A New Tetrahedral Nickel(II) Complex—Bis(*N*-4-methoxyphenyl-3-methoxysalicylideneiminato)nickel(II)

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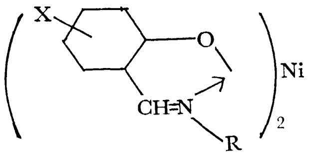
It was concluded[1,2] that bis(*N*-aryl-substituted salicylideneiminato)nickel(II) complexes (abbreviated as Ni(X-SAL·R)$_2$, Formula I) in non-donor solvents existed as an equilibrium mixture composed of various species such as planar, tetrahedral and associated forms, the equilibrium depending upon the nature of X and R as well as upon concentration and temperature. Both a planar and an associated species could be isolated as crystals, but no tetrahedral species has so far been obtained for these complexes. The present communication describes the first isolation of a tetrahedral species, which has been achieved with bis(*N*-4-methoxyphenyl-3-methoxysalicylideneiminato)nickel(II).



Formula I

The crude product of Ni(3-CH$_3$OSAL·4-CH$_3$O–Ph)$_2$ was obtained, Ph being phenyl group, by a reaction of bis(3-methoxysalicylaldehydato)-nickel(II) (0.01 mol) with 4-methoxyphenyl amine (0.02 mol) in ethanol or chloroform. A solution of the crude product in chloroform or benzene was slowly evaporated at about 50°C, until red-brown crystals separated out. The red-brown crystals were filtered off, while the solution was kept warm. Mp 239—240°C. Found: C, 62.66; H, 4.92; N, 4.78%. Calcd for Ni(C$_{15}$H$_{14}$NO$_3$)$_2$: C, 63.07; H, 4.94; N, 4.90%.

Planar coordination is ruled out for this compound, since it is paramagnetic with a magnetic moment of 3.30 B.M. at room temperature. The solid spectrum of this complex displays main features typical of the tetrahedral nickel(II) complex,[3] having *d-d* bands at about 5.7, 8.0, and 14.0 kK. It is concluded that the red-brown form of Ni(3-CH$_3$O–SAL·4-CH$_3$O–Ph)$_2$ has a tetrahedral configuration. Inspection of electronic spectra also reveals that Ni(3-CH$_3$O–SAL·4-CH$_3$O–Ph)$_2$ in chloroform exists predominantly as a tetrahedral species.

It is presumed that the steric hindrance arising from the methoxy-group at the 3-position does not absolutely exclude the planar configuration for Ni(3-CH$_3$O–SAL·4-CH$_3$O–Ph)$_2$, since Ni(3-CH$_3$O–SAL·2,6-(CH$_3$)$_2$Ph)$_2$, in which steric hindrance is much higher, was concluded to have a planar configuration in solid state and in non-donor solvent.[4] For occurrence of the tetrahedral species in crystalline state, the steric condition is not considered to be the only responsible factor. Another important factor might be the suitable field strength produced by the ligand 3-CH$_3$O–SAL·4-CH$_3$O–Ph, which seems to be low enough to disfavour the planar configuration for the complex.

Besides the red-brown crystals, olive-green crystals with composition of Ni(3-CH$_3$O–SAL·4-CH$_3$O–Ph)$_2$·H$_2$O have also been isolated by recrystallization of the crude product from 95% ethanol.

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