A Tetrahedral Zinc(II) Complex of *N*-(*R*)-1-Phenylethylsalicylideneimine. Structural and Circular Dichroism Spectral Investigations on Stereoselectivity†

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The stereoselectivity of bis[*N*-(*R*)-1-phenylethylsalicylideneiminato]zinc(II) has been studied by means of single-crystal *X*-ray analysis and circular dichroism (c.d.) spectra. The complex crystallizes in space group $P2_12_12_1$ with a = 17.738(4), b = 29.632(9), c = 9.968(2) Å, and Z = 4. The unit cell is comprised of four units each containing two complex molecules (A and B). Each molecule adopts a nearly tetrahedral structure with two bidentate ligands; the dihedral angle defined by the two chelate rings is 81.7° for molecule A and 84.9° for molecule B. The absolute configuration along the pseudo-C_2 axis is Λ for both molecules. Based on the *X*-ray analysis it is suggested that intramolecular non-covalent interactions between the chiral N-substituent and the adjacent chelate ring give rise to stereoselectivity and the Λ configuration around the metal ion. The c.d. couplet (+and − signs) induced at the azomethine π–π* transition at around 27 000 cm^{-1} is discussed with respect to the absolute configuration and in comparison with the spectra of related Schiff-base complexes.

It is known[1] that non-covalent interactions often occur between ligands within a metal complex, giving rise to significant effects upon the stability and stereochemistry. In previous papers[2] we have shown that such intramolecular non-covalent interactions are highly effective for controlling configurations of both inert and labile metal complexes, whereas configuration control of labile metal complexes is otherwise difficult. Such sterically controlled complexes are of particular importance in view of the development of new stereoselective reactions.[3]

Tetrahedral or pseudo-tetrahedral complexes with two unsymmetrical bidentate chelates are enantiomeric, affording the Δ and Λ absolute configurations with respect to the C_2 axis of the molecule (see Figure 1). The enantiomers, however, are hardly resolved because tetrahedral complexes are generally labile, with a few exceptions.[4] When a chiral residue is introduced into a bidentate chelate its tetrahedral complexes are diastereomeric with respect to the central metal and the chiral residue, *i.e.* Δ(1,1) and Λ(1,1) [or Δ(d,d) and Λ(d,d)]. Previously we studied the stereoselectivity of bis(*N*-L-menthylsalicylideneiminato)metal(II) complexes (M = Co, Cu, or Zn) and homologues.[5] The tetrahedral cobalt(II) and zinc(II) complexes and pseudo-tetrahedral copper(II) complexes showed circular dichroism (c.d.) bands of significant intensity in the visible region, indicating the predominant formation of one of the diastereomers. The preferred absolute configuration was inferred as Λ from the c.d. pattern induced at the azomethine π–π* transition in comparison with the pattern for *N,N'*-propane-1,2-diylbis(salicylideneiminato)zinc(II).[6] The operation of non-covalent interligand interactions in these complexes was suggested by ^{1}H n.m.r. spectra. However, no direct evidence based on single-crystal *X*-ray analysis has been obtained so far.

In order to gain further insight into the stereoselectivity of tetrahedral salicylideneimine complexes in view of intramolecular non-covalent interactions, in this study we have determined the crystal structure of bis[*N*-(*R*)-1-phenylethylsalicylideneiminato]zinc(II) by single-crystal *X*-ray analysis. Further, the c.d. couplet induced at the azomethine π-π* transition has been studied in comparison with those of related complexes, in the hope of obtaining a correlation between the c.d. pattern and the absolute configuration around the central ion.

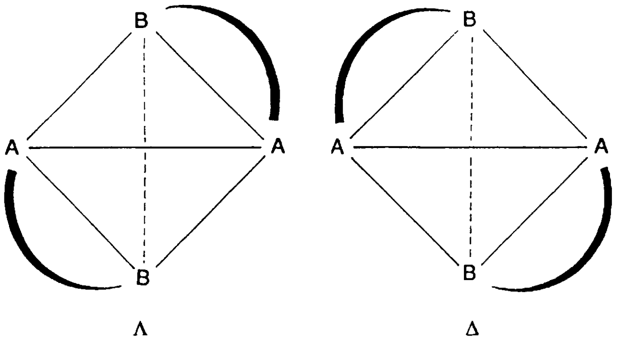

Figure 1. The two absolute configurations (Λ and Δ) for tetrahedral complexes

Experimental

Materials.—All chemicals were of reagent grade and were used as commercially obtained.

Preparation of Bis[N-(R)-1-*phenylethylsalicylideneiminato*]-*zinc*(II).—An ethanolic solution of (*R*)-1-phenylethylamine (0.48 g) and salicylaldehyde (0.48 g) was refluxed for 2 h. To this were added powdered $NaHCO_3$ (0.34 g) and zinc(II) acetate dihydrate (0.44 g), and the mixture was refluxed for 2 h then allowed to stand overnight. The resulting colourless crystals were separated and recrystallized from ethanol (Found: C, 69.85; H, 5.55; N, 5.45. Calc. for $C_{30}H_{28}N_2O_2Zn$: C, 70.10; H, 5.50; N, 5.45%).

Measurements.—Elemental analyses of C, H, and N were obtained at the Elemental Analysis Service Centre, Kyushu University. Electronic spectra in the region 40 000—12 500 cm^{-1} were recorded on a Shimadzu MPS-2000 spectrometer in

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Positional parameters (× 10^4) of the complex with estimated standard deviations (e.s.d.s) in parentheses

	Molecule A			Molecule B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Zn	6 187(1)	4 495(1)	8 089(2)	2 626(1)	3 514(1)	8 778(2)
O(1)	6 245(7)	5 105(4)	7 320(13)	3 160(6)	3 732(3)	7 243(11)
O(2)	6 468(7)	3 999(4)	6 999(14)	3 234(7)	3 493(4)	10 315(12)
N(1)	6 940(7)	4 605(4)	9 522(15)	1 838(7)	4 000(4)	8 861(14)
N(2)	5 116(6)	4 313(5)	8 396(17)	2 456(7)	2 850(3)	8 694(13)
C(1)	6 384(10)	5 457(6)	8 134(23)	2 920(7)	4 067(5)	6 468(12)
C(2)	6 065(10)	5 866(6)	7 631(25)	3 299(10)	4 142(6)	5 326(18)
C(3)	6 201(12)	6 252(6)	8 450(31)	3 098(10)	4 456(7)	4 355(19)
C(4)	6 646(13)	6 227(6)	9 548(28)	2 463(11)	4 726(6)	4 621(16)
C(5)	6 920(13)	5 851(5)	9 950(25)	2 068(10)	4 664(5)	5 776(17)
C(6)	6 801(10)	5 437(6)	9 304(20)	2 268(8)	4 321(4)	6 724(15)
C(7)	7 102(9)	5 021(7)	9 891(19)	1 805(9)	4 294(5)	7 875(16)
C(8)	7 354(11)	4 258(7)	10 234(22)	1 324(11)	4 059(6)	9 999(17)
C(9)	7 902(11)	4 029(7)	9 301(28)	1 784(14)	4 185(7)	11 231(21)
C(10)	6 815(10)	3 942(6)	10 886(17)	840(10)	3 638(5)	10 163(17)
C(11)	6 416(12)	3 599(6)	10 236(23)	1 104(11)	3 277(7)	10 898(21)
C(12)	5 910(14)	3 343(6)	10 909(24)	670(12)	2 904(7)	11 044(21)
C(13)	5 833(12)	3 391(8)	12 221(25)	−31(11)	2 876(7)	10 522(27)
C(14)	6 225(15)	3 741(9)	12 894(26)	−319(10)	3 228(8)	9 818(24)
C(15)	6 700(12)	3 989(7)	12 223(24)	118(10)	3 616(6)	9 662(25)
C(16)	6 053(11)	3 627(5)	6 846(20)	3 293(8)	3 153(6)	11 170(16)
C(17)	6 395(13)	3 253(6)	6 178(20)	3 682(11)	3 211(7)	12 369(20)
C(18)	5 981(14)	2 866(6)	5 945(21)	3 742(11)	2 861(8)	13 311(19)
C(19)	5 226(13)	2 835(6)	6 249(21)	3 422(14)	2 447(7)	13 031(25)
C(20)	4 917(12)	3 199(6)	6 908(26)	3 049(12)	2 393(5)	11 946(22)
C(21)	5 320(9)	3 590(5)	7 223(21)	2 975(9)	2 728(5)	10 931(19)
C(22)	4 883(9)	3 926(6)	7 952(24)	2 599(9)	2 596(5)	9 721(18)
C(23)	4 536(8)	4 593(6)	9 009(22)	2 126(10)	2 614(7)	7 478(19)
C(24)	4 368(11)	4 966(7)	7 999(27)	2 774(15)	2 404(8)	6 687(25)
C(25)	4 815(9)	4 762(6)	10 398(22)	1 653(9)	2 933(5)	6 691(16)
C(26)	5 068(10)	5 217(6)	10 568(26)	1 939(11)	3 157(6)	5 619(19)
C(27)	5 318(14)	5 324(8)	11 865(28)	1 479(14)	3 441(7)	4 841(22)
C(28)	5 278(12)	5 052(8)	12 934(29)	739(13)	3 478(7)	5 132(25)
C(29)	5 022(15)	4 628(8)	12 744(28)	463(12)	3 227(8)	6 215(28)
C(30)	4 773(12)	4 475(6)	11 486(26)	913(11)	2 979(6)	6 979(21)

chloroform at room temperature. C.d. spectra were recorded on a JASCO J-600 spectropolarimeter at room temperature; spectra of solid samples were determined on KBr discs.

X-Ray Structural Analysis.—Single crystals of the complex were grown by slow crystallization from ethanol and a crystal with approximate dimensions 0.5 × 0.4 × 0.6 mm was used for the *X*-ray diffraction study. Diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation (λ = 0.710 73 Å) at 20 ± 1 °C. Lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 2 520 values in the range $15 < 2\theta < 30°$.

Crystal data. $C_{60}H_{56}N_4O_4Zn_2$, M = 1 027.73, orthorhombic, space group $P2_12_12_1$, a = 17.738(4), b = 29.632(9), c = 9.968(2) Å, U = 5 239(2) Å^3, D_m = 1.245 g cm^{-3}, Z = 4, D_c = 1.303 g cm^{-3}, $F(000)$ = 2 144, $\mu(\text{Mo-}K_\alpha)$ = 9.8 cm^{-1}.

For the intensity-data collections, the θ—2θ scan mode was used at a scan rate of 6° min^{-1}. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. A total of 3 844 reflections were collected in the range $1.5 < 2\theta < 48°$, of which 2 762 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. The intensity data were corrected for Lorentz-polarization effects, but not for absorption.

The data were reduced by using the UNICS III program system[7a] at the Computer Centre of Kyushu University. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and equal weight w = 1 for all reflections was adopted. Atomic scattering factors were taken from ref. 7*b*. Hydrogen atoms were entered in calculated positions and unrefined. Final R and R' values were 0.0725 and 0.0755, respectively. Positional parameters of non-hydrogen atoms are given in Table 1

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Crystal Structure.—The unit cell is comprised of four units (Z = 4), each containing two complex molecules (A and B). Perspective views of molecules A and B are given in Figures 2 and 3, respectively, together with the numbering system. Relevant bond lengths and angles are listed in Table 2.

As expected the ligand functions as a bidentate chelate through its azomethine nitrogen and phenolic oxygen to afford four-co-ordination around the zinc(II) ion. The dihedral angle between the plane defined by Zn, N(1), and O(1) and that defined by Zn, N(2), and O(2) is 81.7° for molecule A and 84.9° for molecule B. Thus, the configuration around the metal ion is nearly tetrahedral for both A and B. The Zn–N and Zn–O bond lengths are comparable to those of zinc(II) complexes of related Schiff-base ligands.[8,9]

In the crystal each complex molecule has no symmetry in a

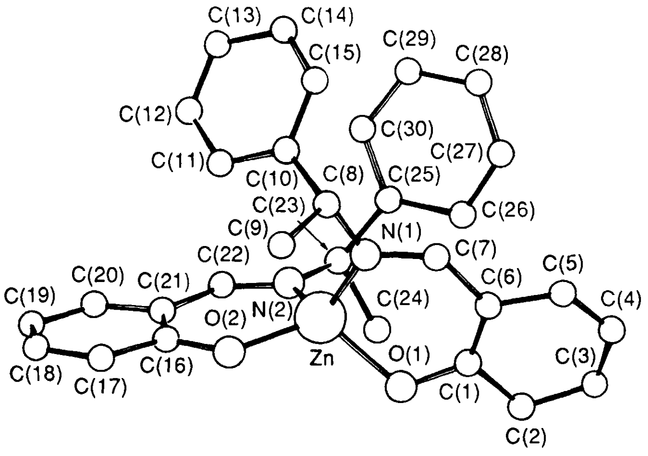

Figure 2. ORTEP view of molecule A with numbering system

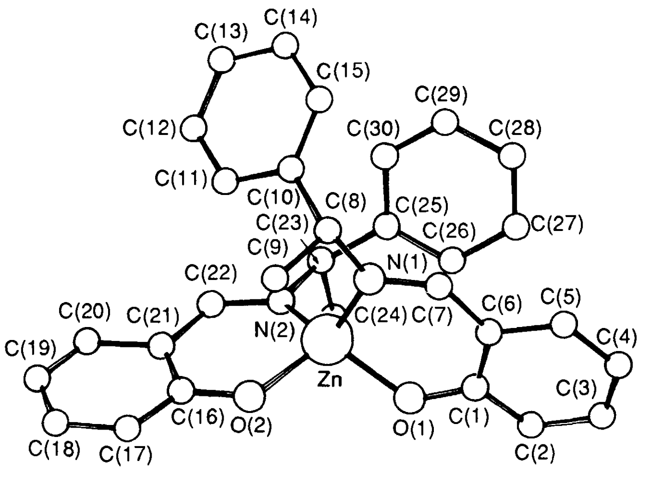

Figure 3. ORTEP view of molecule B with numbering system

Table 2. Relevant bond distances (Å) and angles (°)

	Molecule A	Molecule B
Zn–O(1)	1.96(1)	1.91(1)
Zn–O(2)	1.90(1)	1.88(1)
Zn–N(1)	1.98(1)	2.01(1)
Zn–N(2)	2.00(1)	1.99(1)
O(1)–Zn–O(2)	118.4(6)	112.3(5)
O(1)–Zn–N(1)	95.4(5)	97.7(5)
O(1)–Zn–N(2)	111.0(5)	112.1(5)
O(2)–Zn–N(1)	111.3(5)	112.9(6)
O(2)–Zn–N(2)	97.3(6)	95.2(5)
N(1)–Zn–N(2)	125.1(6)	127.2(5)
Distances between non-bonded atoms		
O(1) $\cdots$ C(24)	3.41(2)	
O(1) $\cdots$ C(26)		3.18(2)
O(2) $\cdots$ C(9)	3.41(3)	3.39(2)
O(2) $\cdots$ C(11)	3.40(3)	
C(1) $\cdots$ C(26)	3.44(3)	3.29(2)
C(6) $\cdots$ C(26)	3.34(3)	

precise sense, but there is a pseudo-C_2 axis passing through the centre of the N(1) $\cdots$ N(2) edge, Zn, and the centre of the O(1) $\cdots$ O(2) edge. We have analyzed the molecular structure by taking into consideration the stereochemistry of the (*R*)-1-phenylethyl group and found the sinistral disposition of two ligands along the pseudo-C_2 axis for both A and B, *i.e.* the Λ configuration around the metal ion. The crystal structure of the corresponding copper complex was recently studied by Kawamoto *et al.*[10] The geometry around the copper has been shown to be pseudo-tetrahedral with a dihedral angle of 39.5° and the absolute configuration along the pseudo-C_2 axis is Δ. Thus, the copper(II) and zinc(II) complexes differ markedly from each other in stereoselectivity.

It is valuable to gain an insight into the origins leading to the different stereoselectivities in these complexes. Kawamoto *et al.*[10] pointed out that in the crystal of the copper(II) complex the hydrogen on the asymmetric carbon of one ligand is bonded to the phenolic oxygen of the other ligand within a molecule. This intramolecular interligand hydrogen bonding probably plays a dominant role in the configuration about the central copper ion. The importance of hydrogen bonding at the phenolic oxygen has been suggested by Fujii *et al.*[11] in their studies on the solvent dependence of the stereoselectivity of Schiff-base complexes.

In the zinc(II) complex, however, such intramolecular hydrogen bonding cannot occur because two ligands are tetrahedrally disposed around the metal ion so that the hydrogen at the asymmetric carbon and the phenolic oxygen of the adjacent ligand are far apart from each other. From careful inspection of the crystal structure we have found that the phenyl and methyl groups of the N-substituent are associated with intramolecular interligand interactions. In molecule A both the phenyl and methyl groups attached to C(8) are in close proximity to the adjacent chelate ring (see Figure 2). In particular the C(9) $\cdots$ O(2) and C(11) $\cdots$ O(2) interatomic distances [3.41(3) and 3.40(3) Å, respectively] are significantly short compared with the distance expected from van der Waals radii (C $\cdots$ O 3.6 Å). Similarly the phenyl and methyl groups attached to C(23) are in close proximity to the other chelate ring. The C(24) $\cdots$ O(1) distance is 3.41(2) Å. The C(26) $\cdots$ C(1) and C(26) $\cdots$ C(6) distances [3.44(3) and 3.34(3) Å, respectively] are also very short compared with the C $\cdots$ C van der Waals radius (4.0 Å).

In molecule B the intramolecular interligand interaction differs slightly from that in molecule A. That is, only the phenyl group attached to C(23) interacts with the chelate ring on one side and only the methyl group attached to C(8) interacts with the chelate ring on the other side (see Figure 3). The C(26) $\cdots$ O(1) and C(26) $\cdots$ C(1) distances are 3.18(2) and 3.29(2) Å, respectively. The C(9) $\cdots$ O(2) distance is 3.39(2) Å. Some important non-bonding interatomic distances are included in Table 2.

Thus, the chiral N-substituent [(*R*)-1-phenylethyl group] is participating in intramolecular interligand interactions in a way different from that of the copper complex. That is, in the zinc complex the substituent is interacting through the phenyl and methyl groups to afford a Λ configuration whereas in the latter complex it interacts through the hydrogen at the asymmetric carbon to afford a Δ configuration.

The operation of similar non-covalent interactions has been demonstrated by *X*-ray analysis for some diastereomeric organic compounds,[12–14] where a conformer with bulky groups in *gauche* position is preferred.

C.D. Spectra.—Electronic and c.d. spectra of the zinc complex in chloroform are given in Figure 4. The absorption band at 26 800 cm^{-1} is assigned to the azomethine π–π* transition.[6] In the c.d. spectrum a negative and a positive band were observed at 25 900 and 28 400 cm^{-1}, respectively. The same pattern of (− and +) was found for a solid sample (KBr disc) as indicated in the insert to Figure 4. Such splitting of the azomethine π–π* transition has been observed previously for related zinc complexes[5,6] and explained in terms of exciton interaction.[15,16]

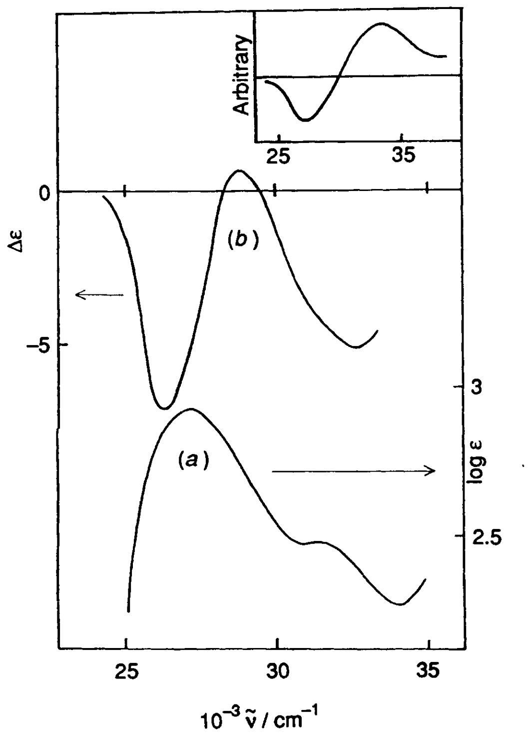

Figure 4. Electronic absorption (*a*) and c.d. (*b*) spectra of the complex in chloroform. The insert is the c.d. spectrum for a KBr disc

Table 3. Absolute configuration and c.d. pattern at the azomethine π–π* transition for some salicylideneimine complexes

Complex[a]	Configuration	C.d. pattern
$[ZnL^1_2]$	Λ	(−, +)
$[CuL^1_2]$	Δ	(+, −)
$[NiL^1_2]$	(Δ)	(+, −)
$[ZnL^2]$	Λ	(+, −)
$[CuL^2]$	Λ	(+, −)
$[NiL^2]$	Λ	(+, −)

[a] L^1 = *N*-(*R*)-1-Phenylethylsalicylideneiminate, L^2 = *N*,*N*′-propane-1,2-diylbis(salicylideneiminate).

It is interesting to examine the correlation between the c.d. spectral feature at the azomethine π–π* transition and the absolute configuration of tetrahedral or pseudo-tetrahedral salicylideneimine complexes. The copper complex of Δ configuration serves as a good reference for this purpose. For this complex the higher-wavenumber component of the c.d. couplet is superposed by the band associated with an absorption at 33 000 cm^{-1}, but the c.d. pattern is undoubtedly (+, −).[10] This pattern is quite opposed to that of the present zinc complex of Λ configuration and thence is consistent with its Δ configuration. The nickel homologue derived from 5-methylsalicylaldehyde instead of salicylaldehyde is known to adopt a pseudo-tetrahedral structure in solution owing to a rapid interconversion between planar and tetrahedral species.[17] Its preferred absolute configuration is presumably Δ in view of the configuration of the pseudo-tetrahedral copper complex above. The observed (+, −) c.d. pattern[17] is also consistent with this configuration. The results are summarized in Table 3. Another example of known configuration is *N*,*N*′-propane-1,2-diylbis(salicylideneiminato)zinc[8] which prefers a Λ configuration about the central metal ion. The same Λ configuration has been assigned to the corresponding copper[18,19] and nickel complexes.[6] These three complexes show the same (+, −) c.d. pattern at the azomethine π–π* transition. The results are also included in Table 3.

It is evident from Table 3 that the 1-phenylethylsalicylideneiminate complexes and the propane-1,2-diylbis(salicylideneiminate) complexes differ from each other in the c.d. pattern at the azomethine π–π* transition, *i.e.* (−, +) for the former and (+, −) for the latter if Λ and *vice versa*. At this stage we can point out an essential difference in structure between the two classes of complexes. That is, the former class adopts a nearly tetrahedral structure with two bidentate chelates whereas the latter class has a tetrahedrally distorted planar configuration with a quadridentate ligand. This difference is probably related to the different c.d. pattern at the azomethine π–π* transition but a rational interpretation is the subject of further investigation. In conclusion, we may say that the use of the c.d. spectral feature at the azomethine π–π* transition as diagnostic of the absolute configuration is valid only among complexes of similar structure. In this connection we have to retract part of our previous conclusions for bis(*N*-L-menthylsalicylideneiminato)metal complexes (M = Co, Cu, or Zn).[5] These complexes exhibiting a c.d. pattern of (+, −) at the azomethine π–π* transition should be assigned as Δ not Λ.

In the course of this investigation we noticed that both the electronic absorption and c.d. spectra in solution are time-dependent. That is, the absorption maximum shifts from 26 800 to 31 600 cm^{-1} with time. In the c.d. spectrum the couplet near 27 000 cm^{-1} decreases with time and a new negative band appears near 31 000 cm^{-1} as the dominant band. Such pronounced spectral changes suggest a structural change of the complex in solution, such as dimerization through a phenolic oxygen to afford five-co-ordination around each metal ion. Such a structure is known for the zinc(II) complex with *N*-methylsalicylideneimine.[9]

Acknowledgements

Thanks are due to Professor Yoshihiko Kushi of Osaka University for kind suggestions. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 62430011).

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Received 25*th January* 1990; *Paper* 0/00400F