, when violet coloured silky needles of the sodium salt of the copper complex separated out. These were washed and dried as usual.

The substance is soluble in water and alcohol. It is not affected by hot alkali, but is decomposed by mineral acids. The substance is paramagnetic ($\mu_{\rm B} = 1.85$).

Found: Cu 13.2; N 5.86; Na 9.62; C₆H₃(COOH)(OH)CHO 69.33; H₂O (by loss at 110 °C) 3.80.

Calculated for Na₂[Cu(C₁₈H₁₂O₆N₂)], H₂O, Cu 13.24; N 5.84; Na 9.59; C₆H₃(COOH)(OH)CHO 69.23; H₂O 3.75 per cent.

Copper 3-aldehydo-salicylic acid-ethylenediamine-barium salt

The barium salt of the copper complex was obtained by adding a solution of barium chloride (1 mol.) to an aqueous solution of its di-sodium salt. The compound forms a light violet precipitate, slightly soluble in water and alcohol.

Found: Cu 11.56; N 5.12; Ba 25.0; $C_6H_3(COOH)(OH)CHO$ 60.2; Calculated for Ba[Cu($C_{18}H_{12}O_6N_2$)],

Cu 11.48; N 5.06; Ba 24.85; C₆H₃(COOH)(OH)CHO 60.04 per cent.

Nickel 3-aldehydo-salicylic acid-ethylenediamine-disodium salt

This was prepared like the corresponding copper compound described above, by using nickel acetate in place of copper acetate. It forms orange-red silky needles, soluble in water and alcohol. The substance is diamagnetic. Found: Ni 12.45; N 6.01; Na 9.72; $C_6H_3(COOH)(OH)CHO$ 70.22; H_2O 4.0; Calculated for $Na_2[Ni(C_{18}H_{12}O_6N_2)]$, H_2O ,

Ni 12.36; N 5.9; Na 9.69; C₆H₃(COOH)(OH)CHO 69.9; H₂O 3.8 per cent.

Cobalt 3-aldehydo-salicylic acid-ethylenediamine-sodium salt

0.71 g. of the SCHIFF's base was dissolved in 40 ml. of a caustic soda solution containing 0.25 g. of NaOH. To this solution was added with stirring a solution of 0.53 g. of hexammine cobaltic chloride dissolved in 30 ml. of water. The mixture was heated on a water-bath till no more smell of ammonia was given off (about 3 hours). The volume of the solution was then reduced to about 25 ml. and kept overnight in the cold. A deep-brown crystalline product was obtained, which was washed with a little cold alcohol and dried in a desiccator.

The substance is highly soluble in water and alcohol. It will be observed that the cobalt complex of the SCHIFF's base with ethylenediamine contains cobalt in the bivalent state though prepared from hexammine cobaltic chloride. This is evident from its composition and magnetic moment value ($\mu_{\rm B} = 4.15$). Presumably a reduction takes place during the reaction.

Found: Co 12.96; N 6.24; Na 10.32; C₆H₃(COOH)(OH)CHO 71.92;

Calculated for $Na_2[Co(C_{18}H_{12}O_6N_2)]$,

Co 12.89; N 6.12; Na 10.06; C₆H₃(COOH)(OH)CHO 72.6 per cent.

Cobalt 3-aldehydo-salicylic acid-ethylenediamine-barium salt

The barium salt of the cobalt complex was obtained as a brown crystalline precipitate on adding a calculated amount of barium chloride solution to an aqueous solution of the sodium salt. The compound is slightly soluble in water and alcohol.

Found: Co 10.90; N 5.12; Ba 25.12; C₆H₃(COOH)(OH)CHO 61.2;

Calculated for $Ba[Co(C_{18}H_{12}O_6N_2)]$,

Co 10.74; N 5.16; Ba 25.06; C₆H₃(COOH)(OH)CHO 60.55 per cent.

Uranyl 3-aldehydo-salicylic acid-ethylenediamine-disodium salt

The uranyl compound was prepared like the corresponding copper complex by using uranyl acetate in place of copper acetate. It forms orange-yellow crystals, soluble in water and alcohol. The substance is diamagnetic.

Found: U 35.58; N 4.23; Na 6.96; C₆H₃(COOH)(OH)CHO, 50.02;

Calculated for $Na_2[UO_2(C_{18}H_{12}O_6N_2)]$,

U 35.63; N 4.19; Na 6.88; C₆H₃(COOH)(OH)CHO 49.7 per cent.

Copper 3-aldchydo-salicylic acid-orthophenylenediamine

A mixture of an alcoholic solutions of the SCHIFF's base (2 g.) and copper acctate (0.8 g.) was refluxed on the water-bath for about an hour. A yellow green product separated out. This was filtered hot, washed with alcohol and dried in air.

The substance is insoluble in water and slightly soluble in hot alcohol, but readily soluble in ammonia and alkali solutions. The substance is paramagnetic ($\mu_{\rm B} = 1.90$).

Found: Cu 13.55; N 6.10; C₆H₃COOH)(OH)CHO 71.6;

Calculated for $Cu(C_{22}H_{14}O_6N_2)$,

Cu 13.64; N 6.01; C₆H₃(COOH)(OH)CHO 71.32 per cent.

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Copper 3-aldehydo-salicylic acid-orthophenylenediamine disodium salt

This was obtained as dark green needles from a solution of the above described compound and a calculated amount of caustic soda solution on evaporation over conc. H_2SO_4 in a desiccator. The substance is readily soluble in water and alcohol.

Found: Cu 12.30; N 5.28; Na 8.84; C₆H₃(COOH)(OH)CHO 63.05; H₂O 3.58; Calculated for Na₂[Cu(C₂₂H₁₂O₆N₂)], H₂O, Cu 12.03; N 5.31; Na 8.72; C₆H₃(COOH)(OH)CHO 62.93; H₂O 3.41 per cent.

Nickel 3-aldehydo-salicylic acid-orthophenylenediamine-disodium salt

Alcoholic solutions of the SCHIFF's base (1 mol.), nickel acetate (1 mol.) and NaOH (2 mols.) were mixed together and refluxed on the water-bath for about 2 hours. The mixture was then allowed to cool when orange-yellow silky needles separated out. These were collected on a filter, washed with a little cold alcohol and finally dried in air.

The compound is highly soluble in water as well as in alcohol and is diamagnetic. Found: Ni 11.30; N 5.52; Na 8.95; $C_6H_3(COOH)(OH)CHO$ 63.7; H_2O 3.20; Calculated for Na₂[Ni($C_{22}H_{12}O_6N_2$)], H_2O , Ni 11.23; N 5.35; Na 8.80; $C_6H_3(COOH)(OH)CHO$ 63.51; H_2O 3.44 per cent.

Cobalt 3-aldehydo-salicylic acid-orthophenylenediamine sodium salt

0.4 g. of the SCHIFF's base and 0.27 g. of hexamine cobaltic chloride were dissolved in 50 ml. of 50% ethanol. 0.12 g. of NaOH dissolved in 30 ml. of water was then added with stirring to the above mixture and heated on the water-bath till no smell of ammonia was perceptible (about 3 hours). The volume of the solution was then further reduced to about 30 ml. and cooled. A deep brown crystalline product was obtained. This was filtered, and washed with a little cold alcohol and finally dried in a desiceator.

The substance is highly soluble in water and alcohol. A brown crystalline precipitate of the corresponding barium salt was obtained by adding a solution of barium chloride to a solution of the sodium salt.

As in the case of the SCHIFF's base of ethylenediamine, the cobalt complex of the SCHIFF's base of ortho-phenylenediamine with 3-aldehydo-salicylic acid also contains cobalt in the bivalent state due to the reduction of Co(III) to Co(II) during the reaction ($\mu_B = 4.1$).

Found: (a) Sodium salt: Co 11.58; N 5.36; Na 9.22; C₆H₃(COOH)(OH)CHO 65.90; (b) Barium salt: Co 9.78; N 4.66; Ba 23.18; C₆H₃(COOH)(OH)CHO 55.24;

Calculated for (a) $Na_2[Co(C_{22}H_{12}O_6N_2)]$,

- Co 11.66; N 5.54; Na 9.11; C₆H₃(COOH)(OH)CHO 65.75;
- (b) Ba[Co($C_{22}H_{12}O_6N_2$)],
- Co 9.88; N 4.70; Ba 23.04; C₆H₃(COOH)(OH)CHO 55.68 per cent.

Uranyl 3-aldehydo-salicylic acid-orthophenylenediamine

The uranyl compound was prepared in a way similar to that of the corresponding copper compound, using uranyl acctate in place of copper acetate. It forms a reddish-yellow product, insoluble in water and alcohol, but soluble in ammonia and caustic soda solutions. The substance is diamagnetic.

Found: U 35.54; N 4.08; C₆H₃(COOH)(OH)CHO 49.80;

Calculated for $UO_2(C_{22}H_{14}O_6N_2)$, U 35.42; N 4.17; $C_6H_3(COOH)(OH)CHO$ 49.40 pcr cent.

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