Synthesis and Properties of Metal Complexes with a New Multidentate Schiff Base Containing Ethereal Oxygen Atoms[1]

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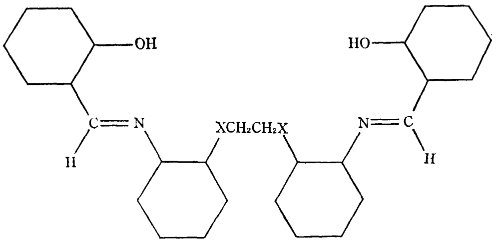
A new multidentate Schiff base, 1,4-bis(*o*-salicylideneaminophenyl)-1,4-dioxabutane having six atoms which may be available for bonding with a metal ion was prepared. With this ligand several metal complexes have been synthesized. From their magnetic properties, electronic absorption spectra and X-ray powder diagrams, it has been concluded that the cobalt(II), nickel(II), and zinc(II) complexes are isomorphous, having a five-coordinated configuration, in which one of the ethereal oxygen atoms of the ligand is bound with the metal ion. The copper(II) complex with a similar composition has a different configuration.

It is well known that the ability of the ethereal oxygen atom to be coordinated with a transition metal ion is significantly lower than that of the alcoholic oxygen atom, and only a small number of complexes which involve the linkage between the ethereal oxygen atom and the metal ion have so far been reported.[2] It is expected, however, that the oxygen atom, when incorporated into a multidentate ligand, may be bound with a metal ion more readily than that in a unidentate ligand.

In the present work, we have synthesized a new multidentate ligand (I), which contains six atoms capable of coordination with a metal ion and may function as a sexa-, a quinqui-, or a quadridentate ligand, depending upon the nature of the metal ion involved.



I: X=O (abbreviated as H_2L)
II: X=S (abbreviated as H_2Ls)

Furthermore, complexes of several transition metal ions with this ligand have been synthesized, and their stereochemistry has been investigated, in order to examine the effect of the metal ions upon the behaviour of the ligand.

Experimental

Materials. 1,4-Bis(*o*-salicylideneaminophenyl)-1,4-dioxabutane. A mixture of ethyleneglycol-bis(2-aminophenyl-ether)[3] (0.0044 mol) and salicylaldehyde (0.016 mol) in 20 m*l* of ethanol was refluxed on a water bath for 2 hr. On cooling, the resulting crystals were collected and recrystallized from a large amount of ethanol; mp 178°C. The yield was almost quantitative. Yellow crystals. Found: C, 73.61; H, 5.33; N, 6.19%. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19%.

[*NiL*]: To a hot solution of the Schiff base H_2L (0.0022 mol) in 50 m*l* of dimethylformamide (DMF) was added nickel(II) acetate (0.0024 mol) in 50% DMF-water, and the mixture was heated on a water bath. The formation of the metal chelate was completed in 10 min. The crystals were filtered and washed with hot ethanol and dried over phosphoric oxide under vacuum at 110°C. Yellow-brown crystals. Found: C, 65.25; H, 4.38; N, 5.6%. Calcd for $C_{28}H_{22}N_2O_4Ni$: C, 66.04; H, 4.36; N, 5.50%.

[*CoL*]: The procedure was the same as described above, except that cobalt(II) acetate was used in place of nickel(II) acetate. Red-violet crystals. Found: C, 65.15; H, 4.31; N, 5.66%. Calcd for $C_{28}H_{22}N_2O_4Co$: C, 65.42; H, 4.32; N, 5.45%.

[*CuL*]: A mixture of the Schiff base (0.0022 mol) and copper(II) acetate (0.0024 mol) in 15 m*l* of DMF was heated on a water bath and the resulting solution was filtered. Methanol was added to the hot filtrate until the solution began to become turbid, and the solution was allowed to cool to room temperature. Brown plates were filtered and washed with hot methanol and dried over phosphoric oxide under vacuum at 110°C. Found: C, 64.66; H, 4.36; N, 5.49%. Calcd for $C_{28}H_{22}N_2O_4Cu$: C, 65.42; H, 4.32; N, 5.45%.

[*ZnL*]: The procedure was the same as described above, except that zinc(II) acetate was used instead of nickel(II) acetate. The product was recrystallized from chloroform to yield yellow-orange crystals. Found: C, 65.17; H, 4.38; N, 5.50%. Calcd for $C_{28}H_{22}N_2O_4Zn$: C, 65.19; H, 4.30; N, 5.43%. The zinc(II) complex is soluble in methanol, ethanol, and chloroform, but insoluble in acetone and benzene.

The other metal complexes, [CoL], [NiL], and [CuL], are almost insoluble in organic solvents, but they were found to be pure and crystalline without recrystallization.

Measurements. Electronic absorption spectra of the ligand and its metal complexes were determined with a Shimadzu MPS-50L spectrophotometer.

Powder diffraction diagrams were obtained with a Toshiba ADX-103 X-ray diffractometer.

Magnetic measurements were carried out by the Gouy method at room temperature.

Infrared spectra of the compounds were determined in the rock-salt region with a Hitachi EPU-2A infrared spectrophotometer using the potassium bromide disc method.

Results and Discussion

It was confirmed by the X-ray powder diagrams that the metal complexes prepared in the present work

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[1] Presented, in part, at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April 1971.

[2] F. Dwyer, N. S. Gill, E. C. Gyarfasand, and F. Lions, *J. Amer. Chem. Soc.*, **75**, 1526 (1953); *ibid.*, **78**, 4905 (1956).

[3] E. Wagner, *J. Prakt. Chem.*, [2] **27**, 201 (1883).

were not polymeric but crystalline.

The ligand, 1,4-bis(*o*-salicylideneaminophenyl)-1,4-dioxabutane, contains an N_2O_4 ligand set consisting of six atoms capable of combining with a metal ion. Judging from the low ability of the ethereal oxygen atom to be bound with a metal ion, however, coordination numbers lower than six may also be possible.

It is presumed that the cobalt(II) complex, [CoL], is not a six-coordinated one, since it is paramagnetic with a magnetic moment of 4.33 B.M. This value is considered to be in the range of magnitude so far observed for a tetrahedral or a five-coordinated cobalt(II) complex, but far below the moment for a six-coordinated one.[4,5] The electronic absorption spectrum of [CoL], as shown in Fig. 1, is quite different from those of octahedral cobalt(II) complexes and tetrahedral ones, but has the main characteristics of the spectrum for the five-coordinated cobalt(II) complex.[6] It is thus concluded that the cobalt(II) ion in [CoL] is five-coordinated, with one of the ethereal oxygen atom bound to the cobalt(II) ion. Any attempt to isolate the cobalt(III) complex with L as a ligand by oxidizing [CoL] has so far been unsuccessful. With 1,4-bis(*o*-salicylideneaminophenyl)-1,4-dithiabutanate (Ls), however, six-coordinated cobalt(III) complexes only were previously reported.[7] This result probably indicates that the ligand field produced by L may be weaker than that produced by Ls, showing significant difference between sulfur and oxygen as a coordinating atom.

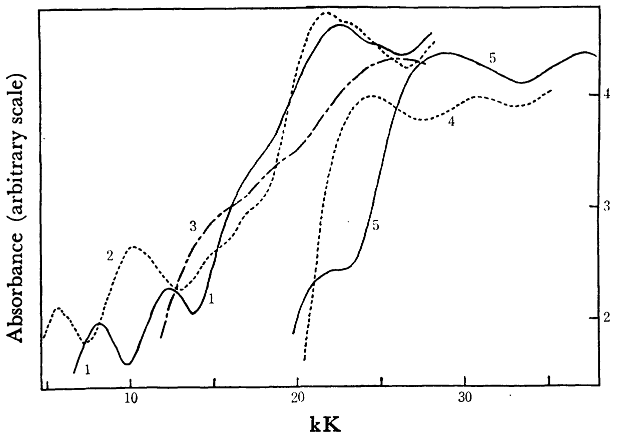


Fig. 1. Electronic absorption spectra of 1,4-bis(*o*-salicylideneaminophenyl)-1,4-dioxabutane (H_2L) and its metal complexes: 1, [CoL], solid; 2, [NiL], solid; 3, [CuL], solid; 4, [ZnL], in chloroform; 5, H_2L, in chloroform. The solid spectra are shown in aribitrary scale.

For the nickel(II) ion in [NiL], the planar four-coordination is excluded, since the nickel(II) complex is paramagnetic with a magnetic moment of 2.86 B.M. at room temperature. The moment observed is much smaller than those reported for tetrahedral nickel(II) complexes.[5] Moreover, the electronic absorption spectrum of [NiL], which is shown in Fig. 1, is similar to that of the typical five-coordinated nickel(II) complex, but is different from that of the octahedral complex.[6] It is concluded that the nickel(II) ion in [NiL] is five-coordinated.

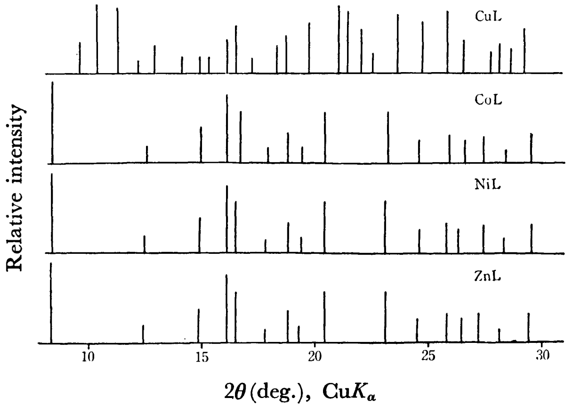
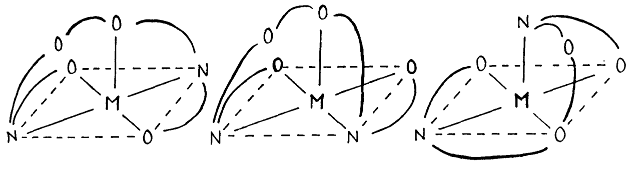


Fig. 2. X-Ray diffraction diagrams of [CuL], [CoL], [NiL], and [ZnL]

The X-ray powder diffraction diagram of [NiL], as shown in Fig. 2 is similar to that of [CoL], indicating that the cobalt(II) and the nickel(II) complexes have a similar configuration, namely the configuration containing the metal ion in five-coordination. Moreover, the infrared spectrum in the rock-salt region of [NiL] is also virtually identical with that of [CoL], in agreement with the conclusion derived above about their structure.

Since the zinc(II) complex, [ZnL], also shows an X-ray powder diagram and an infrared spectrum similar to those of [CoL] and [NiL], it is concluded that the three complexes [CoL], [NiL], and [ZnL] have a similar configuration, in which the metal ion assumes the five-coordination.



(a) (b) (c)

Fig. 3. Some possible configurations for the five-coordinated complexes of the [ML] type.

Some possible configurations for the five-coordinated complexes are shown in Fig. 3. The configuration (a) seems to be more favorable than the other configurations from the steric condition alone, but the definitive conclusion about the precise configuration must await the more detailed X-ray studies. It should be noted, in any case, that the ligand in these complexes is not sexadentate but quinquedentate, with only one of the two ethereal oxygen atoms bound to the metal ion.

The absorption spectrum of [ZnL], which is shown in Fig. 1, may be interpreted on the basis of previous results about *N*-substituted-salicylideneiminato-metal(II) complexes.[8] It is thus considered that the absorp-

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[4] L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 116 (1965).

[5] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

[6] L. Sacconi, *Coordin. Chem. Rev.*, **1**, 192 (1966).

[7] F. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, **76**, 383 (1954).

[8] B. Bosnich, *ibid.*, **90**, 627 (1968).

tion bands at about 24.4 kK (log ε, 4.0) and 30.5 kK (log ε, 4.0) of [ZnL] are originated mainly from excitations involving both the metal ion and the ligand and π-π^* transitions within the ligand, respectively.

The X-ray diffraction diagram of [CuL] is different from those of the other three metal complexes. The infrared spectrum of [CuL] in the region from 1200 to 1275 cm^{-1}, where compounds having an ethereal structure similar to that in the ligand, L, is known to absorb,[9] is very different from that of [ZnL] but similar to that of HL.

The electronic absorption spectrum of [CuL] may be interpreted on the basis of the model having a four-coordinated configuration, scarcely distorted from a planar one. As shown in Fig. 1, [CuL] shows *d-d* absorption bands at frequencies nearly identical with, or even higher than, those of bis(*N*-aryl-salicylideniminato)copper(II) and related complexes;[10,11] their *d-d* bands in the lowest frequency region appear at about 15 kK.

From these data combined, a four-coordinated, essentially planar configuration seems to be likely for [CuL], but any definitive conclusion about its structure may not safely be drawn, except that [CuL] has a different configuration from that of [CoL], [NiL], or [ZnL].

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[9] L. J. Bellamy, "The Infrared Absorption Spectra of Complex Molecules," Methuen, London (1958), p. 117.

[10] S. Yamada, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, This Bulletin, **42**, 131 (1969).

[11] S. Yamada, H. Nishikawa, and E. Yoshida, *ibid.*, **39**, 994 (1966).