

Geometric Selectivity, Hydrogen-Bonding Interaction, and Solvatochromism of Bis[*N*-(aminoalkyl)salicylamidato(2-)]cobaltate(III)

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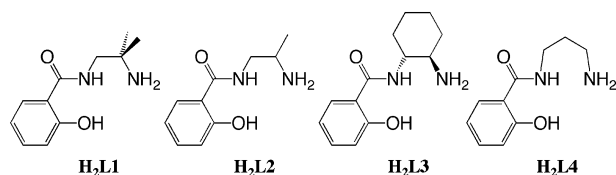
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Cobalt(III) complexes with *N*-(aminoalkyl)salicylamide dianions, L_n^{2-} ($n = 1-4$), have been prepared and their molecular and crystal structures have been determined. The geometric (*mer*- or *fac*-) selectivity of $[Co(L_n)_2]^-$ complexes was dependent on the number of the amine-amidato chelate ring member. Intermolecular homochiral hydrogen-bonds and solvatochromic behavior of the complexes were also observed.

Nitrogen-ligating amidate anions, $[RNC(O)R']^- \kappa N$, are classified as strong σ - and π -donors.¹ In addition, the capability of the uncoordinated amidate-O atom as a hydrogen-bonding acceptor is a key factor in many enzymatic systems,² and would be fascinating for construction of new functional materials.³ Hence, in combination with an aminoalkyl group that can act as a hydrogen-bonding donor upon coordination, transition-metal complexes with amine-amidato type chelate ligands which result from deprotonation of *N*-(aminoalkyl)amides would be good candidates for specific molecular recognition using multiple hydrogen-bonds.⁴ We are interested in such amine-amidato type ligands, particularly unsymmetrical tridentate ligands having an additional phenoxo donor group. Despite of their simple molecular structures, transition-metal complexes with *N*-(aminoalkyl)salicylamidates(2-) have not been widely investigated,^{4,5} although they have often been used as precursors for unsymmetrical tetradentate amidate-Schiff base complexes.^{3c} In this study, we deal with such tridentate ligands, L_n^{2-} ($n = 1-4$) shown in Scheme 1. In order to reveal their fundamental coordination and hydrogen-bonding behaviors, we have prepared and characterized their cobalt(III) complexes, $[Co(L_n)_2]^-$.

The ligands, H_2L_n ($n = 1-4$), were prepared by a reaction of phenyl salicylate and the appropriate diamines (1,2-diamino-2-methylpropane, 1,2-diaminopropane, *trans*-1,2-diaminocyclohexane, and 1,3-diaminopropane, respectively) in 2-propanol.^{3c,6} For H_2L_3 and H_2L_4 , other preparative procedures had been reported,^{2a,7} but the present method was much simpler and gave higher yields. In this method, the desired *N*-(aminoalkyl)salicylamides were precipitated from the reaction mixture due to their low solubility in 2-propanol, which prevents further reaction to give symmetric tetradentate diamides. The products collected by filtration were reasonably pure, even the unsymmetrical di-



Scheme 1. The neutral (doubly protonated) forms of the ligands used in this study.

amines were used (for H_2L_1 and H_2L_2).^{3c} In the preparation of H_2L_4 , if a mixture of methyl salicylate and 1,3-diaminopropane was refluxed without any solvent, then the intramolecular condensation of H_2L_4 took place to give a 2-hydroxyphenyl-substituted *N,N'*-propanediyl-bridged amidine,⁸ whose crystal structure and coordination behaviors will be reported elsewhere.

The cobalt(III) complexes bearing L_n^{2-} ($n = 1-4$) were prepared by addition of a stoichiometric amount of *t*-BuOK to a methanolic mixture of H_2L_n and $Co(OAc)_2 \cdot 4H_2O$ (or $CoCl_2 \cdot 6H_2O$) in the molar ratio of 2:1, followed by stirring the mixture in air, affording a gradual color change of the reaction solution.⁶ When the reaction was performed under a nitrogen atmosphere, no color change of the reaction solution was observed, indicating that air oxidation was necessary to form stable cobalt(III) complexes. The resulting complexes with L_1^{2-} and L_2^{2-} could be isolated as dark purple crystals of $K[Co(L_1)_2] \cdot CH_3OH$ (**1**) and $K[Co(L_2)_2] \cdot 5H_2O \cdot CH_3OH$ (**2**), respectively, by concentration of the reaction mixture and diffusion of diethyl ether vapor. In the cases of L_1^{2-} and L_3^{2-} complexes, cation exchange using PPh_4Br and recrystallization of the crude products from acetonitrile/diethyl ether deposited dark brown platelet crystals of $PPh_4[Co(L_1)_2] \cdot 1.5CH_3CN \cdot 2H_2O$ (**1P**) and purple block crystals of $PPh_4[Co(L_3)_2] \cdot 0.5CH_3CN$ (**3P**). It should be noted that, while both crystals of **1** and **1P** were deeply colored, their powdered samples showed different colors, as seen in their diffuse-reflectance spectra (Figure 1a).

The 1H NMR spectrum of the crude reaction product of $K[Co(L_1)_2]$ indicated the isolation of the sole product. The spectrum showed four kinds of resonances due to phenyl protons and three sets of two signals for methyl, methylene, and amine protons, respectively (Figure S1⁶), with a geminal coupling for the latter two sets. These spectral features suggest the chelate ring formation of amine-amidato moiety and the molecular symmetry of C_2 or C_i for the resulting $[Co(L_1)_2]^-$ complex. In addition, a remarkable solvent-dependency of the 1H NMR and UV-vis spectra of this complex salt **1** or **1P** was observed. As seen from Figure 1b, two absorption bands appearing in the

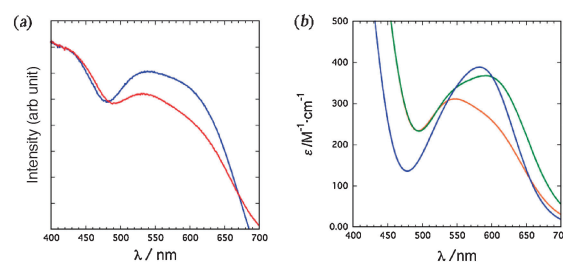


Figure 1. (a) Diffuse-reflectance spectra of **1** (blue) and **1P** (red). (b) Absorption spectra of **1P** in CH_3OH (blue), $CHCl_3$ (green), and CH_3CN (orange).

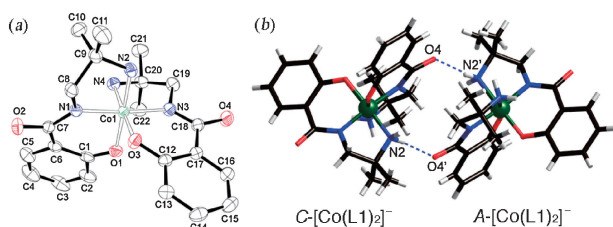


Figure 2. (a) ORTEP (50% probability level, H-atoms omitted) of the anionic part in $\text{PPh}_4[\text{Co}(\text{L}1)_2] \cdot 1.5\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ (**1P**). (b) A schematic view of the heterochiral dimer connected by double hydrogen-bonds in **1P**.

region of 500–650 nm became closer in energy and the band with longer wavelength became more intense in the order of $\text{CH}_3\text{CN} < \text{CHCl}_3 < \text{CH}_3\text{OH}$. Also, the difference in chemical shifts for two methylene resonances became larger in the same order (Figure S1⁶).

In order to interpret the color difference between crystals **1** and **1P** and the solvatochromic behavior observed in the complex salts, crystal structures of **1** and **1P** have been determined by X-ray analysis.⁹ It was revealed that both crystals consisted of the *mer*-isomer of $[\text{Co}(\text{L}1)_2]^-$ complex anion. The molecular structure of the anion in **1P** is shown in Figure 2a. Owing to the planarity of salicylamidato moiety in $\text{L}1^{2-}$, the tridentate ligand forming an aminoethylamidato five-membered chelate ring is sterically restricted to the *mer*-coordination mode. The *mer*-isomer is chiral, and a pair of *clockwise* (*C*-) and *anticlockwise* (*A*-) enantiomers is possible. The space group of the crystal **1P** is *P*1, indicating that the crystal is racemic. In this crystal structure, there are intermolecular hydrogen bonds between the coordinated amino (NH_2) groups and the amidato-O atoms, which form a hetero-chiral (*C*- and *A*-) dimer as illustrated in Figure 2b. In contrast, the crystal structure of $\text{K}[\text{Co}(\text{L}1)_2] \cdot \text{CH}_3\text{OH}$ (**1**) exhibited an explicit interaction between one of the amidate-O atoms and a K^+ cation, which was also surrounded by two coordinated phenoxo-O atoms and an O atom of the methanol of crystallization (Figure 3). The other amidato-O atom was hydrogen-bonded to an amino group of the neighboring complex anion. We expected that such an interaction with K^+ would make the amidato $\text{C}=\text{O}$ bond longer, and hence, the ligand-field strength of the amidato-N donor would be weakened. However, the $\text{C}=\text{O}$ and the coordination ($\text{Co}-\text{N}$) bond lengths in **1** did not differ much from those in **1P**.⁹ This is consistent with the almost unchanged transition energies observed in the range of 500 to 650 nm in the diffuse-reflectance spectra of **1** and **1P** (Figure 1a). Thus, the apparent color change of the crystals would originate not from the transition-energy shift, but from the intensity change of the absorption bands presumably due to the lowering of the molecular symmetry. Similarly, the solvent-dependency of the absorption spectrum of (**1** or) **1P** (Figure 1b) seems to be related to the acceptor numbers of the solvents,¹⁰ because the solvent molecules would interact with the amidato-O atom of the complex anion, likewise K^+ . At this moment, we cannot fully interpret the solvatochromic behavior of UV-vis and ¹H NMR spectra, but this result is an example of the importance of the uncoordinated amidate-O moiety in the chemical and physical properties of the amidato-N complexes.

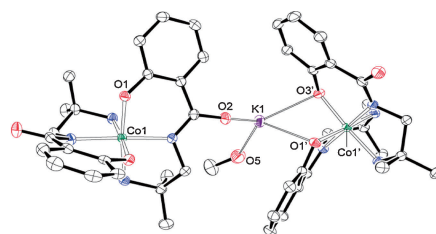


Figure 3. A perspective view illustrating the interaction of $[\text{Co}(\text{L}1)_2]^-$, K^+ , and CH_3OH in **1**.

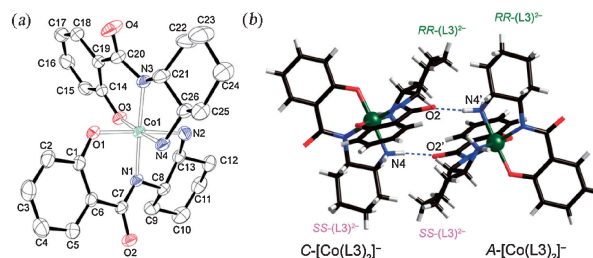


Figure 4. (a) ORTEP (50% probability level, H-atoms omitted) of the anionic part in $\text{PPh}_4[\text{Co}(\text{L}3)_2] \cdot 0.5\text{CH}_3\text{CN}$ (**3P**). (b) A schematic view of the heterochiral dimer connected by double hydrogen-bonds in **3P**.

The molecular structure of $[\text{Co}(\text{L}2)_2]^-$ in **2** (Figure S2⁶) is similar to that of $[\text{Co}(\text{L}1)_2]^-$ in **1**. Because we have used a racemic mixture of 1,2-diaminopropane ($=\text{pn}$) for the preparation of H_2L_2 , an equimolar mixture of *R*- and *S*- $\text{L}2^{2-}$ would be incorporated into the complex. Thus, $\text{C}-[\text{Co}(\text{R}-\text{L}2)_2]^-$, $\text{C}-[\text{Co}(\text{S}-\text{L}2)_2]^-$, and $\text{C}-[\text{Co}(\text{R}-\text{L}2)(\text{S}-\text{L}2)]^-$ diastereomers are possible (in addition to their *A*-enantiomers). The crystal structure analysis of **2** indicated a positional disorder for the methyl groups attached to the C atom next to the amine group over two possible positions.⁶ The ¹H NMR spectrum of **2** in CD_3OD was also indicative of a mixture of the above diastereomers. We also prepared a similar complex using enantiomerically pure *R*-pn. In this case it is expected to form only two isomers, $\text{C}-[\text{Co}(\text{R}-\text{L}2)_2]^-$ and $\text{A}-[\text{Co}(\text{R}-\text{L}2)_2]^-$, and the ¹H NMR spectrum of the products exhibited resonances due to the two complexes with almost equal intensities (Figure S3⁶). These facts suggest that there is no selectivity in the formation of bis($\text{L}2$)-type complexes, as far as their methyl substituents are concerned.

For the preparation of H_2L_3 and its complex, $[\text{Co}(\text{L}3)_2]^-$, we used a racemic mixture (*RR*- and *SS*-) of *trans*-1,2-diaminocyclohexane. Because of the stable diequatorial-chair conformation of the diaminocyclohexane ring, in addition to the planarity of the salicylamidato fragment, the tridentate amine-amidato-phenoxo ligand of $\text{L}3^{2-}$ would be restricted to the *mer*-configuration in the $[\text{Co}(\text{L}3)_2]^-$ complex. Similar to the $\text{L}2$ complex mentioned above, three diastereomers of *mer*- $\text{C}-[\text{Co}(\text{RR}-\text{L}3)_2]^-$, *mer*- $\text{C}-[\text{Co}(\text{SS}-\text{L}3)_2]^-$, and *mer*- $\text{C}-[\text{Co}(\text{RR}-\text{L}3)(\text{SS}-\text{L}3)]^-$ (and their *A*-enantiomers) are possible. The ¹H NMR spectrum of the crude products of $\text{K}[\text{Co}(\text{L}3)_2]$ (**3**) was indicative of the formation of three products in nearly equal ratios. However, the X-ray crystallographic analysis of its PPh_4 salt, $\text{PPh}_4[\text{Co}(\text{L}3)_2] \cdot 0.5\text{CH}_3\text{CN}$ (**3P**), revealed the specific crystallization of one of the products, *mer*- $\text{PPh}_4[\text{Co}(\text{RR}-\text{L}3)(\text{SS}-\text{L}3)]$ (Figure 4a). In this crystal heterochiral dimerization (Figure 4b) took place by the amine...amidato double hydrogen-bonds, as

similarly found in the crystal of **1P**. Interestingly, the hydrogen bonds are formed between the homochiral $L3^{2-}$ ligands (i.e., an amine group of $RR-L3^{2-}$ with an amidato-O of the neighboring $RR-L3^{2-}$ and the analogs of $SS-L3^{2-}$ ligands). In other words, the double hydrogen bonds between amine and amidato groups can recognize the chirality of the ligand itself and the chirality of the metal center, forming a selective homochiral/heterochiral aggregation. We have attempted to compare the formation energies of the three diastereomers (monomeric anions) by the DFT method. The results⁶ indicated that the X-ray-derived structure, $mer-C-[Co(RR-L3)(SS-L3)]^-$, is slightly more stable by 2.25 kcal mol⁻¹ than $mer-C-[Co(RR-L3)_2]^-$, but $mer-C-[Co(SS-L3)_2]^-$ is more stable by 3.31 kcal mol⁻¹ than the X-ray-derived structure. This fact also suggests the importance of the intermolecular hydrogen bonds.

Differing from the above-mentioned ligands, H_2L4 has a trimethylene group connecting the amine and amide donor groups, and this would give a different tendency to stabilize a specific geometric isomer. Aerobic reaction of $Co(OAc)_2 \cdot 4H_2O$, H_2L4 , and $t-BuOK$ (molar ratio of 1:2:4) in methanol at room temperature for 2 h gave a green solution, but ¹H NMR spectroscopy confirmed that this mixture contained at least two products. On stirring the mixture at room temperature for two weeks, or refluxing the mixture for 7 h, the reaction solution turned brown, and brown columnar crystals of $K[Co(L4)_2] \cdot 5H_2O$ (**4**) were deposited by concentration of the reaction solution, followed by diffusion of diethyl ether vapor. The crystal structure of **4** was determined by X-ray analysis. In the asymmetric unit of space group $P\bar{1}$ with $Z = 2$ there are two halves of complex anions, which are similar in their molecular structures (Figure 5). Both complex anions have an inversion center at the Co atom with *fac*-configuration of $L4^{2-}$ ligands (*fac*- C_i -isomer). This is an explicit difference from the corresponding complexes with Ln^{2+} ($n = 1-3$) in the above, and presumably due to the six-membered amine–amidato chelate ring. The C8 (and C18) atom has a conformational restriction from the planar salicylamidato moiety, but the six-membered ring is flexible enough to form a stable chair-like conformation with the amine-N atom in the *cis*-position to the phenoxo-O atom.

In order to compare the stability of the possible geometric isomers for $[Co(L4)_2]^-$, we have calculated the formation energies of a *mer*- and five *fac*-isomers by the DFT method. The results indicated two stable isomers; the most favorable one was the X-ray-derived *fac*- C_i -isomer, and the secondary stable one (4.29 kcal mol⁻¹ above) was the *fac*- C_2 -*trans*(NH_2)-isomer.⁶ Other isomers were higher in energy more than 10 kcal mol⁻¹. Thus, it was suggested that the isomers with *trans*(NH_2)-configuration would be energetically favorable, presumably due to the distribution of the ligand negative charges over the equatorial plane. From these calculations, we presumed that in the preparation of $[Co(L4)_2]^-$ the green intermediate formed kinetically would be the *fac*- C_2 -*trans*(NH_2)-isomer, which converted gradually to the thermodynamically more stable *fac*- C_i -isomer.

In summary, the amine–amidato–phenoxo tridentate ligands exhibited geometric selectivity on coordination, owing to the planarity of salicylamidate moiety and the number of chelate ring members of aminoalkylamidate. The ligand, $L4^{2-}$, with a 3-aminopropyl substituent afforded the *fac*- C_i -isomer of $[Co(L4)_2]^-$, while the other ligands ($L1^{2-}$ – $L3^{2-}$) forming a five-membered amine–amidato chelate ring gave the corresponding

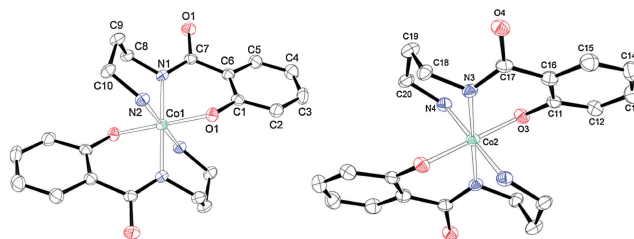


Figure 5. ORTEPs (50% probability level, H-atoms omitted) of two crystallographically independent anionic complexes in $K[Co(L4)_2] \cdot 5H_2O$ (**4**).

mer-isomer exclusively. The X-ray analyses revealed that the coordinated amino ($-NH_2$) group and the uncoordinated amidato-O atom were acting as a hydrogen-bonding donor and an acceptor, respectively. With these hydrogen-bonds, homochiral aggregation between the tridentate ligands was achieved in the $L3^{2-}$ complex **3P**, forming a heterochiral dimer consisting of a pair of *C*- and *A*-enantiomers. This kind of chiral recognition using hydrogen-bonds of amine–amidato moieties may be applicable for the selective molecular recognition of nucleobases or nucleosides. Such studies using complex fragments with a *N*-(aminoalkyl)salicylamide dianion are now in progress.

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References and Notes

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