

Wright of this Department for his interest and encouragement.

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¹ Stahl, E., *Angew. Chem.*, **73**, 646 (1961).

² Wollenweber, P., *J. Chromat.*, **181**, 303 (1961).

³ *Separation and Identification of Food Colours Permitted by the Colouring Matter in Food Regulations, 1957* (Association of Public Analysts, 1960).

⁴ *Data Sheets on Food Colours*. (W.H.O., 1957).

Crystal Structures of Bis-(Salicylaldehydato)-copper(II) and Bis-(8-Hydroxyquinolinato)-copper(II)

ANHYDROUS bis(salicylaldehydato)copper(II) and bis(8-hydroxyquinolinato)copper(II) were obtained by precipitation of the complexes from aqueous solution and recrystallization from water-free chloroform and chlorobenzene respectively. Both compounds formed bronze-green crystals. Their structures have been determined from single-crystal X-ray photographs using copper $K\alpha$ -radiation. Both compounds were found to crystallize in the monoclinic space group $P2_1/c$, details being as follows:

Bis(salicylaldehydato)copper(II) had unit cell dimensions: $a = 8.77$, $b = 6.21$, $c = 12.33$ Å, $\beta = 117.4^\circ$. The structure was solved by three-dimensional Fourier and Patterson methods and refined by the diagonal least-squares technique. There are two centro-symmetric $(C_7H_5O_2)_2Cu$ groups in the unit cell, the metal ion being co-ordinated to the oxygen atoms in a square planar configuration with O—Cu—O angle within the chelate rings 93.0° (e.s.d. 0.4°). The Cu—O distances are 1.87^5 and 1.93^2 Å for the phenolic and aldehydic oxygen atoms respectively (e.s.d. 0.017 Å in each case), and the next nearest atoms to the copper are aromatic carbon atoms from neighbouring molecules at a distance of 3.24 Å above and below the molecular plane.

The observed structure of bis(salicylaldehydato)copper(II) confirms Stackelberg's conclusion from unit cell measurements alone¹ that the molecule is square planar. The distance of 3.24 Å to the nearest neighbours of the copper atom above and below the molecular plane excludes any intermolecular interaction which could be interpreted as giving the copper atom a co-ordination number of six, such as is found in bis(acetylacetonato)copper(II)²; bis(salicylaldehydato)copper thus adds to the still small group of copper(II) compounds in which the metal atom has square planar stereochemistry.

Bis(8-hydroxyquinolinato)copper(II) had unit cell dimensions: $a = 10.90$, $b = 8.61$, $c = 18.16$ Å, $\beta = 102.0^\circ$. Approximate co-ordinates of the metal atoms were obtained from the three-dimensional Patterson function and the rest of the structure solved by Fourier syntheses; refinement was carried out by the differential Fourier method. There are four $(C_8H_7ON)_2Cu$ groups in the unit cell, forming two dimeric units, one oxygen atom of each $(C_8H_7ON)_2Cu$ group completing a square pyramidal arrangement about the copper atom of another. Each copper atom is thus surrounded by two nitrogen atoms at 1.94^5 Å and two oxygen atoms at 2.00 Å very nearly in a plane and a third oxygen atom at the apex of the square pyramid at 2.85 Å; the Cu—O distance in the dimeric unit is 3.49 Å (all distances e.s.d. 0.03 Å) (Fig. 1).

Bridged bimolecular structures with tetragonal pyramidal 5 : co-ordination of the metal atoms have been observed in several other copper(II) complexes. Thus, in bis(dimethylglyoximato)copper(II)³ two planar molecules are linked by co-ordination of one of the oxygen atoms of each to the copper atom of the other, giving an intermolecular Cu—O distance of 2.43 Å, and in dimethylglyoxime-dichloro-copper(II) there is a similar chlorine bridge between the copper atoms of a pair of molecules⁴.

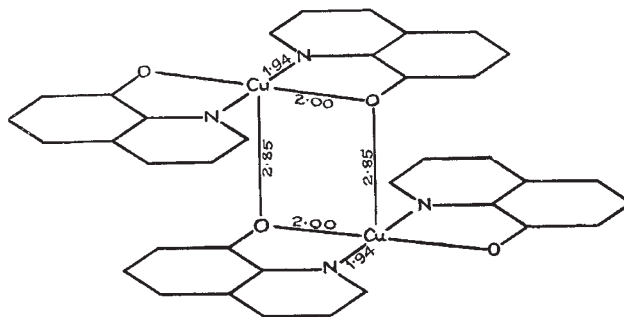


Fig. 1

In disalicylidine-ethylenediamine-copper(II)⁵ dimerization occurs through one of the oxygen atoms, the remainder of the molecule being distorted to allow a Cu—O distance of 2.41 Å in the bridge.

In bis(8-hydroxyquinolinato)copper(II) only slight distortion is observed and the bridging Cu—O distance of 2.85 Å is correspondingly much longer, though still too short to be considered non-bonding. Observations of the spectra of this complex support the interpretation of this distance as representing a weak co-ordinate bond, the visible region, solid-state, reflectance spectrum being shifted about $70 m\mu$ to longer wave-lengths as compared with chloroform solutions; whereas the reflectance and solution spectra for bis(salicylaldehydato)copper(II) are virtually the same. A similar shift to longer wave-length has been observed in 5 : co-ordinated adducts of bis(acetylacetonato)copper(II) and related compounds⁶.

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¹ Stackelberg, M., *Z. Anorg. Chem.*, **253**, 136 (1947).

² Koyama, H., Saito, Y., and Kuroya, H., *J. Inst. Polytech., Osaka*, **4**, C, 43 (1953).

³ Frasson, E., Bardi, R., and Bezzi, S., *Acta Cryst.*, **12**, 201 (1959).

⁴ Barclay, G. A. (private communication).

⁵ Hall, D., and Waters, T. N., *J. Chem. Soc.*, 2644 (1960).

⁶ Graddon, D. P., and Watton, E. C., *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).

A Synthetic Cyclitol Glycoside

THE synthesis of cyclitol glycosides is of interest because of the natural occurrence of these substances as such (galactinol) and as structural moieties of several antibiotics and phospholipids^{1,2}. In this laboratory, attempts have been made to couple activated forms of glucose with protected derivatives³ of myo-inosamine-2 and, more recently, (+)-pinitol. The former efforts were unsuccessful; but the latter provided a glucoside (V) of pinitol in fair yield.

The initial condensation was effected by the Koenigs-Knorr method. Diacetone-(+)-pinitol, which has been shown to be 1,2 : 3,4-di-O-isopropylidene-5-O-methyl-D-inositol (I)⁴ (the numbering used here is that of Fletcher, Anderson and Lardy, reviewed in ref. 1), was prepared by the method of Anderson⁵. It was dissolved in alcohol-free chloroform and the solution was stirred for 1 h with dry silver oxide and anhydrous calcium sulphate ('Drierite'), then tetra-O-acetyl- α -D-glycopyranosyl bromide and iodine were added. Stirring was continued for 24 h, the reaction vessel being protected from light. Inorganic salts were removed by filtration on a 'Celite' pad, which was washed with chloroform, and the filtrate and washings were concentrated to a syrup under vacuum. The crystalline condensation product was obtained by dissolving the syrup in a minimal volume of hot methanol, adding water to