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Synthesis and Properties of Cobalt Complexes with Schiff Bases Obtained from Pyridoxal and Amines

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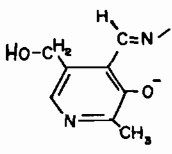
Cobalt(II) and cobalt(III) complexes have been synthesized with Schiff bases obtained from pyridoxal and monoamines (RNH_2) and diamines. The 1:2 type cobalt(II) complexes were obtained with bidentate Schiff bases for $R = iso\text{-}C_3H_7$, $t\text{-}C_4H_9$, cyclohexyl and p-tolyl. Electronic absorption spectra and magnetic data show that they have a tetrahedral configuration. The octahedral 1:3 type cobalt(III) complexes were obtained with the bidentates for $R = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $iso\text{-}C_3H_7$ and p-tolyl. With quadridentate Schiff bases derived from ethylenediamine and 1-methylethylenediamine (propylenediamine) as an amine component, 1:1 type cobalt(II) complexes were obtained in crystals. They consist of low-spin square-planar cobalt(II) complexes, their electronic spectra being very similar to that of the "active form" of N,N′-ethylenebis(salicylaldiminato)cobalt(II).

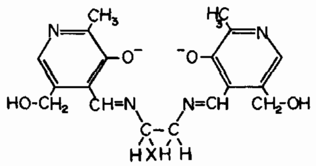
Introduction

In order to obtain basic information, which is expected to be of fundamental significance to discussing the interaction between metal ions and pyridoxal, we recently initiated studies on isolation and characterization of metal complexes with Schiff bases (abbreviated as Pdx–R, I) obtained from pyridoxal. The results about the copper(II) complexes were reported previously.[1]

The present paper describes isolation and properties of the cobalt complexes with the Schiff bases obtained from monoamines (I) and diamines (II) and pyridoxal. Very little work has ever been carried out about such cobalt complexes.



I



II X = H Pdxen
X = CH_3 Pdxpn

Experimental

Pyridoxal hydrochloride of Analar Grade was purchased from Merck and Co. and used as received.

Tris(N-alkylpyridoxaldiminato)cobalt(III) Complexes

These complexes were prepared as dark green crystals, the alkyl groups being methyl, ethyl, *n*-propyl and *iso*-propyl. A typical preparative method is given below. The method is essentially similar to that reported previously for tris(N-alkylsalicylaldiminato)cobalt(III) complexes.[2,3,4]

To a hot solution of cobalt acetate tetrahydrate (0.005 mol) in ethanol (50 ml) were added with stirring pyridoxal hydrochloride (0.015 mol) and a solution of sodium carbonate (0.008 mol) in a small amount of water at about 60° C. An appropriate amine (0.003 mol) was added to this solution, followed by dropwise addition of a 30% aqueous hydrogen peroxide solution (25 ml). The solution was heated at this temperature for 1 hr. A dark-brown precipitate was collected by filtration and recrystallized from methanol or acetone to yield dark green crystals.

For the N-ethyl analogue, the reaction proceeded readily without hydrogen peroxide. For the N-*iso*-propyl analogue, however, the oxidation occurred most slowly and further addition of hydrogen peroxide was often required, as in the case of the corresponding salicylaldiminato-complexes.[4]

All these complexes are soluble in methanol, ethanol and acetone, but almost insoluble in chloroform, benzene and water. Their analytical data are shown in Table I.

Tris(N-p-tolylpyridoxaldiminato)cobalt(III) Monohydrate

Pyridoxal hydrochloride (0.03 mol) and a solution of sodium carbonate (0.02 mol) in a small amount of water were added at about 50° C to a solution of cobalt acetate tetrahydrate (0.01 mol) in ethanol (50 ml). To the resulting solution was added *p*-toluidine (0.03 mol), followed by heating at this temperature for 30 min. The solution was filtered to remove a

TABLE I. Analytical Data of Cobalt Complexes with N-alkyl- and N-aryl-substituted Pyridoxaldiminates.

Complex	M.p.	Calcd., %			Found, %			
	°C	C	H	N	C	H	N	μ
Co(Pdx–CH$_3$)$_3$	288[a]	54.36	5.58	14.09	53.94	5.42	14.45	dia
Co(Pdx–C$_2$H$_5$)$_3$	223	56.42	6.16	13.16	56.03	6.11	13.33	dia
Co(Pdx–*n*-C$_3$H$_7$)$_3$·H$_2$O	221	56.72	6.78	12.03	56.07	6.24	12.80	dia
Co(Pdx–*i*-C$_3$H$_7$)$_3$·H$_2$O	196	56.72	6.78	12.03	56.53	6.36	11.75	dia
Co(Pdx–*p*-tolyl)$_3$·H$_2$O	194	64.12	5.62	9.97	63.97	5.95	9.52	dia
Co(Pdx–*i*-C$_3$H$_7$)$_2$·2.5H$_2$O	232	50.96	6.80	10.81	51.14	6.62	10.69	4.39
Co(Pdx–*t*-C$_4$H$_9$)$_2$·2H$_2$O	175	53.62	7.13	10.42	53.04	6.54	10.20	4.28
Co(Pdx–cychex)$_2$·H$_2$O	158	58.83	7.05	9.80	57.74	6.76	9.67	4.34
Co(Pdx–*p*-tolyl)$_2$(py)$_2$	190[a]	66.02	5.54	11.55	65.93	5.58	11.48	4.81
Co(Pdx–*p*-tolyl)$_2$	185[a]	63.26	5.31	9.84	63.81	5.38	10.41	4.26

[a] Decomposition. μ: magnetic moment at room temperature. Cychex: cyclohexyl. Py: pyridine.

yellow precipitate, and the filtrate was allowed to stand at room temperature for a few days. A dark-coloured precipitate, which formed in the solution, was filtered and recrystallized from methanol to yield dark-green crystals; moderately soluble in methanol, ethanol and chloroform, and insoluble in water and benzene. Analytical data are shown in Table I.

Bis(N-alkylpyridoxaldiminato)cobalt(II) Complexes

These complexes were synthesized by the following general method, the alkyl groups being *iso*-propyl, *t*-butyl and cyclohexyl.

To a solution of cobalt acetate tetrahydrate (0.005 mol) in ethanol (50 ml) were added pyridoxal hydrochloride (0.01 mol) and a solution of sodium carbonate (0.005 mol) in a small amount of water at about 60° C. In a few minutes the colour of the solution changed from green to brown. Then an appropriate amine (0.01 mol) and sodium carbonate (0.003 mol) were added to the solution, and the solution was heated at 60° C for 1 hr. A brown precipitate was collected by filtration and recrystallized from methanol to yield orange crystals of the desired complex.

They are soluble in methanol and ethanol, but insoluble in acetone, chloroform, benzene and water. Analytical data of these complexes are shown in Table I.

Bis(N-p-tolylpyridoxaldiminato)bis(pyridine) cobalt(II)

A solution of sodium carbonate (0.01 mol) in water (5 ml) and that of cobalt acetate tetrahydrate (0.01 mol) in water (10 ml) were added to a solution of pyridoxal hydrochloride (0.02 mol) in ethanol (50 ml) at about 60° C. To the resulting solution was added, drop by drop, a solution of sodium carbonate (0.05 mol) in water (5 ml), and the solution was heated for about 1 h until a brown precipitate began to appear in the solution. A solution of *p*-toluidine (0.02 mol) in pyridine (50 ml) was added slowly to this solution, followed by heating at about 60° C for 30 min. A dark-red crystalline precipitate was recrystallized from acetone. This compound is soluble in methanol, ethanol, chloroform and pyridine, and insoluble in benzene and water. Analytical data are shown in Table I.

Bis(N-p-tolylpyridoxaldiminato)cobalt(II)

This compound was obtained in a very low yield by a method similar to that for the N-alkyl–cobalt(II) complexes described above. However, the compound was prepared in a considerably higher yield by a different method, which is given below. Bis(N-*p*-tolylpyridoxaldiminato)bis(pyridine)cobalt(II) (*loc. cit.*) was heated at about 165–170° C under 50 mmHg for about 6 hr, until the weight of the sample became constant finally after the weight loss corresponding to two pyridine molecules occurred. A yellow-red powder thus obtained almost agreed with the composition of the bis-complex. Further purification was carried out by recrystallization from methanol. This complex is highly soluble in methanol and ethanol, moderately soluble in chloroform and acetone, and insoluble in benzene and water. Analytical data are shown in Table I.

N,N'-Ethylenebis(pyridoxaldiminato)cobalt(II) Dihydrate

This complex was obtained by the following two methods, A and B.

Method A

To a solution of cobalt acetate tetrahydrate (0.01 mol) in ethanol (50 ml) were added pyridoxal hydrochloride (0.02 mol) and sodium carbonate (0.016 mol) with stirring at about 60° C. To the resulting solution was added ethylenediamine (0.01 mol), followed by heating at about 60° C for 1 hr. A dark-red, microcrystalline precipitate was collected by filtration and washed several times with warm methanol.

Method B

An aqueous solution of cobalt acetate tetrahydrate (0.005 mol) was added to an ethanolic solution of the Schiff base (0.01 mol), which had been prepared, in advance, from pyridoxal hydrochloride (0.02 mol), ethylenediamine (0.01 mol) and sodium carbonate (0.01 mol) in ethanol–water. The resulting solution was heated for 30 min at about 60° C with stirring. A dark-red microcrystalline precipitate was filtered and washed with warm methanol. *Anal.* Calcd. for $C_{22}H_{28}CoN_4O_6$, Co(Pdxen)·$2H_2O$: C, 47.90; H, 5.36; N, 12.41%. Found: C, 47.74; H, 5.16; N, 12.01%.

This compound is slightly soluble in water, methanol, ethanol, dimethylformamide and pyridine, but insoluble in chloroform and benzene.

No clear melting point was observed below 300° C, but the compound turned darker in colour above 105° C. The water content of Co(Pdxen)·$2H_2O$ decreased on heating. When Co(Pdxen)·$2H_2O$ was heated for 2 hr at 120° C in the atmosphere under 15 mmHg, the water content reached a constant value, a dark-red powder being finally obtained. The analytical data of thc final product corrcspond with Co (Pdxen)·$^1/_2 H_2O$. *Anal.* Calcd. for $C_{22}H_{25}CoNO_{4.5}$, Co(Pdxen)·$^1/_2 H_2O$: C, 50.95; H, 4.99; N, 13.20%. Found: C, 50.92; H, 4.87; N, 13.51%.

N,N'-1-Methylethylenebis(pyridoxaldiminato) cobalt(II) Monohydrate

This compound was obtained as dark-red microcrystals by methods similar to those for Co(Pdxen)·$2H_2O$. *Anal.* Calcd. for $C_{23}H_{28}CoN_4O_5$, Co(Pdxpn)·H_2O: C, 51.01; H, 5.41; N, 12.52%. Found: C, 50.25; H, 5.16; N, 12.32%.

Its solubility and other properties are similar to those of Co(Pdxen)·$2H_2O$. No melting point was observed below 300° C. When Co(Pdxpn)·H_2O was heated for 2 hr at 120° C under 15 mmHg, the water content decreased at first and reached a constant value; a dark-red powder was finally obtained. The analytical data agree with Co(Pdxpn)·$^1/_2 H_2O$. *Anal.* Calcd. for $C_{23}H_{25}CoN_4O_{4.5}$: C, 52.06; H, 5.29; N, 12.78. Found: C, 52.46; H, 5.19; N, 12.56.

Measurements

Electronic absorption spectra of the complexes in solution and in nujol were recorded on a Hitachi EPS–4T and a Hitachi EPU–2 spectrophotometer. Beer's law was found to hold for all the solution spectra reported in the present paper.

Magnetic measurements were carried out by the Gouy method at room temperature using $CoHg(SCN)_4$ as a calibrant.

Results and Discussion

Complexes with the Bidentate Schiff Bases

With N-*n*-alkyl-pyridoxaldimines, synthetic procedures in the atmosphere tend to yield cobalt(III) complexes, whereas the same procedures yield cobalt(II) complexes with *iso*-propyl- and *t*-butyl-pyridoxaldiminates. Prolonged treatment with hydrogen peroxide results in formation of the cobalt(III) complexes with R = *iso*-propyl, but no appreciable oxidation to cobalt (III) takes place with R = *t*-butyl, probably due to remarkable steric hindrance arising from the bulky *t*-butyl groups. This result is found to be similar to that of the corresponding salicylaldiminato-complexes.[2,4]

With R = methyl, ethyl and *n*-propyl, attempts to synthesize the bis-complexes even in the nitrogen atmosphere have so far been unsuccessful, only yielding complexes of more complicated composition, which were not further studied in the present work.

With R = *p*-tolyl, the bis-complex is obtained by the procedure in the atmosphere. The oxidation to cobalt

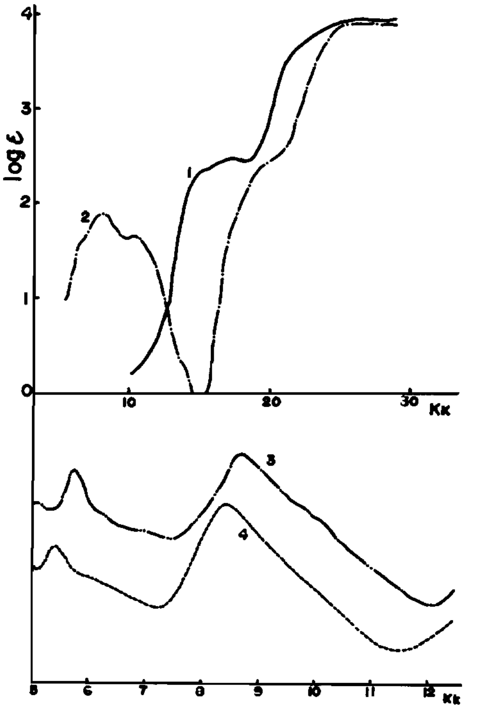


Figure 1. Electronic absorption spectra of cobalt complexes with Schiff bases obtained from pyridoxal amines. 1, Co(Pdx–C_2H_5)$_3$, in methanol (——); 2, Co(Pdx-*t*-C_4H_9)$_2$·H_2O, in methanol (–·–); 3, Co(Pdxen)·$2H_2O$, in nujol (–··–); 4, "active form" of Co(Salen), by reflectance (······). The curves 3 and 4 are shown in arbitrary scale. The curve 4 is taken from ref. 9 of the text.

TABLE II. Absorption Maxima of d–d Bands of Cobalt Complexes with Schiff Bases derived from Pyridoxal.

Complex	Solvent	ν (logε)[a]
Co(Pdx–CH_3)$_3$	methanol	17.3 (2.50)
Co(Pdx–C_2H_5)$_3$	methanol	17.3 (2.46)
Co(Pdx–*n*-C_3H_7)$_3$	methanol	17.8 (2.54)
Co(Pdx–*i*-C_3H_7)$_3$	methanol	17.3 (2.46)
Co(Pdx–*p*-tolyl)$_3$	methanol	16.5 (2.52)
Co(Pdx–*i*-C_3H_7)$_2$	ethanol	7.8 (1.83), 11.0 (1.64)
	pyridine	10.2 (1.08)
Co(Pdx–*t*-C_4H_9)$_2$	methanol	7.9 (1.90), 10.4 (1.65)
Co(Pdx–cychex)$_2$	methanol	7.6 (1.87), 10.3 (1.64)
	pyridine	10.2 (1.09)
Co(Pdx–*p*-tolyl)$_2$	ethanol	7.4 (1.34), 10.3 (1.17)
Co(Pdx–*p*-tolyl)$_2$(py)$_2$	nujol	10.7
Co(Pdxen)·$2H_2O$	nujol	5.38, 8.32
Co(Pdxen)·$0.5H_2O$	nujol	5.45, 8.35
Co(Pdxpn)·H_2O	nujol	5.31, 8.32
Co(Pdxpn)·$0.5H_2O$	nujol	5.35, 8.17

[a] ν: wave-number in 10^3 cm^{-1}.

(III) in this case is more difficult than for the *n*-alkyl-complexes, probably indicating that the aryl-pyridoxaldiminate produces lower ligand field than the alkyl-pyridoxaldiminate. This tendency is similar to that reported previously for the corresponding salicylaldiminato-complexes.[2,5]

The bis-complexes show electronic spectra typical of the tetrahedral cobalt(II) complexes. One of the curves is shown in Figure 1 and data given in Table II. As shown in Table I, they are paramagnetic with magnetic moments lower than 4.5 B.M., in agreement with the tetrahedral stereochemistry.

Bis(N-*p*-tolylpyridoxaldiminato)bis(pyridine)cobalt (II) shows absorption spectrum, which is typical of the octahedral cobalt(II) complex with a low frequency d–d band at 10.7 kK. It is, therefore, most likely that the two pyridine molecules, in addition to the two bidentate ligands, are bound to a cobalt(II) ion.

The cobalt(III) tris-complexes are diamagnetic and show electronic spectra, which are similar to those of tris(N-alkyl-salicylaldiminato)cobalt(III).[2] The data are given in Table II, one of the absorption curves being shown in Figure 1. Their absorption maxima lie at nearly the same frequencies as those of the corresponding salicylaldiminato-complexes, a fact which implies that the ligand field strength may also be nearly the same.

It is interesting to note that the d–d band has a shoulder on the lower frequency side, showing the splitting of the band. The splitting is found to be apparently more pronounced than that of the corresponding salicylaldiminato-complexes, which were concluded previously to have a *mer*-configuration.[6] The appreciable band splitting observed in the present work, as compared with less apparent band splitting for the salicylaldiminato-complexes, suggests that tris (N-alkylpyridoxaldiminato)cobalt(III) complexes may also have a *mer*- rather than a *fac*-configuration. Their solubility, however, is not high enough for PMR measurements.

Complexes with the Quadridentate Schiff Bases

The two complexes Co(Pdxen)·$2H_2O$ and Co (Pdxpn)·H_2O, in which Pdxen and Pdxpn behave as quadridentate ligands, are paramagnetic with magnetic moments of 2.47 and 2.55 B.M., respectively. The magnitude of these moments lies in the range expected for the square-planar cobalt(II) complexes of a low-spin type.[7]

As shown in Figure 1 and Table II, their electronic spectra in nujol are similar to each other and obviously different from those of the tetrahedral and the octahedral cobalt(II) complexes. They are remarkably similar to the spectrum of the active form of N,N′-ethylenebis(salicylaldiminato)cobalt(II), abbreviated as Co(Salen),[8,9] which was concluded by X-ray studies to have a square-planar structure.[10] The d–d band maxima of Co (Pdxen)·$2H_2O$ and Co(Pdxpn)·H_2O lie at nearly the same frequencies as the corresponding band maximum of Co(Salen).

The complexes Co(Pdxen)·$^1/_2\,H_2O$ and Co(Pdxpn)·$^1/_2\,H_2O$, which were obtained by heating the corresponding dihydrate and the monohydrate, respectively, are also of a low spin type, their magnetic moments being 2.48 and 2.54 B.M., respectively. Their spectra in nujol are similar to each other and to those of Co (Pdxen)·$2H_2O$ and Co(Pdxpn)·H_2O, as shown in Table II. It is, therefore, reasonable to conclude that the hemihydrates and the parent hydrates also consist of low spin square-planar cobalt(II) complexes.

In analogy to Co(Salen), some modifications of which are capable of absorbing oxygen molecules in the solid state, it may be anticipated that Co(Pdxen)·nH_2O and Co(Pdxpn)·nH_2O would also have such a property. A preliminary examination, however, has revealed that these compounds in the solid state do not absorb oxygen molecules in the atmosphere near the room temperature. The more detailed investigation regarding this property is now going on at this Institute and will be reported later.

Acknowledgement

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