Commun. Fac. Sci. Univ. Ank. Serie B
V. 35. pp. 53–58 (1989)

THE INVESTIGATION OF SUBSTITUENT EFFECTS ON SOME LIGAND-FIELD PARAMETERS OF SOME PSEUDO-OCTAHEDRAL NICKEL(II) COMPLEXES

PERİHAN ÇERENÇE GÜRKAN* and NECLA GÜNDÜZ

Gazi University, Department on Chemistry, Ankara, Turkey

and

Ankara University, Deparıment of Chemistry, Ankara, Turkey

ABSTRACT

The ligand-field parameters Dq,β′ and β of pseudo-octahedral Ni(II) complex of N–(2–hydroxyphenyl)-salicylaldimine and twelve different derivatives were calculated. Substituent effects on these parameters are discussed.

Dq values were found to be higher and β values to be lower in those complexes bearing electron withdrawing NO_2 groups, than the respective values in the unsubstituted parent complex. On the other hand, Dq's were found to be lower and β's to be higher in complexes carrying electron donating groups like CH_3., Cl and Br in comparison with those of the parent complex.

INTRODUCTION

The Ni^{2+} complexes of N–(2–hydroxyphenyl)-salicylaldimine and its twelve different derivatives were found pseudo-octahedral structure in our previous work (1). This structure was reached by axial polymerization of planar dimer units through Ni–O–Ni bridges.

In this work the ligand-field parameters Dq, B′ and β of all the complexes were calculated and substituent effects on these parameters were discussed.

The general structure of ligands and complexes is shown in Fig. 1 and the abbreviations for the names of the ligands and complexes are given in Table 1.

---

* B, is taken to be 1030 cm^{-1} for the free nickel-II ion.

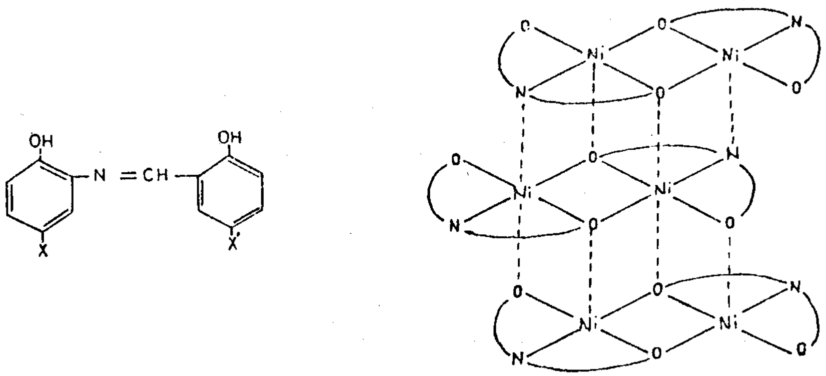


Fig. 1. The general structure of the ligands and pseudo-octahedral structure of the complexes.

Table 1. Abbreviated Names of the Ligands and the Complexes and Key to the Series.

x	x′	Symbol of the ligand	Symbol of the complex	Series
H	H	L-O	C-O	
Cl	H	L-1-Cl	C-1-Cl	1
Br	H	L-1-Br	C-1-Br	
CH$_3$	H	L-1-CH$_3$	C-1-CH$_3$	
NO$_2$	H	L-1-NO$_2$	C-1-NO$_2$	
H	Cl	L-2-Cl	C-2-Cl	2
H	Br	L-2-Br	C-2-Br	
H	CH$_3$	L-2-CH$_2$	C-2-CH$_2$	
H	NO$_2$	L-2-NO$_2$	C-2-NO$_2$	
Cl	Cl	L-3-Cl	C-3-Cl	3
Br	Br	L-3-Br	C-3-Br	
CH$_3$	CH$_3$	L-3-CH$_3$	C-3 CH$_3$	
NO$_2$	NO$_2$	L-3-NO$_2$	C-3-NO$_2$	

EXPERIMENTAL

Preparation of Ligands and complexes, magnetic measurements, elemental analysis and electronic spectra are given in our previous work (1).

RESULTS AND DISCUSSION

In general, the ligand-field spectra of octahedral Ni(II) complexes consist of three spin-allowed transitions from $^3A_{2g}$ to $^3T_{2g}$ (ν_1), $^3T_{1g}$

(F) (ν_2) and ${}^3T_{1g}$ (P), (ν_2), which generally fall within the ranges 7000–13000, 11000–20000 and 19000–27000 cm^{-1} respectively (2). The frequencies and wave numbers of the d–d transitions of all the complexes are tabulated in Table 2. Spectra could be recorded only over the wavelenght range between 1700–350 nm because there was a strong interference beyond 1700 nm possibly due to the nujol used (3) and a very strong absorption of glass plates at around 350 nm. Beside these there were small interference bands of nujol which approximate band widths of 5–25 nm appearing at about 980, 1260 and 1380 nm regions (3).

The values of λ_{max} corresponding to ν_1 transitions in all complexes could not be determined from the spectra obtained. Since λ_{max} of ν_1 transition for C–3–NO_2 fall in the wavelength region of about 1260 nm and for other complexes of about 1380 nm. As it was mentioned above both of these regions are covered with interference bands of nujol.

Because of the above difficulties exact positions of λ_{max} values could not be determined but given as a range of 40–60 nm in the spectra. The exact λ_{max} of each ν_1 transition, which gives the 10 Dq value, was calculated from the energies of ν_2 and ν_3 using the equation given by Tanabe and Sugano (4); for most of the complexes it was found to lie within the given range.

The three ligand-field parameters Dq, B′ and β have been calculated (4,5) and tabulated in Table 2 for the complexes. Then the substituent effects on these parameters were discussed.

The complexes with electron donating Cl, Br or CH_2 groups have lower Dq values and the complexes with electron withdrawing NO_2 groups have higher Dq compared to that of the parent compound. Because of inductive effect Cl and Br are expected to be electron withdrawing atoms, but they act as electron donating atoms because of resonance effect.

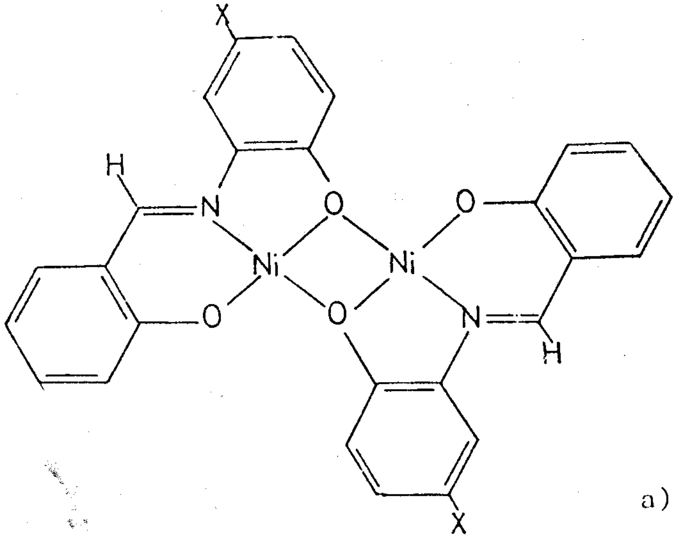
As it is seen in Fig. 1, the donor atoms in the ligands are N and O. If electron withdrawing substituent, NO_2 is present, a decrease in the electron density of the ligand 2p orbitals facilities a interaction to some extent. Thus Dq increases with electron withdrawing substituents. On the contrary if the electron donating substituents Cl, Br, or CH_2 which increase the electron density of N and O atoms are present it becomes difficult ot transfer any electron density from the metal to the ligands

Table II. The electronic transitions and calculated ligand-field parameters of complexes.

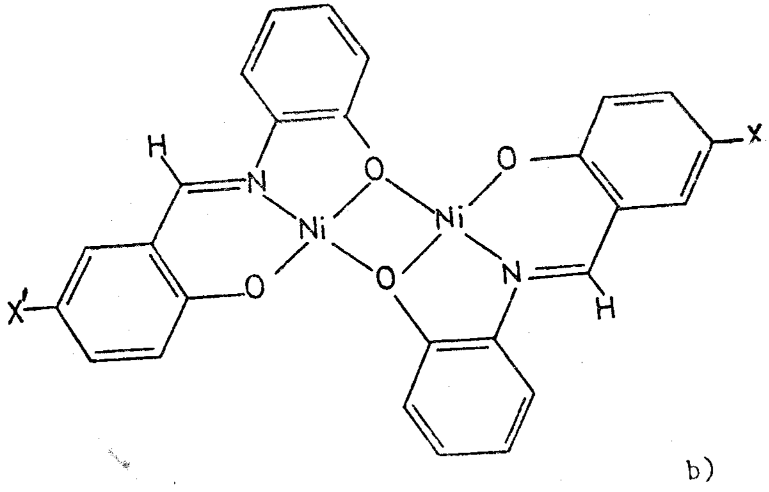
Complex	ν_1 λ_1	ν_2 λ_2	ν_3 λ_3	Calculated values (cm^{-1})			$\beta^* = \frac{B'}{B}$
				Dq (cm^{-1})	ν_1 (cm^{-1})	B′ (cm^{-1})	
C–O	7353–7042 1360–1420	12364 808.8	23381 427.67	734.0	7340 1362.4	915	0.89
C–I–Cl	7576–7143 1320–1400	12231 817.6	23635 423.1	723.3	7233 1382.6	945	0.92
C–I–Br	7326–7143 1365–1400	12241 819.6	23613 423.5	721.3	7213 1386.4	945	0.92
C–I–CH_3	7407–6944 1350–1440	12228 817.8	24355 410.6	719.7	7197 1389.5	1000	0.97
C–I–NO_2	7843–7519 1275–1330	12302 812 9	21519 464.7	744.0	7440 1344.1	767	0.74
C–II–Cl	7407–7042 1350–1420	12226 817.9	22821 438.2	727.6	7276 1374.4	881	0.85
C–II–Br	7463–7042 1340–1420	12161 822.3	22722 440.1	723.6	7243 1381.9	878	0.85
C–II–CH_3	7463–7042 1340–1420	12136 824.0	22712 440.3	721.9	7219 1385.2	879	0.85
C–II–NO_2	7547–7435 1325–1345	12228 817.8	21377 467 8	739.6	7396 1352.1	761	0.74
C–III–Cl	7353–7143 1360–1400	12231 817.6	23781 420.5	722.1	7221 1384.8	957	0.93
C–II–IBr	7407–7194 1350–1390	12194 820.1	23680 422.3	720.5	7205 1387.9	951	0.92
C-III-CH_2	7576–7353 1320–1360	12247 816.5	24284 411.8	721.3	7213 1386.4	993	0.96
C-III-NO_2	8130–8000 1220–1260	12143 823.5	19102 523.5	784.3	7843 1275.0	514	0.50

and therefore the Dq values decrease with respect to the standard parent complex C–O.

Nephelauxetic parameter β is the measure of the covalency of the metal-ligand bond. In a totally ionic metal-ligand interaction β is 1.00. The more the covalency the smaller β is. In all three series β's are smaller than that of C–O for the complexes with NO_2 group. This shows that metal-ligand bonds are more covalent, thus the π interaction is more significant in these complexes. In the series I and III complexes that have Cl, Br and CH_2 groups the values of β is bigger than that of C–O. Thus the covalency is smaller and π interaction is weaker. But there is a deviation from the above general trend in the series II, which can be explained as follows.



X = Cl, Br, CH_3, NO_2



X′ = Cl, Br, CH_3, NO_2

Fig. 2. Dimeric structure of I. series (a) and II. series (b) complexes.

If Fig 2a and Fig 2b are compared it is seen that the bridging oxygens and nitrogen atom are affected from the resonance effect of the substituents in the series I while the only nonbridging oxygens are affected in the series II. As it seen in Fig 1. If the Ni(II) ions are coordinated by the series I ligands the number of donor atoms which are affected by the substituents in either 4 or 5. They are two bridging oxygens and two nitrogen atom or one nitrogen atom and four bridging oxygen atoms. In the case of having the series II ligands, the number of donor atoms which are affected by the substituents is either one or two nonbridging oxygens. As a conclusion we may say that the substituent effect is greater in the series I complexes compared to the series II complexes.

This difference in resonance effect is observed in the Dq values given in Table 2, where the effect of substituents is large in the complexes of series I and small in the series II. Although the above explanation is reflected nicely on Dq values, there are some irregularities in β parameters. In serie II complexes with electron donating groups have smaller β values than C–O. Furthermore, the three complexes have the same β value. It can be said that the metal-ligand bonds are not significantly affected by the substituents which have a very small electron donating effect. The β value of C–2–NO_2, NO_2 being strong electron withdrawing group, is smaller than the C–O as expected.

REFERENCES

GÜRKAN, P., GÜNDÜZ, N.

LEVER, A.B.P., "Inorganic Electronic Spectroscopy" Elsevier, Sci. Publ. Co. Netherlands, 1984, PP. 507–544.

LEE, R.H., GRISWOLD, E., KLEINBERG, J., Inorg. Chem. 3(9), 1278, (1964).

TANABE, Y., SUGANO, S., J. Phys. Soc. Japan 9, 753, (1954).

REEDIJK, J., VON LEEUWEN, P.W.N.M., Groeneveld, L.W., Rec. Trawv. Chim. 87, 129, (1968).