Synthesis and structure of a Co(II) chloride complex with bis-(3,3-dimethyl-3,4-dihydroisoquinolyl-1)methane

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Bis-(3,3-dimethyl-3,4-dihydroisoquinolyl-1)methane (L) is potentially able to form complexes with metal salts in the form of tautomers **A** and **B**.

By means of IR-, electron-, and ^{1}H NMR spectroscopy it was established that both in the crystalline state and in solution L exists as enamine tautomer **B**. Indeed,

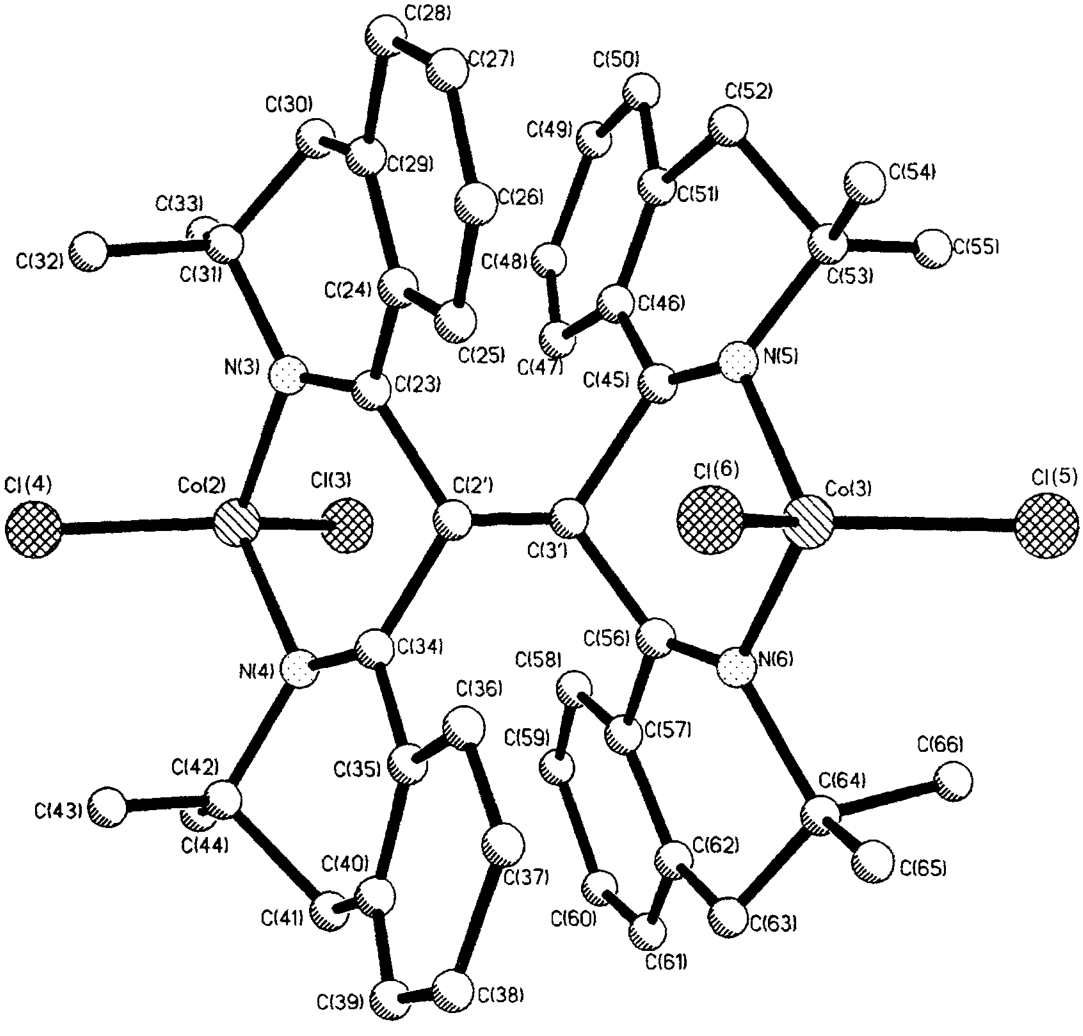

Fig. 1. The structure of tetrakis-(3,3-dimethyl-3,4-dihydroisoquinolyl-1)ethylene dicobalt(II) tetrachloride.

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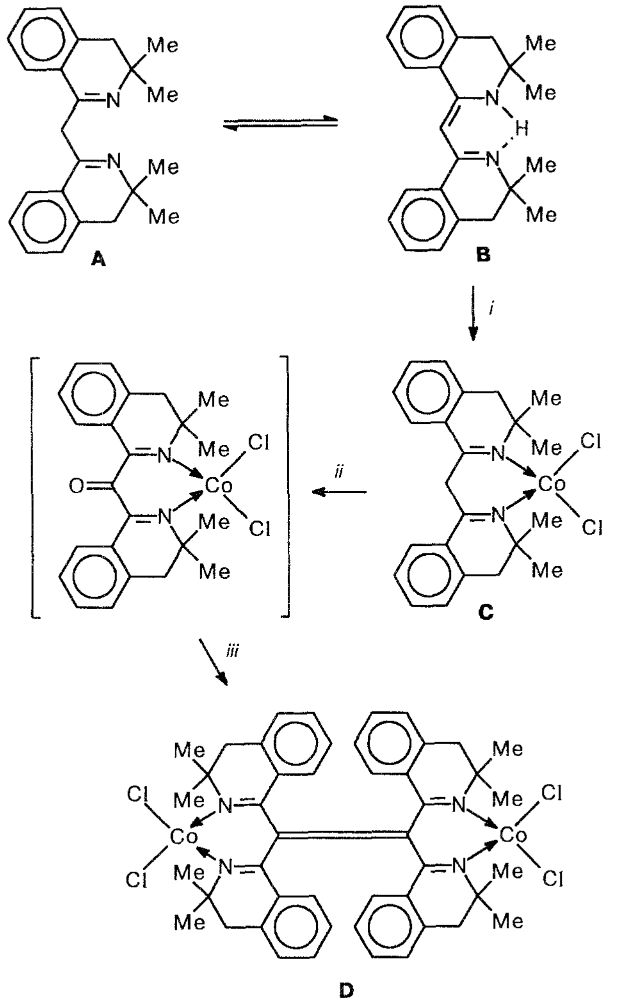

Reagents and conditions: *i.* $CoCl_2 \cdot n\ H_2O$; *ii.* [O]; *iii.* complex **C**

in the IR spectrum of L ν(NH) 3640—3160 cm^{-1} bands are observed, and the ν(C=N) bands of the azomethine bond are shifted to 1615 cm^{-1} in comparison with 1629 cm^{-1} in the spectrum of 1,3,3-trimethyl-3,4-dihydroisoquinoline. In the electron absorption spectrum there is an intense band with a maximum at 396—418 nm indicating strong π conjugation between the heterocyclic fragments of the molecule. Additionally, signals at 12.05 ppm (s, 1H,NH) and at 5.80 ppm (s, 1 H, CH) are observed in the ^1H NMR spectrum (in $CDCl_3$).

The crystal hydrate of Co(II) chloride, partially dehydrated by heating, interacts with L in acetone (M:L = 1:1) to give a complex as a single-phase crystalline bluish-green powder, which has a 1:1 composition according to elemental analysis. In the IR (in KBr) spectrum the bands in the 1650—1500 cm^{-1} region are shifted to higher-frequencies than those in the spectrum of L. This implies the formation of a chelate complex of type **C**. However, addition of a chloride Co(II) solution causes the electron absorption spectrum of L to undergo a bathochromic, not a hypsochromic, shift of the longwave band. X-Ray analysis of the monocrystal grown under these reaction conditions demonstrated (Fig. 1) that the reaction product is a complex (**D**) of chloride Co(II) with a ligand that is a dehydrodimer of ligand L, tetrakis-(3,3-dimethyl-3,4-dihydroisoquinolyl-1)ethylene. We believe that in the course of this reaction chelate complexes **C** are initially formed. Oxidation of these by air oxygen followed by subsequent condensation leads to compounds of type **D** (Scheme).

The ν(C=C) band of the vinyl fragment (1640—1630 cm^{-1}) overlaps with ν(C=N) of the azomethine bond coordinated at nitrogen.

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