Copper(II)-complexes of Schiff Bases Derived from Salicylaldehyde and Alkylamines

By Shoichiro YAMADA and
Hiroaki NISHIKAWA

(Received March 8, 1963)

Four-co-ordinate copper(II) usually demands a planar configuration with comparatively strong ligands, and bis(*N*-*n*-alkyl-salicylideneiminato)copper(II)-complexes ($Cu(O\cdot C_6H_4\cdot CH{:}N\cdot R)_2$) are expected to have a four-co-ordinate, planar configuration. One can, however, expect cupric complexes of the Schiff bases which are distorted from the square-plane, when R denotes a group which causes steric hindrance to the planar co-ordination[1,2]. The present communication deals with the preparation of those anomalous cupric complexes with the Schiff bases which take a co-ordination distorted from the square-plane, it also discusses the stereochemistry of copper(II) in relation to that of cobalt(II) and nickel(II).

Bis(*N*-*n*-alkyl-salicylideneiminato)copper(II)-complexes, which are considered to have a planar configuration of $Cu(N)_2(O)_2$, on the basis of X-ray crystal structure analysis with the methyl-substituted complex[3,4], show almost identical ultraviolet absorption spectra in non-co-ordinating organic solvents and in the crystalline state, regardless of the number of the carbon atoms of the *n*-alkyl groups.

On the contrary, bis(*N*-*t*-butyl-salicylideneiminato)copper(II), which has newly been prepared as dark-red crystals by warming a solution of bis(salicylaldehyde)copper(II) and an excess of *t*-butylamine in ethanol, is expected to be tetrahedral, because of the steric condition imposed by the bulky *t*-butyl group[1,2]. Bis(*N*-*t*-butyl-salicylideneiminato)copper(II) in organic solvents (Fig. 1) displays a ligand field band at a much lower frequency (about $39.0\times 10^{13}\,sec^{-1}$) than the *n*-alkyl-substituted complex (about $53\times 10^{13}\,sec^{-1}$). This is in agreement with the presumption that the *N*-*t*-butyl-substituted complex has a tetrahedral configuration[5]. The ligands show nearly identical absorption curves, whether they contain for R a normal or a branched alkyl. The maxima in the crystal spectra nearly coincide with those in the solution spectra.

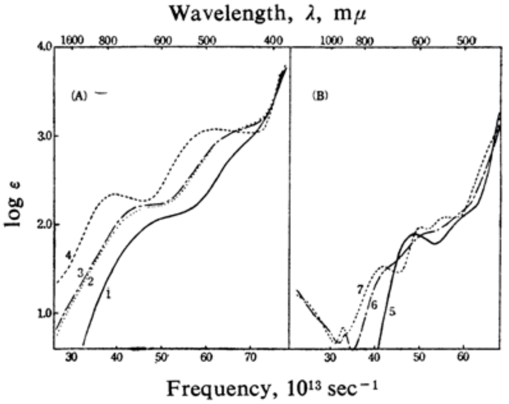

Fig. 1. Visible and near-infrared absorption spectra of (A) $Cu(O\cdot C_6H_4\cdot CH:NR)_2$ in chloroform: 1. R=methyl, 2. cyclohexyl, 3. isopropyl, and 4. *t*-butyl, and (B) $Ni(O\cdot C_6H_4\cdot CH:NR)_2$ in chloroform: 5. R=ethyl, 6. isopropyl and 7. *t*-butyl.

When R represents isopropyl, *sec*-butyl, 1-ethylpropyl or cyclohexyl, steric hindrance to the planar co-ordination may not be as serious as in the case of R=*t*-butyl, but nevertheless it seems significant[1,2]. The copper(II)-complexes with these substituents, which have been prepared in a way similar to that used for the *t*-butyl-substituted complex, show ligand field bands at a much lower frequency (about $47\times 10^{13}\,sec^{-1}$) than when R=*n*-alkyl in non-co-ordinating organic solvents, indicating that the configuration of the cupric complexes with these substituents is not planar but tetrahedral. The absorption spectra of these four complexes are almost superposable with one another, so that the distortion from planarity is to a nearly equal degree in these complexes. The distortion is considered to be greater in the *t*-butyl-substituted complex, which shows a ligand field band at an appreciably lower frequency than when R is any of the other branched alkyls.

Quite a similar type of distortion is concluded for bis(salicylideneiminato)nickel(II) from an inspection of the ligand field bands[6]. The absorption spectra of the *N*-*t*-butyl, isopropyl and cyclohexyl-substituted complexes

---

[1] H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962), etc.

[2] H. Nishikawa and S. Yamada, This Bulletin, **35**, 1430 (1962); S. Yamada, H. Nishikawa and K. Yamasaki, ibid., **36**, 483 (1963).

[3] B. Meuthen and M. V. Stackelberg, *Z. anorg. u. allgem. Chem.*, **305**, 279 (1960).

[4] L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino (*J. Inorg. Nucl. Chem.*, **19**, 73 (1961)) proposed a flattened pyramidal structure.

[5] Bis(*N*-*t*-butyl-salicylideneiminato)cobalt(II) was also prepared and was established as having a tetrahedral configuration (H. Nishikawa and S. Yamada, to be submitted shortly).

[6] A similar conclusion was reached recently from another kind of data by L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini (*Proc. Chem. Soc.* (*London*), **1962**, 255).

in organic solvents (Fig. 1B) have the main features characteristic of tetrahedral nickel(II)-complexes and are quite different from the spectrum of bis(*N*-ethyl-salicylideneiminato)-nickel(II), which is known to be planar in chloroform. Similar by to the case of the cupric complexes, the slight difference in the spectrum between the branched alkyl-substituted complexes seems to be understood on the assumption that the extent of distortion from planarity becomes gradually smaller in the order: R=*t*-butyl, isopropyl, cyclohexyl. The hypothesis of the association of complexes in solution, which has currently been postulated, seems to be superfluous when R is one of the branched alkyls.

Since the bis(*N*-alkyl-salicylideneiminato)-cobalt(II)-complexes take a tetrahedral co-ordination around the cobalt(II) ion, whether the substituent is normal or branched alkyl[1,2,7)], the present work indicates that copper(II) and nickel(II) are more inclined to take a planar co-ordination than cobalt(II), in agreement with the prediction from the simple crystal field theory.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

---

7) L. Sacconi, M. Ciampolini and F. Maggio, *J. Am. Chem. Soc.*, **84**, 3246 (1962), etc.