

A Study of Substituent Effects in Quadridentate Schiff Base Complexes with Nickel(II). ¹³C NMR, Electronic Spectra and Polarographic Measurements

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The effect of peripheral substituents on the electron distribution of a Ni(II) complex with a quadridentate Schiff base ligand has been investigated through ¹³C NMR, electronic spectroscopy and half-wave potential measurements. It has been demonstrated that electron-withdrawing groups such as COCH₃ and COOC₂H₅ decrease the electron density on the Ni(II) atom, and that this effect is responsible for the stabilization of the O₂ adducts of the corresponding Co(II) complexes at ambient temperature.

Introduction

In a series of metal complexes containing π-conjugated macrocyclic ligands, the reactivity of the complexes and the redox potential of the central metal are sensitive to the nature of the peripheral substituents on the chelate ring [1–3]. Figure 1 and Table I show the structures and abbreviations, respectively, of square planar Ni(II) and Co(II) complexes with five Schiff base ligands. Ni(H, COCH₃, CH₃) and Ni(H, COOC₂H₅, CH₃) react with ethylenediamine to form N₄-macrocyclic complexes shown in Fig. 2 while such reactions do not occur for Ni(CH₃, H, CH₃) and Ni(CH₃, H, C₆H₅) [4–6]. Although Co(CH₃, H, CH₃) and Co(CH₃, H, C₆H₅) form 1:1 (Co/O₂) adducts in the presence of pyridine at low temperatures [7, 8], they undergo irreversible oxidation at ambient temperature. On the other hand, Co(H, COCH₃, CH₃) [9] and Co(H, COOC₂H₅,

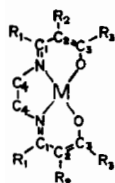


Fig. 1. Structure of the complexes, M(R₁, R₂, R₃).

TABLE I. List of Abbreviations.^a

	R ₁	R ₂	R ₃	Abbreviations
A	CH ₃	H	CH ₃	M(CH ₃ , H, CH ₃)
	CH ₃	H	C ₆ H ₅	M(CH ₃ , H, C ₆ H ₅)
	CH ₃	H	OC ₂ H ₅	M(CH ₃ , H, OC ₂ H ₅)
B	H	COCH ₃	CH ₃	M(H, COCH ₃ , CH ₃)
	H	COOC ₂ H ₅	CH ₃	M(H, COOC ₂ H ₅ , CH ₃)

^aM = Ni(II) or Co(II).

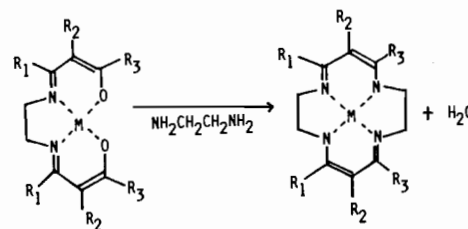


Fig. 2. Condensation reaction of M(R₁, R₂, R₃) with ethylenediamine.

CH₃) [10] react with O₂ to form violet colored O₂ adducts, and these reactions are reversible even at room temperature. Although the importance of an electron-withdrawing group as R₂ in the reaction shown in Fig. 2 was pointed out by Tang *et al.*, [6], no detailed investigations have been made concerning the effect of such a group on the electron distribution in the chelate ring.

It is well known that ¹³C NMR spectroscopy provides valuable information about the electron distribution in organic molecules. In this study, we have measured the ¹³C NMR spectra of the five Ni(II) complexes shown in Table I and Fig. 1 to explore the effect of the substituents on the electron distribution

TABLE II. ^{13}C NMR Chemical Shifts (ppm) and Assignments.

R ₁	R ₂	R ₃	C ₄	C ₁	C ₂	C ₃	R ₁	R ₂	R ₃
CH ₃	H	CH ₃	52.97	164	99.2	176	20.98	—	24.25
CH ₃	H	C ₆ H ₅	53.17	164.8	97.04	171.03	21.56	—	137.2
									128.9
									127.6
									126.2
CH ₃	H	OC ₂ H ₅	52.81	{ 167.5* 167.8	79.88	{ 167.8* 167.5	21.01		59.80 (OCH ₂) 14.70 (CCH ₃)
H	COOC ₂ H ₅	CH ₃	{ 59.54* 58.28	159.69	102.93	187.12	—	166.75 (COO) { 58.28* (OCH ₂) 59.54 14.47 (CH ₃)	27.36
H	COCH ₃	CH ₃	58.44	159.42	113.89	188.0	—	193.99 (CO) { 28.90* (CH ₃) 28.31	{ 28.31* 28.90

*These assignments may be interchangeable. For the numbering of the C atoms, see Figure 1.

TABLE III. ^{13}C NMR Chemical Shifts (ppm)* of X-CH=CH₂.
(α) (β)

X	C _{α}	C _{β}
H	122.8	122.8
OCH ₃	153.1	85.5
OC ₂ H ₅	152.9	84.6
COCH ₃	138.5	129.3
COOC ₂ H ₅	128.7	130.5

*Ref. 12.

in the chelate ring. We have also recorded their electronic spectra and measured polarographic half-wave potentials to gain information about the effect of the electron-withdrawing groups on the d-d transition and the electron density on the Ni atom, respectively. On the basis of these data, we have attempted to elucidate the relationship between the electron distribution and the stability of the O₂ adducts of the corresponding Co(II) complexes.

Experimental

All the compounds shown in Table I were prepared by literature method [4, 5]. ^{13}C NMR data were obtained on dilute solutions (1–10%) of the five compounds (Table I) in CDCl₃ using a JEOL FX-60QD FT spectrometer. Electronic absorption spectra of the five Ni(II) complexes dissolved in 1,2-dichloroethane were measured on a Shimadzu multi-purpose spectrophotometer Model MPS-5000 at room temperature.

All polarographic measurements were made in DMF containing 0.1 M tetraethylammonium perchlorate at room temperature. All solutions were deoxygenated by bubbling nitrogen through them. The saturated calomel reference electrode was separated from the working electrode by a bridge. The dropping mercury electrode was constructed from commercially available tubing. The counter electrode was platinum.

Results and Discussion

^{13}C NMR Spectra

The assignments of the ^{13}C NMR spectra of the five compounds studied are tabulated in Table II. These assignments were made based on known chemical shift values and off-resonance experiments. The results obtained for Ni(CH₃, H, CH₃) are in perfect agreement with those reported by Lindoy *et al.* [11]. As stated before, the five compounds listed in Tables I and II can be classified into two groups (A and B) according to their reactivity with ethylenediamine and the stability of the O₂ adducts of their analogous Co(II) complexes.

(A) M(CH₃, H, CH₃), M(CH₃, H, C₆H₅),
M(CH₃, H, OC₂H₅)

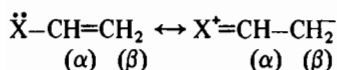
(B) M(H, COCH₃, CH₃), M(H, COOC₂H₅, CH₃)

The chemical shifts of each carbon atom will be discussed separately for these two groups.

C₂ chemical shifts

According to Table II, the C₂ chemical shifts differ markedly between groups A and B. This is expected

since electron-withdrawing groups such as COCH₃ and COOC₂H₅ decrease the electron density on the C₂ atom ($\text{C}=\text{O} \leftrightarrow \text{C}^+-\text{O}^-$), thus causing downfield shifts of the C₂ signal relative to group A compounds. The same effect is also seen in a series of vinyl compounds shown in Table III. In both cases, the C₂ (or C_α) chemical shift is *ca.* 10 ppm further downfield for the COCH₃ than for the COOC₂H₅ derivative. This indicates that the electron-withdrawing property of the COCH₃ group is stronger than that of the COOC₂H₅ group. The C₂ chemical shift of Ni(CH₃, H, OC₂H₅) is upfield relative to that of Ni(CH₃, H, CH₃) and Ni(CH₃, H, C₆H₅) because the electron-donating property of the OC₂H₅ group increases the C₂ electron density via resonance similar to:



The chemical shift data of simple vinyl derivatives shown in Table III (C_β) support this interpretation.

C₃ chemical shifts

The C₃ chemical shifts are also different between groups A and B: The former are in the range of 176–167 ppm, whereas the latter are in the range of 188–187 ppm. This may be accounted for in terms of the resonance [12–14] shown in Fig. 3. Thus, substituents such as COCH₃ and COOC₂H₅ decrease the electron density on the C₃ atom via resonance participation of structure b, and cause downfield shifts of the C₃ signals. As stated before, ethylenediamine reacts with the Ni(II) complexes only when R₂ is COCH₃ or COOC₂H₅. This reaction (Fig. 2) is initiated by the attack of the negatively charged nitrogen atom of ethylenediamine on the positively charged C₃ atom. Therefore, it proceeds more easily when R₂ contains the C=O group which decreases the electron density at C₃.

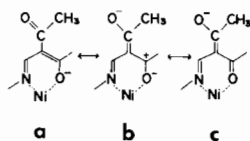


Fig. 3. Resonance structures for Ni(H, COCH₃, CH₃).

Chemicals shifts of other C atoms

The C₁ chemical shifts of group B complexes are 5–8 ppm further upfield than those of group A compounds. This is due to the difference in the R₁ substituent between these two groups. For example, the ¹³C chemical shift of benzene is 128.5 ppm whereas that of the C atom bonded to the CH₃ group of toluene is 137.4 ppm [15].

TABLE IV. ¹³C NMR Chemical Shifts (ppm)* of RCOX Type Compounds.

X	R = CH ₃	R = C ₆ H ₅
H	199.6	191.0
CH ₃	205.08	196.0
OC ₂ H ₅	169.52	164.0

*Ref. 14.

TABLE V. Lowest-energy d–d Bands.

Complex	$\nu/10^3 \text{ cm}^{-1}$
Ni(CH ₃ , H, CH ₃)	17.6
Ni(CH ₃ , H, C ₆ H ₅)	17.7
Ni(CH ₃ , H, OC ₂ H ₅)	16.8
Ni(H, COOC ₂ H ₅ , CH ₃)	19sh ^a
Ni(H, COCH ₃ , CH ₃)	19sh

^ash denotes shoulder.

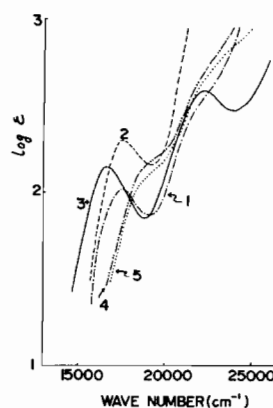


Fig. 4. Absorption spectra of Ni(II) complexes (in 1,2-dichloroethane). 1: Ni(CH₃, H, CH₃); 2: Ni(CH₃, H, C₆H₅); 3: Ni(CH₃, H, OC₂H₅); 4: Ni(H, COCH₃, CH₃); 5: Ni(H, COOC₂H₅, CH₃).

The chemical shifts of the C₄ atoms (CH₂–CH₂ chains) are also different between the two groups: Group A complexes give 52–53 ppm while group B complexes give 58–59 ppm. This may be explained in terms of the inductive effect of the COCH₃ and COOC₂H₅ groups which operate via one N and two C atoms. The chemical shifts (C*) of the C*OCH₃ and C*OOC₂H₅ groups attached to the π-conjugated chelate ring are 193.99 and 166.75 ppm, respectively. These values are close to those found for C₆H₅C*–OCH₃ (196.0 ppm) and C₆H₅C*OOC₂H₅ (164 ppm)

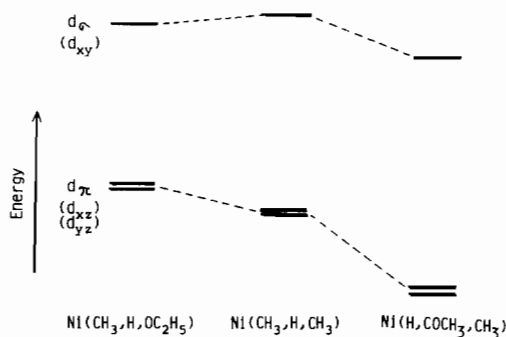


Fig. 5. Schematic illustration of substituent effects on the orbital energies of metal d-orbitals.

but smaller than those of the corresponding aliphatic compounds (Table IV) [14], suggesting some delocalization of electron density from the chelate ring to these C=O groups.

Electronic Spectra

The electronic absorption spectra of the five Ni(II) complexes are shown in Fig. 4, and the frequencies of their lowest-energy bands are listed in Table V. It is to be noted that group B complexes (with electron-withdrawing groups) exhibit bands at much higher frequencies than group A complexes. Previously, the same trend was observed for some Ni(II) complexes with N_4 -macrocyclic ligands [16]. Since these bands are due to the transition from the $d\pi$ (d_{xz} and d_{yz}) to the $d\sigma$ (d_{xy}) orbital [17], the observed blue-shift for group B complexes should be attributed to the lowering of the $d\pi$ or raising of the $d\sigma$ level (Fig. 5). However, the introduction of the electron-withdrawing group on the chelate ring may lower, but cannot raise, the metal $d\sigma$ orbitals. Thus, the observed blue-shift must be interpreted in terms of the lowering of the $d\pi$ level caused by the reduction of the electron density on the coordinating oxygen atom. The contribution of resonance structure c (Fig. 3) is responsible for this electron drift. In Ni(CH₃, H, OC₂H₅), the OC₂H₅ group is expected to function as an electron-releasing group and to raise the $d\pi$ level, thereby bringing about the red-shift of the $d\pi$ – $d\sigma$ transition. In fact, Table V shows that this complex exhibits the band at the lowest frequency among the complexes studied here. These results are quite consistent with those of the ¹³C NMR studies which indicate that the COCH₃ and COOC₂H₅ groups are functioning as electron-withdrawing substituents while the OC₂H₅ group is acting as an electron-releasing substituent on the chelate ring.

Half-wave Potentials

Jäger *et al.* [18] measured polarographic half-wave potentials ($[\text{Ni}(\text{R}_1, \text{R}_2, \text{R}_3)] + e^- \rightarrow [\text{Ni}(\text{R}_1, \text{R}_2,$

$\text{R}_3)]^-$) of a series of Ni(II) complexes, and discussed the effect of the substituents on the electron density of the Ni atom. According to their results, the $-E_{1/2}$ values decrease markedly (by 0.25 ~ 0.27 volt) when the CH₃CO group is substituted for H (*viz.*, the CH₃CO complex is more reducible). This is seen in Table VI where the data for the complexes of interest are listed. Although two different solvents are used in these measurements, the solvent effect seems to be small as exemplified by the constant $-E_{1/2}$ values of Ni(CH₃, H, CH₃) obtained in them. These data clearly indicate that the introduction of the COCH₃ or COOC₂H₅ group reduces the electron density on the Ni atom as indirectly suggested by the ¹³C NMR and electronic spectral studies.

TABLE VI. Polarographic Half-wave Potentials $[\text{Ni}(\text{R}_1\text{R}_2\text{R}_3)] + e^- \rightarrow [\text{Ni}(\text{R}_1\text{R}_2\text{R}_3)]^-$.

Complex	$E_{1/2}$ volts (S.C.E.)	Solvent
Ni(CH ₃ , H, CH ₃)	-2.04	acetonitrile [18]
Ni(CH ₃ , H, CH ₃)	-2.04	DMF
Ni(CH, H, OC ₂ H ₅)	-1.86	DMF
Ni(H, COOC ₂ H ₅ , CH ₃)	-1.71	acetonitrile [18]
Ni(H, COCH ₃ , CH ₃)	-1.68	acetonitrile [18]

Stability of the O₂ Adduct

According to Carter *et al.* [19], there is a linear relationship between the anodic half-wave potential ($-E_{1/2}^{\text{ox}}$) for the Co(II) → Co(III) oxidation and the equilibrium constant, K_{O_2} , of the reaction, $\text{Co}(\text{L}_4)\text{py} + \text{O}_2 \rightleftharpoons \text{Co}(\text{L}_4)\text{py}(\text{O}_2)$ where L_4 denotes a series of Schiff base ligands and porphyrins. According to their results, the larger the electron density on the Co atom (larger $-E_{1/2}^{\text{ox}}$ value), the more stable the O₂ adduct (larger log K_{O_2} value). When the electron density on the Co atom exceeds a certain limit, the reversibility of the reaction is lost, and the complex is completely oxidized to Co(III). As stated before, the O₂ adducts of Co(CH₃, H, CH₃) and Co(CH₃, H, C₆H₅) are only stable at low temperatures and readily undergo irreversible oxidation at ambient temperature. This may be attributable to the relatively high electron density on the Co atom which can be inferred from our studies on the corresponding Ni(II) complexes. On the other hand, the Co atom in Co(H, COCH₃, CH₃) and Co(H, COOC₂H₅, CH₃) have relatively low electron densities as shown by our studies on the analogous Ni(II) complexes. Thus, their reactions with O₂ are reversible even at room temperature.

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