2976 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2976—2981 (1973) [Vol. 46, No. 10

The Electronic Structure of Nickelocene by Means of the Configurational Interaction Method

Shunsuke Kobinata

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

(Received Auguest 1, 1972)

The electronic structures of nickelocene have been investigated by means of the configurational interaction method. The locally-excited configurations of the central metal ion and the charge-transfer configurations corresponding to an electron transfer from the ligand system to the central metal ion have been taken into account. A correspondence with the crystal-field treatment has been obtained using the partitioning technique of solving the secular equation. The energies of the charge-transfer configurations, the resonance integrals, and the Racah parameters were determined so as to obtain the best fit with the observed d-d transition energies.

The nature of the bonding in the sandwich complexes has been the subject of extensive experimental and theoretical investigations. Many calculations based on the MO theory or the crystal-field (CF) theory have been made, but they had led to rather scattered results.[1–7] With regard to the spectral assignment of the low-lying absorption bands (d-d transitions), the CF treatment seems more reliable than the MO treatment for the present.

Recently, a detailed study of the electronic state of nickelocene has been successfully made by I. Pavlik *et al.* using the CF treatment.[8] This method is based on an electrostatic model. On the other hand, many experiments, for example, NMR[9,10] and ESR,[11,12] clearly show the presence of a considerable covalency between nickel and cyclopentadienyl rings.

In this respect it is interesting to inquire into the origin of the validity of the CF treatment and the physical contents of the CF parameters (D_s and D_t) of nickelocene. Previously we have dealt with Cu(II) complexes by means of the configurational interaction (CI) method and have shown that the CF and CI methods give approximately equivalent results with regard to the d-d transition energies. The comparison of the CF parameters with the CI parameters gives useful information about the nature of bonding of Cu(II) complexes.[13]

In this study the electronic structures of nickelocene were treated by means of the CI method, and the physical content of the CF parameters and the nature of bonding in nickelocene were investigated.

Method

In the treatment of the CI method[14,15] nickelocene is considered to be a composite of two component groups: nickel ion and a ligand system composed of two cyclopentadienyl (cp) rings. The total electronic state is described as a superposition of various configurational wave functions: the ionic configurations (locally-excited configurations of the central metal ion or the ligand system) and the charge-transfer (CT) configurations, which correspond to an electron transfer from the ligand system, and *vice versa* if necessary. The ionic configurations are defined as those configurations in which the nickel ion has eight valence electrons (Ni^{2+}).

With regard to the ionic configurations, we took into account only the locally-excited configurations of the central metal ion, which arise from the rearrangement of d electrons within the d-shells, because we are interested primarily in the d-d transitions. In the ionic configurations the fivefold degenerate d AO's of the central metal ion are split into three levels:[16]

$$\left.\begin{aligned} <\mathrm{d}_0|V_\mathrm{c}|\mathrm{d}_0> &= 2D_\mathrm{s}^\mathrm{ion} - 6D_\mathrm{t}^\mathrm{ion} \\ <\mathrm{d}_{\pm1}|V_\mathrm{c}|\mathrm{d}_{\pm1}> &= D_\mathrm{s}^\mathrm{ion} + 4D_\mathrm{t}^\mathrm{ion} \\ <\mathrm{d}_{\pm2}|V_\mathrm{c}|\mathrm{d}_{\pm2}> &= -2D_\mathrm{s}^\mathrm{ion} - D_\mathrm{t}^\mathrm{ion} \end{aligned}\right\} \quad (1)$$

as a result of the electrostatic potential (V_c) from the ligands, where $D_\mathrm{s}^\mathrm{ion}$ and $D_\mathrm{t}^\mathrm{ion}$ are the CF parameters. They are usually determined so as to obtain the best coincidence between the calculated and the observed d-d transition energies. Here, they are considered to be the quantities which contain only the contribution of the electrostatic potential from the ligands. The energies of various terms of Ni^{2+} (d^8 configuration; ^3F, ^3P, ^1D, ^1G, ^1S) under the influence of V_c are shown in Ref. 8. The basic wave functions used in the CF method, $\Phi_\mathrm{M}^\mathrm{ion}(\mathrm{S}, \mathrm{M_S}, \mathrm{L}, \mathrm{M_L})$, should be replaced by:

$$\Phi_\mathrm{M}^\mathrm{ion}(\mathrm{S},\mathrm{M_S},\mathrm{L},\mathrm{M_L}) = A\Phi_\mathrm{L}^0\Phi_\mathrm{M}^\mathrm{ion}(\mathrm{S},\mathrm{M_S},\mathrm{L},\mathrm{M_L}) \quad (2)$$

in the CI treatment, where $\Phi_\mathrm{L}{}^0$ is the wave function of two cp anions in their ground state. A is the antisymmetrizer for the exchange of the electrons between

---

1) W. Moffitt, *J. Amer. Chem. Soc.*, **76**, 3386 (1954).

2) A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *J. Chem. Phys.*, **47**, 1104 (1967).

3) R. D. Fisher, *Theoret. Chim. Acta*, **1**, 418 (1963).

4) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3603 (1971).

5) A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.*, **11**, 207 (1957).

6) D. R. Scott and F. A. Matsen, *J. Phys. Chem.*, **72**, 16 (1968).

7) R. Prins and J. D. W. Voost, *J. Chem. Phys.*, **49**, 4665 (1968).

8) I. Pavlik, V. Cerny, and E. Maxova, *Collect. Czech. Chem. Commun.*, **35**, 3063 (1970).

9) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

10) H. M. Mcconell and C. H. Holm, *J. Chem. Phys.*, **28**, 749 (1958); **27**, 314 (1957).

11) R. Prins, *ibid.*, **50**, 4804 (1969).

12) R. E. Robertson and H. M. Mcconnell, *J. Phys. Chem.*, **64**, 70 (1960).

13) S. Kobinata, to be published.

14) J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, *Proc. Phys. Soc.*, **88**, 13 (1966).

15) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265 (1969).

16) D. R. Scott and R. S. Becker, *J. Organometal. Chem.*, **4**, 409 (1965). See also Ref. 2—8.

the nickel ion and the ligand system. S, M_S and L, M_L are the quantum numbers of the spin and the orbital angular momentum.

As to the CT configurations, those which are formed by an electron transfer to 3d AO of the central metal ion from the filled ligand π MO were considered first (3d-CT). The filled π MO's which belong to the same irreducible representation as the d AO under the D_{5d} molecular symmetry group are given as:[17]

$$\left.\begin{array}{ll}(d_0); & \phi(a_{1g}) = 1/\sqrt{2}(\phi_a(a_2) + \phi_b(a_2)) \\ (d_{\pm1}); & \phi(e_{1g}\pm) = 1/\sqrt{2}(\phi_a(e_1\pm) + \phi_b(e_1\pm))\end{array}\right\} \qquad (3)$$

where the suffixes a and b indicate the two cp rings. $\phi(a_2)$ and $\phi(e_1)$ are the π MO's of a cp ring, corresponding to the lowest and highest occupied π MO of the cp anion respectively.

$$\left.\begin{array}{l}\phi(a_2) = 1/\sqrt{5}(x_1+x_2+x_3+x_4+x_5) \\ \phi(e_1\pm) = 1/\sqrt{5}(x_1+\sigma^{\pm1}x_2+\sigma^{\pm2}x_3+\sigma^{\pm3}x_4+\sigma^{\pm4}x_5)\end{array}\right\} \qquad (4)$$

where x_i is the $2p\pi$ AO of the carbon atom. $\sigma=\exp(2\pi i/5)$.

The energies of 3d-CT configurations were represented as $E_0^{CT}(a_{1g})$ or $E_1^{CT}(e_{1g})$, depending on whether an electron was transferred from $\varphi(a_{1g})$ or $\varphi(e_{1g})$. The wave functions of the CT configurations are written as:

$$\Phi_\alpha^{CT}(S,M_s,L,M_L) = \sum A\Phi_L^{CT}(S',M_s'',M_L')\Phi_M^{CT}(S'',M_s'',L'',M_L'')$$
$$<S',M_s',S'',M_s''|S,M_s><M_L',M_L''|M_L> \qquad (5)$$

where summation is taken over S',M_S',S'',M_S'',M'_L and M_L''. $<S,'M_S',S,''M_S''|S,M_S>$ and $<M_L',M_L''|M_L>$ are the vector coupling coefficients for the spin angular momentum and the irreducible representation of the molecular symmetry group, D_{5d}.[18] $\Phi_M^{CT}(S, M_S, L, M_L)$, and $\Phi_L^{CT}(S, M_S, M_L)$ are the wave functions of the central metal ion (d^9 configuration) and the ligand system in a 3d-CT configuration (11π electrons). α is used to distinguish the independent Φ^{CT}'s belonging to the same irreducible representation. They are tabulated in Table 1. For the triplet state (S=1), we considered exclusively the state with the spin magnetic quantum number $M_S=1$.

The resonance interactions between the ionic configurations and CT configurations are calculated by the method of Longuett-Higgins and Murrell,[19] which lead to the group resonance integrals (β_0 and β_1) between the 3d AO of the central metal ion and the $2p\pi$ MO of cp rings,

$$\left.\begin{array}{l}\beta_0 = <d_0|\mathcal{H}|\phi(a_{1g})> \\ \beta_1 = <d_{\pm1}|\mathcal{H}|\phi(e_{1g}\pm)>\end{array}\right\} \qquad (6)$$

The diagonal and off-diagonal matrix elements of the secular equations are tabulated in Table 2, in which the Φ^{ion} (S=1, L=3) state, corresponding to the lowest state of the Ni^{2+} ion, *i.e.*, ^3F, is chosen as the standard of energy. *B* and *C* are the Racah parameters.

TABLE 1. THE WAVE FUNCTIONS OF CT CONFIGURATIONS

$$\Phi^{CT}(^3A_{2g}) = (1/\sqrt{2})(L(1/2,E_1{}^+)M(1/2,E_1{}^-) - L(1/2,E_1{}^-)M(1/2,E_1{}^+))$$
$$\Phi_1^{CT}(^3E_{1g}) = L(1/2,E_1{}^-)M(1/2,E_2{}^+)$$
$$\Phi_2^{CT}(^3E_{1g}) = L(1/2,E_1{}^+)M(1/2,A_1)$$
$$\Phi_3^{CT}(^3E_{1g}) = L(1/2,A_1)M(1/2,E_1{}^+)$$
$$\Phi_1^{CT}(^3E_{2g}) = L(1/2,E_1{}^+)M(1/2,E_1{}^+)$$
$$\Phi_2^{CT}(^3E_{2g}) = L(1/2,E_1{}^-)M(1/2,E_2{}^-)$$
$$\Phi_3^{CT}(^3E_{2g}) = L(1/2,A_1)M(1/2,E_2{}^+)$$
$$\Phi_1^{CT}(^1A_{1g}) = (1/2)(L(1/2,E_1{}^+)M(-1/2,E_1{}^-) - L(-1/2,E_1{}^+)M(1/2,E_1{}^-) + L(1/2,E_1{}^-)M(-1/2,E_1{}^+) - L(-1/2,E_1{}^-)M(1/2,E_1{}^+))$$
$$\Phi_2^{CT}(^1A_{1g}) = 1/\sqrt{2})(L(1/2,A_1)M(-1/2,A_1) - L(-1/2,A_1)M(1/2,A_1))$$
$$\Phi_1^{CT}(^1E_{1g}) = (1/\sqrt{2})(L(1/2,E_1{}^+)M(-1/2,A_1) - L(-1/2,E_1{}^+)M(1/2,A_1))$$
$$\Phi_2^{CT}(^1E_{1g}) = (1/\sqrt{2})(L(1/2,E_1{}^-)M(-1/2,E_2{}^+) - L(-1/2,E_1{}^-)M(1/2,E_2))$$
$$\Phi_3^{CT}(^1E_{1g}) = (1/\sqrt{2})(L(1/2,A_1)M(-1/2,E_1{}^+) - L(-1/2,A_1)M(1/2,E_1{}^+))$$
$$\Phi_1^{CT}(^1E_{2g}) = (1/\sqrt{2})(L(1/2,E_1{}^+)M(-1/2,E_1{}^+) - L(-1/2,E_1{}^+)M(1/2,E_1{}^+))$$
$$\Phi_2^{CT}(^1E_{2g}) = (1/\sqrt{2})(L(1/2,E_1{}^-)M(-1/2,E_2{}^-) - L(-1/2,E_1{}^-)M(1/2,E_2{}^-))$$
$$\Phi_3^{CT}(^1E_{2g}) = (1/\sqrt{2})(L(1/2,A_1)M(-1/2,E_2{}^+) - L(-1/2,A_1)M(1/2,E_2{}^+))$$

$L(1/2,E_1{}^+)$ and $M(-1/2,E_1{}^-)$ indicate $\Phi_L^{CT}(S=1/2,M_s=1/2, M_L=1)$ and $\Phi_M^{CT}(S=1/2,M_s=-1/2,M_L=-1)$, respectively. (Eq. (5)).

The CT configurations, formed by an electron transfer from a filled π-MO of the ligand system to the 4s or 4p AO of the central metal ion (4s-CT or 4p-CT), can easily be constructed using the vector coupling coefficients, in a manner similar to that used to construct the 3d-CT configurations. It is apparent that the effect of the 4s and 4p-CT configurations on the low-lying d^8 configurations is a uniform stabilization of these energies. Hence, these configurations do not affect the d AO splittings in a higher approximation.[14] The CT configurations corresponding to an electron transfer from the ligand σ orbital to the central metal ion can also be neglected in a higher approximation, because ESR[11] and NMR[20] experiments have shown that, in nickelocene, the electron delocalization between the cp rings and the nickel ion takes place mainly through the π orbitals of the cp rings.

To see the relation between the cf and CI treatments, it is necessary first to transform the basis of the CI method (ionic and CT configurations) to the ionic configurations which appear in the CF treatment.

By means of the partitioning technique,[21,22] the secular equation in the CI treatment (Table 2) is transformed to:

$$\sum_{j=1}^{N_1}\left\{<\Phi_i^{ion}|\mathcal{H}|\Phi_j^{ion}> - \sum_{p=N_1+1}^{N_1+N_{CT}}\frac{<\Phi_i^{ion}|\mathcal{H}|\Phi_p^{CT}><\Phi_p^{CT}|\mathcal{H}|\Phi_i^{ion}>}{<\Phi_p^{CT}|\mathcal{H}|\Phi_p^{CT}>-E}\right\}c_i^{ion} = Ec_i^{ion} \qquad (7)$$

---

[17] W. Moffitt, *J. Amer. Chem. Soc.*, **76**, 3386 (1954).

[18] J. S. Grifith, "The Theory of Transition-Metal Ions", Cambridge University Press, London (1961).

[19] H. C. Longuett-Higgins and Murrell, *Proc. Phys. Soc., Ser, A*, **68**, 601 (1955).

[20] M. F. Retting and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 1361 (1969).

[21] P. O. Löwdin, *J. Mol. Spectrosc.*, **10**, 12 (1963).

[22] P. O. Löwdin, *J. Math. Phys.*, **3**, 969 (1962).

Table 2a. The matrix elements between Φ^{ion} and Φ^{CT} for triplet states

	Diagonal		Off-diagonal	
$^3\text{A}_{2g}$	$^3\text{F}(0)$	$-0.8D_s^{\text{ion}}-6D_t^{\text{ion}}$	$^3\text{F}(0)\sim{}^3\text{P}(0)$	$2.4D_s^{\text{ion}}+4D_t^{\text{ion}}$
	$^3\text{P}(0)$	$15B+2.8D_s^{\text{ion}}$	$^3\text{F}(0)\sim\Phi^{\text{CT}}(^3\text{A}_{2g})$	$-\sqrt{8/5}\,\beta_1$
	$\Phi^{\text{CT}}(^3\text{A}_{2g})$	E_1^{CT}	$^3\text{P}(0)\sim\Phi^{\text{CT}}(^3\text{A}_{2g})$	$\sqrt{2/5}\,\beta_1$
$^3\text{E}_{1g}$	$^3\text{F}(1)$	$-0.6D_s^{\text{ion}}-D_t^{\text{ion}}$	$^3\text{F}(1)\sim{}^3\text{P}(1)$	$(\sqrt{6}/5)(4D_s^{\text{ion}}-5D_t^{\text{ion}})$
	$^3\text{P}(1)$	$15B-1.4D_s^{\text{ion}}$	$^3\text{F}(1)\sim\Phi_1^{\text{CT}}(^3\text{E}_{1g})$	$\sqrt{3/5}\,\beta_1$
	$\Phi_1^{\text{CT}}(^3\text{E}_{1g})$	E_1^{CT}	$^3\text{F}(1)\sim\Phi_2^{\text{CT}}(^3\text{E}_{1g})$	$-\sqrt{2/5}\,\beta_1$
	$\Phi_2^{\text{CT}}(^3\text{E}_{1g})$	E_1^{CT}	$^3\text{F}(1)\sim\Phi_3^{\text{CT}}(^3\text{E}_{1g})$	$-\sqrt{2/5}\,\beta_0$
	$\Phi_3^{\text{CT}}(^3\text{E}_{1g})$	E_0^{CT}	$^3\text{P}(1)\sim\Phi_1^{\text{CT}}(^3\text{E}_{1g})$	$\sqrt{2/5}\,\beta_1$
			$^3\text{P}(1)\sim\Phi_2^{\text{CT}}(^3\text{E}_{1g})$	$\sqrt{3/5}\,\beta_1$
			$^3\text{P}(1)\sim\Phi_3^{\text{CT}}(^3\text{E}_{1g})$	$\sqrt{3/5}\,\beta_0$
$^3\text{E}_{2g}$	$^3\text{F}(-3)$	$D_s^{\text{ion}}-3D_t^{\text{ion}}$	$^3\text{F}(-3)\sim\Phi_2^{\text{CT}}(^3\text{E}_{2g})$	$-\beta_1$
	$\Phi_2^{\text{CT}}(^3\text{E}_{2g})$	E_1^{CT}		
$^3\text{E}_{2g}$	$^3\text{F}(2)$	$7D_t^{\text{ion}}$	$^3\text{F}(2)\sim\Phi_3^{\text{CT}}(^3\text{E}_{2g})$	$-\beta_0$
	$\Phi_3^{\text{CT}}(^3\text{E}_{2g})$	E_0^{CT}		

$^3\text{F}(0)$ indicates $\Phi^{\text{ion}}(\text{S}=1,\text{M}=1,\text{L}=3,\text{M}_\text{L}=0)$ of Eq. (2).

Table 2b. The matrix elements between Φ^{ion} and Φ^{CT} for singlet states

	Diagonal		Off-diagonal	
$^1\text{A}_{1g}$	$^1\text{D}(0)$	$5B+2C$	$^1\text{G}(0)\sim{}^1\text{D}(0)$	$(24\sqrt{5}/35)D_s^{\text{ion}}-(20\sqrt{5}/7)D_t^{\text{ion}}$
		$+(6/7)D_s^{\text{ion}}+(24/7)D_t^{\text{ion}}$	$^1\text{G}(0)\sim{}^1\text{S}(0)$	$2\sqrt{14}\,D_t^{\text{ion}}$
	$^1\text{G}(0)$	$12B+2C$	$^1\text{D}(0)\sim{}^1\text{S}(0)$	$2\sqrt{14}/5D_t^{\text{ion}}$
		$-(20/7)D_t^{\text{ion}}+(18/7)D_t^{\text{ion}}$	$^1\text{D}(0)\sim\Phi_1^{\text{CT}}$	$-\sqrt{2/7}\,\beta_1$
	Φ_1^{CT}	E_1^{CT}	$^1\text{D}(0)\sim\Phi_2^{\text{CT}}$	$\sqrt{4/7}\,\beta_0$
	Φ_2^{CT}	E_0^{CT}	$^1\text{G}(0)\sim\Phi_1^{\text{CT}}$	$-\sqrt{32/35}\,\beta_1$
			$^1\text{G}(0)\sim\Phi_2^{\text{CT}}$	$-\sqrt{36/35}\,\beta_0$
			$^1\text{S}(0)\sim\Phi_1^{\text{CT}}$	$\sqrt{4/5}\,\beta_1$
			$^1\text{S}(0)\sim\Phi_2^{\text{CT}}$	$-\sqrt{2/5}\,\beta_0$
$^1\text{E}_{1g}$	$^1\text{D}(0)$	$5B+2C$	$^1\text{D}(1)\sim{}^1\text{G}(1)$	$(4\sqrt{6}/7)D_s^{\text{ion}}-(5\sqrt{6}/7)D_t^{\text{ion}}$
		$+(3/7)D_s^{\text{ion}}-(16/7)D_t^{\text{ion}}$	$^1\text{D}(1)\sim\Phi_1^{\text{CT}}$	$-\sqrt{1/7}\,\beta_1$
	$^1\text{G}(1)$	$12B+2C$	$^1\text{D}(1)\sim\Phi_2^{\text{CT}}$	$\sqrt{6/7}\,\beta_1$
		$-(17/7)D_s^{\text{ion}}+(9/7)D_t^{\text{ion}}$	$^1\text{D}(1)\sim\Phi_3^{\text{CT}}$	$\sqrt{1/7}\,\beta_0$
	Φ_1^{CT}	E_1^{CT}	$^1\text{G}(1)\sim\Phi_1^{\text{CT}}$	$\sqrt{6/7}\,\beta_1$
	Φ_2^{CT}	E_1^{CT}	$^1\text{G}(1)\sim\Phi_2^{\text{CT}}$	$\sqrt{1/7}\,\beta_1$
	Φ_3^{CT}	E_0^{CT}	$^1\text{G}(1)\sim\Phi_\alpha^{\text{CT}}$	$-\sqrt{6/7}\,\beta_0$
$^1\text{E}_{1g}$	$^1\text{G}(-4)$	$12B+2C+4D_s^{\text{ion}}+2D_t^{\text{ion}}$		
$^1\text{E}_{2g}$	$^1\text{D}(2)$	$5B+2C$	$^1\text{D}(2)\sim{}^1\text{G}(2)$	$(4\sqrt{3}/7)D_s^{\text{ion}}+(30\sqrt{3}/7)D_t^{\text{ion}}$
		$-(6/7)D_s^{\text{ion}}+(4/7)D_t^{\text{ion}}$	$^1\text{D}(2)\sim\Phi_1^{\text{CT}}$	$-\sqrt{6/7}\,\beta_1$
	$^1\text{G}(2)$	$12B+2C$	$^1\text{D}(2)\sim\Phi_2^{\text{CT}}$	$-\sqrt{4/7}\,\beta_0$
		$-(8/7)D_s^{\text{ion}}-(11/7)D_t^{\text{ion}}$	$^1\text{G}(2)\sim\Phi_1^{\text{CT}}$	$\sqrt{8/7}\,\beta_1$
	Φ_1^{CT}	E_1^{CT}	$^1\text{G}(2)\sim\Phi_2^{\text{CT}}$	$-\sqrt{3/7}\,\beta_0$
	Φ_2^{CT}	E_0^{CT}		
$^1\text{E}_{2g}$	$^1\text{G}(-3)$	$12B+2C+D_s^{\text{ion}}-3D_t^{\text{ion}}$	$^1\text{G}(-3)\Phi_2^{\text{CT}}$	$-\beta_1$

$^1\text{D}(0)$ indicates $\Phi^{\text{ion}}(\text{S}=0,\text{M}_\text{S}=0,\text{L}=2,\text{M}_\text{L}=0)$ of Eq. 2.

where N_I and N_CT are the numbers of bases of the ionic and CT configurations respectively. c_i^{ion} and c_p^{CT} are the CI coefficients acting on $\Phi_\text{i}^{\text{ion}}$ and $\Phi_\text{p}^{\text{CT}}$ respectively. E is the eigenvalue. The secular equation obtained above is different from those ordinarily obtained, because E is present in the denominator. An eigenvalue, E, is composed of the uniform stabilization energies produced by the 4s-CT and 4p-CT configurations, ΔE(4s-CT) and ΔE(4p-CT), and of the stabilization energy produced by 3d-CT (Fig. 1). Writing the average stabilization energy by 3d-CT as ΔE(3d-CT), a constant

$$\Delta E=\Delta E(\text{3d}-\text{CT})+\Delta E(\text{4s}-\text{CT})+\Delta E(\text{4p}-\text{CT}) \quad (7)$$

may be added to E without any influence on the splitting of 3d levels. If the E in the denominator is replaced by an average energy, $\bar{E}$, after the above procedure, the secular equation (7) is reduced to an ordinary one, the basis of which is the same as that of the CF treatment. Each matrix element depends only on 3d-CT, not on 4s-CT and 4p-CT. The above replacement would be a good approximation for low-lying d-d transition energies if $E_1^{\mathrm{CT}}-\bar{E}$ is much larger than the breadth of the eigenvalues corresponding to the locally-excited configurations of the central metal ion, *i.e.*, the d-d transition energies. As will be shown in the next section, the quite large value of $E_1^{\mathrm{CT}}-\bar{E}$ estimated by means of the CI treatment confirms that this is the case. Furthermore, the success of the CF treatment itself implies that this replacement is a good approximation. Therefore, using these definitions:

$$\left.\begin{aligned}\sigma_1 &= \beta_1^2/(E_1^{\mathrm{CT}}-\bar{E})\\ \sigma_0 &= \beta_0^2/(E_0^{\mathrm{CT}}-\bar{E})\end{aligned}\right\} \tag{8}$$

the average stabilization energy by 3d-CT can be represented, so as to satisfy the center of gravity rule, as:

$$\Delta E(\mathrm{3d-CT}) = (4/5)\sigma_1 + (2/5)\sigma_0 \tag{9}$$

We obtain exactly the same form of the secular equations as those obtained by means of the CF treatment by defining as follows:

$$D_s = D_s^{\mathrm{ion}} + D_s^{\mathrm{cov}}$$
$$D_t = D_t^{\mathrm{ion}} + D_t^{\mathrm{cov}}$$

where:

$$\left.\begin{aligned}D_s^{\mathrm{cov}} &= (5/35)\sigma_1 + (5/35)\sigma_0\\ D_t^{\mathrm{cov}} &= (4/35)\sigma_1 - (3/35)\sigma_0\end{aligned}\right. \tag{10}$$

The only differences are the replacement of the D_s^{ion} and D_t^{ion} of the CF treatment by the D_s and D_t in Eq. 10. These differences lose all meaning when the D_s^{ion} and D_t^{ion} are considered as parameters which should be determined so as to obtain the best fit with the observed d-d transition energies, as is usually done in the CF calculations. This implies that the CF parameter treatment is approximately equivalent to the CI treatment with respect to the d-d transition energies. Hence, the CF treatment is valid even in the presence of considerable covalency.

Results and Discussion

CI Parameters. In order to calculate the d-d transition energies theoretically by means of the CI method, it is necessary to estimate the eight quantities, D_s^{ion}, D_t^{ion}, E_1^{CT}, E_0^{CT}, B, C, β_1 and β_0, shown in Table 2. At present, it is difficult to estimate these quantities theoretically with sufficient confidence. Therefore, it seems justifiable to use an alternative method of estimating these quantities empirically, considering them as CI parameters which should be determined so as to obtain the best fit with the observed d-d transition energies.

In order to reduce the number of unknown parameters, the following approximations were made. In the first place, the D_s^{ion}, and D_t^{ion} in Table 2 were assumed to be negligible, because it is known that the effect of the electrostatic terms on the d-orbital splitting is generally rather small.[24] The validity of this approximation was confirmed by the consistency of the results obtained under this approximation. E_0^{CT} was estimated to be equal to E_1^{CT} plus the difference between the second and the first ionization potentials of the cp anion. This difference was calculated by the method of Pariser-Parr-Pople,[25,26] and using Koopmans' theorem, as 5.145 eV. Hence, we obtained:

$$E_0^{\mathrm{CT}} = E_1^{\mathrm{CT}} + 5.145\ \mathrm{eV}$$

Table 3. The calculated d-d transition energies and the CI parameters

	Calcn. 1	Calcn. 2	Obsd.[8]
$^3E_{1g} \leftarrow {}^3A_{2g}$	13.12 kK	14.12 kK	14.4 kK
$^3E_{2g} \leftarrow {}^3A_{2g}$	15.78	16.68	16.9
$^3E_{1g} \leftarrow {}^3A_{2g}$	24.46	23.99	23.45
$^3E_{2g} \leftarrow {}^3A_{2g}$	32.64	35.46	
$^3A_{2g} \leftarrow {}^3A_{2g}$	52.82	52.77	
$^1E_{2g} \leftarrow {}^3A_{2g}$	10.83	11.68	11.72
$^1A_{1g} \leftarrow {}^3A_{2g}$	17.93	18.96	19.15
$^1E_{1g} \leftarrow {}^3A_{2g}$	24.54	26.51	
$^1E_{1g} \leftarrow {}^3A_{2g}$	28.70	30.10	
$^1E_{2g} \leftarrow {}^3A_{2g}$	32.14	32.98	
$^1A_{1g} \leftarrow {}^3A_{2g}$	43.42	47.78	
$^1E_{2g} \leftarrow {}^3A_{2g}$	48.37	52.35	
β_0	−3.901 eV	−3.712 eV	
β_1	−6.40	−6.40	
E_1^{CT}	10.64	9.53	
E_0^{CT}	15.785	14.675	
B	1030 cm^{-1}	824 cm^{-1}	
C	4B	5650 cm^{-1}	
E_G(3d−CT)	−4.959 eV	−5.282 eV	

We carried out two types of calculation, Calcn. 1 and Calcn. 2. In Calcn. 1, $C/B=4.0$ was assumed, as is usually done in a CF treatment.[23] In Calcn. 2, B and C were considered to be independent parameters. With these assumptions, the number of independent CI parameters to be determined is reduced to four in Calcn. 1 (β_1, β_0, E_1^{CT} and B) and to five in Calcn. 2 (β_1, β_0, E_1^{CT}, B and C). Because five d-d bands have been observed for nickelocene, we can determine these CI parameters uniquely so as to obtain the best coincidence with the observed d-d transition energies. The results are shown in Table 3. The average deviation is about 1 kK for Calcn. 1 and 0.2 kK for Calcn. 2. This small deviation must result from the neglect of the two-electron charge-transfer configurations and the locally-excited configurations of the ligand system. Calcn. 2 gives the $B/C=6.85$ ratio, which is rather large compared with the value of the free ion. It is very near to that of $C/B=6.87$ obtained in the CF treatment of nickelocene by Pavlik *et al.*[8] The ratio of B to the free ion value B_{ion}, the nephelauxetic ratio, was obtained as $\beta=0.80$ by means of Calcn. 2, using $B_{\mathrm{ion}}=1030\ \mathrm{cm}^{-1}$. In the CF treatment, $\beta=0.56$ has been obtained.[8] Calc. 1 gives the unreasonable value of $\beta=1.0$. This probably results from the unreasonable

---

[23] H. L. Schläfer and G. Gliemann, "Basic Principles of Ligand Field Theory," Wiley-Interscience (1969).

[24] C. K. Jørgensen, "Modern Aspects of Ligand Field Theory," North-Holland Publishing Company, Amsterdam-London (1971).

[25] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[26] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

assumption that the C/B ratio is independent of the complex formation, that is, $C/B=4.0$.[27] It is known that the nephelauxetic ratio consists of two factors, the central-field covalency and the symmetry-restricted covalency.[24] Because, in the CI treatment, the latter effect is taken into account to some extent, it seems reasonable that the nephelauxetic ratio in the CI treatment is larger than in the CF method.

As to the resonance integral the value of $\beta_1=-6.40$ eV and $\beta_0=-3.712$ eV were obtained. At first sight these values seem too large compared with the corresponding values of ferrocene, which is known to be more covalent than nickelocene, for which $\beta_1=-3.3468$ eV and $\beta_0=0$ have been used in the MO calculation.[28] In the Wolfsberg-Helmholz approximation, the resonance integral, β_{ij}, is estimated to be:

$$\beta_{ij} = -F(I_i+I_j)G_{ij}/2 \tag{11}$$

where G_{ij} is the group overlap integral and where F is a constant, for which a value of about 2 has usually been used. I_i and I_j are the valence-state ionization potentials of the relevant AO's. I_i and I_j depend strongly on the electronic charge and the electronic configuration of the relevant atom. The β_{ij} in the MO calculation is related to the value for the self-consistent charge distribution and electron configuration, whereas the β_{ij} in the CI treatment would be more closely related to the value for the "zeroth-order" charge distribution and the electron configuration. In nickelocene the β_1 and β_0 of the CI treatment may be estimated as:

$$\left.\begin{aligned}\beta_1 &= -(1/2)F(I(\mathrm{Ni}^{2+}) + I(\mathrm{C}^{-1/5}))\langle d_1|\phi(e_{1g}{}^+)\rangle \\ \beta_0 &= -(1/2)F(I(\mathrm{Ni}^{2+}) + I(\mathrm{C}^{-1/5}))\langle d_0|\phi(a_{1g})\rangle\end{aligned}\right\} \tag{12}$$

where $I(\mathrm{Ni}^{2+})$ and $I(\mathrm{C}^{-1/5})$ are the ionization potentials of Ni^{2+} and $I(\mathrm{C}^{-1/5})$, which were estimated to be 35.17 eV and 9.10 eV respectively.[30] The group overlap integrals, $\langle d_1/\phi(e_{1g}{}^+)\rangle$ and $\langle d_0/\phi(a_{1g})\rangle$, were calculated, on the basis of the radial 3d functions tabulated by Richardson *et al.*, to be 0.139 and 0.059 respectively.[31] This calculation made use of the geometry reported by Ronova and Alekseev.[32] With these values and taking $F=2$, the values of $\beta_1=-6.16$ eV and $\beta_0=-2.64$ eV are obtained from Eq. (12). These values coincide fairly well with the values obtained empirically by the CI method (Table 3). Hence, the values of the resonance integrals obtained from the CI treatment seem not to be unreasonable.

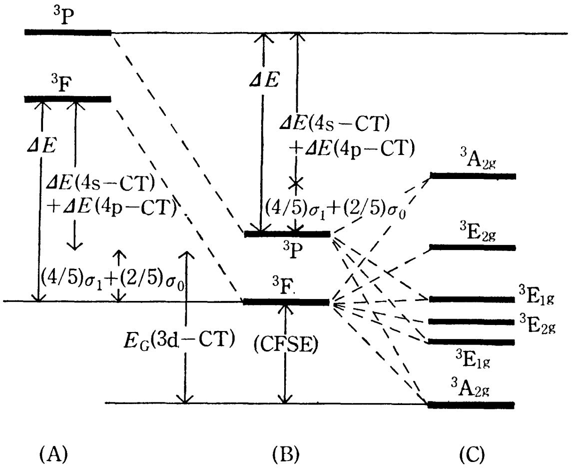

Fig. 1. Schematic illustration of the relation between the quantities ΔE, ΔE(4s-CT)+ΔE(4p-CT), $(4/5)\sigma_1+(2/5)\sigma_0$, E_G(3d-CT) and CFSE.
(A) represents the position of energy level of the ionic configurations. (B) represents the energy level after the uniform shift of Eq. 7. (C) is the final energy level.

As to the energy of CT configuration, the value of $E_1^{CT}=9.53$ eV was obtained. The electronic absorption band at about 32700 cm^{-1} of nickelocene has been assigned to an intramolecular CT band by Scott and Becker.[33] Therefore, the above value of E_1^{CT} implies that the CT state is the state of the strong mixing of the CT and the appropriate locally-excited configurations. A more detailed study of the resonance integrals in the CI and MO treatments and an analysis of the CT states will be undertaken in the future.

The E_G (3d-CT) value of -5.28 eV was obtained for the ground-state stabilization energy due to the 3d-CT, which is considerably larger than the value of $\mathrm{Cu(en)_2(NCS)_2}$, $E_G(\text{3d-CT})=-2.35$ eV. As can be seen from Fig. 1, E_G(3d-CT) is equal to the sum of the ground-state stabilization energy measured from the center of gravity of the ^{3}F term and the average stabilization energy due to 3d-CT, ΔE(3d-CT) of Eq. (9). The former should be equal to the crystal-field stabilization energy (CFSE) of the CF treatment, CFSE$=-2.89$ eV. From the values of $D_s=3290$ cm^{-1} and $D_t=1696$ cm^{-1} obtained in the CF treatment, we can estimate

$$\sigma_1 = 18.38\ \mathrm{kK}: \qquad \sigma_0 = 4.66\ \mathrm{kK}$$

following to Eqs. (8) and (10), neglecting D_s^{ion} and D_t^{ion}. Thus, we obtain:

$$E_G(\text{3d}-\text{CT}) = \text{CFSE} - (4/5)\sigma_1 - (2/5)\sigma_0 = -4.94\ \text{eV}$$

which agrees reasonably well with the value obtained from the CI calculation, $E_G(\text{3d-CT})=-5.28$ eV. Hence, the large value of E_G(3d-CT) of nickelocene seems reasonable.

Although, the physical meaning of the average energy of Eq. (8) is complicated, it is expected, for the theory to be self-consistent as a whole, that the $\overline{E}$ derived from σ_1 and σ_0 are equal. Substituting the values of β_1, β_0, E_1^{CT}, and E_1^{CT} tabulated in Table 3 into the right-hand side of Eq. 8, the average energy, $\overline{E}$, is determined to be:

$$\text{Calcn. 1}\quad \left.\begin{aligned}\overline{E} &= -7.32\ \text{eV from } \sigma_1 \\ \overline{E} &= -9.35\ \text{eV from } \sigma_0\end{aligned}\right\}$$

$$\text{average } \overline{E} = -8.34 \pm 1.0\ \text{eV}$$

---

[27] H. Witzke, *Theoret. Chim. Acta*, **20**, 171 (1971).

[28] E. M. Shustorovish and M. E. Dyatkina, *J. Struct. Chem. USSR*, **1**, 98 (1960).

[29] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[30] C. E. Moore, *Natl. Bur. Std., Circ.* No. 467 (1949).

[31] J. W. Richardson, W. C. Nieuwpoort, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

[32] I. A. Ronova and N. V. Alekseev, *Zh. Struk. Khim.*, **7**, 886 (1966).

[33] D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961).

$$\text{Calcn. 2}\quad \left.\begin{array}{l}\bar{E} = -8.43\,\text{eV from }\sigma_1\\ \bar{E} = -9.03\,\text{eV from }\sigma_0\end{array}\right\}$$

$$\text{average }\bar{E} = -8.76 \pm 0.3\,\text{eV}$$

In Calcn. 2 a much smaller deviation of $\bar{E}$ was obtained, similarly to the case of the d-d transition energies. The good agreement between the $\bar{E}$'s obtained above implies that the values of β_1, β_0, E_1^{CT} and E_0^{CT} obtained in the CI treatment are "self-consistent."

The author would like to thank Professor Ichiro Hanazaki of Osaka University for his helpful discussions and advice.