^{1}H Nuclear Magnetic Resonance Investigation of the Formation of Molecular Salicylideneiminato-cobalt(II), -nickel(II), -copper(II), and -zinc(II) Complexes with 1,3,5-Trinitrobenzene

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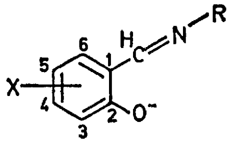
1 : 1 Molecular complexes of tetrahedral cobalt(II), nickel(II), copper(II), and zinc(II) salicylideneiminates and 1 : 2 complexes of square-planar nickel(II) and copper(II) salicylideneiminates with 1,3,5-trinitrobenzene (tnb) have been isolated, and molecular-complex formation in chloroform solution has been demonstrated by ^{1}H n.m.r. probe methods. In some cases the direction of the shift of the tnb resonance could be reversed by the introduction of a nitro-substituent into the salicylideneiminato-chelate. ^{1}H N.m.r. spectra of several salicylideneiminato-cobalt(II) complexes and the temperature dependence of a zinc(II) derivative are also described.

METAL chelate complexes are known [1] to form molecular complexes with a number of nitroarenes. In an attempt to determine the influence of the structure of the metal chelate complex on that of the molecular complex, we have investigated a series of complexes in which the co-ordination geometry of the metal ion is that of a distorted tetrahedron. A secondary interest has been the comparison of different transition-metal complexes as 'shift reagents' in the attempt, not so much to aid spectral analysis, but to elucidate electronic and molecular interactions in solution.[2] These two objectives combine in this report of an investigation of molecular complexes formed by bis(salicylideneiminato) derivatives of cobalt(II), nickel(II), copper(II), and zinc(II).

EXPERIMENTAL

3-Nitro- and 5-nitro-salicylaldehyde were obtained from Eastman Kodak Company, while the 4-methyl derivatives were prepared by the Duff reaction [3] on *m*-cresol. 1,3,5-Trinitrobenzene (tnb) was twice recrystallized from ethanol. Most of the metal salicylideneiminato-complexes were prepared in crystalline form by published procedures [4] and had satisfactory analyses and melting points. Data for complexes not previously reported are given in Table 1.



(I); R = Pr^i, X = 4-Me
(II); R = Pr^i, X = 3-NO$_2$
(III); R = Bu^s, X = 3-NO$_2$
(IV); R = Bu^s, X = 5-NO$_2$
(V); R = Bu^t, X = 3-NO$_2$
(VI); R = Bu^t, X = 5-NO$_2$
(VII); R = Bu^t, X = H
(VIII); R = Bu^s, X = H
(IX); R = Pr^i, X = H
(X); R = Bu^n, X = H
(XI); R = Bu^i, X = H

TABLE 1

Analyses and melting points of new salicylideneiminato-cobalt(II) complexes, [Co(L)$_2$]

	Found (%)			Calc. (%)			
L	C	N	H	C	N	H	M.p.(*t*/°C)
(I)	64·2	7·0	6·6	64·3	6·8	6·8	230—232
(II)	50·6	11·7	4·5	50·7	11·8	4·7	270—272
(III)	53·1	11·3	5·1	52·8	11·2	5·2	264—267
(IV)	53·3	11·3	5·2	52·8	11·2	5·2	203—204
(V)	52·8	11·5	5·1	52·8	11·2	5·2	>360
(VI)	52·5	11·4	5·2	52·8	11·2	5·2	302—304

Molecular Complexes.—The same experimental procedure was used for each of these preparations. The acceptor (0·5 or 1 mmol), usually tnb, was dissolved in a slight excess of warm solvent and the metal chelate complex donor (0·5 mmol) was added. After heating and stirring for a few minutes, the solution was filtered and allowed to cool slowly. The crystalline molecular complex was obtained after 1—3 days provided that the solubility relation between the two components was correct. It was filtered off, washed with a little cold solvent, and dried *in vacuo*. *Bis*[N-(*t-butyl*)-*salicylideneiminato*]*cobalt*(II)–1,3,5-*Trinitrobenzene* (1/1). Red prisms from ethanol (Found: C, 53·9; H, 5·1; N, 11·4. Calc. for $C_{22}H_{28}H_2O_2{\cdot}C_6H_3N_3O_6$: C, 53·85; H, 5·0; N, 11·0 %). *Bis*[N-(*s-butyl*)*salicylideneiminato*]*nickel*(II)–1,3,5-*Trinitrobenzene* (1/2). Dark red needles from cyclohexane (Found: C, 49·0; H, 4·0; H, 13·55. Calc. for $C_{22}H_{28}NiN_2O_2{\cdot}2C_6H_3N_3O_6$: C, 48·75; H, 4·1; N, 13·4 %). *Bis*[N-(*t-butyl*)*salicylideneiminato*]*nickel*(II)–1,3,5-*Trinitrobenzene* (1/1). Brown, double-truncated bipyramids from cyclohexane (under anhydrous conditions) (Found: C, 53·5; H, 5·1; N, 10·85. Calc. for $C_{22}H_{28}NiN_2O_2{\cdot}C_6H_3N_3O_6$: C, 53·85; 5·05; N, 11·2 %). *Bis*[N-(*i-propyl*)*salicylideneiminato*]*nickel*(II)–1,3,5-*Trinitrobenzene* (1/2). Reddish brown needles from ethanol; m.p. 118—119 °C (Found: C, 47·55; H, 3·65; N, 13·6. Calc. for $C_{20}H_{24}NiN_2O_2{\cdot}2C_6H_3O_6$: C, 47·5; H, 4·0; N, 13·85 %). *Bis*[N-(*n-butyl*)-*salicylideneiminato*]*nickel*(II)–1,3,5-*Trinitrobenzene* (1/2). Reddish black prisms from dry cyclohexane, recrystallized from ethanol; m.p. 133—134 °C (Found: C, 48·7; H, 3·75; N, 13·35. Calc. for $C_{22}H_{28}NiN_2O_2{\cdot}2C_6H_3N_3O_6$: C, 48·75; H, 4·1; N, 13·4%). *Bis*[N-(*i-propyl*)*salicylideneiminato*]-*copper*(II)–1,3,5-*Trinitrobenzene* (1/2). Yellowish brown needles from n-hexane; m.p. 111—112 °C (Found: C, 47·3; H, 3·35; N, 13·7. Calc. for $C_{20}H_{24}CuN_2O_2{\cdot}2C_6H_3N_3O_6$: C, 47·2; H, 3·7; N, 13·8 %). *Bis*[N-(*s-butyl*)-*salicylideneiminato*]*copper*(II)–1,3,5-*Trinitrobenzene* (1/2). Brown microcrystals from ethanol; m.p. 83—84 °C (Found: C, 48·2; H, 3·95; N, 13·05. Calc. for $C_{22}H_{28}CuN_2O_2{\cdot}2C_6H_3N_3O_6$: C, 48·45; H, 4·05; N, 13·3 %). *Bis*[N-(*n-butyl*)-*salicylideneiminato*]*copper*(II)–1,3,5-*Trinitrobenzene* (1/2).

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[1] C. K. Prout and J. D. Wright, *Angew. Chem.*, 1968, **80**, 688.

[2] H. A. O. Hill, P. J. Sadler, R. J. P. Williams, and C. D. Barry, *Ann. New York Acad. Sci.*, in the press.

[3] J. C. Duff, *J. Chem. Soc.*, 1941, 547.

[4] R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

Brownish yellow prisms from ethanol; m.p. 126—127 °C (Found: C, 48·6; H, 3·95; N, 13·25. Calc. for $C_{22}H_{28}CuN_2O_2{\cdot}2C_6H_3N_3O_6$: C, 48·45; H, 4·05; N, 13·3%). *Bis-*[N-*(t-butyl)salicylideneiminato*]*copper*(II)–1,3,5-*Trinitrobenzene* (1/1). Dark red bipyramids from ethanol (Found: C, 53·5; H, 4·4; N, 10·9. Calc. for $C_{22}H_{28}CuN_2O_2{\cdot}C_6H_3N_3O_6$: C, 53·45; H, 4·95; N, 11·15%). *Bis*[N-(*t-butyl*)*salicylideneiminato*]*zinc*(II)–1,3,5-*Trinitrobenzene* (1/1). Well formed red prisms from yellow solution in ethanol; m.p. 168—169 °C (Found: C, 52·85; H, 5·15; N, 11·1. Calc. for $C_{22}H_{28}N_2O_2Zn{\cdot}C_6H_3N_3O_6$: C, 53·3; H, 4·9; N, 11·1%). I.r. spectra of all the molecular complexes were recorded and consisted of bands from both components with small or no shifts in their positions. An unsuccessful attempt was made to prepare the complex of bis[*N*-(i-propyl)salicylideneiminato]cobalt(II) with tnb from ethanol.

^1H N.m.r. spectra were recorded on a JEOL-JNM-C-60HL spectrometer operating at 60 MHz or a JNM-4H-100 machine at 100 MHz. Solutions were made up in $CDCl_3$ (99·8%), with tetramethylsilane as internal standard. The 300 p.p.m. spectra of the cobalt salicylideneiminato-complex were calibrated by the sideband technique, and shifts were accurate to ±0·5 p.p.m. Temperature variations over the range 220—330 K were monitored by the method of van Geet.[5]

RESULTS AND DISCUSSION

Although much work has been reported on the n.m.r. spectra of nickel(II) salicylideneiminato-complexes,[4] and a brief report has appeared on a cobalt(II) salicylideneiminato-complex,[6] we describe here the ^1H n.m.r. spectra of a wide variety of cobalt(II) salicylideneiminato-complexes and an interesting feature of the spectrum of a zinc(II) derivative.

Cobalt(II) *Salicylideneiminato-complexes.*—Paramagnetic (Knight) shifts for a series of cobalt complexes at 298 K are given in Table 2. Negative values indicate downfield shifts of the proton resonances from their positions in the corresponding zinc chelate complexes, and positive values shifts to higher fields. Considerable difficulty was encountered in distinguishing the $-CH{=}N-$ signal, which has not previously been reported, presumably on account both of its great breadth (width at half height *ca.* 30 p.p.m.) and its large low-field shift.

TABLE 2

Paramagnetic (Knight) shifts (p.p.m.) of cobalt(II) salicylideneiminato-complexes $[Co(L)_2]$ at 298 K

L	3-H	4-H	5-H	6-H	$-CH{=}N-$	α-CH or α-CH_2	β-CH_2	β-CH_3	γ-CH_2 or γ-CH_3	Others
(IX)	+17·4	−47·1	+10·6	−36·9	−422	−152		+26·3		
(I)	+16·8		+11·2	−37·0	−440	−155		+24·1		4-Me, +16·0
(II)		−42·5	+11·0	−32·5	*a*	−149		+28·5		
(X)	+15·9	−49·0	+12·0	−39·2	*a*	−124	+37·0		+5·0	CH_3 + 5·0
(VIII)	*b*	−46·3	+10·6	−37·7	−436	−152	+29·0	+28·0	+8·8	
(III)		−43·5	+9·1	−34·5	*a*	−155	+30·5	+30·5	+9·2	
(IV)	*b*	−46·5		−35·5	*a*	−155	+27·8	+27·8	+7·3	
(VII)	+13·0	−45·3	+10·5	−36·4	−432			+7·5		
(V)		−41·8	*b*	−33·5	*a*			+6·0		
(VI)	+13·5	−45·0		−33·6	*a*			+6·3		

[a] Not searched for. [b] Unresolved at 298 K.

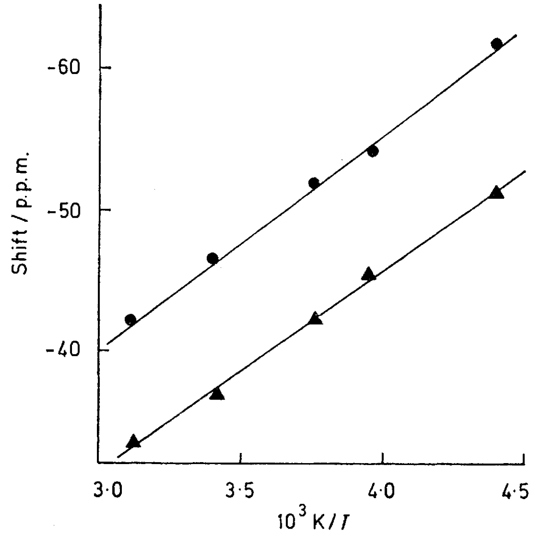

FIGURE 1 Temperature variation of the paramagnetic shifts of the 4-H (●) and 6-H(▲) protons of the complex $[Co(L)_2]$-[L = (VIII)]

The variation with temperature of the chemical shift of all the well resolved signals was measured for the complexes $[Co(L)_2]$ [L = (VII) and (VIII)]. In all cases a linear dependence of shift on T^{-1} (Curie Law) was seen. This dependence is illustrated in Figure 1 for the 4-H and 6-H resonances of the L = (VIII) complex.

Very little work has been reported on the separation of the shifts of pseudo-tetrahedral cobalt(II) complexes into contact and dipolar (pseudo-contact) contributions. It has been suggested[7] that the pseudo-contact term arising from zero-field splitting effects might be considerable. But in the absence of *g* values, and particularly of single-crystal susceptibility measurements, no reliable estimates of the dipolar contribution can be made. Comparison of shifts in analogous nickel and

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[5] A. L. van Geet, *Analyt. Chem.*, 1968, **40**, 2227.

[6] C. Benelli, I. Bertini, and D. Gatteschi, *J.C.S. Dalton*, 1972, 661.

[7] R. J. Kurland and B. R. McGarvey, *J. Mag. Res.*, 1970, **2**, 286.

cobalt complexes by use of the 'ratio method'[8] is not applicable to tetrahedral species.

Some trends are apparent from the data in Table 2. The introduction of an NO_2 group at the 3-position gives rise to high-field shifts of 3—5 p.p.m. for the 4-H and 6-H relative to the unsubstituted cobalt salicylideneiminato-complexes. When the NO_2 group is placed at the 5-position, the 6-H is again shifted to high field (*ca.* 2 p.p.m.) whereas the resonance position of the 4-H, and also that of the 3-H, is unchanged. It might be thought that these effects could be rationalized by considering the electron-withdrawing properties normally associated with the nitro-group, and that the changes in the n.m.r. spectra could be attributed solely to variations in the contact term associated with the redistribution of electronic charge. However, in the study of the interaction of metal salicylideneiminato-complexes with some aromatic acceptor molecules (*vide infra*), it will be seen that the introduction of nitro-groups into the salicylideneiminato-donor molecules causes considerable changes in the magnitude and direction of the shifts induced in the acceptors, and these shifts are ascribed mainly to the dipolar contribution. Thus in considering the n.m.r. spectra of the metal chelate complexes themselves, variations induced by the presence of substituents must be interpreted in terms of changes in both contact *and* pseudo-contact contributions.

Zinc(II) *Salicylideneiminato-complexes.*—In the spectrum of the complex $[Zn(L)_2]$ [L = (IX)] at ambient temperature (298 K) the methyl protons of the alkyl side chains appear as a 1 : 2 : 1 triplet. It was only at higher temperatures that the expected doublet appeared. At lower temperatures two doublets arising from the now non-equivalent methyl groups were present in the spectrum, coupling to the neighbouring C–H proton being still the same with $J = 6{\cdot}5$ Hz. These effects are illustrated in Figure 2. The coalescence temperature was *ca.* 303 K.

This behaviour is reminiscent of that which has been analysed in detail for amines such as *NN*-dimethylformamide.[9] As expected, the spectrum of the zinc(II) chelate complex with the less-bulky substituent [L = (X)] was not temperature dependent (233—323 K). On the other hand, the $CH-CH_3$ methyl peak of the L = (VIII) complex showed similar splittings to those in Figure 2 and an additional splitting of the $-CH{=}N$ peak was observed. However the L = (VII) and (XI) complexes gave only slightly broadened methyl resonances as the temperature was lowered. Curiously there was no temperature effect on the resonances of the L = (IV) chelate complex.

It seems likely that these effects arise from known steric interactions in metal salicylideneiminato-complexes, as can be seen by comparing chemical shifts of the $-CH{=}N-$ proton, in the 'tetrahedral' zinc chelate complex with those of the 'square-planar' palladium chelate complex. On changing from L = (X) to L = (VII), there is an upfield shift of 0·08 p.p.m. (from −8·18 to −8·10 relative to Me_4Si) for the zinc complex, and one of 0·30 p.p.m. (from −7·60 to −7·30) for the palladium complex. The aromatic resonances are at about the same positions in all four complexes. Whereas square-planar nickel(II) complexes tend to relieve steric strains introduced by bulky groups by distorting towards tetrahedral configurations, palladium(II) complexes are square planar irrespective of the nature of R. Consequently the intramolecular contact between the methyl and $-CH{=}N-$ protons in crystals of $[Pd(L)_2]$ [L = (VII)][10] is 0·9 Å less than the sum of the van der Waals radii. The electronic spectrum is also different from that when L = (X),[11] although both complexes are diamagnetic.

Molecular Complexes.—1 : 1 Complexes of the metal salicylideneiminates with 1,3,5-trinitrobenzene (tnb) have been isolated for L = (VII) and M = Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, and the crystal structures determined[12] for all except the zinc(II) complex. The complexes contain stacks of *isolated* donor–acceptor *pairs* of molecules (unlike most molecular complexes of metal chelate complexes, usually square planar, which contain[1] alternating stacks of 'donor' and 'acceptor' molecules). There is a plane-to-plane interaction between tnb and one of the salicylideneiminato-ligands of a given chelate complex (Figure 3) and no specific interactions with the metal. The overlapping ligand showed deviations from

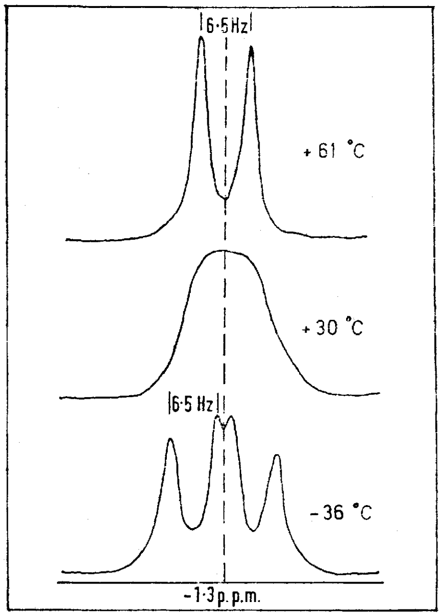

FIGURE 2 Temperature dependence of the methyl resonances of the complex $[Zn(L)_2]$ [L = (IX)]

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[8] W. De W. Horrocks jun., *Inorg. Chem.*, 1970, **9**, 690.

[9] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.

[10] V. W. Day, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1968, **90**, 4803.

[11] S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Japan*, 1969, **42**, 2543.

[12] E. E. Castellano, O. J. R. Hodder, C. K. Prout, and P. J. Sadler, *J. Chem. Soc.* (*A*), 1971, 2620.

planarity and the O_2N_2 tetrahedron around the metal ion was flattened in the order Cu > Ni > Co.

1 : 2 Molecular complexes have now been isolated for the nickel(II) and copper(II) chelate complexes with L = (VIII)—(X). The stoicheiometry of these molecular complexes suggests that a plane-to-plane stacking arrangement of tnb molecules with *both* salicylideneiminato-ligands of a given metal chelate complex can be accommodated in the crystal only when the metal chelate complex is square planar or can distort towards this geometry. Cobalt(II), like zinc(II) salicylideneiminates, are usually tetrahedral irrespective of R, whereas those of copper(II), like nickel(II), are square planar unless [4] R is bulky (*e.g.*, t-butyl).

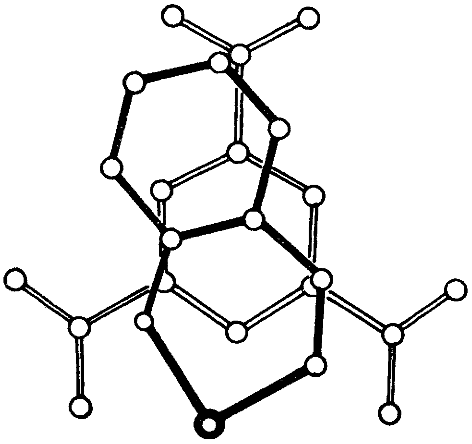

FIGURE 3 Overlap of the metal salicylideneiminato-complex and 1,3,5-trinitrobenzene found in the crystal [12]

N.M.R. Probes.—The effects of increasing concentrations of the complexes $[M(L)_2]$ [M = Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}; L = (VII)] on the tnb proton resonance at $-9{\cdot}38$ p.p.m. are shown in Figure 4. There is a fast exchange between complexed and uncomplexed species. The relative broadenings, determined from plots of linewidths at half height against metal concentration, are Co : Ni : Cu : Zn = 100 : 15 : 125 : 0, probably a consequence of the long electronic spin-relaxation time of tetrahedral Cu^{II}, and the large magnetic moment of Co^{II}. The equilibrium constant, K, and shift, Δ_0, in the fully formed Ni^{II} complex were determined by the method of Foster *et al.*,[13] by measuring the shift of tnb in the presence of a large excess of the metal chelate complex and were obtained from a plot of (shift/$[Ni^{II}(L)_2]$) against shift, which has a gradient of $-K$ and an intercept of $\Delta_0 K$ for a 1 : 1 association, giving $K = 0{\cdot}9 \pm 0{\cdot}6$ mol^{-1} and $\Delta_0 = 5 \pm 3$ p.p.m. Small high-field shifts with the diamagnetic zinc(II) chelate complex arise from increased shielding of the tnb protons, which suggests that they may lie over the aromatic system of the salicylideneiminato-ligand as they do in crystals of the cobalt(II), nickel(II), and copper(II) complexes (Figure 3).

The cobalt, nickel, and copper complexes shift the aromatic and methyl protons of 2,4,6-trinitrotoluene (tnt) in the same direction. At equal concentrations (0·1M) of tnt and $[M(L)_2]$ [L = (VII)] complex in $CDCl_3$ the shifts of the aromatic H and CH_3 protons were +0·92 and +0·79 for Co^{II}, −0·15 and −0·10 for Ni^{II}, and −0·16 and −0·05 p.p.m. for Cu^{II}, respectively. The lack of alternation in the direction of the shifts of the methyl and aromatic protons suggests that no significant amount of spin is transferred from the chelate complex to the acceptor molecule and that the Knight shifts may be determined mainly by the dipolar contribution. If no significant spin is transferred, this may provide additional evidence that the principal contribution to the formation of molecular complexes arises from 'electrostatic' interactions. The cobalt(II) complex gives rise to the largest shifts (Figure 4) those from the nickel(II) and copper(II) complexes being smaller and in the opposite direction. The dipolar shifts in axial symmetry [7] should be proportional to the anisotropy in the susceptibility tensor, $\chi_{\parallel} - \chi_{\perp}$, and $(3\cos^2\theta - 1)r^{-3}$, the geometrical term which describes the position of the proton with respect to the metal and the symmetry axis of the complex. Although magnetic anisotropies of the nickel(II) and copper(II) chelate complexes have been reported [14,15] to be in opposite directions, the shifts observed here suggest that in the complex $\chi_{\parallel} - \chi_{\perp}$ is positive for Ni^{II} and Cu^{II}, and negative for Co^{II}.

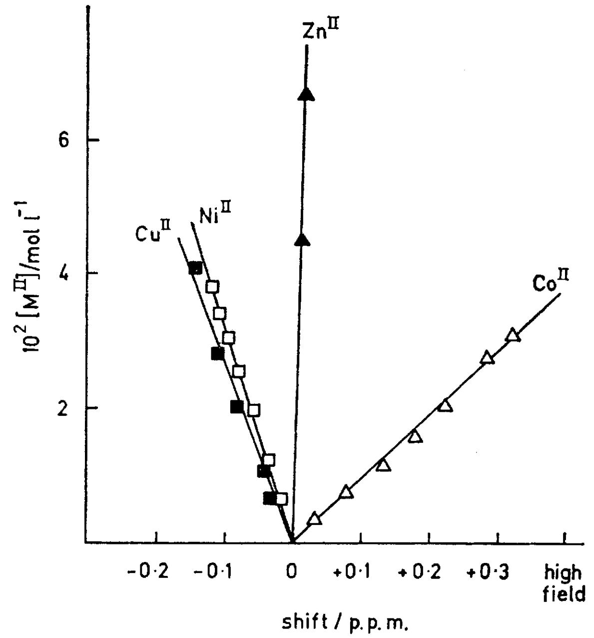

FIGURE 4 Effect of $[M(L)_2]$ [M = Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}; L = (VII)] complexes on the shift of tnb (0·09M) at 100 MHz and 34 °C in $CDCl_3$

Figures 5 and 6 illustrate the effect of the addition of cobalt(II) and nickel(II) nitrosalicylideneiminato-com-

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[13] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626.

[14] M. Gerloch, *J. Chem. Soc.* (*A*), 1968, 2023.

[15] M. Gerloch, *J. Chem. Soc.* (*A*), 1969, 1022.

plexes on the tnb resonance. In all the cases observed, the presence of a 3-nitro-group enhanced the shift of the tnb resonance compared to that of the unsubstituted salicylideneiminato-complexes (which may be due to a change in K and/or Δ_0), whereas a 5-nitro-group *reversed* the *direction* of the shift, which can only be due to a change in the *sign* of Δ_0. It is possible that the structures of the complexes with L = (IV) and (VI) are different from those of the other complexes, caused by some specific interaction with the 5-nitro-group, but two other factors could be important. First the substituents may change the magnitude of the components of the susceptibility tensor (if the real symmetry is lower than D_{2d} the dipolar shift will depend on χ_{xx}, χ_{yy}, and χ_{zz}). Secondly the dipolar term should include contributions from spin density delocalized on to the salicylideneiminato-ligand. If this alters on introduction of the substituent, then the sign of the dipolar contribution may be reversed. These points highlight the difficulty of assessing accurately the dipolar contribution in the absence of information on the susceptibility tensor and when a contact contribution is also present. However it is obvious that molecular-complex formation is readily detected by n.m.r. spectroscopy and that, when more detailed information on the magnetic properties of the metal complexes becomes available, it should be possible to reach more definite conclusions about the *structures* of the molecular complexes *in solution.*

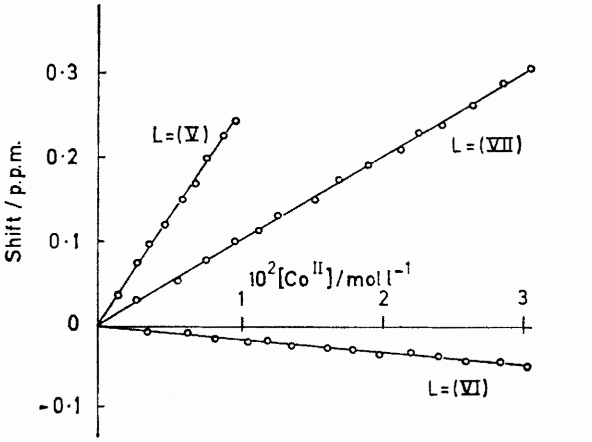

FIGURE 5 Effect of the complexes [Co(L)$_2$] [L = (V), (VI), and (VIII)] on the shift of tnb (0·09M) at 60 MHz and 25 °C in CDCl$_3$

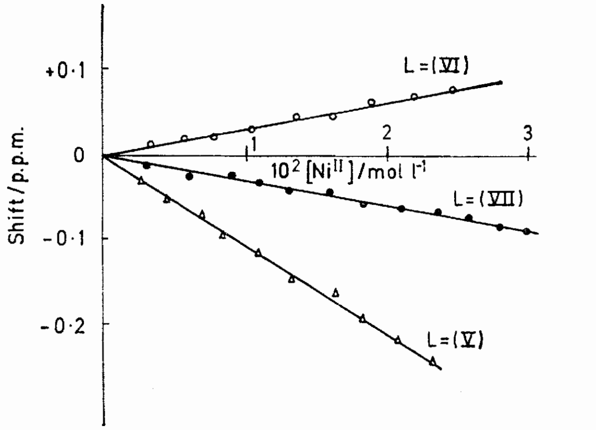

FIGURE 6 Effect of the complexes [Ni(L)$_2$] [L = (V), (VI), and (VII)] on the shift of tnb (0·09M) at 60 MHz and 25 °C in CDCl$_3$

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