Study of Ligand Isomeric Complexes of *N*-Furfurylsalicylaldimine

By **Urmila A. Bhagwat, Vasudha A. Mukhedkar,** and **Anant J. Mukhedkar,*** Department of Chemistry, The University, Poona 411007, India

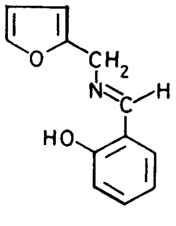
The ligand isomeric complexes ($OC_4H_3CH_2N{=}CHPhOH$, A, and $OC_4H_3CH{=}NCH_2PhOH$, B) of *N*-furfurylsalicylaldimine with Co^{III}, Ni^{II}, Cu^{II}, and Pd^{II} have been synthesised. The nature of the isomerism was characterised by the ^1H n.m.r. spectral data for the azomethine group, C=N group frequencies, and electric polarization. The complexes with $V^{IV}O$, Cr^{III}, Mn^{II}, Fe^{III}, Pt^{II}, Be^{II}, and Zn^{II} were obtained in the A isomeric form. The ^1H n.m.r. spectra of both the isomers of the cobalt(III) complexes indicated a *trans* configuration. An electric polarization study of nickel(II) complexes also suggested that both isomeric complexes had the *trans* configuration and that they were linkage isomers containing ligand isomers A and B. The participation of the furan oxygen in co-ordination was indicated in the A isomeric form of complexes with Pd^{II} and Zn^{II}. The characterisation of the isomers was supplemented by u.v. spectra.

SYNTHESIS of Schiff-base complexes using thiophen-2-carbaldehyde and different amines[1] has been reported However, a similar series of complexes using furan-2-carbaldehyde could not be obtained. It has also been reported that *NN'*-difurfurylidene-ethylenediamine-copper(II) could not be separated[2] due to its hydrolysis, even in alcohol. We have therefore tried to synthesise metal complexes of a Schiff base derived from furfurylamine and salicylaldehyde. This paper reports the results of this problem.

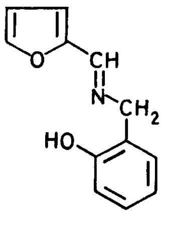
RESULTS AND DISCUSSION

The ^1H n.m.r. spectra of *N*-furfurylsalicylaldimine (L) gave a very broad signal between τ —0.5 and —2.5. On deuterium exchange, this band disappeared. It was therefore assigned to O*H*. Since there was no observable concentration effect on the position of the ^1H n.m.r. signal of O*H*, the hydroxy-group was assumed to be involved mainly in intramolecular hydrogen bonding[3] with the N of the azomethine group. This intramolecular hydrogen bond, OH · · · N, was shown to be stronger than those involving other groups,[4] thus, the equilibria involving self association seemed to be of minor importance.

Two ^1H n.m.r. signals were observed for $-N{=}CH$ (τ 0.24, 1.99), and two for $-N{-}CH_2$ (τ 4.48, 5.05). There was no effect of the deuterium exchange experiment on the positions and intensities of these signals. Since the self association and related equilibria for L seemed to be of little significance the ^1H n.m.r. data suggested that L was present in two isomeric forms, A and B.



A



B

Although, there was an appreciable concentration effect on the intensity ratio of the two signals associated with the azomethine proton, no such effect was observed on the positions of the ^1H signals of $-N{=}CH$ and $-N{-}CH_2$. (It should be noted here that these protons were not directly involved in hydrogen bonding.) The intensity ratio *I* (τ 0.24) : *I*(τ 1.99) increased with dilution in carbon tetrachloride. This observation suggested that there was a dielectric effect on the concentrations of A and B, the less polar form being favoured in a dilute solution. A similar concentration effect had been reported for the keto–enol equilibrium of pentane-2,4-dione in cyclohexane,[5] and for the equilibrium between the spatial isomers of D-camphorquinone in n-heptane.[6]

The suggested isomerisation of L is similar to the methylene–azomethine isomerisation proposed for *N*-benzylidene-α,*p*-diphenylbenzylamine[7] and could be demonstrated by the isolation of the corresponding isomeric imine complexes (see below).

Separation of the isomers A and B was found to be impractical either by fractional distillation or by conventional column chromatography. The gas chromatogram of L on a Lubrol MO column gave a characteristic broad band. Infrared spectra also indicated the probable isomerisation of L. It seemed plausible that out of the four bands observed in the region 1 613—1 667 cm^{-1}, the two bands observed at 1 651 and 1 640 cm^{-1} were associated with the C=N group[8] of these two isomers.

In the preparation of the metal complexes with L, two isomeric complexes with similar elemental analyses were separated for cobalt(III), nickel(II), copper(II), and palladium(II). These complexes were initially separated using the solubility difference of the two isomers in chloroform and were then further purified on a silica column.

The ^1H n.m.r. spectra of the palladium(II) isomeric complexes, (7) and (8), were distinctly different. The resonances of the azomethine proton in (7) and (8) appeared at τ 1.86 and —2.19 respectively. The i.r. spectra also showed a difference in the position of the characteristic bands associated with the C=N group and the CH_2 deformation mode[9] of vibration in the two isomeric complexes (Table 1). On comparison of the spectra of the ligand with those of (7) and (8) we were tempted to propose that (7) and (8) were linkage isomers. Geometrical isomerism for complexes containing ligands A or B would also be possible. However, the difference in polarization effects between *cis* and *trans* isomers would not be expected to influence the shielding constants of the azomethine proton to such an extent that their chemical shifts would differ by as much as *ca.* τ 4. The problem of isomerisation was analysed further using the data of electric polarization (see below). It should be noted that there is not yet a confirmed report of synthesis of both *cis* and *trans* isomers of complexes with bidentate Schiff bases.[10]

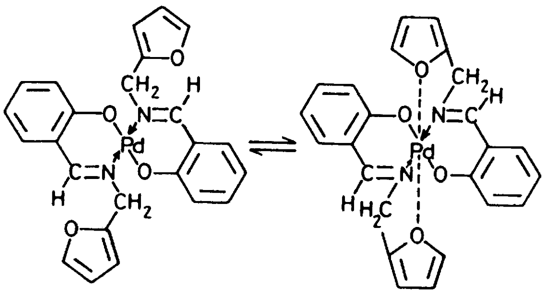
The higher ν(C=N) frequency and the lower ^{1}H n.m.r. chemical shift of the azomethine proton for (8) as compared to that for (7) suggested that complex (8) contained ligand isomer B and complex (7) ligand isomer A. Hydrogen-1 n.m.r. spectra of (7) showed an additional band with weak intensity in the low-field region (τ 1.70). This observation suggested the presence of an equilibrium between a square-planar (C) and an octahedral (D) configuration of (7). The octahedral configuration would involve bonding through the furan oxygen. A similar equilibrium for (8) was not evident from its spectra. This might be due to steric reasons; free rotation of the azomethine group in ligand isomer B, as would be required for octahedral geometry, would not be possible.

TABLE 1

Physical data of metal complexes with *N*-furfurylsalicylaldimine

	Complex	Ligand isomer	Colour	I.r. spectra		^{1}H n.m.r. spectra	
				ν(C=N)/cm^{-1}	δ(CH$_2$)/cm^{-1}	τ_{CH}	τ_{CH_2}
(1)	$Co(C_{12}H_{10}NO_2)_3$	A	Green	1 603	1 462	2.00	5.56 5.58 5.60
(2)	$Co(C_{12}H_{10}NO_2)_3$	B	Pale green	1 629	1 458	0.2	5.34 5.40 5.44
(3)	$Ni(C_{12}H_{10}NO_2)_2$	A	Green	1 619	1 464		
(4)	$Ni(C_{12}H_{10}NO_2)_2$	B	Yellowish green	1 635	1 454		
(5)	$Cu(C_{12}H_{10}NO_2)_2$	A	Green	1 608	1 462		
(6)	$Cu(C_{12}H_{10}NO_2)_2$	B	Yellowish green	1 627	1 458		
(7)	$Pd(C_{12}H_{10}NO_2)_2$	A	Orange	1 603	1 467	1.86 1.70	4.92
(8)	$Pd(C_{12}H_{10}NO_2)_2$	B	Yellow	1 619	1 462	−2.19	4.88
(9)	$VO(C_{12}H_{10}NO_2)_2$	A	Pale green	1 614	1 458		
(10)	$Cr(C_{12}H_{10}NO_2)_3$	A	Green	1 619	1 454		
(11)	$Mn(C_{12}H_{10}NO_2)_2$	A	Brown	1 608	1 454		
(12)	$Fe(C_{12}H_{10}NO_2)_3$	A	Red	1 598	1 466		
(13)	$Pt(C_{12}H_{10}NO_2)_2$	A	Orange	1 603	1 466	1.82	4.90
(14)	$Be(C_{12}H_{10}NO_2)_2$	A	Pale yellow	1 629	1 462	2.08	5.68
(15)	$Zn(C_{12}H_{10}NO_2)_2$	A	Pale yellow	1 634	1 456	1.95 1.64	5.59 5.26
L	$C_{12}H_{11}NO_2$	A	Pale yellow	1 651	1 484	1.99	5.05
		B		1 640	1 466	0.24	4.48

Similarly to the complexes with palladium(II), the isomeric complexes with cobalt(III) were obtained. For complexes of formula ML_3 the facial–meridional pair was expected. The observed large difference of τ 1.8 between the azomethine proton resonances of (1) and (2), however, could not be attributed to such isomerism. A comparative study suggested that these complexes contained ligand isomers A and B. The ^{1}H n.m.r. spectra of both the isomeric complexes gave three resonances of equal intensity for the -N-CH$_2$ group indicating the *trans* configuration.[11] As these complexes were co-ordinatively saturated, the furan oxygen could not take part in co-ordination in (1). The azomethine proton resonances in both the isomers were broad and the expected three component bands could not be observed.



C D

The ^{1}H n.m.r. spectra of nickel(II) complexes could not be analysed as the bands were very broad. This observation indicated that both the isomers of nickel(II) complexes were paramagnetic in solution, although they were found to be diamagnetic in the solid state. Thus, both the isomers might be quasi-octahedral or tetrahedral in solution;[12] complex (3) would also be octahedral, involving bonding through the furan oxygen as suggested for (7). The i.r. spectra of the isomeric nickel(II) and copper(II) complexes showed the characteristic differences in the positions of ν(C=N) and δ(CH$_2$) modes of vibrations (Table 1).

The question of the nature of isomerisation reported in the present work has been partially resolved by determining the electric dipole moments. Due to the solubility limitations in non-polar solvents such as benzene or dioxane, the electric polarization of isomeric nickel(II) complexes only could be determined. It is beyond the scope of the present work to go into details concerning the contribution of atom polarization, model of dipole, and related topics.[13] The complexes (3) and (4) may be considered to be polar although their dipole-moment values were found to be low [D.C.M. model:[14] μ_3, 0.26 D;* μ_4, 0.31 D. M.C.S. model:[6,15] μ_3, 0.52 D; μ_4, 0.60 D] since the total polarization values of these complexes were temperature-dependent.[16] It was difficult to predict the value of the dipole moment of (3) and (4) using the vector model due to the structural complexities. These results, however, suggested that the isomeric complexes had similar geometrical (probably *trans*) configurations[17] and that they were the linkage isomers containing ligands A and B.

TABLE 2

Analytical data of metal complexes with *N*-furfurylsalicylaldimine

Complex	Decomposition temperature θ_c/°C	Found % C	Found % H	Found % N	Found % Metal	Calc. % C	Calc. % H	Calc. % N	Calc. % Metal
(1)	136—139	64.9	3.7	6.1	8.7	65.5	4.6	6.4	8.9
(2)	160—164	64.8	3.8	6.0	8.6	65.5	4.6	6.4	8.9
(3)	190—195	61.9	4.9	5.9	12.5	62.8	4.4	6.1	12.8
(4)	220—225	61.8	4.6	5.8	12.3	62.8	4.4	6.1	12.8
(5)	208—212	61.6	4.2	5.8	13.2	62.1	4.3	6.0	13.7
(6)	230—235	61.7	4.4	5.7	13.5	62.1	4.3	6.0	13.7
(7)	164—168	56.6	3.8	5.2	20.7	56.8	4.0	5.5	21.0
(8)	222—225	56.5	3.8	5.0	20.8	56.8	4.0	5.5	21.0
(9)	195—200	61.2	4.1	5.5	10.7	61.7	4.3	6.0	10.9
(10)	202—205	65.9	4.4	6.2	7.5	66.2	4.6	6.4	8.0
(11)	176—180	63.0	4.2	5.8	11.7	63.3	4.4	6.1	12.1
(12)	156—160	65.1	4.2	6.1	8.0	65.9	4.6	6.4	8.5
(13)	175—180	48.2	3.1	4.3	32.2	48.4	3.4	4.7	32.8
(14)	180—182	70.1	4.5	6.3	1.8	70.4	4.9	6.8	2.2
(15)	196—198	61.7	4.0	5.7	13.8	61.9	4.3	6.0	14.0
L b.p.	155—157	71.8	4.8	6.9		72.0	5.0	7.0	

Of the 15 complexes studied, the complexes of $V^{IV}O$, Cr^{III}, Mn^{II}, Fe^{III}, Pt^{II}, Be^{II}, and Zn^{II} were obtained in only one isomeric form. (The complex of Pt^{II} was prepared by treating the preformed salicylaldehyde complex with amine, as the product obtained using L could not be characterised.) The ^1H n.m.r. spectra of (15) indicated that it contained ligand isomer A and that an equilibrium similar to C $\rightleftharpoons$ D prevailed in this complex. It might be suggested, with caution, on the basis of ν(C=N), that the complexes (9) to (15) contained ligand isomer A.

The evidence for ligand isomerisation among the complexes was supplemented by u.v. spectral data. Gaussian analysis of the broad asymmetric band observed for L in the region 345—380 nm in methanolic K[OH] solution revealed two bands, at 350 and 372 nm. The band with lower energy was assigned to the A isomer, on the basis of the resonance contribution. It was interesting to observe that all the complexes [except (14) and (15)] which were thought to contain ligand isomer A, on the basis of i.r. and n.m.r. spectra, showed a red shift of *ca.* 12 to 15 nm in the band position assigned to A. The zinc and beryllium complexes [(14) and (15)] showed a red shift of less than 2 nm. This observation indicated that the nature of the metal–ligand bonding in beryllium and zinc complexes was mainly ionic, whereas that of the other transition-metal complexes was appreciably covalent in character. A similar shift, of *ca.* 10—12 nm, was observed for all the complexes which were thought to contain the B isomer.

The results of the present work suggest that the complexes with Schiff bases derived from furan-2-carbaldehyde could be stabilised by using an appropriate amine. The complexes containing ligand isomer B could be synthesised by using the Schiff base formed from furan-2-carbaldehyde and *o*-hydroxybenzylamine. This has been confirmed by preparing a palladium(II) complex by treating *o*-hydroxybenzylaminepalladium(II) with furan-2-carbaldehyde; the spectroscopic properties of this complex were identical with those of (8).

EXPERIMENTAL

Infrared spectra were measured in the range 665—4 000 cm^{-1} on a Beckman IR-4 spectrophotometer for Nujol and hexachlorobutadiene mulls. Electronic spectra were recorded in the range 200—800 nm on a Beckman DK-2 ratio recording spectrophotometer (1.00-cm matched quartz cells) using methanol and chloroform as solvents. The magnetic susceptibility measurements were performed at 27 ± 1 °C on a Faraday balance with a 7 000-G magnetic field, assembled in this Department.[18] Hydrogen-1 n.m.r. spectra were recorded on a Perkin-Elmer R-32 spectrometer at 90 MHz using $CDCl_3$ as solvent and hexamethyldisiloxane for lock signal. Dielectric constant measurements of benzene solutions at different temperatures were made with a WTW dipole meter using an oil-circulated experimental cell. Dipole moments were calculated using the Debye-Clausius-Mosotti model (D.C.M.) and a model for comparative study (M.C.S.) by plotting total polarization against reciprocal temperature.

Furfurylamine (b.p. 142 °C, lit.,[19] 145 °C) and *o*-hydroxybenzylamine (m.p. 127 °C, lit.,[20] 129 °C) were synthesised by the reduction of the corresponding oxime with zinc dust–acetic acid. All other chemicals were of AnalaR B.D.H. grade.

* Throughout this paper: 1 D $\approx 3.336 \times 10^{-30}$ C m.

Analytical data for the complexes are summarised in Table 2. The important spectral data are summarised in Table 1.

Synthesis of N-*Furfurylsalicylaldimine*, $C_{12}H_{11}NO_2$.—A mixture of salicylaldehyde (12.21 g, 0.1 mol) and furfurylamine (9.70 g, 0.1 mol) in methanol (100 cm^3) was refluxed for 0.5 h. The methanol was removed *in vacuo* and the residue triturated with diethyl ether affording *N*-furfurylsalicylaldimine, L (b.p. 155—157 °C).

Synthesis of Metal Complexes.—Bis(N-*furfurylsalicylaldiminato*)*nickel*(II), $Ni(C_{12}H_{10}NO_2)_2$. To a solution of nickel chloride (2.39 g, 0.01 mol) in methanol was added slowly, with constant stirring, a solution of Schiff base (4.04 g, 0.02 mol) in methanol. A suspension of sodium acetate in methanol was added to this mixture with constant stirring till a green precipitate was formed. The solid was filtered off, washed with methanol, and dissolved in hot chloroform. The chloroform solution was allowed to stand overnight at room temperature giving yellowish green crystals of (4) (0.90 g, 20%). The mother-liquor was reduced to a small volume *in vacuo* and the residue was chromatographed on a silica-packed column. Elution with chloroform gave green crystals of (3) (2.75 g, 60%).

The isomeric complexes of cobalt(III), copper(II), and palladium(II) were synthesised using a similar procedure (Table 1 and 2). The palladium(II) complexes were separated by using acetone instead of chloroform. In the preparation of the cobalt(III) complex, H_2O_2 was used to oxidise Co^{II} to Co^{III}.

The complexes of $V^{IV}O$, Cr^{III}, Mn^{II}, Fe^{III}, Be^{II}, and Zn^{II} were obtained in one isomeric form. The complex of Pt^{II} was prepared by treating bis(salicylaldehyde)platinum(II) with furfurylamine in refluxing methanol.

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