Metal Complexes of *N*-2-Thenylsalicylaldimine †

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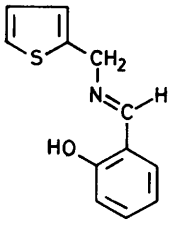
The ligand isomeric complexes of *N*-2-thenylsalicylaldimine with Pd^{II} were synthesised. The nature of the isomerism was characterised by the ^1H n.m.r. spectral data for the azomethine group, C=N group i.r. frequencies, and u.v. spectra. The complexes with Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, and Pt^{II} were obtained in the isomeric form (A), *i.e.* $SC_4H_3CH_2N{=}CHC_6H_4OH$-*o*, and those of V^{IV} and Zn^{II} were obtained in the isomeric form (B), *i.e.* $SC_4H_3CH{=}NCH_2C_6H_4OH$-*o*. From its solubility characteristics and ^1H n.m.r. spectra, the palladium(II) complex containing ligand isomer (A) was shown to be a binuclear complex in which the phenolic oxygen displays three-co-ordination. The subnormal magnetic moment at room temperature and the cryomagnetic data of the copper(II) complex suggested a similar binuclear configuration having a large antiferromagnetic interaction ($J = -175\ cm^{-1}$, $g = 2.4$). The cryomagnetic data of the iron(III) complex indicated a thermal equilibrium between nearly equi-energetic spin-paired ($^2T_2$) and spin-free ($^6A_1$) configurations of iron(III). Co-ordination of the thiophene sulphur was indicated in the (B) isomeric form of the complexes of Pd^{II} and Zn^{II}.

Separation and characterisation of the ligand isomeric complexes of *N*-furfurylsalicylaldimine [1] suggested that the heteroatom participated directly or indirectly in controlling the observed ligand isomerisation. The complexes of Co^{III}, Ni^{II}, Cu^{II}, and Pd^{II} were obtained with both the *N*-furfurylsalicylaldimine and *N*-*o*-hydroxybenzylfuran-2-carbaldimine ligand isomers. The yields with the latter isomer were, however, less than 20%. With other metals only the complex containing the *N*-furfurylsalicylaldimine ligand isomer was obtained. These results prompted us to obtain data on the related ligand containing sulphur as the heteroatom, and this paper reports metal complexes of the Schiff base derived from 2-thenylamine and salicylaldehyde (Tables 1 and 2).

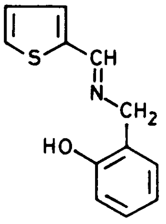
Results and Discussion

The deuterium exchange and concentration dependence of the ^1H n.m.r. spectra of *N*-2-thenylsalicylaldimine (L^1) were found to be similar to that of *N*-furfurylsalicylaldimine (L^2).[1] The OH signal was broad (10.4—11.2 p.p.m.), and there was no observable concentration effect on its position. The hydroxy-group was therefore assumed to be involved mainly in intramolecular hydrogen bonding [2] with the N of the azomethine group, and the self association and related equilibria of L^1 seemed to be of little significance. The intensity ratios of the two signals of N=CH, 9.75 and 8.28 p.p.m., and of $N{-}CH_2$, 5.58 and 4.76 p.p.m., increased with dilution in carbon tetrachloride. A similar dielectric effect due to the concentration variation has been reported for the keto–enol equilibrium of pentane-2,4-dione in cyclohexane [3] and for the equilibrium between the special isomers of D-camphorquinone in n-heptane.[4] The positions of the signals of N=CH and $N{-}CH_2$ were independent of concentration. Moreover, deuterium exchange had no effect on the positions and intensities of these signals. These results suggested that L^1 was present in two isomeric forms, *N*-2-thenylsalicylaldimine (A) and *N*-*o*-hydroxybenzylthiophene-2-carbaldimine (B). The ^1H n.m.r. signals at 8.28 and 4.76 p.p.m. were assigned to isomer (A) and those at 9.75 and 5.58 p.p.m. to (B). By analysing the i.r. spectrum of L^1 using a procedure similar to that reported earlier,[1] the bands at 1 632 and 1 650 cm^{-1} were asigned to ν(C=N) of isomers (A) and (B) respectively.

A separation of the ligand isomers (A) and (B) by usual physical techniques was found to be impracticable. However, they were separated as the palladium(II) complexes, one insoluble (1) and the other soluble (2) in benzene, with similar elemental analyses. Complex (2) was found to be stable only in benzene and dichloromethane. In other solvents (and also in refluxing dichloromethane) it was immediately transformed into a benzene-insoluble product which was found to



(A)



(B)

Table 1. Analytical data for metal complexes of 2-*N*-thenylsalicylaldimine

		Analyses (%)					
		Found			Calc.		
Complex	M.p. (°C)	C	H	N	C	H	N
(1) $[PdL^1_2]$	190—192 (decomp.)	53.1	3.9	5.0	53.3	3.7	5.2
(2) $[PdL^1_2]$	60.5	53.0	3.8	4.9	53.3	3.7	5.2
(3) $[CoL^1_3]$	98.0	60.5	4.5	5.5	60.8	4.3	5.7
(4) $[PtL^1_2]$	126.5	45.9	3.4	4.1	45.8	3.2	4.5
(5) $[ZnL^1_2]$	155.0	57.8	4.1	5.4	57.7	4.0	5.6
(6) $[VOL^1_2]$	113.0	57.6	4.1	5.5	57.5	4.0	5.6
(7) $[CrL^1_3]$	142—145 (decomp.)	61.8	4.4	5.7	61.4	4.3	5.9
(8) $[FeL^1_3]$ [a]	117.5	60.8	4.5	5.7	61.1	4.2	5.9
(9) $[NiL^1_2]$	120.5	58.7	4.2	5.9	58.5	4.1	5.7
(10) $[CuL^1_2]$	220—223 (decomp.)	57.5	3.8	5.7	57.9	4.0	5.6
L^1	*b*	66.5	4.9	6.1	66.3	5.1	6.4

[a] Molecular weight in benzene: found, 682; required, 704.2. [b] B.p. 108—110 °C at 600 mmHg.

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† *Non-S.I. units employed*: B.M. ≈ $9.27 \times 10^{-24}\ J\ T^{-1}$, mmHg ≈ 133 Pa.

Table 2. Physical data for metal complexes of *N*-2-thenylsalicylaldimine

Complex	Ligand isomer	Colour	I.r. spectra (cm^{-1})			^1H N.m.r.[a] (p.p.m.)		μ/B.M. (at 300 K)
			ν(C=N)	δ(CH_2)	ν(C–S–C)	δ(CH)	δ(CH_2)	
(1)	(A)	Yellow	1 620	1 448	1 320	8.25	5.22	
(2)	(B)	Pale orange	1 638	1 438	1 270, 1 350	9.76, 9.70	5.28	
(3)	(A)	Green	1 612	1 450	1 316	8.18	5.65, 6.50, 5.56	
(4)	(A)	Orange	1 608	1 448	1 315	8.28	5.25	
(5)	(B)	Pale yellow	1 648	1 440	1 275, 1 348	9.80, 9.64	4.90, 4.66	
L^1	(A)	Pale yellow	1 632	1 448	1 270, 1 340,	8.28	4.76	
	(B)		1 650	1 475	1 370	9.75	5.58	
(6)	(B)	Green	1 640	1 460	1 350			1.69
(7)	(A)	Green	1 615	1 445	1 318			3.80
(8)	(A)	Red	1 614	1 450	1 316			4.51
(9)	(A)	Green	1 612	1 448	1 315			*b*
(10)	(A)	Pale green	1 615	1 452	1 320			1.46

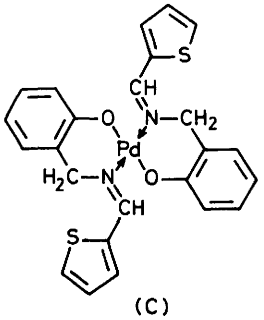
[a] Solvents used: for (1), [$^2H_5$]pyridine; (2), [$^2H_6$]benzene; other compounds, $CDCl_3$. [b] Diamagnetic, but paramagnetic in solution.

be identical with complex (1) from the analytical and spectral data. The complexes containing other metal ions prepared in the present work were obtained in only one isomeric form. It should be noted that with metal ions other than palladium(II), no observable reaction occurred in benzene and it was necessary to use polar solvents for the synthesis of the other metal complexes.

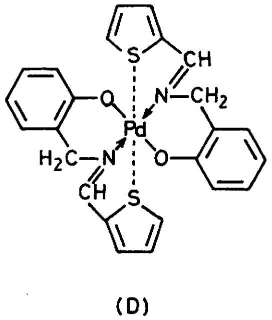
The resonance of the azomethine proton in complex (1) (determined in [$^2H_5$]pyridine) appeared at 8.25 p.p.m. and that of the CH_2 group at 5.22 p.p.m. The corresponding values for complex (2) (in C_6D_6) were 9.70 and 9.76 p.p.m. (both N=CH) and 5.28 p.p.m. Thus complex (1) contains isomer (A) and complex (2) contains isomer (B). The appearance of two signals for the azomethine proton in complex (2) suggested the presence of an equilibrium between a square-planar (C) and an octahedral configuration.[1] The latter would involve bonding through the thiophene sulphur expanding the co-ordination sphere of the monomeric complex from four to six.[5] It would be a mixture of different geometrical isomers. The meridional isomer is illustrated by structure (D). The ^1H n.m.r. spectrum of the zinc(II) complex (5) was similar to that of (2) displaying two signals at 9.64 and 9.80 p.p.m. due to the azomethine proton and two at 4.90 and 4.66 p.p.m. due to the CH_2 group. These results suggested that here also the thiophene sulphur participated in metal–ligand bonding. Bonding through the heterocyclic group seemed to be absent in complex (1) from the ^1H n.m.r. spectra. It should be noted that this complex was insoluble in common solvents, but could be brought into solution in solvents which behaved as Lewis bases. This suggests that the co-ordination number of the phenolic oxygen in (1) is three,[6] forming the binuclear complex (E).[7]

The i.r. spectra of complexes (1) and (2) substantiated the structural features suggested from the ^1H n.m.r. data. The position of ν(C=N) was [8] at 1 638 cm^{-1} for complex (2) and at 1 620 cm^{-1} for (1). Another characteristic region was 1 270—1 350 cm^{-1} which was assigned to the C–S–C stretching vibration in thiophene and its derivatives.[9] Complex (2) showed two bands in this region, at 1 270 and 1 350 cm^{-1}, while its isomer (1) showed only one band at 1 320 cm^{-1}.

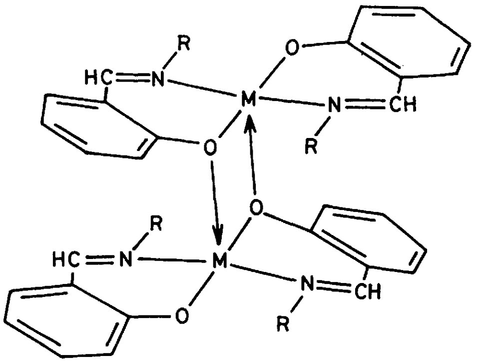
The C=N group frequencies of complexes (3), (4), and (7)—(10) were in the region 1 608—1 620 cm^{-1}, and that of complex (6) was at 1 640 cm^{-1} (Table 2). A comparison of these data with ν(C=N) of complexes (1) and (2) suggested that complexes (3), (4), and (7)—(10) contained isomer (A) and complex (6) contained isomer (B) of L^1. The ^1H n.m.r. spectra of complexes (3) and (4) substantiated this. The resonance of the azomethine proton in complex (3) appeared at 8.18 p.p.m. and that in complex (4) appeared at 8.28 p.p.m. The ^1H n.m.r. spectra of other complexes were broad, probably due to their paramagnetic nature.



(C)

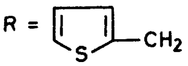


(D)



(E) M = Cu^{II} or Pd^{II}

R =



A comparison of the u.v. spectra of the complexes with that of ligand L^1 gave further evidence for the ligand isomerisation. Gaussian analysis of the broad asymmetric band observed for L^1 in methanolic K[OH] solution revealed two bands at 350 and 365 nm, that at lower energy being assigned to isomer (A) and the other to (B), on the basis of the resonance contribution. In the isomer (A) the C=N group favours the mesomeric

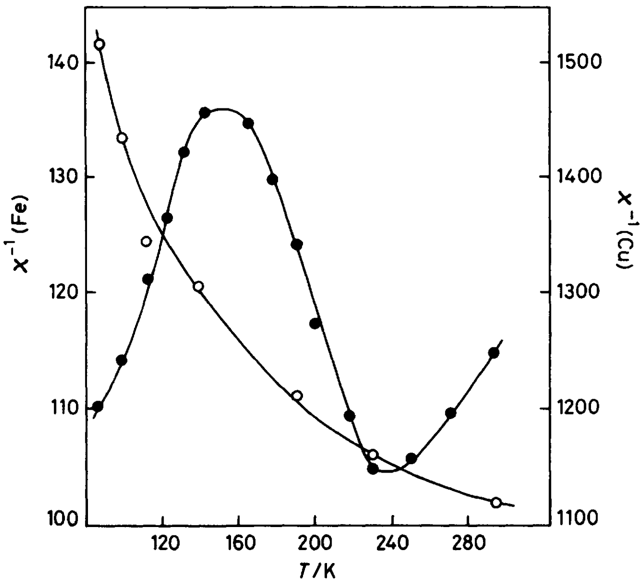


Figure. Temperature variation of reciprocal magnetic susceptibility of [FeL$^1_3$] (●) and [CuL$^1_2$] (○)

polarization of the benzene ring. It was interesting to observe that all the complexes which were thought to contain ligand isomer (A), on the basis of i.r. and ^{1}H n.m.r. spectra, showed a red shift of *ca.* 10—25 nm in the band assigned to the isomer (A). A similar shift of *ca.* +5 nm was observed for complex (2) and of *ca.* −6 nm for complex (5) which were thought to contain the isomer (B).

The magnetic properties of the iron(III) complex (8) and copper(II) complex (10) gave further insight into the interesting structural aspects of these complexes. The solubility of complex (10) was negligible, similar to that of (1), in the usual organic solvents but it was soluble in Lewis bases such as pyridine. The subnormal magnetic moment (1.46 B.M.) of complex (10) at room temperature is attributed to a binuclear configuration [10] similar to (E). A plot of the reciprocal molar magnetic susceptibilty (χ_M^{-1}) *vs.* temperature (T) (Figure) indicated the presence of antiferromagnetic interaction between the electron spins on the metal ions in the binuclear complex. The values of the exchange integral J and Landé g factor were determined by computer fitting of the Bleaney–Bowers equation (i).[11] Here N is the Avogadro number, β the

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\cdot\frac{3e^{2J/kT}}{1+3e^{2J/kT}} + N\alpha \qquad \text{(i)}$$

Bohr magneton, k the Boltzmann constant, and $N\alpha$ the temperature-independent magnetic susceptibility (assumed to be 60×10^{-6} c.g.s. units). The values of J (-175 cm^{-1}) and g(2.4) calculated for complex (10) were much higher than those reported for similar binuclear Schiff-base complexes for which a comparatively low value of the singlet-triplet separation was observed.[12,13] This observation suggested a significantly large antiferromagnetic interaction between the electron spins on the two metal ions in complex (10).

The magnetic moment of iron(III) complex (8) at room temperature was much lower (4.51 B.M.) than that expected (5.92 B.M.) for the high-spin iron(III) complex.[14] This anomalous behaviour could not be due to intramolecular antiferromagnetic interaction similar to that observed for the trinuclear [Fe$_3$O(O$_2$CMe)$_6$]$^+$ cation,[15] since the molecular weight of complex (8) in benzene solution indicated that it was monomeric. The intermolecular interactions in the solid state would be also insignificant for an octahedral complex such as (8) as it was freely soluble in organic solvents such as benzene and chloroform. These observations suggested a thermal equilibrium between nearly equi-energetic spin-paired ($^2T_2$) and spin-free ($^6A_1$) configurations of iron(III) in complex (8). Assuming the magnetic moments at room temperature associated with the low-spin configuration to be 2.30 B.M. and that with the high-spin configuration to be 5.92 B.M., the observed magnetic moment of complex (8) suggested that, at room temperature, it contains 50% of the high-spin isomer.[16]

Further support for an equilibrium between the spin-paired and the spin-free configurations [17] of iron(III) in complex (8) was obtained from its cryomagnetic susceptibility data in the temperature range 85—295 K (Figure). The magnetic moment varied smoothly between 2.51 B.M. (at 86.5 K) and 4.51 B.M. (at 292 K). The temperature variation of the reciprocal magnetic susceptibility revealed both a minimum and a maximum. This is typical of the behaviour of an iron(III) complex in which the energy separation between the zero-point levels of the $^2T_2$ and $^6A_1$ states ($|E|$) is less than the one-electron spin–orbit coupling constant (ξ), *i.e.* $|E|/\xi < 1.0$ (for $g \approx 2$).[18] In the near-i.r. region this complex in solution displayed a weak broad band at 1 300 nm, possibly due to overlap of the $^6A_1 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_1$ ligand-field transitions in the high- and low-spin octahedral isomeric complexes respectively.

Experimental

Infrared spectra were measured in the range 400—4 000 cm^{-1} on a Perkin-Elmer 337 spectrophotometer for Nujol and hexachlorobutadiene mulls. Electronic spectra were recorded in the range 200—900 nm on a Beckman DK-2 ratio recording spectrophotometer using methanol and dichloromethane as solvents. Hydrogen-1 n.m.r. spectra were obtained on a Perkin-Elmer R-32 spectrometer at 90 MHz using [^{2}H$_5$]pyridine, [^{2}H$_6$]benzene, and CDCl$_3$ as solvents and tetramethylsilane for the lock signal. The cryomagnetic measurements were performed in the temperature range 85—295 K on a Faraday balance assembled at the Tata Institute of Fundamental Research, Bombay. Molecular weights were determined in benzene solution using a Wescan model 232 A vapour-pressure osmometer. The elemental analyses were obtained from the Microanalytical Division of the National Chemical Laboratory, Pune. Computations were done on an ICL 1904S computer at the Regional Computer Centre, Pune.

2-Thenylamine (b.p. 62—64 °C, 4 mmHg; lit.,[19] 63—65 °C, 4 mmHg) was synthesised by aminomethylation of thiophene. All other chemicals were of AnalaR B.D.H. grade.

Synthesis of N-2-*Thenylsalicylaldimine*, L^1.—A mixture of salicylaldehyde (12.21 g, 0.1 mol) and 2-thenylamine (11.31 g, 0.1 mol) in methanol (100 cm^3) was refluxed for 0.5 h. The methanol was removed *in vacuo*, and the residue was triturated with diethyl ether affording N-2-thenylsalicylaldimine, b.p. 108—110 °C (600 mmHg).

Synthesis of Metal Complexes: Reaction of N-2-*Thenylsalicylaldimine with Palladium*(II) *Chloride*.—To a solution of L^1 (4.34 g, 0.02 mol) in benzene (50 cm^3) was added powdered palladium(II) chloride (1.79 g, 0.01 mol). The mixture was stirred for 8 h and the volume was reduced *in vacuo* when a solid separated. The solid was filtered off, washed thrice with benzene, then with acetone, and finally with diethyl ether, affording yellow crystals of complex (1) (3.20 g, 60%). The benzene filtrate was evaporated to dryness *in vacuo*, and the solid was purified by two successive crystallisations from benzene–light petroleum (b.p. 60—80 °C) (2 : 1 v/v) yielding pale orange crystals of (2) (1.30 g, 25%).

The complexes of V^{IV}, Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}, and Cu^{II} were obtained using methanol instead of benzene as a reaction medium in the above procedure, and that of Zn^{II} was obtained using benzene–methanol (3 : 1 v/v). The complex of Pt^{II} was obtained by treating bis(salicylaldehydato)platinum(II) with 2-thenylamine in ethanol at 40 °C.

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