

Synthesis and Physico-Chemical Properties of Alcoholato Cobalt(II) Chlorides

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Z. Naturforsch. **35b**, 1555-1558 (1980); received July 1, 1980

Alcoholato Complexes, Cobalt(II) Chlorides

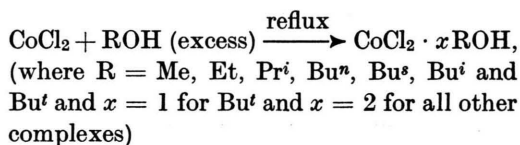
Alcoholato complexes of cobalt(II) chloride with the general formula, $\text{CoCl}_2 \cdot x\text{ROH}$ (where $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^n, \text{Bu}^s, \text{Bu}^i$ and Bu^t) have been synthesised by the reactions of anhydrous CoCl_2 with an excess of the appropriate alcohols under reflux. Physico-chemical studies such as electronic, infra-red spectra, magnetic and conductivity measurements have been carried out to throw light on the structure of these complexes. Magnetic and electronic spectra suggest an octahedral environment for cobalt(II) in the methanolato complex and tetrahedral geometry for all other complexes.

Introduction

A considerable amount of work has been carried out in our laboratories on alkoxides and alcoholato complexes of chromium [1, 2] and nickel [3, 4] in recent years, but very little work has been reported on the corresponding derivatives of cobalt(II). It was, therefore, considered worthwhile to synthesize some of these derivatives and study their physico-chemical properties.

Results and Discussion

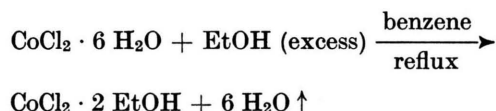
Anhydrous cobalt(II) chloride dissolves in a number of alcohols forming clear blue solutions. Blue adducts with the general formula, $\text{CoCl}_2 \cdot x\text{ROH}$ can be isolated either by crystallization or by distilling of the solvents from the above solutions.



The methanol, ethanol and isopropanol adducts of cobalt(II) chloride could be crystallised from their solutions in the respective alcohols. However, other alcoholato complexes could not be crystallised and were, therefore, isolated by removal of excess of solvent (parent alcohol) under reduced pressure. These alcoholato complexes are blue (except meth-

anolato, which is a light pink) coloured solid (Table I). These are insoluble in other common organic solvents except in the parent alcohol.

The ethanol adduct has also been isolated by the reaction of hydrated CoCl_2 with ethanol in benzene medium; the water formed in the reaction has been removed azeotropically:



After removing the azeotrope and excess of solvent, the clear solution was kept overnight when blue crystals were obtained which were dried at $20-25^\circ\text{C}/0.5\text{ mm}$. Analysis of the product corresponded to the formula $\text{CoCl}_2 \cdot 2\text{EtOH}$.

Infrared spectra

The $\nu(\text{OH})$ stretching band in the IR spectra of all these alcoholato complexes appear at $\sim 3160\text{ cm}^{-1}$ which is much lower than the 3300 cm^{-1} region in which the same band appears in the free alcohols; thus lowering in the value appears to arise from coordination of the alcohol molecules to the central cobalt atom [5, 6].

Visible spectra

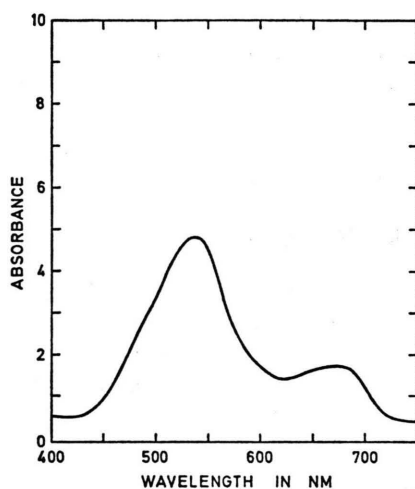
The visible spectra of all the alcohol adducts of CoCl_2 have been recorded in the parent alcohols. The spectrum (Fig. 1) of $\text{CoCl}_2 \cdot 2\text{MeOH}$ shows two well defined bands with maxima at $18,590$ and $14,790\text{ cm}^{-1}$. The third band at 7550 cm^{-1} is observed for this compound in the near infrared region. These bands are characteristic for Co^{2+} in

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Table I. Reactions of anhydrous CoCl_2 with various alcohols.

Reagent	Drying Temp. [°C/mm]	Product	Found Co	(Calcd) Cl	[%] OR	λM [ohm ⁻¹ cm ² mol ⁻¹]
CoCl_2 (1.62 g) MeOH (~10 ml)	40–45°/5.0	$\text{CoCl}_2 \cdot 2 \text{MeOH}$ (Light pink crystalline solid)	30.21 (30.40)	37.24 (36.57)	31.90 (33.03)	170.9
CoCl_2 (3.41 g) EtOH (~30 ml)	20–25°/5.0	$\text{CoCl}_2 \cdot 2 \text{EtOH}$ (Blue crystalline solid)	26.49 (26.50)	32.40 (31.96)	40.50 (41.48)	47.8
CoCl_2 (2.27 g) Pr^iOH (~15 ml)	20–25°/5.0	$\text{CoCl}_2 \cdot 2 \text{Pr}^i\text{OH}$ (Blue crystalline solid)	22.95 (23.58)	27.64 (28.37)	47.51 (48.05)	1.3
CoCl_2 (1.87 g) Bu^nOH (~12 ml)	35–40°/5.0	$\text{CoCl}_2 \cdot 2 \text{Bu}^n\text{OH}$ (Blue solid)	21.42 (21.19)	26.53 (25.86)	—	1.0
CoCl_2 (1.45 g) Bu^sOH (~25 ml)	20–25°/5.0	$\text{CoCl}_2 \cdot 2 \text{Bu}^s\text{OH}$ (Blue solid)	20.98 (21.19)	25.08 (25.86)	—	—
CoCl_2 (3.44 g) Bu^iOH (~50 ml)	40–45°/0.5	$\text{CoCl}_2 \cdot 2 \text{Bu}^i\text{OH}$ (Blue solid)	20.19 (21.19)	26.34 (25.86)	—	—
CoCl_2 (1.31 g) Bu^tOH (~20 ml)	20–25°/0.5	$\text{CoCl}_2 \cdot \text{Bu}^t\text{OH}$ (Blue solid)	29.19 (28.90)	36.34 (35.24)	—	—

Fig. 1. Visible spectrum of $\text{CoCl}_2 \cdot 2 \text{MeOH}$ in MeOH .

octahedral (O_h) environment [1, 8] in this compound and can be assigned to the following transitions:

$$7550 \text{ cm}^{-1}: {}^4T_{1g} \rightarrow {}^4T_{2g} (\nu_1)$$

$$14790 \text{ cm}^{-1}: {}^4T_{1g} \rightarrow {}^4T_{2g} (\nu_2)$$

$$18590 \text{ cm}^{-1}: {}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P}) (\nu_3)$$

Moreover, the visible spectrum of this compound is similar to the spectra [7, 9] of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $\text{Co}(\text{OMe})_2$ in which Co^{2+} ions are also present in octahedral environment. With the help of these three transitions, *i.e.*, ν_1 , ν_2 and ν_3 , the following values of spectroscopic parameters like $10 Dq$, interelectronic repulsion parameter (B) and covalency factor (β) have been calculated using Underhill and Billing's equation [10]:

$$10 Dq = 7600 \text{ cm}^{-1}, B = 845 \text{ cm}^{-1} \text{ and } \beta = 0.87$$

However, the visible spectra of all the other alcoholato derivatives, $\text{CoCl}_2 \cdot x \text{ROH}$ (where $x = 2$, $R = \text{Et}$, Pr^i , Bu^n , Bu^s , Bu^i ; when $x = 1$, $R = \text{Bu}^t$) in parent alcohols, gave a band towards the higher energy side in the range $14850 \pm 150 \text{ cm}^{-1}$. The near-infrared bands for all these derivatives have been observed in the range $6325 \pm 125 \text{ cm}^{-1}$. Some representative spectra are shown in Fig. 2. These transitions are characteristic for Co^{2+} in tetrahedral environment [7] and can be assigned transitions as $\nu_3[{}^4A_2 \rightarrow {}^4T_1(\text{P})]$ and $\nu_2[{}^4A_2 \rightarrow {}^4T_1(\text{F})]$ respectively. Also the visible spectra of all these latter compounds are comparable with the spectrum [7, 11] of $[\text{CoCl}_4]^{2-}$ in which Co^{2+} is in tetrahedral environment. The intense blue colour also

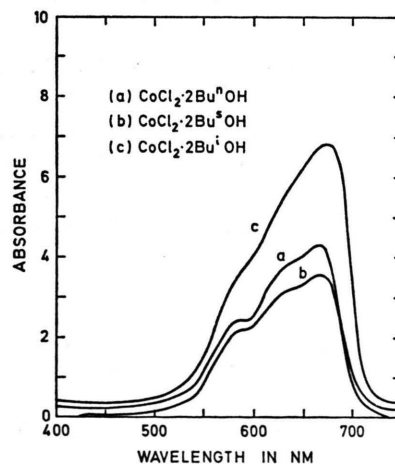


Fig. 2. Visible spectra in parent alcohols.

Table II. Electronic spectra and magnetic moments of alcoholato complexes of CoCl₂.

S. No.	Compound	Observed transitions [cm ⁻¹]		10 Dq [cm ⁻¹]	B [cm ⁻¹]	β	μ_{eff} (BM)
		⁴ A ₂ – ⁴ T _{1g} (F) ν_2	⁴ A ₂ – ⁴ T ₁ (P) ν_3				
1	CoCl ₂ · 2 EtOH	6450	15010	3730	684	0.61	4.61
2	CoCl ₂ · 2 Pr ⁱ OH	6250	15060	3610	698	0.62	4.62
3	CoCl ₂ · 2 Bu ⁿ OH	6250	14970	3605	693	0.62	4.66
4	CoCl ₂ · 2 Bu ^s OH	6250	14970	3605	693	0.62	4.68
5	CoCl ₂ · 2 Bu ⁱ OH	6410	14970	3710	671	0.60	4.67
6	CoCl ₂ · Bu ^t OH	6350	15010	3670	690	0.61	4.60

supports the above view. Various spectroscopic parameters like 10 Dq, B and β , calculated using the Underhill and Billing equation [10], are given in Table II.

It has been observed that the obtained values of B for all the alcoholato complexes of CoCl₂ are lower than the free ion value (1120 cm⁻¹) for Co²⁺ in the CoCl₂ · 6 H₂O. The apparent lowering in the value of B indicates a higher covalent nature of these derivatives.

Magnetic studies

Magnetic susceptibility measurements have been made in their parent alcohols at room temperature by the Gouy method.

Cobalt(II) derivatives should show magnetic moments values between $[4S(S+1)]^{1/2}$ ($\mu_{\text{eff}} = 3.90$ BM) and $[4S(S+1) + L(L+1)]^{1/2}$ ($\mu_{\text{eff}} = 5.2$ BM) when Co²⁺ is present in high-spin state ($S = 3/2$) in an octahedral geometry (d⁷ configuration) [12]. Experimental values reported for cobalt(II) in octahedral geometry lie in the range of 4.7–5.2 BM. For Co(II) in tetrahedral geometry [12], the magnetic moment values are given by

$$\mu_{\text{eff}} = 2 \left(1 - \frac{4\lambda}{10 Dq} \right) [S(S+1)]^{1/2} \text{ and the experi-}$$

mental values are generally known to lie in the range 4.4–4.7 BM. Among the compounds studied during the present investigations, only the methanol adduct shows a magnetic moment of 4.85 BM which corresponded to the range typical for octahedral geometry. Magnetic moments of the other homologues lie in the range 4.64 ± 0.04 BM. (Table II) which are suggestive of Co²⁺ in tetrahedral environment. These magnetic studies also, therefore, support the conclusions tested on the electronic spectra.

Conductance studies

Molar conductance measurements were made in parent alcohols (Table I).

The molar conductance ($\lambda_M = 170.9$ ohm⁻¹ cm² mol⁻¹) of CoCl₂ · 2 MeOH solution in methanol indicates that it behaves as a 1 : 2 electrolyte [13] which may be represented by the formula $[\text{Co}(\text{MeOH})_6]^{2+} \cdot 2 \text{Cl}^-$. The ethanol derivative CoCl₂ · 2 EtOH in ethanol solution appears to behave as a 1 : 1 electrolyte ($\lambda_M = 47.6$ ohm⁻¹ cm² mol⁻¹) whereas the isopropanol derivative in isopropanol appears to be a weak electrolyte ($\lambda_M = 1.3$ ohm⁻¹ cm² mol⁻¹). Other alcohol adducts behave as non-electrolytes in parent alcohols, which may be partly due to decreasing value of dielectric constants of the solvents.

Experimental

All glass apparatus with standard joints were used throughout the experiments. Stringent precautions were taken to exclude moisture.

Anhydrous CoCl₂ was prepared by heating the hydrated CoCl₂ (B. D. H.) in a current of dry HCl gas and analysed.

Analysis for CoCl₂

Found	Co 45.45	Cl 54.50,
Calcd	Co 45.39	Cl 54.61.

Benzene and alcohols were dried by the standard literature procedures.

IR spectra were recorded in the range 4000 to 400 cm⁻¹ in Nujol mulls on a Perkin-Elmer 621 spectrophotometer. Electronic spectra were recorded on a Beckman-26 spectrophotometer in parent alcohols using 10 mm quartz cell. Magnetic susceptibility measurements were carried out in parent alcohols by the Gouy method. Conductivity measurements were made using a Systronics Conductivity bridge having a specially fabricated conductivity cell of cell constant 0.135 cm⁻¹ in these compounds.

Cobalt in these compounds was estimated as cobalt anthranilate [14], chloride as AgCl, and alcohol as reported earlier [15].

One of the authors (J. V. S.) thanks to the University Grants Commission, New Delhi for the financial support.

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