

Preliminary communication

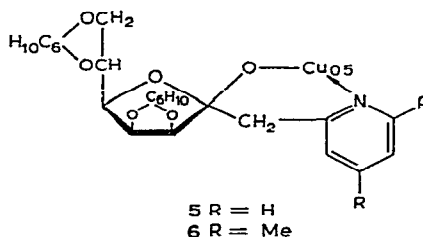
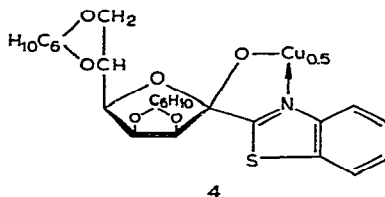
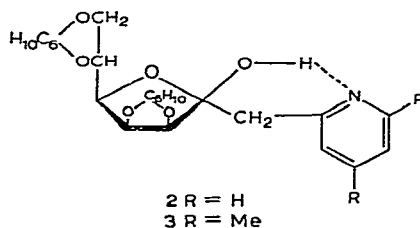
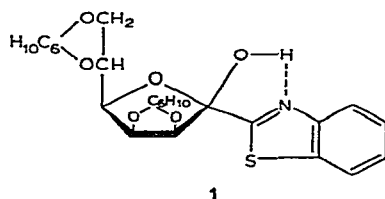
Metal complexes of carbohydrates: chelate complexes of some nitrogen heterocycle-monosaccharide derivatives

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Studies on the complexing of nucleosides¹ and nucleotides² with metals have increased during the last few years due to the biological significance of this phenomenon³. We now report on the complexing of the nitrogen heterocycle-monosaccharide derivatives⁴ 1-3, which are structurally related to naturally occurring C-nucleosides⁵. These compounds were expected to form complexes readily because of hydrogen bonding between the anomeric hydroxyl groups and the nitrogen atom of the heterocyclic residue.



Complexes with copper(II) ion were formed by storage of solutions of 1, 2, or 3 with copper(II) acetate in methanol. The respective complexes 4 (m.p. 295°), 5 (m.p. 92°), and 6 (m.p. 93°) were isolated in moderate yield by slow concentration of the

solutions. They were coloured powders having satisfactory analytical data corresponding to the general formula CuL_2 , where L is a ligand (i.e., 1, 2, or 3).

The electrochemical method⁶ for preparing metal complexes of nitrogen heterocycles was applied to 1–3, and electrolysis using a copper anode gave 4–6 in high yields. It is noteworthy that potentials of formation of the complexes decreased in the order $4 > 5 > 6$.

The structures of 4–6 were revealed by physical methods. Each complex exhibited the expected chiroptical properties, as c.d. absorptions in the visible spectral region: $[\theta]_{722} 0$, $[\theta]_{655} 1165$, $[\theta]_{595} 0$ for 4; and $[\theta]_{686} 0$, $[\theta]_{628} 100$, $[\theta]_{556} 0$ for 5; from $[\theta] = M\theta/cl$, where M = molecular weight, c = concentration (mole/dl), and l = path-length (dm). The observed c.d. bands are indicative of a metal centre adjacent to a chiral carbon atom.

The absence of hydroxyl absorption in the i.r. spectrum of each complex, together with the frequency shifts of the C=N absorptions relative to those in 1–3, indicated the presence of both ionized ligand and heterocycle nitrogen atom co-ordinated with the copper atom, and, therefore, the chelate structure of the complexes. This conclusion is also confirmed by the ready dissolution of the complexes in organic solvents.

The magnetic moments of 4 and 5, as determined by the Goug method⁷, had the values of ~ 1.8 B.M. characteristic⁸ of mononuclear complexes.

The e.p.r. spectrum of 4 showed a distinct, superfine structure. A similar spectrum, although complicated by line broadening, was shown by 5. These observations also indicate⁹ the co-ordination of copper with nitrogen and confirm the chelate nature of the complexes.

Measurements of the dipole moments of 4 and 5 gave values of 3.17 and 4.74 D, respectively (cf. 1.77 and 3.02, respectively, for 1 and 2), which indicate a possible tetrahedral structure of the copper atoms.

Thus, the complexes may be formulated as bis[1-C-(benzothiazol-2-yl)-2,3,5,6-di-O-cyclohexylidene-D-mannofuranose] copper(II) (4), bis[3,4:6,7-di-O-cyclohexylidene-1-deoxyl-1-C-(pyrid-2-yl)-D-manno-heptulo-2,5-furanose] copper(II) (5), and bis[3,4:6,7-di-O-cyclohexylidene-1-deoxy-1-C-(4,6-dimethylpyrid-2-yl)-D-manno-heptulo-2,5-furanose]-copper(II) (6).

Complex formation of 1–3 with cobalt(II) and nickel(II) was successful, and some of the complexes were obtained sufficiently pure to establish an empirical formula of MeL_2 .

REFERENCES

- 1 H. J. Heitner, S. J. Lippard, and H. R. Sunshine, *J. Amer. Chem. Soc.*, **94** (1972) 8936; S. Shimokawa, H. Fukui, J. Sohma, and K. Hotta, *ibid.*, **95** (1973) 1777; T. J. Yokono, S. Shimokawa, H. Fukui, and J. Schma, *Nippon Kagaku Kaishi*, (1973) 201; *Chem. Abstr.*, **78** (1973) 124833d; L. Y. Tan and A. Beck, *Biochim. Biophys. Acta*, **299** (1973) 500.
- 2 M. Ogawa and T. Sakaguchi, *Yakugaku Zasshi*, **92** (1972) 1166; *Chem. Abstr.*, **78** (1973) 58719t; C. M. Frey, J. L. Bayasz, and J. E. Stuehr, *J. Amer. Chem. Soc.*, **94** (1972) 9198; J. Torrielles and A. C. dePaulet, *Biochimie*, **55** (1973) 845.
- 3 H. R. Mahler and E. H. Cordes, *Basic Biological Chemistry*, Harper and Row, New York, 1968.
- 4 Yu. A. Zhdanov, V. G. Alexeeva, and V. N. Fomina, *Dokl. Akad. Nauk SSSR*, **212** (1973) 99; *Tsesisy Vses. Konf. Khim. Heterocycl. Soed.*, **1st**, Chernogolovka, (1973) 36.

- 5 S. Hanessian and T. H. Haskell, in W. Pigman and D. Horton (Eds.), *The Carbohydrates: Chemistry and Biochemistry*, Vol. IIA, Academic Press, New York, 1970, p. 139; R. J. Suhadolnic, *Nucleoside Antibiotics*, Wiley-Interscience, New York, 1970, pp. 50 and 58.
- 6 N. N. Bogdashev, A. D. Garnovsky, V. P. Grigoriev, and O. A. Osipov, *Izv. Severo-Kavkazskogo Nauchn. Zentra Vysshei Shkoly, Ser. Estv. Nauk*, 2 (1973) 28.
- 7 W. Selwood, *Magnetochemistry*, Interscience, New York, 1956.
- 8 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edition, 1966.
- 9 A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 29 (1958) 35.