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Synthesis and Characterization of a New Quinquedentate Ligand Consisting of Salen Skeleton and Phenolic Tail Capable of Axial Coordination and Its Metal Complexes

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A New quinquedentate ligand *N,N'*-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine (H_2(sal-Hpen)) has been prepared, which is a salen derivative containing a phenolic tail capable of axial coordination. It formed the complexes of a general formula [M(sal-Hpen)] with copper(II), nickel(II), and cobalt(II) ions. Based on infrared, electronic and ESR spectra, the complexes were revealed to assume a planar coordination, free from axial coordination of the phenolic tail. On the other hand, distorted octahedral cobalt(III) and tetragonal pyramidal iron(III) complexes, [Co(sal-pen)py] and [Fe(sal-pen)], were obtained, where sal-pen^{3-} acts as a quinquedentate ligand.

Metal complexes of *N,N'*-disalicylideneethylenediamine (H_2salen) and its derivatives are known to assume planar coordination and show some characteristics relevant to biological systems, such as reversible oxygen adducts[1—11] and alkyl-cobalt(III) complexes[12,13] formations and catalytic function in substrate oxidation.[14—17] In these complexes, the fifth and sixth coordination at the axial positions plays a key role in the biomimetic functions. Therefore, it is interesting to synthesize salen derivatives possessing a tail group capable of axial coordination. However, synthesis of quinquedentate salen derivatives are limited to those with a thioether[18] or a pyridyl group[19] as an axial coordinating group.

In this study, a quinquedentate salen derivative, *N,N'*-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine (abbreviated as H_2(sal-Hpen)), has been prepared. The complexes of this ligand may serve for elucidating the effects of the axial coordination of a phenolic oxygen on the electronic property and the reactivity of complexes and as a model for an intermediate in oxygenase reaction.[20]

In order to examine the net effect of axial phenolato donation, *N,N'*-disalicylidene-2-methyl-4-(2-methoxy-5-methylphenyl)-1,2-butanediamine (H_2(sal-mpen)) and its metal complexes were also prepared, where methyl group was substituted for phenolic hydrogen of H_2(sal-Hpen) so that practically no axial coordination is feasible. The synthetic methods for H_2(sal-Hpen) and H_2(sal-mpen) are schematically shown in Fig. 1.

Experimental

Syntheses. *Methyl 2-(2-Methoxy-5-methylphenyl)ethyl Ketone*: Ethyl acetoacetate (52 g) was added with stirring to a sodium ethoxide solution prepared by dissolving sodium (9.2 g) in absolute ethanol (350 cm^3). To this solution was added 2-methoxy-5-methylbenzyl chloride (68 g) with gentle boiling, and the mixture was refluxed for 3 h. When the reaction was completed, the mixture was cooled and sodium chloride separated was removed by filtration. The salt was washed with a small amount of ether and washings were combined with the main solution. The solution was evaporated to dryness to give a pale yellow substance. It

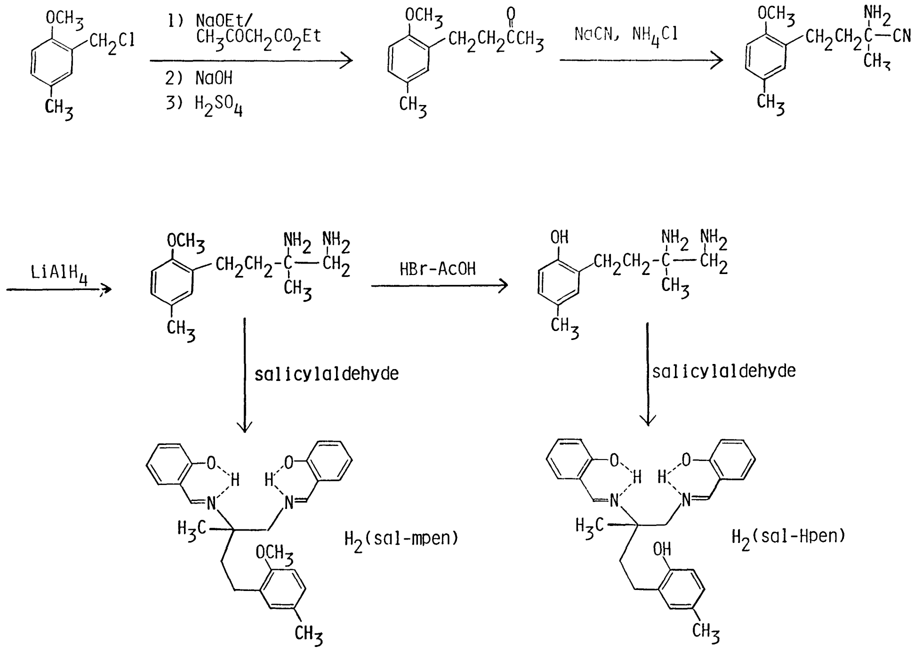

Fig. 1. Synthetic method for H_2(sal-Hpen) and H_2(sal-mpen).

was suspended in a 5% aqueous sodium hydroxide solution (640 cm^3) and the solution was stirred at room temperature overnight. The insoluble oily substance was removed and the aqueous solution was acidified by adding 50% sulfuric acid (160 cm^3). The mixture was refluxed for 2 h and the resulting yellow oily substance was separated with a separatory funnel. The aqueous layer was shaken with benzene and the extracts were combined and dried over anhydrous sodium sulfate. After the solvent was evaporated, the residue was distilled at 149—151 °C/13 mmHg (1 mmHg $\approx$133.322 Pa) to give a colorless liquid (30 g).

Found: C, 76.64; H, 8.42%. Calcd for $C_{12}H_{16}O_2$: C, 74.79; H, 8.39%.

2-Amino-2-methyl-4-(2-methoxy-5-methylphenyl)butanenitrile: A solution of ammonium chloride (5 g) in water (20 cm^3), sodium cyanide (4 g), and aqueous ammonia (28%, 11 cm^3) were mixed in a 500 cm^3 round-bottomed flask. To this was added methyl 2-(2-methoxy-5-methylphenyl)ethyl ketone (15 g), and the flask was sealed with a glass stopper and heated at 60 °C on a water bath for 5 h. The reaction mixture was shaken with five 60 cm^3 portions of ether, and the etherial extracts were combined and dried over sodium sulfate. On evaporating the solvent, the amino nitrile was obtained as an orange paste. It was used for the following reaction without purification.

2-Methyl-4-(2-methoxy-5-methylphenyl)-1,2-butanediamine Dihydrochloride (mpen·2HCl): To a stirred suspension of $LiAlH_4$ (25 g) in absolute ether (400 cm^3) was added a solution of the aminonitrile (10 g) in ether (50 cm^3). The reaction mixture was refluxed for 13 h and decomposed by adding water under ice cooling. The ethereal layer was separated and the residue was extracted with three 100 cm^3 portions of ether. The ethereal solutions were combined and dried over sodium sulfate. When dry hydrogen chloride was bubbled into the solution, crude mpen·2HCl was separated as a milky white precipitate. It was used for the following reaction without further purification because of its high hygroscopicity.

2-Methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine Dihydrobromide (Hpen·2HBr): A mixture of crude mpen·2HCl (3.2 g), acetic acid (35 cm^3), hydrobromic acid (40%, 35 cm^3), and hydroiodic acid (55%, 3.5 cm^3) was refluxed for 20 h. The reaction mixture was evaporated to dryness to give dark brown mass. It was dissolved in methanol and decolorated with activated charcoal. When the solvent was evaporated, Hpen·2HBr was obtained as yellow mass. Since it was very hygroscopic, it was used for the preparation of H_2(sal-Hpen) without purification.

N,N′-*Disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine (H_2(sal-Hpen))*: This was obtained as yellow needles by the reaction Hpen·2HBr (0.3 g) and salicylaldehyde (0.2 g) in methanol (20 cm^3) in the presence of triethylamine (0.17 g).

Found: C, 74.74; H, 6.83; N, 6.74%. Calcd for $C_{26}H_{28}N_2O_3$: C, 74.79; H, 7.00; N, 6.89%.

N,N′-*Disalicylidene-2-methyl-4-(2-methoxy-5-methylphenyl)-1,2-butanediamine (H_2(sal-mpen))*: This was obtained as yellow needles in nearly the same way as that of H_2(sal-Hpen) except for using mpen·2HCl (0.2 g) instead of Hpen·2HBr.

Found: C, 75.15; H, 7.11; N, 6.52%. Calcd for $C_{27}H_{30}N_2O_3$: C, 75.32; H, 7.02; N, 6.51%.

[Cu(sal-Hpen)]: To a methanolic solution (30 cm^3) of H_2(sal-Hpen) (0.2 g) was added a methanolic solution of copper(II) acetate monohydrate (0.1 g). The mixture was heated at 60 °C for 5 h and allowed to stand overnight. Purple crystals separated were filtered and recrystallized from methanol.

Found: C, 64.58; H, 5.72; N, 5.79%. Calcd for $C_{26}H_{26}N_2O_3Cu\cdot\frac{1}{2}H_2O$: C, 64.12; H, 5.59; N, 5.75%.

[Ni(sal-Hpen)]: This complex was obtained as red crystals by the reaction of H_2(sal-Hpen) (0.2 g) and nickel (II) acetate tetrahydrate (0.12 g) in methanol. It was recrystallized from methanol.

Found: C, 65.69; H, 5.62; N, 6.00%. Calcd for $C_{26}H_{26}N_2O_3Ni$: C, 65.99; H, 5.53; N, 5.92%.

[Co(sal-Hpen)]: This complex was obtained as orange powder by the reaction of H_2(sal-Hpen) (0.2 g) and cobalt (II) acetate tetrahydrate (0.12 g) in absolute ethanol in an atmosphere of nitrogen.

Found: C, 65.60; H, 5.61; N, 5.94%. Calcd for $C_{26}H_{26}N_2O_3Co$: C, 65.96; H, 5.54; N, 5.92%.

[Fe(sal-pen)]: This complex was obtained as brownish purple crystalline powder by the reaction of H_2(sal-Hpen) (0.2 g) and iron(III) acetate (0.08 g) in absolute ethanol.

Found: C, 65.58; H, 5.44; N, 5.78%. Calcd for $C_{26}H_{25}N_2O_3Fe\cdot\frac{1}{2}H_2O$: C, 65.28; H, 5.47; N, 5.86%.

[Co(sal-pen)py]: [Co(sal-Hpen)] (0.1 g) was dissolved in dichloromethane (30 cm^3) containing pyridine (0.02 g), and to this was bubbled air for 3 h. On concentrating the solution, reddish brown crystalline powder was separated.

Found: C, 65.16; H, 5.39; N, 7.35%. Calcd for $C_{31}H_{30}N_3O_3Co\cdot H_2O$: C, 65.38; H, 5.66; N, 7.37%.

[Cu(sal-mpen)]: This complex was obtained as purple needles in the same way as that of [Cu(sal-Hpen)] except for using H_2(sal-mpen) (0.2 g) instead of H_2(sal-Hpen).

Found: C, 65.65; H, 5.74; N, 5.68%. Calcd for $C_{27}H_{28}N_2O_3Cu$: C, 65.77; H, 5.92; N, 5.68%.

[Ni(sal-mpen)]: This complex was obtained as red needles in the same way as that of [Ni(sal-Hpen)] except for using H_2(sal-mpen) (0.2 g) instead of H_2(sal-Hpen).

Found: C, 65.97; H, 5.86; N, 5.73%. Calcd for $C_{27}H_{28}N_2O_3Ni$: C, 66.42; H, 5.98; N, 5.73%.

[Co(sal-mpen)]: This complex was obtained as orange microcrystalline powder in the same way as that of [Co(sal-Hpen)] except for using H_2(sal-mpen) (0.2 g) instead of H_2(sal-Hpen).

Found: C, 66.34; H, 5.75; N, 5.79%. Calcd for $C_{27}H_{28}N_2O_3Co$: C, 66.39; H, 5.98; N, 5.73%.

Measurements. Infrared spectra were recorded on a Hitachi Infrared Spectrometer Model 215 on KBr disks or hexachlorobutadiene mulls. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 and a Shimadzu UV-VISIBLE Recording Spectrometer Model UV-240 in dichloromethane. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.[21] Diamagnetic corrections were carried out using Pascal's constants and effective magnetic moments were calculated by the equation $\mu_{\text{eff}}=2.828(\chi_A\times T)^{1/2}$.

Results and Discussion

Infrared spectra of [M(sal-Hpen)](M=Cu^{II}, Ni^{II}, and Co^{II}) are quite similar to those of [M(sal-mpen)], except for a band at 3300—3200 cm^{-1} which is absent in the spectra of [M(sal-mpen)]. This band should be due to the stretching vibration of the phenolic hydroxy group in the tail.

Electronic spectra of [M(sal-Hpen)] and [M(sal-mpen)] were measured in dichloromethane and are shown in Fig. 2. The spectra of [Cu(sal-Hpen)] and [Cu(sal-mpen)] resemble each other in the region (15—35)$\times10^3$ cm^{-1}, exhibiting a d-d band centered around

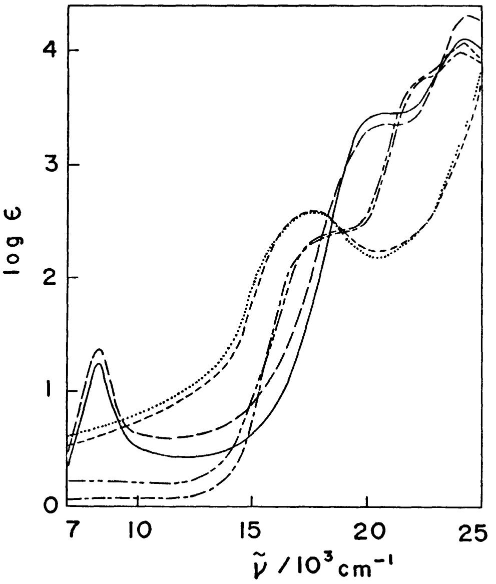

Fig. 2. Electronic spectra of (— — —)[Cu(sal-Hpen)], (······) [Cu(sal-mpen)], (—·—·—) [Ni(sal-Hpen)], (—··—) [Ni(sal-mpen)], (——)[Co(sal-Hpen)], and (— — — —) [Co(sal-mpen)].

18×10^3 cm^{-1}. Furthermore, these spectra are nearly the same as that of [Cu(salen)].[22–24] These facts clearly indicate that the geometry around the metal in the present complexes is essentialy planar without coordination of the hydroxyl or methoxyl group of the tail. Planar configuration for [Cu(sal-Hpen)] and [Cu(sal-mpen)] was also supported by their ESR spectra showing a tetragonal pattern, whose ESR parameters ([Cu(sal-Hpen)]: $g_{\parallel}=2.18$ and $A_{\parallel}=203$ G(1 G$=10^{-4}$T); [Cu(sal-mpen)]: $g_{\parallel}=2.18$ and $A_{\parallel}=201$ G) are practically the same as those of [Cu(salen)] ($g_{\parallel}=2.20$ and $A_{\parallel}195$ G).[25]

Electronic spectra of [Ni(sal-Hpen)] and [Ni(sal-mpen)] resemble each other in the region $(15\text{—}35)\times 10^3$ cm^{-1}. Both showed a d-d band at 18.5×10^3 cm^{-1}, which is nearly the same in frequency as that of [Ni(salen)].[24,26,27] Planar configuration around the metal in [Ni(sal-Hpen)] and [Ni(sal-mpen)] appeared to be reasonable, considered from the facts that [Ni(salen)] and its congeners are known to retain the planar configuration even in polar solvents such as pyridine.[26]

Effective magnetic moments of [Co(sal-Hpen)] and [Co(sal-mpen)] are *ca.* 2.4 BM at room temperature. Electronic spectra of these complexes show a weak band at 8.3×10^3 cm^{-1}, which is characteristic of low-spin, planar cobalt(II) complexes with salen-like Schiff bases.[28–30] Powder ESR spectra of [Co(sal-Hpen)] and [Co(sal-mpen)] both showed a typical ESR pattern of a low-spin, planar cobalt(II) with the $(d_{yz})^1$ ground state[31,32] (Fig. 3). The ESR parameters of the signal at the lower magnetic field are as follows: $g_{\parallel}=3.50$ and $A_{\parallel}=127$ G for [Co(sal-Hpen)]; $g_{\parallel}=3.50$ and $A_{\parallel}=121$ G for [Co(sal-mpen)]. From these facts we may conclude that the present cobalt(II) complexes are of square planar coordination.

Despite marked resemblance in electronic and ESR spectra, [Co(sal-Hpen)] distinctly differ from [Co(sal-mpen)] in reactivity to atmospheric oxygen; the former is very sensitive to molecular oxygen while the latter is practically insensitive in dichloromethane. This suggests that the hydroxy group in the tail exerts some effect on the oxygenation or oxidation at the metal though this group is free from coordination in the cobalt(II) complex.

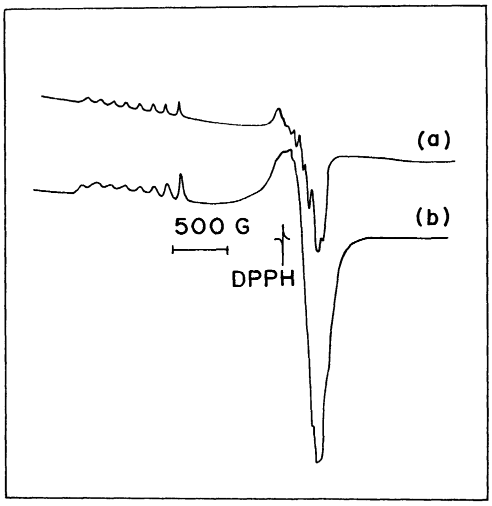

Fig. 3. ESR spectra of (a) [Co(sal-mpen)] and (b) [Co(sal-Hpen)].

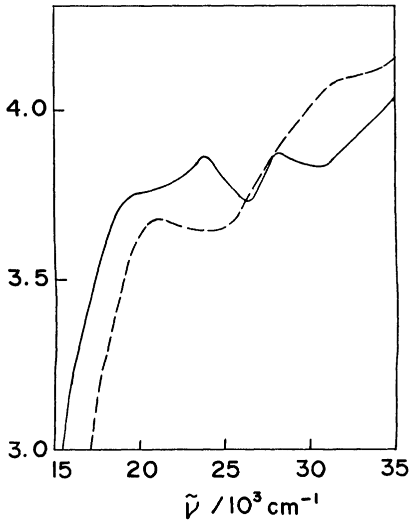

Fig. 4. Electronic spectra of (——) [Co(sal-pen)py] and (— — —) [Fe(sal-pen)].

Reddish brown [Co(sal-pen)py] prepared by air-oxidation of [Co(sal-Hpen)] in dichloromethane-pyridine is diamagnetic. Electronic spectrum of this complex shows an absorption at 20×10^3 cm^{-1} with a shoulder near 16.5×10^3 cm^{-1} (Fig. 4). Coordination of pyridine to the cobalt(III) ion was deduced by an IR band at 690 cm^{-1}. The absence of band due to O-H stretching mode in the region 3300—3200 cm^{-1} implies deprotonation of the phenolic OH group in the tail. All these facts suggest that H_2(sal-Hpen) acts as a quinquedentate ligand to form a six-coordinate cobalt(III) complex with the phenolic oxygen of the tail at the fifth donating site and a pyridine molecule at the sixth site.

Magnetic susceptibility of [Fe(sal-pen)] is 5.8 BM at room temperature, which falls in the range for high-spin iron(III) complex. This complex exhibits no IR band in the region 3300—3200 cm^{-1}, implying the formation of a five-coordinate iron(III) complex with the deprotonated phenolic oxygen in the tail at the apex. It exhibits a visible spectrum with an absorption at 21×10^3 cm^{-1} ($\varepsilon\approx4800$ M^{-1} cm^{-1}), which can be attributed to the charge transfer from the phenolic oxygen in the tail to the iron(III) ion (Fig. 4). Notably, this spectrum differs from those of [Fe(salen)-X] with phenolate or unidentate catecholate group as X; the latter complexes show the CT band in the region $(24.0—24.5)\times10^3$ cm^{-1} ($\varepsilon\approx7000$ M^{-1} cm^{-1}).[20] The reason for the absorption spectral difference between [Fe(sal-pen)] and [Fe(salen)X] is unclear at present. It is likely that the phenolic tail incorporated into the salen moiety affects the electronic property of iron(III) ion in a manner different from a monodentate phenolic donor. It is notable that the spectrum of [Fe(sal-pen)] resembles those of catechol 1,2-dioxygenase[33] and protocatechuate 3,5-dioxygenase,[34] which show the CT band from tyrosinate to iron at $(22.0—21.7)\times10^3$ cm^{-1} ($\varepsilon\approx3000—4000$ M^{-1} cm^{-1}).

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