The Structure and Bond Type of Co\textsuperscript{II} Chelates of 7-Iodo-8-Quinolinol-5-Sulphonic Acid

**Teuvo Nortia**

*Laboratory of Physical Chemistry, Institute of Technology, Helsinki, Finland*

During recent investigations on metal chelates of 8-quinolinol-5-sulphonic acid, Nässänen and Usitalo\textsuperscript{1} have observed that aqueous solutions of Co\textsuperscript{II} (C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) are subject to some change with time. A similar effect has also been observed in the Co\textsuperscript{II} chelate of 7-iodo-8-quinolinol-5-sulphonic acid (Ekman\textsuperscript{2}). The yellow colour of the solution becomes intensified and the shape of the ultraviolet absorption spectrum changes, while its maximum shifts towards longer wavelengths. The phenomenon indicates the formation of a new complex compound, which has been assumed to have the composition X\textsubscript{4}[Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3}]. The structures of these two Co\textsuperscript{II} chelates are represented in Fig. 1.

![Fig. 1. The structure of Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) (a) and Na\textsubscript{2}[Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3}] (b).](image)

The magnetic criterion shows that the bond type in Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3} is, as expected, essentially ionic while the bond type in Na\textsubscript{2}[Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3}] is essentially covalent, corresponding to one unpaired electron. There are two possible configurations of Co\textsuperscript{II} complexes which have one unpaired electron, namely the square planar (coordination number 4) and the octahedral (coordination number 6) structures. The especially low value of the magnetic moment could be interpreted as indicating the octahedral structure\textsuperscript{4}. Since there are only two C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5} groups to one Co atom, the octahedral structure should have the composition Na\textsubscript{2}[Co\textsuperscript{II}(H\textsubscript{2}O)\textsubscript{4}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3}] · 2 H\textsubscript{2}O. By heating the substance to 130\textdegree C all the crystal water can, however, be removed without any marked change in the magnetic moment. It is therefore assumed that the coordination number is four and the structure square planar, involving 3d\textsuperscript{4}s\textsuperscript{4}p\textsuperscript{4} orbitals in the bond formation.

The ultraviolet absorption spectra of the compounds are given in Fig. 2. The broken line in Fig. 2a represents the molar extinction of Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) in 1 M HCl and the dotted line that of the chelating agent C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}. The curves show that the freshly prepared chelate has decomposed to the chelating agent. In Fig. 2b the two curves, representing the molar extinction of Na\textsubscript{2}[Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3}] in distilled water and in 1 M HCl are similar, showing that the covalent compound is stable even in relatively strong mineral acids.

**Preparation of compounds.** Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) can be prepared by adding some soluble Co\textsuperscript{II} salt to a neutralised solution of 7-iodo-8-quinolinol-5-sulphonic acid. The precipitate contains transparent brown-red crystals of the composition Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) · 3 H\textsubscript{2}O. On heating the compound to about 40\textdegree C the third molecule of the crystal water is irreversibly removed, giving yellowish brown crystals. At about 130\textdegree C the rest of the crystal water is reversibly removed while the substance turns greenblack. The experiments were made with the substance Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) · 2 H\textsubscript{2}O.

Na\textsubscript{2}[Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5})\textsubscript{3}] · 4 H\textsubscript{2}O can be prepared by dissolving equivalent amounts of solid Na\textsubscript{2}C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5} · 2 H\textsubscript{2}O and Co\textsuperscript{II}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}N\textsubscript{5}) · 2 H\textsubscript{2}O in water. The reaction between the compounds is slow. By raising the temperature to about 40—50\textdegree C (higher temperatures were avoided to prevent decomposition of the compounds\textsuperscript{4}) the reaction can be carried

*Acta Chem. Scand. 9 (1955) No. 5*
Fig. 2a. The molar extinction of CoII (C₆H₄O₄NIS) in distilled water — — — — in 1 M HCl — — — — and the molar extinction of C₆H₄O₄NIS in 1 M HCl — — — —

Fig. 2b. The molar extinction of Na₃[CoII (C₆H₄O₄NIS)₃] in distilled water — — — and in 1 M HCl — — — —

out more rapidly but not quantitatively. After repeated evaporations an almost black precipitate can be isolated. According to magnetic and spectrophotometric measurements the composition and structure of the precipitate is given by the formula Na₃[CoII(C₆H₄O₄NIS)₃]. The compound is very soluble in water and soluble in alcohol. The solubility is not incompatible with the covalent bond because of the SO₃ groups. The corresponding acid H₃[CoIII(C₆H₄O₄NIS)₂] can be prepared by exchange reaction from the sodium salt. Potentiometric titration of the acid dissolved in water has shown it to be a strong acid.

Similar compounds with 8-quinolinol-5-sulphonic acid and its other derivatives as chelating agent are expected.

Further investigations are in progress.

2. Ekman, A. Personal communication.


Received May 9, 1955.

Sialic Acid in Human Serum Protein and in Meconium

LARS ODIN

Institute of Medical Chemistry, University of Uppsala, Uppsala, Sweden

The presence of sialic acids or closely related substances in many glycoproteins and in gangliosides has been indicated by more or less specific colour reactions. In some materials the presence of these substances has been definitively proved by their isolation in pure form and identi-

Acta Chem. Scand. 9 (1955) No. 5