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Studies in Coordination Chemistry. IX.[1] Investigation of the Stereochemistry of Some Complex Compounds of Cobalt(II) with N-Substituted Salicylaldimines

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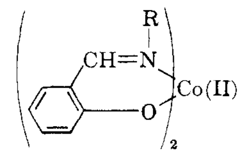
Magnetic and spectrophotometric measurements are reported for cobalt(II) complexes with N-substituted salicylaldimines. The magnetic moments have values ranging between 4.27 and 4.48 B.M. which are those predicted for a tetrahedral structure. This structure was confirmed by X-ray investigations, and it was found to persist in benzene solution. In pyridine, however, hexacoördinate adducts are formed. These have magnetic moments of about 4.8 B.M. and can be isolated in the solid state.

Introduction

The stereochemistry of cobalt(II) complexes is a subject of considerable current interest and one in need of further study. Rather extensive magnetochemical investigations have been reported for the complexes of cobalt(II) which are often assigned structures on this basis. For example, tetracoördinated cobalt(II) complexes are given tetrahedral structures if the values of magnetic moments are in the range 4.2–4.7 B.M., whereas values of 2.1–2.9 B.M. are said to designate square planar structures.[2] Octahedral cobalt(II) complexes have μ_{eff} values of 1.7–2.0 or 4.4–5.6 B.M.[2] It was claimed recently that planar complexes of the type $[CoO_4]$ may be of higher spin and have μ_{eff} values in the range 4.8–5.2 B.M.[3,4] However, it is possible that these compounds are in reality octahedral due to intermolecular association.[5] As far as the spectral properties are concerned, it was observed that the crystal field bands in the spectra of the tetrahedral complexes of cobalt(II) have molar extinction coefficients which are much larger than those found in either planar or octahedral complexes.[4,6] This effect was found also in complexes of other metal ions.[7] Very recently, however, Cotton and Soderberg[8] have shown that the visible band of the tetrahedral bis-(dipivaloylmethano)-cobalt(II) complex has an extinction coefficient of about 40.

In any case, it appears that the correlation between magnetic as well as spectroscopic data and the structure of cobalt(II) complexes is not yet completely understood. In order to obtain more information on this subject, the synthesis and an investigation of magnetic and spectral properties of a series of cobalt(II) compounds containing N-substituted salicylaldimines were undertaken. These compounds, which have the general formula (R = alkyl, aryl and cyclohexyl), are red crystalline solids which are stable to dry air. In solution, they are to some extent oxidized by atmospheric oxygen with the formation of the corresponding green tris-(R-N-salicylaldimino)-cobalt(III) complexes. Thus the preparation of these cobalt(II) complexes was carried out in the absence of air. This tendency toward oxidation depends on the nature of the substituent R. Complexes in which R is a normal alkyl group are most easily oxidized. To date only a few compounds of this series have been described.[9]



Experimental

Preparation of the Bis-(R-N-salicylaldimino)-cobalt(II) Complexes. (a) **Compounds with R = *n*-butyl, *n*-amyl, benzyl, phenylethyl.**—Owing to the sensitivity of these cobalt(II) complexes toward atmospheric oxygen, all procedures were carried out under an inert atmosphere (nitrogen or carbon dioxide). To a suspension of 0.01 mole of bis-salicylaldehyde-cobalt(II) dihydrate[10] in 25 ml. of benzene a solution of 0.022 mole of the amine in 15 ml. of 95% ethanol was added. A brownish-red solution resulted, which was first taken to a small volume under reduced pressure and then diluted with ethanol until a few red crystals started to separate. At this point, just enough benzene was added to dissolve the precipitate. The clear solution was heated to boiling, filtered while hot and again slowly evaporated under reduced pressure at 40–50° to incipient crystallization. On cooling, a red crystalline mass separated, which was collected on a filter, washed on the filter with a few ml. of ethanol and dried *in vacuo*. The compounds are extremely soluble in chloroform, readily soluble in benzene and pyridine, slightly soluble in ethanol, dioxane and cyclohexane, insoluble in diethyl ether and petroleum ether. In the crystalline state they are fairly stable to air, while in solution they are easily converted into the corresponding green oxidation products.

Bis-(N-butylsalicylaldimino)-cobalt(II).—*Anal.* Calcd. for $C_{22}H_{28}O_2N_2Co$: N, 6.81; Co, 14.33. Found: N, 7.00; Co, 14.32.

Bis-(N-amylsalicylaldimino)-cobalt(II).—*Anal.* Calcd. for $C_{24}H_{32}O_2N_2Co$: N, 6.37; Co, 13.41. Found: N, 6.35; Co, 13.69.

Bis-(N-benzylsalicylaldimino)-cobalt(II).—*Anal.* Calcd. for $C_{28}H_{24}O_2N_2Co$: N, 5.84; Co, 12.29. Found: N, 5.77; Co, 12.20.

Bis-(N-β-phenylethylsalicylaldimino)-cobalt(II).—*Anal.* Calcd. for $C_{30}H_{28}O_2N_2Co$: N, 5.52; Co, 11.61. Found: N, 5.41; Co, 11.46.

(b) **Compounds with R = Phenyl and Cyclohexyl.**—A mixture of bis-salicylaldehyde-cobalt(II) dihydrate

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(0.010 mole) and of the amine (0.022 mole) in 25 ml. of ethanol was refluxed on a water bath. The color of the solution gradually turned to deep red, and after a while dark-red crystals started to separate. The mixture was kept refluxing until the suspended solid appeared homogeneous under the microscope After cooling, the solid was filtered off and washed with ethanol. The crude product was recrystallized by dissolving it in chloroform and reprecipitating by addition of ethanol. The compounds are very soluble in chloroform, fairly soluble in benzene, toluene and pyridine, slightly soluble in ethanol, dioxane and cyclohexane, insoluble in diethyl ether and petroleum ether. They are stable to air, both in the solid state and in solution.

The bis-(N-phenylsalicylaldimino)-cobalt(II)·2 pyridine adduct was obtained by adding light petroleum to the pyridine solution of the parent complex. The product was collected on a filter, washed with diethyl ether and dried in the open air.

Bis-(N-phenylsalicylaldimino)-cobalt(II).—*Anal.* Calcd. for $C_{26}H_{20}O_2N_2Co$: C, 69.18; H, 4.47; N, 6.21; Co, 13.06. Found: C, 69.08; H, 4.47; N, 6.25; Co, 13.20. Mol. wt. calcd. 451.4; found in benzene, 480.

Bis-(N-cyclohexylsalicylaldimino)-cobalt(II).—*Anal.* Calcd. for $C_{26}H_{32}O_2N_2Co$: C, 67.37; H, 6.96; N, 6.04; Co, 12.72. Found: C, 67.36; H, 6.96; N, 6.06; Co, 12.60. Mol. wt. calcd. 463.5; found in benzene, 456.

Bis-(N-phenylsalicylaldimino)-cobalt(II)·2 pyridine.—*Anal.* Calcd. for $C_{36}H_{30}O_2N_4Co$: N, 9.19; Co, 9.67. Found: N, 9.28; Co, 9.55.

Magnetic Susceptibility Measurements.—The measuring apparatus and the experimental technique have been described in a previous paper.[1]

Spectrophotometric Measurements.—The absorption spectra have been measured with a Beckman DK 2 recording spectrophotometer over the 290–1,700 mμ wave length range. Benzene and pyridine were purified by the standard procedures used for spectrophotometric measurements. The reflectance spectrum was obtained using the standard Beckman reflectance attachment and MgO as the blank material.

Molecular-weight Determination.—The determination of molecular weights was carried out by the conventional cryoscopic method in benzene.

Results and Discussion

The magnetic susceptibilities of the bis-N-butyl-, bis-N-cyclohexyl- and bis-(N-phenylsalicylaldimino)-cobalt(II) complexes, as measured in the solid state over the 89–293°K. range of temperature, follow strictly the Curie–Weiss law and have values of θ approaching zero (actually varying from -3 to $3°$) (Table I). This very low value of θ indicates, as was found for the analogous compounds of copper(II),[1] that intermolecular interactions are very small.

The values of the magnetic moments of these complexes, ranging between 4.27 and 4.48 B.M., are those predicted for a tetrahedral structure.[2] Their independence of temperature is also in agreement with the ground state, being an orbital singlet as expected for a tetrahedral arrangement.[11] This stereochemical arrangement was established by comparing the X-ray powder diagrams of the compounds bis-(N-butylsalicylaldimino)-cobalt(II) and bis-(N-butylsalicylaldimino)-zinc(II). The cobalt complex is isomorphous with the zinc derivative which is known to have a tetrahedral structure.[12]

The magnetic moments of benzene solutions of the phenyl and cyclohexyl derivatives, which are more resistant toward oxidation when in solution, are identical (4.41–4.42 B.M., see Table I) with those of the solids. Since cryoscopic measurements show that the bis-(R-N-salicylaldimino)-cobalt(II) derivatives are monomeric in benzene solution, it is concluded that they maintain their tetrahedral structure in solution. This is supported by a comparison of the spectra of the complexes in the solid state with that in benzene solution (Fig. 1) over the range 6,000–35,000 cm.$^{-1}$. The reflectance spectrum is very similar in shape to the absorption spectrum of the benzene solution which shows maxima at 7,700, 11,200, 25,000 and 34,100 cm.$^{-1}$

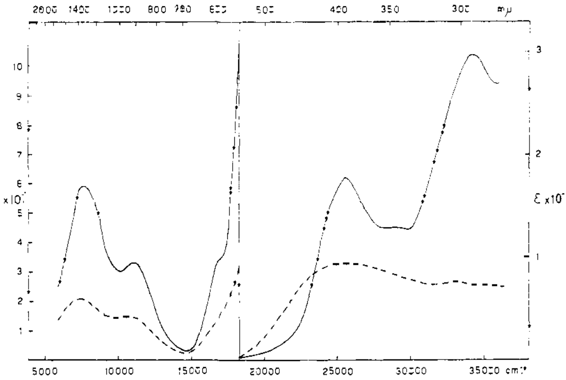

Fig. 1.—Spectra of bis-(N-phenylsalicylaldimino)-cobalt-(II): ———, in benzene; -- -----, by reflectance, absorption scale arbitrary.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR BIS-(R-N-SALICYLALDIMINO)-COBALT (II) COMPLEXES IN THE SOLID STATE AND IN SOLUTION

Bis-R-N-salic. Co(II) complex R-	Concn. (mmole %)	Temp. (°K.)	$\chi_g \times 10^6$	$\chi_A \times 10^6$	μ_{eff} (B.M.)	θ
Butyl		90	63.99	26.541	4.44	−3
		123	47.26	16.658	4.47	
		169	34.30	14.326	4.46	
		220	26.18	10.895	4.44	
		254	22.91	9.640	4.47	
		291	19.95	8.422	4.47	
Amyl		293	18.23	8.250	4.42	
Benzyl		291	15.65	7.745	4.27	
β-Phenylethyl		293	15.62	8.193	4.40	
Phenyl		91	58.11	26.450	4.48	
		124	42.83	19.553	4.47	
		182	28.93	13.279	4.45	
		220	23.85	10.896	4.44	
		262	20.23	9.352	4.47	
		293	17.97	8.332	4.46	
	5.05[a]	297	17.47	8.106	4.41	
	5.18[b]	297	20.67	9.551	4.78	
	5.71[b]	297	20.72	9.573	4.79	
Cyclohexyl		91	59.80	27.986	4.46	+3
		133	40.71	19.138	4.48	
		176	29.80	14.081	4.43	
		212	24.54	22.644	4.43	
		259	20.24	9.651	4.45	
		293	17.59	8.422	4.44	
	4.66[a]	297	16.96	8.130	4.41	
	6.19[a]	297	17.30	8.288	4.42	
	4.72[b]	297	18.73	8.951	4.63	
	6.40[b]	297	18.77	8.969	4.63	

[a] In benzene. [b] In pyridine.

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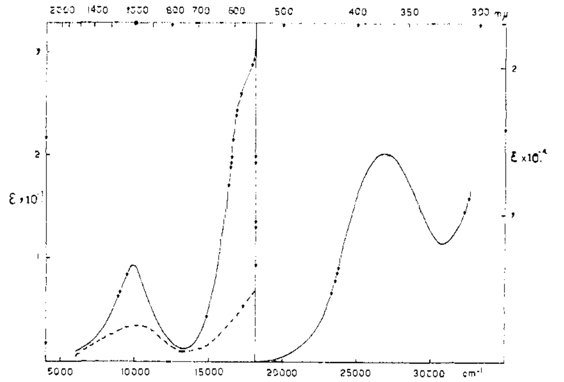

Fig. 2.—Absorption spectrum of bis-(N-phenylsalicylaldimino)-cobalt(II) in pyridine: ———; reflectance spectrum of bis-(N-phenylsalicylaldimino)-cobalt(II)·2 pyridine, absorbance scale arbitrary: --------.

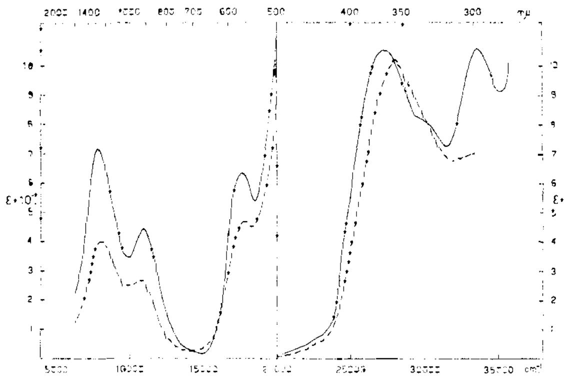

Fig. 3.—Absorption spectra of bis-(N-cyclohexylsalicylaldimino)-cobalt(II): ———, in benzene; --•-----, in pyridine.

and shoulders at about 17,000 and 28,000 cm.$^{-1}$. The bands beyond 20,000 cm.$^{-1}$ are very intense (log $\epsilon > 4$) and occur at frequencies which are almost identical with those of the corresponding bands of the bis-(N-alkylsalicylaldimino)-copper(II) compounds.[1] They may be attributed either to intraligand transitions or to charge transfer between the ligands and the cation. The weaker bands (log $\epsilon < 2$) occurring at lower wave numbers may be ascribed to crystal-field transitions.

The magnetic moment of the complex bis-(N-phenylsalicylaldimino)-cobalt(II) in pyridine solution (4.78 B.M., see Table I) is higher than in benzene solution. This suggests that in pyridine the complex coördinates two molecules of solvent becoming six-coördinate and octahedral. This is confirmed by the isolation of the solid adduct bis-(N-phenylsalicylaldimino)-cobalt(II)·2 pyridine with a μ_{eff} = 4.81 B.M. Further evidence for the formation of this adduct is provided by the reflection spectrum of the di-pyridine derivative and that of a pyridine solution of the unsolvated complex (Fig. 2). These two are very similar. The latter shows maxima at 10,000, 26,000, 33,100 cm.$^{-1}$ and a shoulder at about 17,000 cm^{-1}. This differs from the spectrum of a benzene solution of the tetrahedral complex, the major difference being the markedly higher extinction coefficients of the crystal-field bands in the tetrahedral complex.

The magnetic moment of the complex bis-(N-cyclohexylsalicyl-aldimino)-cobalt(II) in pyridine is 4.62 B.M. (see Table I). This value can be accounted for if it is assumed that only approximately 50% of the molecules of this complex are in the octahedral form. Spectrophotometric measurements are in agreement with this hypothesis. Thus it is evident from Fig. 3 that the spectrum of this complex in pyridine shows the same maxima as that in benzene, at least in the region 6,000–20,000 cm.$^{-1}$, but lower extinction coefficients. This is due to the fact that the tetrahedral complex has extinction coefficients which are larger than those for the bands of the octahedral complex. If one makes use of the observation that the dipyridine adduct has a negligible absorption at 7,700 cm.$^{-1}$, where the tetrahedral complex shows its maximum absorption, from the ratio of the extinction coefficients in both solvents one obtains a value of about 50% for each form.

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[Contribution from the Chemistry Department, Victoria University of Wellington, Wellington, New Zealand]

Transition-metal Complexes with Aliphatic Schiff Bases. IV. Compounds Formed by the Reaction of Copper(II) and Nickel(II) Triethylenetetramine Complexes with Acetone

By D. A. House and N. F. Curtis

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Coördination compounds containing a cyclic quadridentate ligand having three secondary amine and one azomethine donor groups have been prepared by the reaction of copper(II) and nickel(II) triethylenetetramine chlorides with acetone.

It has been reported[1-3] previously that acetone can condense with 1,2-diamine complexes of nickel(II) and copper(II). This paper describes compounds prepared similarly from the triethylenetetramine metal(II) complexes.

If copper(II) or nickel(II) complex chlorides of triethylenetetramine are heated in sealed tubes with acetone, reaction occurs, and an acid stable material can be isolated. Analytical data indicate

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