# The Steric Requirements of *N,N'*-Bis(salicylidene)-2-aminobenzylamines on Metal Chelate Formation

Hajime Kanatomi, Yoichi Demura, and Ichiro Murase
*Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810*

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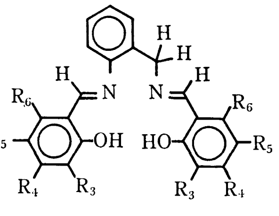
Copper(II), Ni(II), Co(II), Zn(II), and Be(II) chelates of *N,N'*-bis(salicylidene)-2-aminobenzylamine and its methyl and dimethyl salicylidene derivatives have been prepared and characterized. According to the molecular models, the ligands are favorable to tetrahedral arrangement on complex formation. The spectral and magnetic properties revealed that all the Co(II) and some of the Cu(II) chelates were pseudo-tetrahedral, while the Ni(II) and other Cu(II) chelates were square-planar, with a considerable angle strain. This ligand property is somewhat inconsistent with the conclusion derived from *N,N'*-bis(salicylidene)polymethylenediamine chelates, in which the trimethylene analogue could not take a pseudotetrahedral arrangement around a metal ion. The difference in stereochemistry between the two ligands with the same number of bridging carbon atoms will be discussed on the basis of the flexibility and the steric requirement of the central chelate ring.

Several reports have revealed that metal chelates of *N,N'*-bis(salicylidene)polymethylenediamine change in their stereochemistry with an expansion of the central chelate ring size.[1–7] *N,N'*-Bis(salicylidene)ethylenediamine imposes a square-planar structure for transition-metal chelates due to the steric requirement of the ligand in which the central chelate ring was five-membered. On the other hand, *N,N'*-bis(salicylidene)trimethylenediamine forms a high-spin Co(II) chelate with a structure of a very flattened tetrahedron,[5] and in the square-planar Cu(II) and Ni(II) chelates a significant decrease of the apparent ligand field strength is observed relative to the corresponding ethylenic chelates.[1] The fact that the Co(II) chelate could not take a pseudotetrahedral geometry was explained by the insufficient flexibility of the six-membered central chelate ring consisting of a trimethylene chain.



$LH_2$

$LaH_2$: $R_3=R_4=R_5=R_6=H$
$LbH_2$: $R_5=CH_3, R_3=R_4=R_6=H$
$LcH_2$: $R_3=R_5=CH_3$, $R_4=R_6=H$
$LdH_2$: $R_4=R_6=CH_3$, $R_3=R_5=H$

In this report, *N,N'*-bis(salicylidene)-2-aminobenzylamine (abbreviated $LaH_2$ hereafter) and its 5-methyl, 3,5-dimethyl, and 4,6-dimethylsalicylidene derivatives ($LbH_2$, $LcH_2$, and $LdH_2$ respectively) are chosen as quadridentate ligands in order to study the stereochemistry of the metal chelates with regard to the effect of the central chelate ring flexibility. When these ligands combine with metal ions to form three condensed chelate rings, the central ring is six-membered, as is the trimethylene analogue. The flexibility of the ring is, however, suppressed much more than that of the trimethylene analogue because the two carbon atoms of the benzene ring are constituents of the central chelate ring. Molecular models suggest that a square-planar configuration around a metal ion is difficult without a deformation of bond angles; otherwise, the two phenolic oxygen may overlap on the same plane. A favorable arrangement is one which is distorted from square-planar bending at the flexible methylenic linkage of the central chelate ring. In the derivatives, the methyl groups will exert an electronic influence on the ligand-field strength through the donor atoms; this may affect the chelating tendencies or the metal chelate configuration.

## Experimental

The infrared spectra were determined in potassium bromide disks by means of a Hitachi EPI-S2 spectrophotometer, while the electronic spectra were measured with a Hitachi EPS-3T spectrophotometer. The PMR spectra were recorded at 60 MHz in $CDCl_3$ with a Hitachi Model R-24 NMR spectrometer, and the chemical shifts are quoted as ppm values relative to tetramethylsilane. The magnetic moments were measured at room temperature by means of a recording magnetometer specially designed by Hirakawa.[14]

*Preparation of the Schiff Bases ($LaH_2$, $LbH_2$, $LcH_4$, and $LdH_2$).* A mixture of 0.02 mol of salicylaldehyde (for $LaH_2$) and 0.01 mol of 2-aminobenzylamine in 30 ml of methanol was refluxed for 20 min. The yellow crystals which resulted from cooling the reaction mixture in an ice bath were recrystallized from methanol. For $LbH_2$, $LcH_2$, and $LdH_2$, 5-methylsalicylaldehyde, 3,5-dimethylsalicylaldehyde, and 4,6-dimethylsalicylaldehyde were reacted respectively in place of salicylaldehyde. The melting points were: $LaH_2$, 82—83.5 °C; $LbH_2$, 118—120 °C; $LcH_2$, 105—106.5 °C; $LdH_2$, 123—125.5 °C.

*Preparation of the 1:1 Chelates.* A warm methanol solution of the Schiff base was mixed with an equimolar amount of a metal acetate[Cu(II), Ni(II), Co(II), and Zn(II)] or beryllium nitrate in a minimum amount of warm methanol, after which the mixture was refluxed for 20 min. The crystals of the desired chelates were deposited on refluxing or after cooling the reaction mixture. They were collected by filtration, recrystallized from an ethanol–chloroform mixture if necessary, and dried at 90 °C for 8 hr *in vacuo*. The yield was 70—80% for every chelate. The Cu(II) chelate of Lb prepared in this procedure consisted of brown crystals carrying 1/2 mol of water.

*Preparation of the Green Cu(II) Chelate(LbCu).* To each mol of *o*-aminobenzylamine and Cu(II)-acetate in a minimum amount of hot methanol, we added a slight excess of double molar 5-methylsalicylaldehyde in methanol, after which the mixture was heated on a water bath for 30 min. After the solution had stood overnight at room temperature, the dark green crystals which resulted were filtered off, washed with a small amount of methanol, and dried at 90 °C *in vacuo*.

*Preparation of the 1: 2 Ni(II) Chelates.* Although the reaction of $LaH_2$ or $LdH_2$ with the Ni(II) ion under the conditions described above inevitably afforded the 1 : 2 chelates, they were best prepared by reacting the ligands with a double amount of the metal ion. The reaction was carried out with Ni(II)-acetylacetonate in benzene for $LaH_2$ and with Ni(II)-acetate in dimethylformamide for $LdH_2$. The chelates were crystallized out by heating the reaction mixture; they were filtered after cooling, washed with methanol, and dried at 90°C *in vacuo*.

The results of the elemental analyses of the free ligands and the metal chelates are summarized in Table 1.

TABLE 1. ELEMENTAL ANALYSES OF THE SCHIFF BASES AND THEIR METAL CHELATES

| Compound | Formula | Found (Calcd) C% | H% | N% |
|---|---|---|---|---|
| $LaH_2$ | $C_{21}H_{18}N_2O_2$ | 76.40 | 5.45 | 8.49 |
| | | (76.34 | 5.49 | 8.48) |
| LaCo | $C_{21}H_{16}N_2O_2Co$ | 65.05 | 4.35 | 7.27 |
| | | (65.12 | 4.16 | 7.23) |
| LaZn | $C_{21}H_{16}N_2O_2Zn$ | 63.25 | 4.24 | 6.83 |
| | | (64.06 | 4.10 | 7.12) |
| LaBe | $C_{21}H_{16}N_2O_2Be$ | 74.30 | 4.88 | 8.18 |
| | | (74.76 | 4.78 | 8.30) |
| $(LaH)_2Ni$ | $C_{42}H_{34}N_4O_4Ni$ | 70.37 | 4.82 | 7.64 |
| | | (70.31 | 4.78 | 7.80) |
| $LbH_2$ | $C_{23}H_{20}N_2O_2$ | 77.24 | 6.20 | 7.81 |
| | | (77.07 | 6.19 | 7.81) |
| LbCu | $C_{23}H_{18}N_2O_2Cu$ | 65.60 | 4.77 | 6.71 |
| | | (65.78 | 4.80 | 6.67) |
| LbCu $1/2H_2O$ | $C_{23}H_{19}N_2O_{2.5}Cu$ | 64.65 | 4.81 | 6.59 |
| | | (64.40 | 4.93 | 6.53) |
| LbNi | $C_{23}H_{18}N_2O_2Ni$ | 66.21 | 4.83 | 6.67 |
| | | (66.54 | 4.86 | 6.75) |
| LbCo | $C_{23}H_{18}N_2O_2Co$ | 65.92 | 4.88 | 6.58 |
| | | (66.51 | 4.85 | 6.75) |
| $LcH_2$ | $C_{25}H_{26}N_2O_2$ | 77.42 | 6.73 | 7.29 |
| | | (77.69 | 6.78 | 7.25) |
| LcCu | $C_{25}H_{24}N_2O_2Cu$ | 66.89 | 5.53 | 6.24 |
| | | (67.02 | 5.40 | 6.25) |
| LcNi | $C_{25}H_{24}N_2O_2Ni$ | 67.88 | 5.49 | 6.37 |
| | | (67.75 | 5.46 | 6.32) |
| LcZn | $C_{25}H_{24}N_2O_2Zn$ | 66.68 | 5.39 | 6.25 |
| | | (66.75 | 5.38 | 6.23) |
| $LdH_2$ | $C_{25}H_{26}N_2O_2$ | 77.52 | 6.78 | 7.17 |
| | | (77.69 | 6.78 | 7.25) |
| LdCu | $C_{25}H_{24}N_2O_2Cu$ | 66.88 | 5.36 | 6.22 |
| | | (67.02 | 5.40 | 6.25) |
| LdCo | $C_{25}H_{24}N_2O_2Co$ | 67.45 | 5.49 | 6.29 |
| | | (67.72 | 5.46 | 6.32) |
| LdZn | $C_{25}H_{24}N_2O_2Zn$ | 66.77 | 5.38 | 6.12 |
| | | (66.75 | 5.38 | 6.23) |
| $(LdH)_2Ni$ | $C_{50}H_{30}N_4O_4Ni$ | 72.09 | 6.06 | 6.84 |
| | | (72.38 | 6.08 | 6.75) |

## Results and Discussion

The infrared spectra of the free ligands reveal a difference between the two azomethine bondings. Each ligand shows two absorption bands in the 1600 cm$^{-1}$ region, as is illustrated in Table 2. The higher one can be assigned to the double bond of the CH=N-($CH_2$) stretching vibration, and the lower one, to the CH=N-(phenyl) stretching vibration, by analogy with the azomethine frequencies of salicylidenebenzylamine (1634 cm$^{-1}$)[8] and salicylideneaniline (1625 cm$^{-1}$)[9] respectively. In the case of $LdH_2$, only one band appeared, at 1625 cm$^{-1}$; this is because the bond order of the CH=N-($CH_2$) was lowered by the electronic effect of the substituted methyl groups and the absorption overlapped with the CH=N-(phenyl) band.

TABLE 2. C=N STRETCHING FREQUENCIES OF *N,N'*-BIS-(SALICYLIDENE)-2-AMINOBENZYLAMINES AND THEIR 1 : 1 METAL CHELATES (cm$^{-1}$)

| Ligand | Metal | | | | | |
|---|---|---|---|---|---|---|
| | $H_2$ | Cu(II) | Ni(II) | Co(II) | Zn(II) | Be(II) |
| La | 1636 | * | * | 1608 | 1625 | 1632 |
| | 1625 | | | | 1613 | 1618 |
| Lb | 1641 | 1627[a] | 1628 | 1624 | — | — |
| | 1630 | | | | | |
| Lc | 1633 | 1627 | 1627 | * | 1624 | — |
| | 1629 | | | | 1611 | — |
| Ld | 1625 | 1607 | * | 1604 | 1610 | — |

*: no chelate was isolated. —: no reaction was examined. a): anhydrous green chelate.

TABLE 3. PMR DATA RECORDED AT 60 MHz IN $CDCl_3$ (ppm VALUES RELATIVE TO INTERNAL TMS)

| Compound | CH=N-($CH_2$) | CH=N-(phenyl) | OH |
|---|---|---|---|
| $LaH_2$ | 8.63 | 8.49 | 13.10 |
| $LbH_2$ | 8.50 | 8.36 | 12.82 |
| $LcH_2$ | 8.48 | 8.33 | 13.05 |
| $LdH_2$ | 8.86 | 8.72 | 13.41 |

The PMR spectra exhibit two peaks arising from different azomethine protons. The chemical shifts of the two pairs are about 0.15 ppm different, as may be seen in Table 3; the one at the higher magnetic field belongs to the CH=N-($CH_2$) proton, while the lower one is due to the CH=N-(phenyl) proton. This assignment is supported by analogy with the azomethine PMR of salicylidenebenzylamine (8.23 ppm)[8] and of salicylideneaniline (8.50 ppm).[9] The methyl groups *ortho* and *para* to the azomethine groups increase, and the *meta* methyls decrease, the deshielding effect of the phenyl ring current. The OH proton resonance appears as a broad band; the band broadening is attributed to the proton exchange which is taking place at a high rate between the two OH bondings. The chemical shifts shown in Table 3 indicate the mean value due to the two OH protons. Judging from these values, the *para* and/or *ortho* methyl derivatives ($LbH_2$ and $LcH_2$) have more shielded OH protons than the nonsubstituted one ($LaH_2$), while that of the *meta* derivative ($LdH_2$) is less shielded.

Metal chelates isolated as pure crystals with the 1 : 1 metal-ligand composition are listed in Table 2, which shows the CH=N stretching frequencies. It may be seen that the two CH=N absorptions shift to lower frequencies on complex formation and that many of them are overlapped into one band. As is to be expected from the molecular model and from the fact that Cu(II) and Ni(II) chelates could not be isolated with La, the ligand is not likely to have a square-planar arrangement. Furthermore, the tetrahedrally distorted arrangement seems most likely for La because the ligand affords chelates with Zn(II) and Be(II) ions, which are believed to prefer to form tetrahedral complexes. It was shown that, in the case of *N*,*N*′-bis(salicylidene)-polymethylenediamine, the tetramethylene bridge was the smallest chain which would allow the four donor atoms to occupy truly tetrahedral sites around a metal ion. Since beryllium would not tolerate even a slight departure from tetrahedral stereochemistry, the trimethylene derivative did not form a 1:1 complex with the Be(II) ion, but instead gave a 1:2 complex in which the ligand functioned as a bidentate chelate.[3] This explanation is, however, inconsistent with the present finding, where La could form a 1:1 Be(II) chelate despite having a less flexible three-carbon bridge.

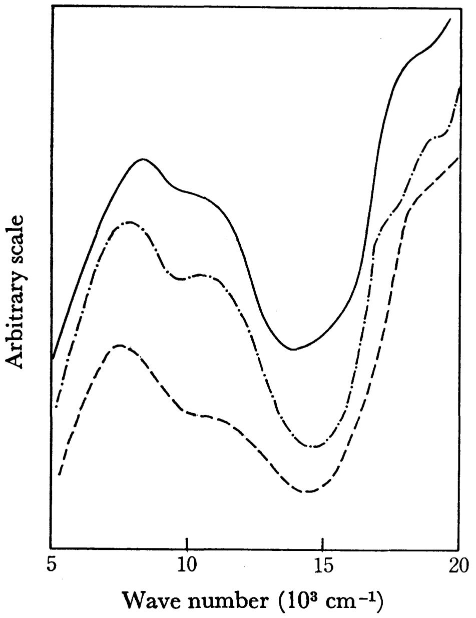


Fig. 1. Electronic reflectance spectra of La-Co(II), -·-·-; Lb-Co(II), ——; Ld-Co(II), ----.

With La, Lb, and Ld, 1:1 Co(II) chelates were isolated as orange-red crystals. The spectral patterns of these chelates, shown in Fig. 1, are quite similar to that obtained for bis(*N*-phenylsalicylaldiminato)cobalt(II), which exhibited absorption bands at 7600, 10700, 16700 (shoulder), and 19300 cm$^{-1}$ in the near-infrared and visible region[10] and which has been shown by crystallographycal evidence to have a pseudotetrahedral geometry.[11] The magnetic moment of the Co(II) chelate with La was $\mu_{\mathrm{eff}}=4.2$ B.M. ($\chi=18.69\times10^{-6}$ egsu$^{-1}$) at room temperature; this is in agreement with those expected for tetrahedral Co(II) complexes.[12] On the bases of these similarities in spectral and magnetic properties with complexes of a known structure, it may be concluded that these Co(II) chelates adopt the pseudotetrahedral geometry around the metal ion. In *N*,*N*′-bis(salicylidene)polymethylenediaminatocobalt(II), those with four to six bridging methylene groups were found to be pseudotetrahedral; however, the trimethylene derivative showed an anomalous electronic spectrum and was assumed to be a highly flattened tetrahedron on the basis of the magnetic high-spin character (4.56 B.M.).[5]

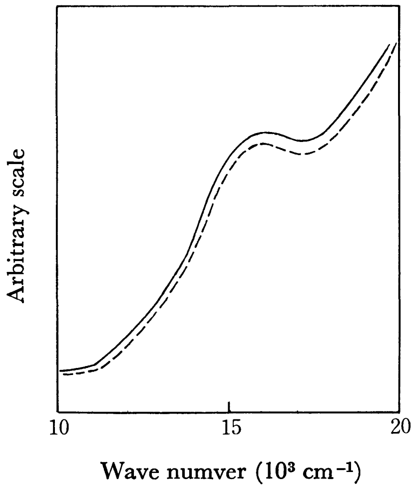


Fig. 2. Electronic reflectance spectra of Lb-Ni(II), ----; Lc-Ni(II), ——.

Nickel(II) chelates with a 1:1 metal-ligand composition were isolated with Lb and Lc. It is seen the presence of *para* and/or *ortho* methyl groups, which increase the electron density of the phenolic oxygens, is necessary for the chelate formation. These chelates were diamagnetic and exhibited *d-d* bands at 15900 cm$^{-1}$ for the Lb-chelate and at 16000 cm$^{-1}$ for the Lc-chelate in their reflectance spectra; the patterns are shown in Fig. 2. It thus appears that these chelates have a basically planar configuration, though it is not necessarily strictly planar. In *N*,*N*′-bis(salicylidene)polymethylenediaminatonickel(II), the planar structures were retained even when the bridging methylene groups increased to 3, 4, or 5, while a significant decrease in the apparent ligand-field strength was observed with an increase in the number of methylene groups.[1,7] The bands for the present Ni(II) chelates were in lower energy region than those of the tetra- and pentamethylene complexes; this may be attributed to the distortion of the bond angles produced when the ligand molecules are forced to adopt the square-planar configuration on the metal-chelate formation.

The PMR spectra of Ni(II) and Zn(II) chelates with Lc are shown in Fig. 3. It is interesting that the separate PMR peaks of the CH=N–(CH$_2$) and the CH=N–(phenyl) protons in the free ligand become a single peak in the Ni(II) chelate and shift to a higher magnetic field (7.34 ppm). Therefore, the two azomethine linkages are equivalent in the metal chelate rings; this agrees with the fact that the azomethine stretching vibration appears as a single band. On the contrary, the two PMR peaks in the corresponding Zn(II) chelate are merely shifted to the respective

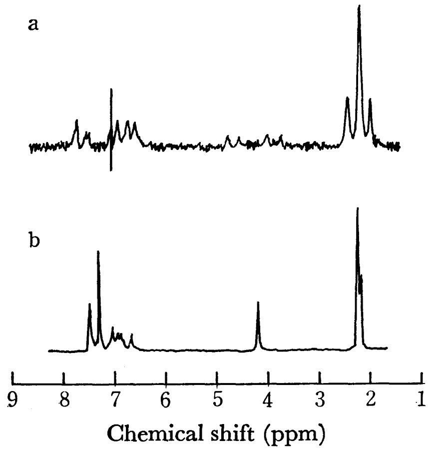


Fig. 3. PMR spectra of Lc-Zn(II) (a) and Lc-Ni(II) (b).

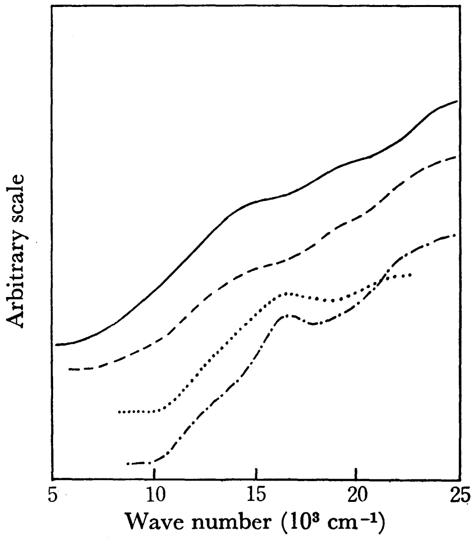


Fig. 4. Electronic reflectance spectra of Lb-Cu(II) (green), ······; Lb-Cu(II) (brown), ----; Lc-Cu(II), -·-·-; Ld-Cu(II), ——.

higher magnetic fields (7.87 and 7.77 ppm), indicating that each azomethine retains a different character in this case. Furthermore, the bridging methylene protons, which appear as a single peak at 4.76 ppm in the free ligand, shift to 4.28 ppm in the Ni(II) chelate, while it splits into an AB pattern centered at 4.30 ppm ($J_{AB}$=8 Hz) in the Zn(II) chelate. The different features; in the methylene PMR can be explained in terms of the central chelate ring flexibility when it is retained at the methylenic linkage in the Ni(II) chelate and fixed in the Zn(II) chelate. The characteristics of the ring flexibility probably arise from the difference in the configuration that is, the Ni(II) chelate is square-planar, while the Zn(II) chelate is tetrahedral.

La and Ld do not form 1:1 Ni(II)-chelates, but instead form 1:2 complexes in which these ligands function as a bidentate chelate. The presence of the uncoordinated salicylaldimino moiety in each ligand molecule is evidenced by the presence of a free OH group which exhibits a broad and weak infrared absorption around 2700 cm$^{-1}$. To distinguish the coordination site of the molecule, the CH=N stretching vibration were compared with the corresponding free ligand; however, they appeared as one rather broad band at 1618 cm$^{-1}$ in $(LaH)_2Ni$ and at 1608 cm$^{-1}$ in $(LdH)_2Ni$. Therefore, it was not clear that either CH=N–($CH_2$) or CH=N–(phenyl) nitrogen coordinated to the metal ion. The reflectance spectral patterns are typical for a square-planar Ni(II) complex exhibiting one *d-d* band at 16000 cm$^{-1}$ in the La-complex and at 16400 cm$^{-1}$ in the Ld-complex.

Copper(II) chelates were isolated with Lb, Lc, and Ld. La could not be a chelate ligand; they must be due to an insufficient electron density of the donor atoms in the same sense as are the Ni(II) chelates. It should be noted that the chelate with Ld was brown and that with Lc was green, while Lb gave chelates of both color types, of which the brown one contained 1/2 mol of water. The difference in color was apparent in their reflectance spectral patterns, as may be seen in Fig. 4. The green chelates show a distinct absorption maximum at 16200 cm$^{-1}$ in Lb-Cu(II) and 16400 cm$^{-1}$ in Lc-Cu(II), with a shoulder both around 13500 cm$^{-1}$, while the brown chelates exhibit absorption only as a shoulder or broad band around 15000 cm$^{-1}$. According to the criteria established by several investigators with regard to the Cu(II) chelates of bissalicylaldimines,[13] these types of absorptions are a result of tetrahedral distortion. The difference in the spectral patterns between the green and the brown chelates depends on the degree of distortion from a square-planar configuration; the green chelates are essentially square-planar, while the brown chelates are pseudotetrahedral.

In the present Cu(II) chelates, the degree of distortion may be attributed to the degree of the ligand-field strength, because the only structural difference in these ligands is in the presence of the methyl groups at the salicylidene moieties, which exert no steric effect on the chelate configuration. A relatively high electron density at the oxgen atoms, which is achieved by the electronic effect of *ortho* and *para* methyl groups, seems to be necessary to enforce the planar configuration on the chelate, as in the case of Lc. The ligand-field strength of Lb is likely to be intermediate in taking a planar or pseudotetrahedral arrangement, because it can from chelates of either type, depending upon the reaction conditions. However, this argument is partly hypothetical, since the role of the 1/2 mol of water has not been made clear.

## Conclusion

In *N,N'*-carbon-bridging bissalicylaldimine derivatives, the three carbon-chain compounds are not necessarily unfavorable for tetrahedral arrangement around a particular metal ion. The stereochemistry of the metal chelates is governed not only by the steric requirement of the metal ion, but also by the steric preference of the bridging carbon linkages in addition to the chain flexibility. This has been evidenced by the present investigation, where *N,N'*-bis(salicylidene)-2-aminobenzylamines formed tetrahedral 1:1 chelates with Be(II) and Co(II) ions which were impossible with the trimethylene analogue. Since a Ni(II) ion enforced a square-planar coordination on the ligands, a decrease in the ligand-field strength was observed and the derivatives with insufficient donor powder could not form a 1 : 1 chelate. In the Cu(II) chelates, the degree of tetrahedral distortion depended upon the donor power in each ligand. It may tentatively be considered that Lb is in a boundary condition in taking a planar or pseudotetrahedral arrangement around a Cu(II) ion.

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