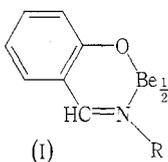


BERYLLIUM COMPLEXES OF SCHIFF BASES*

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Recent solvent distribution studies¹ have shown that beryllium is extractable into non-aqueous solvents by some chelating Schiff bases derived from salicylaldehyde. We describe here the preparation of two such crystalline beryllium complexes.

The complex formed from *N*-*n*-butylsalicylideneimine corresponds in composition to a bis-complex of the bidentate ligand, and n.m.r. measurements show the expected absence of phenolic hydrogen atoms. It is evidently quite analogous to the well-known chelates of Schiff bases with other metals, and its formula may be written as (I) with R = *n*-butyl.



The Schiff base of ethylenediamine is known to behave towards some metals as a quadridentate ligand. However, scale models suggest the impossibility of fitting its four donor atoms around a tetrahedral metal atom, so that it is not surprising that it behaves towards beryllium as a bidentate ligand. The composition corresponds to (I) with R = (CH₂)₂N=CHC₆H₄OH, and this formula is supported by its low solubility and yellow colour, both characteristic of the free hydrogen-bonded salicylaldimine groups.

Both complexes are unusual in that they contain Be-N bonds and yet may be easily prepared from aqueous ethanol. The high stability constants reported^{1,2} in aqueous solution leave no doubt that here are two examples of chelates with Be-N bonds stable to hydrolysis in the pH range 6-10.

Experimental

Melting points are uncorrected. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Sydney. Beryllium was determined by the Analytical Group of the Australian Atomic Energy Commission Research Establishment.

Beryllium Complex of the Schiff Base of n-Butylamine

To beryllium sulphate tetrahydrate (17.1 g; 0.1 mole) in water (200 ml) was added a solution of salicylaldehyde (21 ml; 0.2 mole) and *n*-butylamine (20 ml; 0.2 mole) in ethanol (200 ml). Just enough aqueous sodium hydroxide was added to cause a faint precipitate of Be(OH)₂, and the solution was heated almost to boiling for 30 min with mechanical stirring. It was filtered hot and the filtrate on cooling deposited fine cream-coloured crystals, which were washed with water and dried in the air. The dry solid was recrystallized from a hot mixture of equal volumes of chloroform and light petroleum as fine white crystals, m.p. 128°, readily soluble in ethanol or chloroform, almost insoluble in water, yield 35% (Found: C, 72.8; H, 7.8; Be, 2.4. Calc. for Be(C₁₁H₁₄NO)₂: C, 73.1; H, 7.8; Be, 2.5%).

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¹ Green, R. W. and Alexander, P. W., *Aust. J. Chem.*, 1965, **18**, 651.

² Green, R. W. and Alexander, P. W., unpublished data.

Beryllium Complex of the Schiff Base of Ethylenediamine

To beryllium sulphate tetrahydrate (1.77 g; 0.01 mole) in water (50 ml) was added a solution containing excess of the Schiff base, *NN'*-ethylenebis(salicylideneimine) (13.4 g; 0.05 mole), in ethanol (200 ml). Again just enough aqueous alkali was added to cause slight precipitation of $\text{Be}(\text{OH})_2$ but, after heating the solution to boiling with continuous stirring, yellow crystals separated out. After filtration from the boiling solution, the solid was washed with ethanol and dried in the air, but because of its poor solubility in the common solvents, recrystallization was found to be impossible. Instead, the dry crystals were washed with aqueous hydrochloric acid (1*N*) to remove any unchanged $\text{Be}(\text{OH})_2$ and then with ethanol to remove any excess Schiff base. There remained fine, bright yellow crystals (yield 45%), insoluble in water and only very sparingly soluble in ethanol or chloroform, which decomposed at 290–300° (Found: C, 68.3; H, 5.6; Be, 1.8. Calc. for $\text{Be}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}$: C, 68.4; H, 5.7; Be, 1.6%).