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Preparation of New Cobaloximes and their Use as Precursors of Active Catalyst for Hydrogenation of Nitrobenzene

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The only known cobaloxime of Co^{II} which neither contains coordinated amine nor phosphine is diaquocobaloxime: $Co(dmgH)_2 \cdot 2H_2O$ (I). This compound is a precursor of a catalyst for hydrogenation of nitrobenzene. Preparation of a catalyst involves interaction with amine B:

$$I + B \xrightarrow[\text{solvent}]{} \text{cat.} \quad (1)$$

Diaquocobaloxime is prepared by reaction of hydrated cobalt acetate with dimethylglyoxime in methanol [1]:

$$Co(OAc)_2 \cdot 4H_2O + 2dmgH_2 \xrightarrow[\text{methanol}]{Ar} I \quad (2)$$

We noticed that minor changes in preparative procedure afforded new cobaloximes. Reaction of anhydrous cobalt acetate (0.025 *M*) with $dmgH_2$ (0.05 *M*; $1Co{:}2dmgH_2$) in acetone (70 ml) under nitrogen gave rise to $Co(dmgH)(dmgH_2)OAc$ (II). Yield 60%.

$$Co(OAc)_2 + 2dmgH_2 \xrightarrow[\text{acetone}]{N_2} II \quad (3)$$

The reaction must be performed under strictly anaerobic conditions at room temperature, over 24 hours. At the beginning of reaction (3) starting materials dissolved and after a certain time compound II precipitated.

Reaction of cobalt carbonate is quite similar:

$$CoCO_3 + 2dmgH_2 \xrightarrow[\text{acetone}]{N_2}$$

$$\underset{\text{(III)}}{[Co(dmgH)(dmgH_2)]_2CO_3} \quad (4)$$

The yield of III was 50%. Compounds II and III were more soluble in acetone, THF and dioxane than I.

Reaction of II and III with neat EtI afforded $CH_3(NOH)C(NOC_2H_5)$ (II: yield 40%; III: 35%). In the reaction of II with EtI ethyl acetate was also formed (55% yield). Upon acidification (20% HCl) of III carbon dioxide was evolved in the expected amounts. Analytical data for II and III are shown in Table I.

TABLE I. Analytical Data for New Cobaloximes.[a]

Cobaloxime	C %	H %	N %
II	33.1 (34.3)	4.9 (5.1)	16.0 (16.1)
III	32.0 (31.9)	4.9 (4.7)	17.5 (17.5)

[a] Calculated values in parentheses.

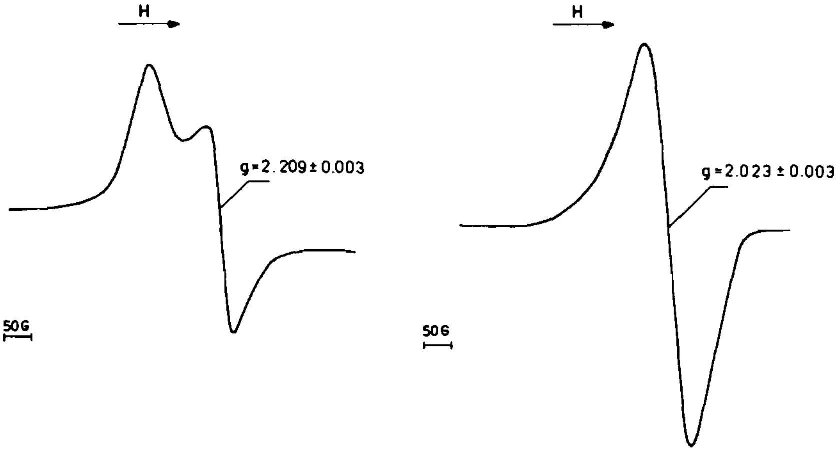

Fig. 1. EPR spectra of $Co(dmgH)_2 2H_2O$ (A) and $Co(dmgH)(dmgH_2)OAc$ (B).

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In the IR of II there was a broad absorption centered at 3400 cm^{-1} attributable to ν_{OH}. An absorption at 1710 cm^{-1} is ascribed to $\nu_{OH\ldots O}$ of strongly hydrogen bonded OH group [2]. The strongest bonds are consistent with the presence of dmgH$^-$ and CH$_3$COO$^-$; 1552 cm^{-1} (superposition of $\nu_{C=N}$ [3] and ν_{COO^-} [4]); 1470 cm^{-1} ν_{COO^-}; 1216 cm^{-1} $\nu_{N=O}$.

In the IR of III there was broad band centered at 3250 cm^{-1}, 1555 cm^{-1} ($\nu_{C=N}$ and ν_{C-O} carbonate); 1420 cm^{-1} ν_{C-O}; 1210 cm^{-1} ν_{N-O}.

The EPR spectra of I and II are shown on Fig. 1. The EPR spectrum of III is virtually identical with that of II but both are distinctly different from the EPR spectrum of diaquocobaloxime.

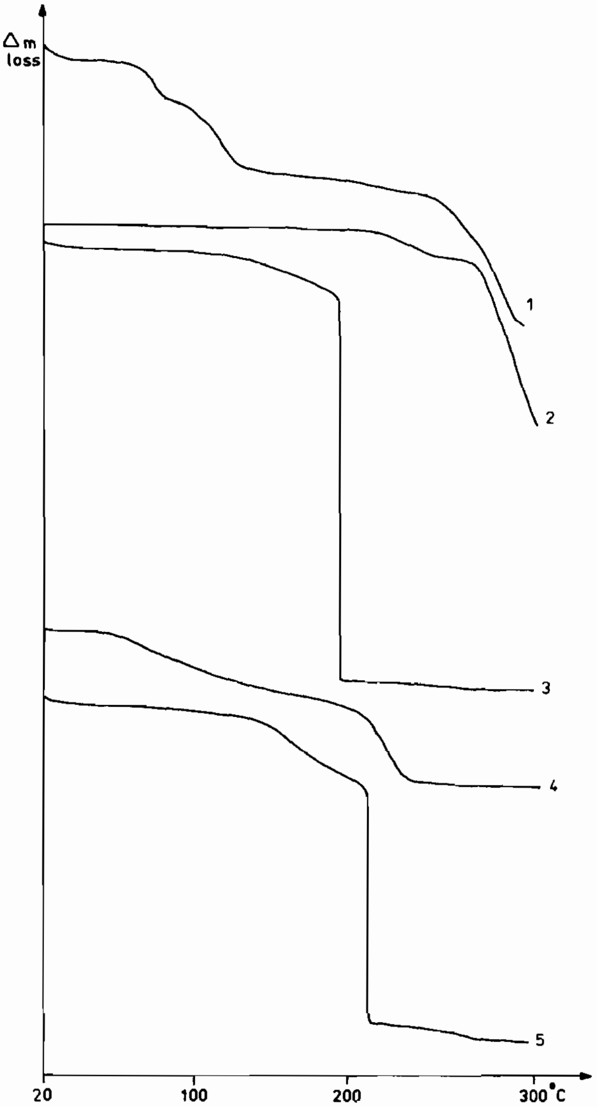

Fig. 2. Mass loss curves of cobaloximes and reference substances: 1) Co(OAc)$_2$4H$_2$O; 2) Co(OAc)$_2$; 3) cobaloxime II; 4) CoCO$_3$; 5) cobaloxime III.

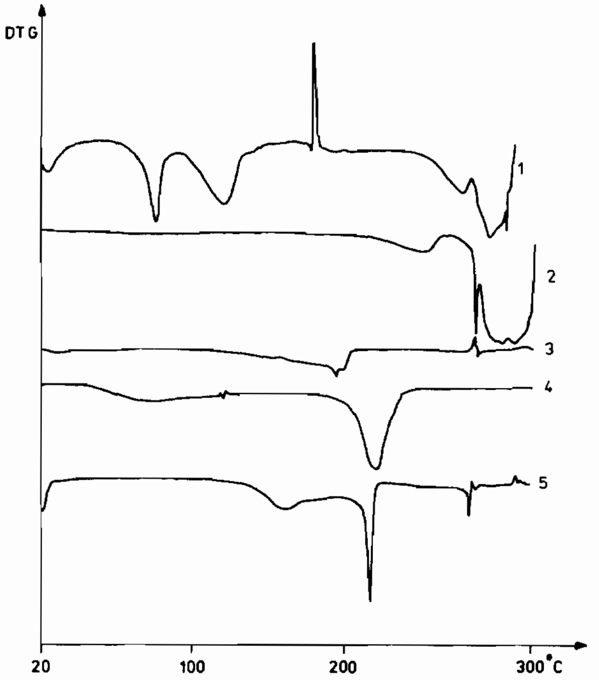

Fig. 3. DTG curves of cobaloximes and reference substances: 1) Co(OAc)$_2$4H$_2$O; 2) Co(OAc)$_2$; 3) cobaloxime II; 4) CoCO$_3$; 5) cobaloxime III.

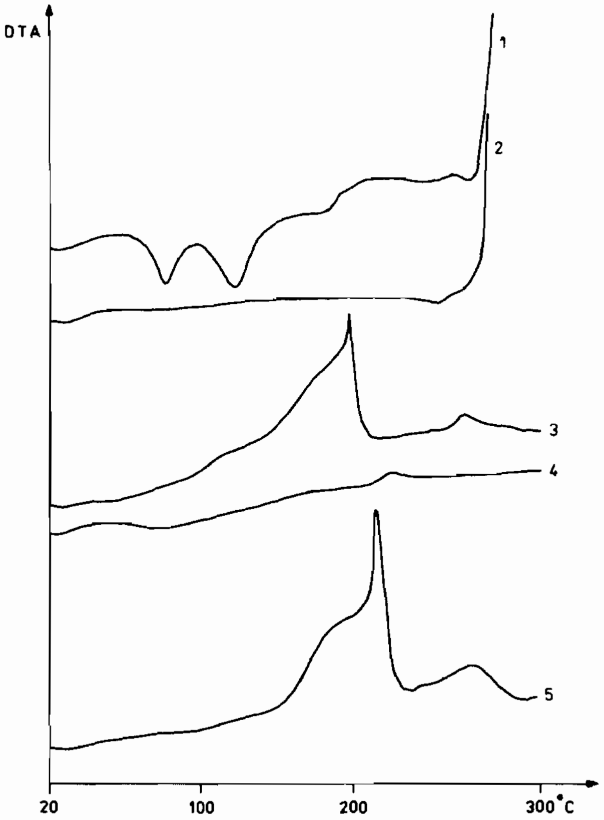

Fig. 4. DTA curves of cobaloximes and reference substances: 1) Co(OAc)$_2$4H$_2$O; 2) Co(OAc)$_2$; 3) cobaloxime II; 4) CoCO$_3$; 5) cobaloxime III.

The polycrystalline EPR spectrum of I was not published in the literature. The spectra of polycrystalline $Co(dmgH)_2 \cdot 2Py$ (IV) and $Co(dmgH)_2 \cdot 2P(nBu)_3$ (V) are known [5]. Spectrum of V is rather similar in shape to the spectrum of II and III but differs considerably in the value of g.

We also characterized the new compounds by thermogravimetric analysis. Corresponding thermograms are shown in Figs. 2, 3 and 4.

During thermal decomposition of diaquocobaloxime and aquo–acetone cobaloxime [6] there was a loss of water in the range 80–105 °C, water and acetone in the range 75–95 °C. For II and III there was no loss of mass in those temperature ranges. At higher temperatures (120–270 °C) there was a continuous loss of weight (products: acetic acid and $dmgH_2$ in the case of II, $dmgH_2$ for III). For the acetate complex there was a violent decomposition at 207 °C as for the corresponding carbonate at 218 °C. Both new cobaloximes are also precursors of catalysts for hydrogenation of nitrobenzene.

The activity of catalytic solutions prepared according to (1) using I, II and III is compared in Table II. Morpholine was used as the amine. The conditions of the catalytic reaction are: Co:morpholine = 1:2; $c_{Co} = 20$ m*M*; $Co:PhNO_2 = 1:70$; $p_{H_2} = 1$ atm; t = 25 °C; acetone solution.

The new cobaloximes, therefore, give rise to better homogeneous catalysts than I.

TABLE II Comparison of the Activity of Catalysts Formed from Different Cobaloximes.

Cobaloxime	Initial turnover of catalytic hydrogenation mol H_2/mol Co L min
I	0.142
II	0.243
III	0.213

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