Journal of Molecular Structure, 102 (1983) 355—363
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

STRUCTURAL INFORMATION ON SOME BERYLLIUM(II) COMPLEXES OF *N*-ARALKYLSALICYLALDIMINES

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(Received 9 December 1982)

ABSTRACT

A series of stable beryllium(II) complexes of newly synthesized *N*-aralkylsalicylaldimine Schiff bases has been prepared and characterized. Structures have been elucidated on the basis of analytical, conductance and IR and PMR spectral data. A tetrahedral symmetry has been proposed for all these complexes which are non-ionic.

INTRODUCTION

Metal complexes of *N*-substituted salicylaldimines have interested chemists for a long time because of their stability and wide structural and configurational diversity [1—3]. Very little work, however, appears to have been done on the beryllium(II) complexes of this group of ligands [4—8]. It has been suggested [9—10] that the weakness of the Be—N bond, as reflected by its tendency to be replaced by the more stable Be—O bond, is the underlying cause. Very recently, however, Deshmukh [11] et al. have reported a series of stable beryllium complexes derived from *N*-arylsalicylaldimines which apparently contradict the conventional view of Be—N bond stability.

As a part of our interest in metal detoxification, we prepared a series of new *N*-aralkylsalicylaldimines by reacting salicylaldehyde and its ring-substituted analogues with benzylamine and β-phenylethylamine. This communication reports the preparation and characterization of beryllium(II) complexes of these new ligands. Analytical, conductance, and IR and PMR spectral data are discussed to elucidate the structural characteristics of the metal chelates.

EXPERIMENTAL

Materials and Methods

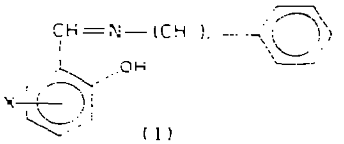
Beryllium nitrate trihydrate was of analytical-reagent grade. All other chemicals were of at least reagent grade. Salicylaldehyde, *O*-vanillin and the amines were purified by distillation under reduced pressure before use. Nitrosalicylaldehydes were prepared from salicylaldehyde [12].

Elemental analyses were performed on a Hosli microcombustion apparatus. Metal content was estimated by igniting the complexes to constant weight and weighing the residue as BeO [13]. Room temperature conductances were measured on solutions in chloroform using a Toshniwal Model CL.01.07 conductivity meter.

Infrared spectra in the 4000–400 cm^{-1} range were recorded in KBr pellets on a Model 577 Perkin—Elmer spectrophotometer. A Model R-32 Perkin—Elmer spectrometer operating at 90 MHz was used to obtain PMR spectra in deuterated chloroform solutions with TMS as internal standard.

Preparation of ligands

The *N*-aralkylsalicylaldimine ligands (designated B_1 to B_8) were obtained by refluxing a mixture of the appropriate aldehyde (0.1 mol) and amine (0.1 mol) in ethanol (50 ml) for five minutes. The crude compounds were purified by crystallization from ethanol, except for B_1 and B_2 which were purified by distillation under reduced pressure. The yields were almost quantitative.



(I)

B_1: X = H, $n = 1$
B_2: X = H, $n = 2$
B_3: X = 3—OCH_3, $n = 1$
B_4: X = 3—OCH_3, $n = 2$
B_5: X = 5—NO_2, $n = 1$
B_6: X = 5—NO_2, $n = 2$
B_7: X = 3—NO_2, $n = 1$
B_8: X = 3—NO_2, $n = 2$

The analytical and conductance data for the *N*-aralkylsalicylaldimines (I) are reported in Table 1.

Preparation of metal complexes

A solution of beryllium nitrate trihydrate (0.01 mol) in the minimum quantity of aqueous ethanol (3:1) was added with stirring to a solution of the ligand (0.02 mol) in ethanol (50 ml). To facilitate deprotonation of the phenolic group, an aqueous solution of sodium hydroxide or diethylamine (0.02 mol) was also added. The mixture was refluxed for five minutes and then filtered hot. The complex deposited as the filtrate cooled and was purified by crystallizing from dry methanol or ethanol. It should be noted that the phenolic proton in the Schiff bases of 3- and 5-nitrosalicylaldehydes are sufficiently labile without addition of base.

The complexes obtained above (Table 2) have been abbreviated as MB_1, MB_2 . . . . . . MB_8 wherein B_1, B_2 etc., identify the ligand from which a particular complex has been obtained.

TABLE 1

Analytical and physical data of *N*-aralkylsalicylaldimines

Compound	Colour/ crystal shape	m.p. (°C)	Molecular formula	Elemental analysis (%)		
				C	H	N
B_1	Yellow oil	Oil[a]	$C_{14}H_{13}NO$	79.60 (79.62)	6.30 (6.16)	6.50 (6.63)
B_2	Thick yellow crystals	45	$C_{15}H_{15}NO$	79.61 (80.00)	6.95 (6.66)	6.33 (6.22)
B_3	Thin yellow needles	59	$C_{15}H_{15}NO$	74.32 (74.69)	6.50 (6.22)	5.92 (5.81)
B_4	Thin yellow needles	79	$C_{16}H_{17}NO_2$	75.05 (75.29)	6.81 (6.66)	5.66 (5.49)
B_5	Lustrous yellow needles	153	$C_{14}H_{12}N_2O_3$	65.34 (65.62)	4.88 (4.68)	10.90 (10.94)
B_6	Lustrous yellow needles	157	$C_{15}H_{14}N_2O_3$	66.65 (66.67)	5.07 (5.18)	10.56 (10.37)
B_7	Orange powder	148	$C_{14}H_{12}N_2O_3$	66.09 (65.62)	4.85 (4.68)	11.16 (10.94)
B_8	Orange needles	131	$C_{15}H_{14}N_2O_3$	66.28 (66.67)	5.44 (5.18)	10.65 (10.37)

[a] G. O. Dudek and R. H. Holm have reported this compound to have a melting point of 24–26°C.

RESULTS AND DISCUSSION

Except for *N*-benzylsalicylaldimine [14] (B_1), the Schiff bases are believed to be new. They are fairly soluble in common organic solvents and possess characteristic yellow/orange colours. Their elemental analysis data (Table 1) agree with their molecular composition. Spectral data, discussed below, are also consistent with the structure (I).

The IR spectra, both of the ligands and of their metal complexes, are in general very complicated and consist of closely spaced bands, particularly in the 1650—500 cm^{-1} region. This complexity, caused mainly by the presence of differently-substituted aromatic rings and extensive vibrational coupling, precludes definitive assignment of the bands, though otherwise the spectra are quite informative. For example, there is little uncertainty in assigning a broad band spread over the 3200—2500 cm^{-1} region to an intramolecularly hydrogen-bonded (OH• • •N) phenolic group in the case of free *N*-aralkylsalicylaldimines [15]. This band disappears in the corresponding beryllium(II) complexes. Evidently, the phenolic group undergoes deprotonation with simultaneous Be—O covalent bond formation in the chelation process.

TABLE 2

Analytical and physical data of beryllium complexes

Complex	Colour/ crystal shape	Molecular formula	M.p. (°C)	Analyses (%)				Molar conductance at 20 ± 1°C (mhos cm² mol⁻¹)
				C	H	N	BeO	
MB_1	Off-white needles	$C_{28}H_{24}N_2O_2Be$	198—9	77.95 (78.32)	5.78 (5.59)	6.20 (6.53)	5.80 (5.83)	0.20
MB_2	Off-white needles	$C_{30}H_{28}N_2O_2Be$	166	78.00 (78.77)	6.12 (6.13)	6.00 (6.13)	5.15 (5.47)	0.23
MB_3	Lustrous off-white plates	$C_{30}H_{28}N_2O_4Be$	205—6	73.18 (73.61)	5.95 (5.72)	5.84 (5.2)	5.41 (5.11)	0.29
MB_4	Lustrous off-white plates	$C_{32}H_{32}N_2O_4Be$	95—6	73.62 (74.27)	6.52 (6.19)	5.84 (5.42)	4.61 (4.84)	0.32
MB_5	Pale-yellow powder	$C_{28}H_{22}N_4O_6Be$	232—3	64.15 (64.74)	4.60 (4.24)	11.17 (10.79)	4.54 (4.82)	0.29
MB_6	Pale-yellow powder	$C_{30}H_{26}N_4O_6Be$	261—2	65.07 (65.81)	5.12 (4.75)	10.44 (10.24)	4.72 (4.57)	0.25
MB_7	Light-yellow powder	$C_{28}H_{22}N_4O_6Be$	215—7	64.16 (64.74)	4.42 (4.24)	11.20 (10.79)	4.40 (4.82)	0.49
MB_8	Light-yellow powder	$C_{30}H_{26}N_4O_6Be$	180—2	65.08 (65.81)	4.98 (4.75)	10.52 (10.24)	4.42 (4.57)	0.50

N-Salicylaldimines usually display two spectral bands, one each in the 1650—1600 cm^{-1} and 1600—1550 cm^{-1} regions, characteristic of C=N stretching vibration and in-plane ring deformation. Conflicting assignments have been reported for these bands [16—18]. The general concensus, however, seems to be in favour of assigning the higher frequency band to ν(C=N), though relatively recent N^{15} isotopic studies [18] suggest otherwise. It is, however, now accepted that neither of these bands is vibrationally pure and instead they involve contribution from both the vibrational modes to varying degrees. Assuming that the band with the greater contribution from ν(C=N) would be relatively stronger because of the greater dipole moment change involved, the stronger band in the 1650—1615 cm^{-1} region is assigned to the C=N stretching mode in the free salicylaldimines. On complexation, this band undergoes a downward shift (~10 cm^{-1}). Further, the greater displacement associated with the band in question suggests its greater involvement in coordination because the band placed immediately below it (1600—1550 cm^{-1}) shows hardly any shift. Hence, the assignment proposed for ν(C=N) is justified.

A rather broad band in the 1275—1260 cm^{-1} region, usually displaying a shoulder towards the higher frequency side, is assigned to the coupled ν(C—O) (phenolic) + δ OH vibrations in the case of uncoordinated ligands [19]. In beryllium(II) complexes, this band is replaced by a new one in the 1325—1300 cm^{-1} region which is assignable to bonded ν(C—O) [20], confirming the loss of the phenolic proton on chelation. The complexes of Schiff bases derived from 5-nitrosalicylaldehyde, however, display a broad band (1340—

1300 cm^{-1}), probably due to the merger of symmetric $\nu(NO_2)$ and ν(C—O) modes. The scissoring vibrations of the methylene group absorb consistently in the 1460—1450 cm^{-1} region [21] for the free ligands and at marginally (~5 cm^{-1}) lower values in the metal complexes.

Be—O stretching modes have been reported [11, 22, 23] to absorb around 950, 800 and 500 cm^{-1}. Identification of the first two spectral bands was precluded in this study by the presence of other bands in this region, arising from in-plane and out-of-plane CH deformations. Nevertheless, two medium intensity bands appearing in the 550—510 and 460—430 cm^{-1} regions are tentatively assigned to Be—O and Be ← N stretching modes, respectively.

In contrast to the IR spectra, the PMR spectra (Table 3) were found to be simple and easier to interpret, particularly in the case of the free ligands. Two singlets, a broader one in the 13—16 δ range and the other in the 8—9 δ range, can be unequivocally ascribed to the intramolecular hydrogen-bonded phenolic proton and the azamethine proton, respectively [24]. These assignments are confirmed by deuterium exchange experiments. Appearance of the azamethine proton as an unsplit singlet is a sure indication that the salicylaldimines exist solely in the phenol—imine form [14].

It is noteworthy that the phenolic proton of the Schiff bases derived from 3-nitrosalicylaldehyde appears at significantly higher δ-values (15—16) as compared with its analogues. Higher δ-values indicate that the degree of hydrogen bonding is stronger in the 3-nitro compounds. Apparently, the *meta*-nitro group affects the basicity of the azamethine nitrogen lone pair much less than it affects the acidity of the OH group. The net result is a stronger hydrogen bond. Depending upon whether the ligand contains one or two methylene groups, the PMR spectra show a singlet (4.62—4.90 δ) or two triplets (3.68—3.75 and 2.92—3.02 δ), respectively.

In metal complexes, deprotonation and Be—O covalent bond formation are evident from the disappearance of the broad singlet (13—16 δ) characteristic of an intramolecular hydrogen-bonded phenolic group. This confirms the conclusion drawn earlier from IR spectra. Qualitatively, ligand—metal coordinate bond formation amounts to withdrawal of electrons from the donor atom. Consequently, the signal due to a proton or group of protons, either directly linked with the donor atom or placed close to it, is expected to shift to higher δ-values because of deshielding [25]. In contrast, the azamethine proton is shifted marginally (0.3—0.6 δ) up-field in the beryllium complexes. Some sort of shielding process, the exact nature of which is not yet clear, must also operate simultaneously. As already stated, the Schiff bases derived from benzylamine give a singlet in the 4.62—4.90 δ range characteristic of the two methylene protons. This singlet is replaced by an AB quartet in the corresponding beryllium(II) complexes (Fig. 1). For example, bis(*N*-benzylsalicylaldiminate)beryllium(II) yields a quartet with δ_A (4.40), δ_B (4.12) and J_{AB} (14 Hz). Spin—spin coupling interaction between the methylene protons and the azamethine proton is ruled out because in that case the spectrum would, instead, display a doublet and a triplet.

TABLE 3

PMR spectral data of some *N*-aralkylsalicyaldimes and corresponding beryllium(II) complexes

Compound	Description[a] of proton and signal frequencies (δ)				
	–CH	$\overset{\overset{H}{\vert}}{-C}=N$	C=N=CH$_2$–	–CH$_2$–Ph	3–OCH$_3$	H$_{aromatic}$
B$_1$	13.30 b, s	8.26 s	4.64 s	—	—	6.70–7.60 m
MB$_1$	—	7.86 s	AB quartet $\delta_A = 4.40$, $\delta_B = 4.12$ $J_{AB} = 14$ Hz	—	—	6.55–7.45 m
B$_2$	13.30 b, s	8.10 s	3.75 t, $J = 7$ Hz	2.92 t, $J = 7$ Hz	—	6.60–7.50 m
MB$_2$	—	7.84 s	3.38–3.55 t (with perturbations)	2.72–2.92 t (with perturbations)	—	6.50–7.50 m
B$_3$	13.70 b, s	8.43 s	4.82 s	—	3.93 s	6.70–7.60 m
MB$_3$	—	7.78 s	AB quartet $\delta_A = 4.37$, $\delta_B = 4.00$ $J_{AB} = 14$ Hz	—	—	6.50–7.20 m
B$_4$	13.0 b, s	8.26 s	3.86 t (up-field component merges with methoxy signal)	3.03 t, $J = 7$ Hz	3.92 s	6.70–7.40 m
MB$_4$	—	7.80 s	3.70–3.92 m (+ 3–OCH$_3$)	2.73–3.05 (with perturbations)	Signal merges with that of =N–CH$_2$	6.63–7.38 m
B$_7$	15.1 b, s	7.83	4.90 s	—	—	6.50–7.80 m
MB$_7$	—	8.00 (with shoulders)	AB quartet $\delta_A = 4.54$, $\delta_B = 4.22$ $J_{AB} = 7$ Hz	—	—	6.60–8.10 m
B$_8$	15.4 b, s	7.96 s	3.80 t, $J = 7$ Hz	2.93 t, $J = 7$ Hz	—	6.43–7.90 m

[a] b = broad, s = singlet, m = multiplet, t = triplet.

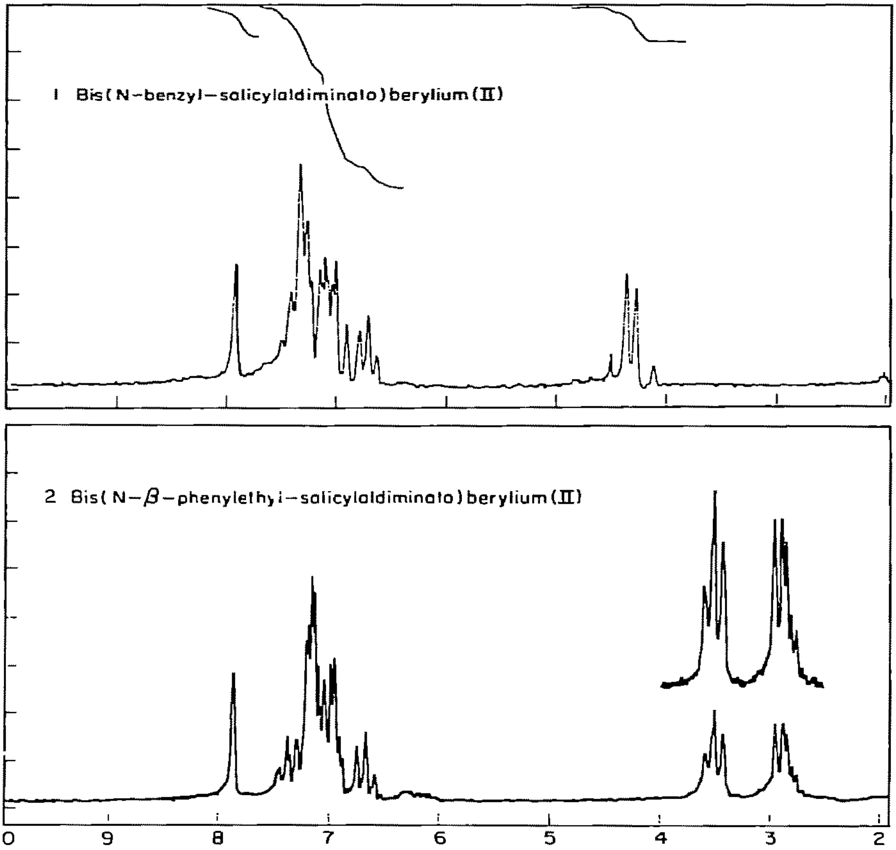


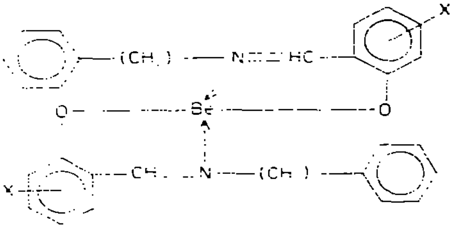
Fig. 1. PMR spectra of two *N*-aralkylsalicylaldimine complexes of Be(II).

It seems quite probable that the observed AB quartet is a direct consequence of the two methylene protons becoming non-equivalent, as rigidity is introduced into the structure by the chelate ring. This effect also appears, albeit to a lesser extent, in the complexes of β-phenylethylamine Schiff base analogues. The triplets relating to the methylene protons in bis(*N*-β-phenethylsalicylaldiminato)beryllium(II), for example, have perturbations which impart almost a multiplet character to these signals (Fig. 1).

The spectra of the Schiff bases of 3- and 5-nitrosalicylaldehydes and the corresponding metal complexes are rather complicated, mainly because of the strong deshielding effect of the nitro group, which causes a considerable downfield shift from adjacent protons. For example, the signal around 8 δ, observed both for *N*-benzyl-3-nitrosalicylaldimine and its beryllium complex, which had earlier been attributed to the azamethine proton, has shoulders on both sides. Since the integral value of this signal corresponds to two protons, it is evident that the nitro group causes the adjacent (4-H) proton in the aldehyde ring to shift downfield and the shoulders arise, presumably, from its coupling with the 5-H (*ortho*) and 6-H (*meta*) protons.

Molar conductance values in the 0.2—0.5 ohm^{-1} cm^2 mol^{-1} range indicate that the beryllium compounds do not dissociate in chloroform and are predominantly covalent in character. Further the complexes show no sign of decomposition or of weight-loss when heated for one hour at a temperature slightly below their melting points. This suggests that the compounds are anhydrous and of high thermal stability.

Analytical data for the beryllium(II) complexes are in fair agreement with a 1:2 (metal—ligand) stoichiometry. On the basis of this and the other evidence presented above, a tetrahedral geometry is proposed for the metal complexes (II). This is in conformity with the strong tendency of Be^{2+} ions to form compounds having sp^3 hybrid bonds [26].



(II)

where n = 1 or 2; X = H, $3—OCH_3$, $3—NO_3$, $5—NO_2$.

It is concluded that the beryllium(II) complexes described above owe their stabilities to the Be—O covalent bonds which presumably have a stabilizing effect on the Be ← N bonds as well.

ACKNOWLEDGEMENT

One of the authors (R. N.) expresses his sincere thanks to Dr. P. K. Ramachandran, Director, Defence Research and Development Establishment, Gwalior, for providing the necessary facilities and encouragement.

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