General Synthesis of Chelate Conjugates of Amino Sugars and Metals; Salicylideneamine Schiff's Bases

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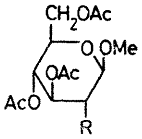
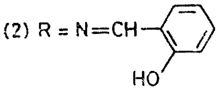
Summary Copper(II) acetate reacts with methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-salicylideneamino-β-D-glucopyranoside (**2**) in methanol solution to form the Schiff's base complex (**3**), the symmetry of which changes from pseudotetrahedral in the solid to a more flattened tetrahedral symmetry in solution; the zinc and cobalt complexes of (**2**) have also been synthesized.

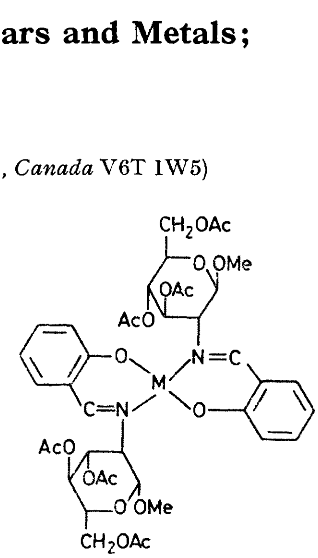
THE ability of sugar derivatives to sequester metals is of current interest for a wide variety of reasons, including the possible development of novel classes of metal-based affinity chromatography materials,[1] of chiral homogeneous catalysts,[2] of metal-chelators for clinical use,[3] and of models for biologically important chelates.[4] Further interests include n.m.r. studies of the interaction of many metals with sugars.[5] These, and many other studies, would clearly be advanced by the development of general methods whereby a metal binding site could be readily attached to a sugar. We now report typical examples of the use of the salicylideneamine Schiff's base (**2**) to form metal complexes† from amino-sugars.

Reaction of the hydrobromide (**1**) with salicylaldehyde in aqueous solution readily afforded the Schiff's base conjugate (**2**),[6] in 80% yield. This conjugate (**2**) reacted smoothly with copper(II) acetate in methanolic solution to form a brown complex (**3**) in 90% yield, m.p. 250 °C, which was purified by slow crystallization from an acetone solution; (**3**) was soluble in chloroform and other organic solvents but insoluble in water.



(1) R = $\overset{+}{N}H_3$ Br$^-$

(2) 



(3) M = Cu
(4) M = Zn
(5) M = Co

In addition to elemental analytical data, the structure of (**3**) was proved by spectroscopic methods. The electron impact, ambient temperature mass spectrum gave intense parent peaks at *m/e* 907 and 909 corresponding to the presence of ^{63}Cu (69·09%) and ^{65}Cu (30·91%) in the complex. Although the resonances were broad, the 270 MHz ^{1}H n.m.r.

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† All derivatives reported here have satisfactory elemental analysis.

spectrum clearly indicated the overall integrity both of the sugar and of the salicylideneamine units. The i.r. spectrum showed a shift in the C=N absorption to lower frequency compared with the ligand [(**2**), 1630 cm^{-1}; (**3**), 1590 cm^{-1}] indicating[7] the co-ordination of the nitrogen atom to the copper ion. The room temperature e.s.r. spectrum of (**3**) in acetone solution was characteristic of other large, copper-containing chelates tumbling slowly enough to show different line widths for the hyperfine components.[8] The presence of the copper atom was also indicated by the characteristic magnetic moment of *ca.* 1·9 B.M.[9]

In common with other copper(II) Schiff's base complexes derived from bulky amines, (**3**) exhibits a significant distortion from square-planar symmetry at the copper towards tetrahedral symmetry; furthermore, the extent of this distortion appears to be greater in the solid state than in solution. Thus the solid-mull electronic spectrum showed three bands at 9500, 13,500, and 20,000 cm^{-1} characteristic of a pseudo-tetrahedral salicylideneamine–copper complex,[7,9,10] whereas the CH_2Cl_2 solution spectrum showed a single band at 15,150 cm^{-1} (ϵ *ca.* 130), indicating a structure intermediate between square-planar and tetrahedral symmetry.

The e.s.r. spectrum at −196 °C in chloroform indicated that a single structural species is present, and comparison of the $g_{\|}$ (2·248) and g_0 (2·128) values, which have been shown to be sensitive to the geometry of these complexes,[10] with $g_{\|}$ and g_0 values obtained for other salicylideneamine copper complexes of known structure, indicates a substantial distortion towards tetrahedral symmetry.

Complex formation between (**2**) and zinc(II) acetate and cobalt(II) acetate occurred readily giving yellow crystals of (**4**), m.p. 272 °C, in 41% yield and green crystals of (**5**), m.p. 260 °C, in 58% yield.

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