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N-ARYL SALICYLALDIMINE COMPLEXES: INFRARED AND PMR SPECTRA OF THE LIGANDS AND VIBRATIONAL FREQUENCIES OF THEIR METAL(II) CHELATES

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Abstract—The i.r. and PMR spectra of 28 *N*-aryl salicylaldimines are reported. Assignments of characteristic i.r. bands are derived by ^{15}N-labelling of *N-p*-tolylsalicylaldimine. The PMR spectra establish that the bases exist in the phenol-imine form at room temperature in deuterochloroform and that electron withdrawing *N*-aryl substituents reduce the magnetic shielding of the hydroxyl proton. The i.r. spectra of 38 Co(II), Ni(II), Cu(II) and Zn(II) chelates derived from the salicylaldimines are discussed. Assignments are based on ^{15}N-labelling of the Cu(II) complex of *N-p*-tolylsalicylaldimine. Support for the νCu–N assignments in the i.r. spectra of the Cu(II) chelates is provided by observing the frequency shifts induced by metal ion substitution and by varying the *N*-aryl substituents. Electron withdrawing substituents shift νCu–N to higher frequencies which is consistent with substituent-induced Cu → N π-bonding.

INTRODUCTION

SCHIFF bases derived from the reaction of salicylaldehyde with primary amines represent a versatile series of ligands, the metal complexes of which have been widely studied[1–3] in recent years. Spectroscopic studies have been largely confined to PMR investigations of the keto-enol equilibria of the free bases[3–6] and the application of electronic spectra to the structures of the metal chelates[3]. The limited extent to which i.r. spectra have been studied[7–8] is undoubtedly due to the structural diversity of the complexes, the impracticability of applying normal coordinate methods to the assignment problem and the complexity of the spectra resulting from the presence of phenyl vibrations, two different metal-ligand bonds (*M*–N and *M*–O) and extensive vibrational coupling. Reported assignments are largely empirical and generally restricted to the ligand bands, νC=N and νC–O.

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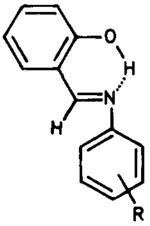
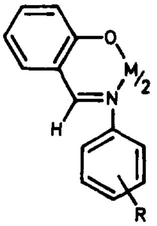
This paper reports the details and extension of preliminary work[9] on the application of ^{15}N-labelling and metal ion substitution to the assignment problem in the i.r spectra of the ligands (I) and their complexes (II) and the effect of varying the *N*-aryl substituents (*R*) on the i.r. and PMR spectra.



(I)



(II)

EXPERIMENTAL

The ligands were prepared by addition of a slight excess of the amine in ethanol to a warm solution of salicylaldehyde in ethanol. After cooling, the precipitated product was collected, recrystallized from ethanol and dried at 25°C and 0·1 mm Hg. Where this method failed to yield the crystalline product, the amine and salicylaldehyde were boiled under reflux for 1 hr. After cooling, the product was collected and purified as described above.

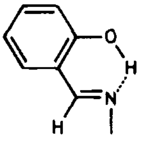
The metal(II) complexes were prepared by the methods referenced: Cu(II) complexes[10]; Co(II) complexes[11]; Ni(II) complexes[12]. The Zn(II) chelates were prepared by addition of the amine (0·02 mole) in methanol to a mixture of zinc(II) acetate dihydrate (0·01 mole) and salicylaldehyde (0·02 mole) in methanol. After 3 hr at 25°C, the crystalline product was collected, washed (methanol) and dried at 25°C and 0·01 mm Hg. The ^{15}N-labelled compounds were prepared from ^{15}N-*p*-toluidine of 96·7 atom-% isotopic purity supplied by Prochem Ltd.

I.R. spectra were determined on Nujol or hexachlorobutadiene mulls between caesium bromide plates on a Beckman IR-12 spectrophotometer calibrated against carbon dioxide and water vapour. Spectra of the ^{15}N-labelled compounds and their unlabelled analogues were repeated at least eight times. Reproducibility of quoted frequencies for these compounds is better than 0·3 cm^{-1}. PMR spectra were determined in deuterochloroform on a Varian A-60 spectrometer (internal standard: tetramethylsilane).

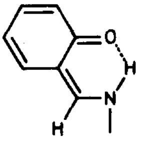
RESULTS AND DISCUSSION

PMR and infrared spectra of the ligands

PMR spectra provide the most direct route for investigating tautomeric equilibria in solutions of Schiff bases. It has been shown[5] that the base (I; $R = H$) exists solely in the phenol-imine form (IIIa) in non-hydroxylic solvents at normal ambient temperatures. Any significant presence of the keto-amine form (IIIb)



(IIIa)



(IIIb)

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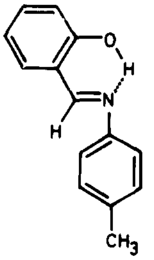
would split the signal arising from the methine proton. No splitting of this signal is observed in the PMR spectra of any of the ligands studied here nor is the aromatic proton signal displaced from its normal benzenoid position as would be implied by the quinoid form (IIIb). We conclude that the phenol-imine form (IIIa) pertains to all the ligands (I). The PMR data are given in Table 1.

Extensive vibrational coupling is likely to occur in the free bases (I). For this reason, interpretation of the i.r. spectra is best approached by isotopic labelling since this technique yields reliable assignments and provides an estimate of the vibrational purity of the frequencies. Two ^{15}N-sensitive bands ($\Delta\nu - 5$ and $-8\,cm^{-1}$) near $1600\,cm^{-1}$ occur in the spectrum (Fig. 1) of the N-aryl compound (IV). Only the higher frequency band has been empirically assigned[8] to $\nu C{=}N$ but the lower frequency band exhibits the greater ^{15}N-induced shift and is therefore vibrationally purer. Since a maximum ^{15}N-induced shift of $-40\,cm^{-1}$ is expected[13] for uncoupled $\nu C{=}N$, it is clear that both bands are extensively coupled. The assignment of both bands to $\nu C{=}N$ is supported by their sensitivity to metal ion complexation and to variation of the substituent, R. Vibrational coupling is also likely to interfere with the realization of a satisfactory correlation between vibrational frequency and the electronic effects of the substituents, R. It is therefore not surprising to find that there is no regularity in the dependence of the frequencies of the bands assigned to $\nu C{=}N$ on the substituent parameter, σ (Table 1).



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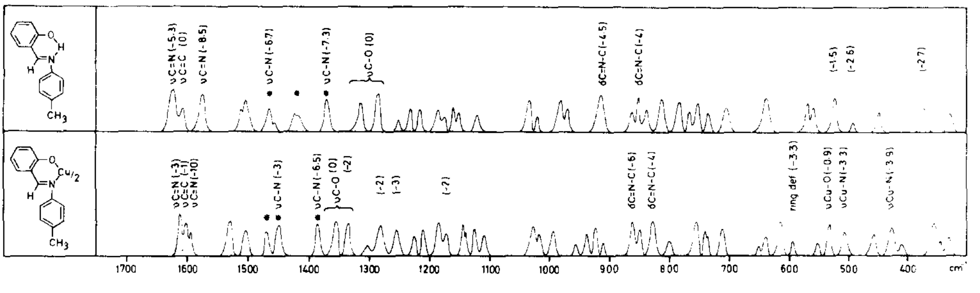

Fig. 1. I.R. spectra of N-p-tolylsalicylaldimine and its Cu(II) chelate. Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling. For all other bands, the shifts are $< 1{\cdot}5\,cm^{-1}$. Bands marked * are taken from hexachlorobutadiene mull spectra.

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Table 1. Data on substituted *N*-aryl salicylaldimines (formula I)*

Subst. Ref.	R	σ	%C	%H	%N	νC=N	Chem. shift†
			Calc./Found			(cm^{-1})	δOH/δ ≥CH (ppm)
1	4-N $(CH_3)_2$	−0·60	75·0	6·7	11·7	1619	13·46
			75·2	7·0	11·9	1571	8·55
2	4-OC_6H_5	−0·32	78·9	5·2	4·8	1624	insol.
			78·8	5·1	4·9	1576	
3	4-OCH_3	−0·27	74·0	5·8	6·2	1627	12·96
			73·9	5·7	6·3	1579	8·46
4	4-OC_2H_5	−0·25	74·6	6·3	5·8	1621	13·05
			74·5	6·6	5·9	1572	8·70
5	3,4-di-CH_3	−0·24	79·6	7·1	6·2	1625	12·83
			79·8	6·7	6·4	1576	8·43
6	4-CH_3‡	−0·17	79·6	6·2	6·6	1625	12·88
			79·5	6·4	6·5	1576	8·55
7	4-C_2H_5	−0·15	80·0	6·7	6·2	1625	12·66
			79·8	6·7	6·2	1576	8·56
8	3-CH_3§	−0·07	79·6	6·2	6·6	1626	12·86
			79·6	6·5	6·8	1579	8·35
9	4-C_6H_5	−0·01	83·5	5·5	5·1	1624	insol.
			83·3	5·7	5·2	1575	
10	H	0	79·2	5·6	7·1	1625	12·73
			78·5	5·7	7·3	1579	8·50
11	4-F	+0·06	72·6	4·7	6·5	1618	
			72·4	4·7	6·5	1576	
12	3-OCH_3	+0·11	74·0	5·8	6·2	1624	12·83
			74·2	5·8	6·2	1577	8·48
13	3-Cl,4-CH_3	+0·20	68·2	5·3	5·6	1616	12·46
			68·5	5·3	5·6	1572	8·43
14	4-Cl	+0·23	67·4	4·4	6·0	1613	12·23
			67·3	4·1	5·9	1573	8·53
15	4-Br	+0·23	56·5	3·7	5·1	1620	12·18
			56·7	3·8	5·1	1573	8·60
16	4-CO_2H	+0·27	69·7	4·6	5·8	1624	insol.
			69·8	4·6	5·6	1574	
17	4-I	+0·28	48·3	3·1	4·3	1622	12·16
			48·3	3·9	4·3	1572	8·55
18	3-$COCH_3$	+0·31	75·3	5·5	5·9	1624	12·13
			75·3	5·2	5·7	1577	8·65
19	3-F	+0·34	72·6	4·7	6·5	1629	12·53
			72·9	4·6	6·6	1582	8·51
20	3-I	+0·35	48·3	3·1	4·3	1619	12·40
			48·4	3·4	4·5	1574	8·46
21	3-Cl	+0·37	67·4	4·4	6·0	1622	12·16
			67·8	4·5	6·1	1578	8·55
22	3-Br	+0·39	56·5	3·7	5·1	1617	12·13
			56·8	4·0	5·3	1576	8·53
23	4-$CO_2C_2H_5$	+0·45	71·4	5·6	5·2	1625	12·36
			71·1	5·5	5·4	1578	8·46
24	4-COC_6H_5	+0·46	79·7	5·0	4·7	1625	11·83
			79·5	5·1	4·7	1578	8·53
25	4-$COCH_3$	+0·52	75·3	5·5	5·9	1622	12·36
			74·6	5·7	5·8	1571	8·60

Table 1 (*Contd.*)

Subst. Ref.	*R*	σ	%C	%H	%N	νC=N (cm^{-1})	Chem. shift† δOH/$\delta \geqslant$CH (ppm)
			Calc./Found				
26	3-NO$_2$,4-CH$_3$	+0·54	65·4	5·1	10·9	1627	12·10
			66·1	5·0	10·7	1570	8·53
27	4-CN	+0·63	75·7	4·5	12·6	1619	12·16
			75·8	4·7	12·4	1570	8·60
28	3, 5-di-Br	+0·78	43·9	2·8	3·9	1621	11·83
			43·8	2·9	4·1	1568	8·53

*Each of the following vibrations yields a pair of bands within the regions given: νC–N (1454–1471 and 1351–1375 cm^{-1}); νC–O (1301–1327 and 1275–1291 cm^{-1}); δC=N–C (891–919 and 830–877 cm^{-1}).

†In deuterochloroform; all shifts are downfield of tetramethylsilane; δOH = chemical shift of hydroxyl proton; $\delta \geqslant$CH = chemical shift of methine proton.

‡Analytical data for ^{15}N-labelled base: Calc.: 79·2%C, 6·2%H, 7·1%N; found: 79·0%C, 6·2%H, 7·0%N.

§Liquid compound (νC=N frequencies from liquid film spectrum).

Presumably because of masking by Nujol absorption, no assignments have previously been proposed for νC–N (the single bond is used as a formal distinction of the exocyclic C–N bond from the C=N bond of the heterocyclic ring). Two bands in the hexachlorobutadiene mull spectrum of the base (IV) within the range 1375–1475 cm^{-1}, exhibit shifts of -7 cm^{-1} on ^{15}N-substitution and their assignment to νC–N is therefore indicated. The phenolic C–O stretching frequency has been empirically assigned[8] to the band near 1280 cm^{-1} in the spectra of *N*-aryl salicylaldimines on the grounds that increased covalence resulting from metal ion coordination shifts this band some 50 cm^{-1} towards higher frequency. Since the neighbouring band near 1310 cm^{-1} exhibits a similar shift (Fig. 1) while neither band is shifted by ^{15}N-labelling, we propose that both bands be similarly assigned.

The strong intramolecular hydrogen bonding present in the ligands leads to very broad and weak hydroxyl absorption near 2700 cm^{-1} so that the PMR spectra are more informative than the i.r. spectra with respect to the nature of the O–H bonding. The electronic effects of the substituents, *R*, may be transmitted to affect the strength of the hydrogen bond either via the conjugation of the heterocyclic ring or, more directly, by modifying the capacity of the nitrogen atom for participating in hydrogen bonding. Since some bond fixation is implied by the predominance of the tautomer (IIIa), the latter route appears more likely. The fact that neither the methine proton shielding nor νC=N exhibits any correlation with the substituent parameters while the hydroxyl proton shielding is dependent on the electronic effects of the substituents (Fig. 2) is consistent with the more direct route. Consequently, increased O–H bond strength is reflected as increased shielding of the OH proton. Certainly, the substituent effect favours (IIIa) as the predominant species. If the tautomeric equilibrium favoured (IIIb), electron releasing substituents would increase the shielding of the proton now primarily resident on the nitrogen atom. This is not observed.

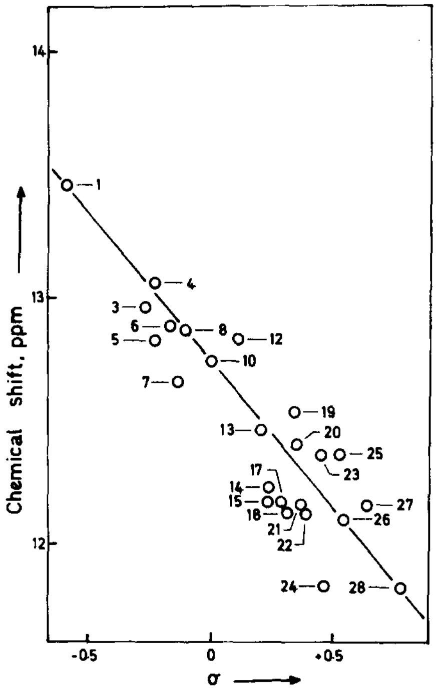

Fig. 2. Relationship between downfield chemical shift of hydroxyl proton (in $CDCl_3$, relative to TMS) and the Hammett substituent parameter (σ) of substituted *N*-aryl salicylaldimines (for key to substituents, see Table 1).

Infrared spectra of the complexes

I.R. data for the complexes are given in Table 2. Compared with the free ligands, the spectra of the Cu(II) chelates exhibit additional complexity below 600 cm^{-1} where the metal–ligand bands are expected. Above 600 cm^{-1}, the only bands in the spectrum of the Cu(II) complex (II; $R = 4\text{-}CH_3$) with ^{15}N-induced shifts exceeding 2 cm^{-1} are at 1615 ($\Delta\nu - 3$), 1596 ($\Delta\nu - 10$), 1450 ($\Delta\nu - 3$), 1387 ($\Delta\nu - 6$), 1256 ($\Delta\nu - 3$), 867 ($\Delta\nu - 6$) and 829 ($\Delta\nu - 4$) cm^{-1} (Fig. 1). In conformity with the spectrum of the free base, assignment of the two bands of highest frequency to coupled νC=N is indicated. The two ^{15}N-sensitive bands at 1450 and 1387 cm^{-1} are almost certainly νC–N(aryl) and the two bands near 850 cm^{-1} probably C=N–C deformation frequencies. Below 600 cm^{-1}, only three bands exhibit significant shifts exceeding 2 cm^{-1}. That at 595 cm^{-1} is very little affected by substitution in the *N*-aryl ring or by replacement of Cu(II) by other metal(II) ions. The remaining bands at 505 and 427 cm^{-1} are sensitive to both modes of substitution and are therefore assigned to νCu–N although there is undoubtedly a significant contribution to each from coupled νCu–O. (Extensive coupling between the metal–ligand vibrations ν*M*–N and ν*M*–O undoubtedly exists in all the complexes discussed in this paper. νCu–N is intended to signify the coupled vibration, νCu–N + νCu–O, which is vibrationally purer in νCu–N. Conversely νCu–O represents the coupled vibration, νCu–O + νCu–N which is vibrationally purer in νCu–O).

In seeking substantiation for the assignment of νCu–N proposed on the basis

Table 2. Data on metal(II) complexes of substituted *N*-aryl salicylaldimines (formula II)*

		%C	%H	%N	νC=N	νM-N	νM-O†
R	σ		Calc./Found		(cm^{-1})	(cm^{-1})	(cm^{-1})
		4-Substituted Cu(II) complexes					
4-OC$_6$H$_5$	−0·32	71·3	4·4	4·4	1615	491	540
		71·4	4·4	4·2	1589	438	
4-OCH$_3$	−0·27	65·2	4·7	5·4	1617	497	537
		65·9	4·7	5·4	1590	425	
4-OC$_2$H$_5$	−0·25	66·2	5·2	5·1	1612	509	532
		66·0	5·3	5·0	1588	417	
4-CH$_3$‡	−0·17	69·5	5·0	5·8	1615	505	533
		69·6	5·1	5·9	1596	427	
4-C$_2$H$_5$	−0·15	70·4	5·5	5·5	1615	514	495
		70·7	5·6	5·3	1593	439	
4-C$_6$H$_5$	−0·01	75·1	4·6	4·6	1612	521	477
		74·8	4·5	4·6	1591	444	
H	0	68·5	4·4	6·1	1611	529	495
		68·9	4·8	5·8	1594	448	
4-F	+0·06	63·5	3·7	5·7	1611	532	473
		63·5	3·8	5·6	1594	445	
4-Cl	+0·23	60·0	3·5	5·4	1610	534	416
		59·8	3·6	5·5	1589	469	
4-Br	+0·23	50·9	3·0	4·6	1610	532	415
		51·0	3·1	4·6	1586	467	
4-I	+0·28	44·1	2·6	4·0	1608	533	409
		43·8	3·4	3·9	1581	465	
4-CO$_2$C$_2$H$_5$	+0·45	64·0	4·7	4·7	1605	534	395
		63·9	4·9	4·6	1593	485	
4-COCH$_3$	+0·52	66·7	4·5	5·2	1612	550	388
		67·4	4·8	5·0	1590	505	
4-CN	+0·63	66·5	3·6	11·1	1617	559	370
		66·4	3·5	10·7	1592	507	
		3-Substituted Cu(II) complexes					
3-CH$_3$	−0·07	69·5	5·0	5·8	1606	542	568
		69·2	4·8	5·9	1585	471	
3-COCH$_3$	+0·31	66·7	4·5	5·2	1612	547	557
		66·5	4·3	5·3	1579	460	
3-F	+0·34	63·5	3·7	5·7	1607	540	575
		63·5	3·6	5·8	1594	482	
3-I	+0·35	44·1	2·6	4·0	1609	538	562
		44·1	2·5	3·9	1580	468	
3-Cl	+0·37	60·0	3·5	5·4	1612	540	568
		59·8	3·2	5·3	1588	472	
3-Br	+0·39	50·9	3·0	4·6	1611	540	565
		50·9	2·8	4·6	1584	470	
3,5-di-Br	+0·78	40·6	2·1	3·6	1615	540	571
		40·3	2·1	4·4	1579	461	
		3, 4-Disubstituted Cu(II) complexes					
3,4-di-CH$_3$	−0·24	70·4	5·5	5·5	1610	510	550
		68·8	5·5	5·6	1588	431	

Table 2 (*Contd.*)

R	σ	%C	%H	%N	νC=N	νM–N	νM–O†
		Calc./Found			(cm^{-1})	(cm^{-1})	(cm^{-1})
3-Cl,4-CH$_3$	+0·20	60·8	4·0	5·1	1614	514	555
		60·7	4·0	4·6	1586	417	
3-NO$_2$,4-CH$_3$	+0·54	58·6	3·9	9·8	1614	515	560
		58·2	3·7	9·4	1597	417	
4-Substituted Ni$_3$II$_4$ complexes							
4-CH$_3$	−0·17	70·2	5·0	5·8	1616	492	524
		69·4	5·0	5·8	—	420	
H	0	69·2	4·5	6·2	1618	542	516
		70·2	4·3	7·3	1588	466	
4-Substituted Zn(II) complexes							
4-OCH$_3$	−0·27	64·9	4·7	5·4	1613	496	527
		65·0	4·8	5·9	1588	408	
4-CH$_3$	−0·17	69·2	5·0	5·8	1616	491	525
		69·6	5·9	5·8	1590	389	
H	0	68·2	4·4	6·1	1609	516	493
		67·9	4·9	6·0	1589	454	
4-Cl	+0·23	59·7	3·5	5·4	1605	524	387
		59·9	3·6	5·3	1584	460	
4-Br	+0·23	50·7	2·9	4·6	1604	522	379
		50·8	2·9	4·6	1582	459	
4-I	+0·28	44·0	2·6	3·9	1607	521	372
		44·3	2·8	4·1	1578	457	
4-Substituted Co(II) complexes							
4-OCH$_3$	−0·27	65·8	4·7	5·5	1611	497	529
		66·1	5·0	5·9	1582	411	
4-CH$_3$	−0·17	70·2	5·0	5·8	1613	491	526
		70·1	5·1	5·9	1583	396	
H	0	69·2	4·5	6·2	1607	519	494
		69·1	4·3	6·2	1580	457	
4-Cl	+0·23	60·0	3·5	5·4	1604	525	393
		59·9	3·6	5·4	1577	465	
4-Br	+0·23	51·3	3·0	4·6	1602	524	387
		51·5	3·3	4·6	1577	460	
4-I	+0·28	44·4	2·6	4·0	1608	523	380
		44·1	3·0	4·0	1574	455	

*Each of the following vibrations yields a pair of bands within the ranges given: νC–N (1434–1454 and 1370–1403 cm^{-1}); νC–O (1338–1363 and 1322–1338 cm^{-1}); δC=N–C (854–893 and 823–858 cm^{-1}).

†Tentative assignment (see text).

‡Analytical data for ^{15}N-labelled complex: Calc.: 69·2%C, 5·0%H, 6·2%N; found: 68·9%C, 5·0%H, 6·2%N.

of ^{15}N-labelling, we make use of the established[14–15] relationship between crystal field stabilization energy (CFSE) and νM–L for transition metal com-

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15. J. M. Haigh, R. D. Hancock, L. G. Hulett and D. A. Thornton, *J. molec. Structure* **4**, 369 (1969).

plexes. Knowledge of the basic structures of the complexes is a prerequisite to this method of assignment. All currently available structural evidence[3] points to tetrahedral coordination in the Co(II) and Zn(II) chelates of *N*-aryl Schiff bases while the Cu(II) complexes have nominally square planar coordination although minor deviations from true planarity commonly occur. Crystal field theory predicts[16] that a series of three complexes with identical ligand composition containing tetrahedral Co(II) and Zn(II) and square planar Cu(II) will have CFSE's in the order Co < Cu > Zn. Accordingly, any band assigned as νCu–N is expected to exhibit a similar order of frequency variation on substitution of Co(II) or Zn(II) for Cu(II). With only one exception, the frequencies of the bands assigned to νCu–N reflect the predicted CFSE sequence for six differently substituted salicylaldimine complexes (Fig. 3).

A further test of the assignments is possible by extending this method to include Ni(II) Schiff base complexes of known structure. Crystallographic studies [3] have confirmed that *N*-phenylsalicylaldimine (I; $R = H$) yields square planar complexes with Ni(II) and Cu(II). Crystal field theory predicts the stability order Ni > Cu for this pair of complexes since the orbital of highest energy is necessarily occupied in the Cu(II) chelate but is unoccupied in the diamagnetic Ni(II) analogue. The νCu–N bands are observed to exhibit this frequency order (Fig. 3). It is now useful to examine the spectra of a pair of complexes (M = Ni, Cu) for which the opposite stability order, i.e. the Irving–Williams[17] stability sequence, Ni < Cu, is expected. The chelates of *N*-*p*-tolylsalicylaldimine (IV) are appropriate since the paramagnetic Ni(II) compound has[3] trinuclear octahedral structure while the Cu(II) analogue is square planar. The change in the stability sequence is reflected by the frequency shifts observed for both bands assigned to νM–N (Fig. 3).

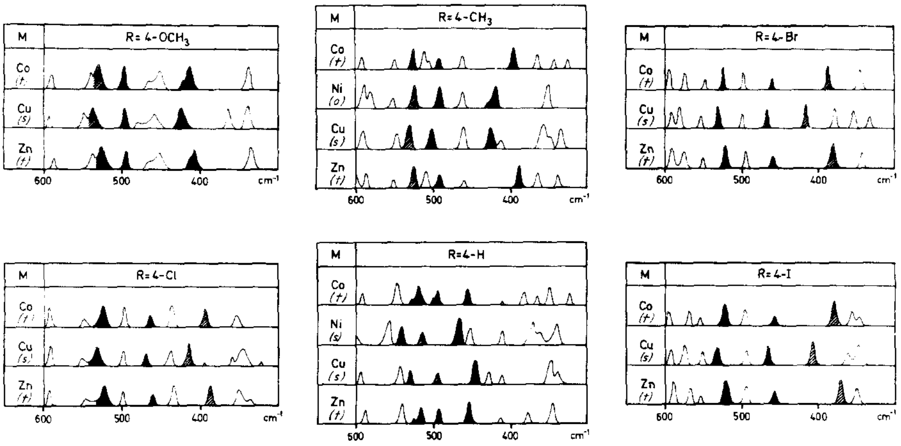

Fig. 3. Effect of metal ion substitution on infrared spectra of metal(II) salicylaldimine complexes (formula II). Solid peaks: νM–N; shaded peaks: νM–O (tentative). Structures: *t* = tetrahedral; *s* = square planar; *o* = octahedral.

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16. R. D. Hancock and D. A. Thornton, *J. S. Afr. chem. Inst.* **23**, 71 (1970).
17. H. Irving and R. J. P. Williams, *J. chem. Soc.* 3192 (1953).

Next, we examine the effect of varying the *N*-aryl substituent (*R*) in the Cu(II) complexes (II; *M* = Cu) on the i.r. spectra. The two bands assigned to νCu–N on the basis of the isotopic labelling and metal ion substitution studies both shift to higher frequency with increased electron withdrawing capacity of the substituents (Fig. 4). Since electron withdrawing substituents would facilitate Cu → N π-bonding, this result is not surprising. As concluded for the free bases, it is unlikely that the electronic effect is transmitted via the conjugation of the chelate ring, since νC=N and νC–O are insensitive to substitution in the *N*-aryl ring. In this connection it is interesting to observe that (by contrast with *para* substitution) *meta*-*N*-aryl substituents induce very little shift in νCu–N (Table 2). Since the electronic effects of *meta* substituents are transmitted almost entirely by an inductive mechanism[18], this suggests that the transmission of the substituent effects in the Schiff base complexes is propagated largely by a mesomeric mechanism. This conclusion was further examined in two ways. Firstly, it is found that two similar *meta* substituents, as in the 3,5-dibromo-substituted complex, yield values of νCu–N which are closely similar to those observed for the *meta*-bromo complex. Secondly, where a *meta* substituent is present in addition to a *para*-methyl substituent, as in the 3,4-di-CH_3-, 3-Cl,4-CH_3- and 3-NO_2,4-CH_3-substi-

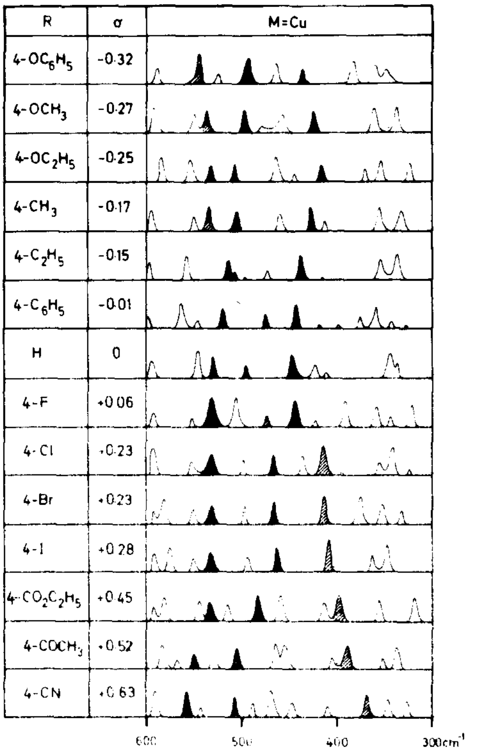

Fig. 4. I.R. spectra of 4-substituted *N*-aryl salicylaldimine complexes of Cu(II) (formula II; *M* = Cu). Solid peaks: νCu–N; shaded peaks: νCu–O.

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18. R. W. Taft, In *Steric Effects in Organic Chemistry*, (Edited by M. S. Newman) p. 591. Wiley, New York (1956).

tuted complexes, the values of νCu–N are similar to those of the *para*-methyl substituted complex. The relevant data are given in Table 2.

Assignment of νCu–O cannot be conclusively established from the present work. Undoubtedly any band so assigned will be coupled with νCu–N so that ^{15}N-substitution will induce some shift in νCu–O. A band at 533 cm^{-1} in the N-p-tolyl complex is in the observed[14, 16, 19] region of νM–O in metal(II) acetylacetonates and is shifted 1 cm^{-1} towards lower frequency on ^{15}N-labelling. Furthermore, a band is observed in the spectra of the *para*-substituted N-aryl complexes (Fig. 4) which is conceivably this band shifted to lower frequencies by electron withdrawing substituents, i.e. in the opposite direction to νCu–N. Finally, as would be expected, this band exhibits precisely similar shifts to those observed for νCu–N on substitution of the coordinated metal ion (Fig. 3). Assignment of this band to νCu–O is indicated but confirmation must await ^{18}O labelling studies reported[7] to be in progress.

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19. S. Pinchas, B. L. Silver and I. Laulicht, *J. chem. Phys.* **46**, 1506 (1967).