Electronic Structure of Transition Metal Complexes. IV. d–d* Transitions

E. KAI, T. ARAKAWA and K. NISHIMOTO

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Received January 5, 1982

d–d* Transition is one of many interesting problems in the study of the transition metal complexes. Therefore, many experimental and theoretical works have been made for several decades. As a result some empirical rules, for example the spectrochemical series, nephelauxetic series, hyperchromic series, averaged potential field rule, *etc.*, have been proposed [1] and are used even now for deciding the structure of the transition metal complexes. The crystal field and ligand field theories [2] have been used for theoretical study of d–d* transitions in most case.

In the previous papers [3–5] we have investigated the electronic structure of the various transition metal complexes in the ground states using the CNDO method, and have explained the binding energy, ionization potential, *trans* influence, *etc.* Our next target is d–d* transition. In the present study we take into consideration three kinds of six-coordinate complexes, $[Co(OH_2)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$, which have been investigated experimentally in detail, and calculate the first and second excitation energies with both INDO and CNDO methods. From the calculated results we attempted to elucidate theoretically the spectrochemical and nephelauxetic series.

The exchange integrals play an important role in the d–d* transitions which are mainly intra atomic transitions. Therefore, we must use the INDO method. For a comparison we have done also a CNDO calculation of the three hexacoordinate Co(III) complexes mentioned above. Recently, some INDO calculations for the transition metal complexes have been done [6–9]. However, the present paper is the first work for the systematic study of d–d* transition with the INDO method.

The energy of d–d* transition is calculated by the following two steps. At first, the ground state is calculated by INDO and CNDO methods. Then SECI calculation (Singly Excited Configuration Interaction) is carried out using the MO's which are contributed mainly by d-orbitals of the central metal ion. The matrix elements in INDO scheme are as follows:

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB} + G^A_{\mu\mu};\ \mu \text{ on atom A}$$

$$F_{\mu\nu} = G^A_{\mu\nu};\ \mu \neq \nu \text{ both on atom A}$$

$$F_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}(\beta^0_\mu + \beta^0_\nu) - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu};\ \mu \text{ on atom A and } \nu \text{ on atom B}$$

$$\text{where } G^A_{\mu\nu} = \sum_{\sigma\lambda} [P_{\sigma\lambda}\langle\mu\nu|\sigma\lambda\rangle - \tfrac{1}{2}P_{\sigma\lambda}\langle\mu\sigma|\nu\lambda\rangle].$$

Clack and Smith [10, 11] neglected exchange integrals except only $\langle\mu\mu|\nu\nu\rangle$ and $\langle\mu\nu|\mu\nu\rangle$ among one-center exchange integrals, $G^A_{\mu\nu}$. However, their approximation is not rotational invariant as pointed out by Bacon and Zerner [6]. For that reason, when we have applied the same type of calculation that Clack and Smith used in d–d* transition, a breakdown of space symmetry of d–d* levels occurred by CI calculation. Therefore, it is necessary to use the INDO scheme which includes all one-center exchange integrals.

The values of one-center core integrals of Co, $U_{\mu\mu}$, used are as follows:

$$U_{ss} = -84.36,\ U_{pp} = -79.18,\ U_{dd} = -150.33 \text{ (a.u.)}$$

For example, U_{ss} is expressed by

$$U_{ss} = -I_s - [F^0(s,p) - {}^1\!/_6\,G^1(s,p)] - 7[F^0(s,d) - {}^1\!/_{10}\,G(s,d)]$$

The ionization potentials I_μ are estimated by the following manner:

$$I_s = E(4s^0 4p^1 3d^7) - E(4s^1 4p^1 3d^7) = -10.62 \text{ (eV)}$$

$$I_p = E(4s^1 4p^0 3d^7) - E(4s^1 4p^1 3d^7) = -5.16 \text{ (eV)}$$

$$I_d = E(4s^1 4p^1 3d^6) - E(4s^1 4p^1 3d^7) = -14.70 \text{ (eV)}$$

The values of two-center core integral, β^0_μ, overlap integral, $S_{\mu\nu}$, two-center repulsion integral, $\gamma^{AB}_{\mu\nu}$, are taken to be the same as those in CNDO scheme of our previous paper [3]. We used Slater Condon parameters given by Anno and Teruya [12], which are necessary to calculate one-center repulsion integral.

The experimental values of Co–N (1.97 Å) and Co–C (1.90 Å) distances and ligands, CN^-, NH_3 and H_2O, are used in the calculations [13, 14]. We estimated Co–O distance to be 1.95 Å.

The calculated excitation energies are summarized in Table I. For a comparison, the results obtained by the *ab initio* MO method [15, 16] and by experiment are also given [17, 18].

As seen from Table I, in the CNDO calculation the splitting between the first ($^1T_{1g}$) and second ($^1T_{2g}$) levels is considerably smaller than the experimental values. Furthermore, the excitation energy is calculated to be much larger than that of the experimental one. The reason is as follows: In the CNDO scheme, one-center exchange integrals in the central metal ion are neglected, which contribute to the localized

0020-1693/83/$3.00

TABLE I. d–d* Transition Energies (in eV).

		INDO	CNDO	*ab initio*	obs.
$[Co(OH_2)_6]^{3+}$	I[a]	2.34	3.74	–	2.06[b]
	II	3.48	3.83	–	3.09
$[Co(NH_3)_6]^{3+}$	I	2.89	3.46	2.64[c]	2.60[d]
	II	3.97	3.52	4.26	3.66
$[Co(CN)_6]^{3-}$	I	4.42	4.77	3.46[e]	4.02[d]
	II	5.31	4.84	4.18	4.84

[a] I: $^1T_{1g}$; II: $^1T_{2g}$. [b] Ref. 17. [c] Ref. 15. [d] Ref. 18. [e] Ref. 16.

excitation such as d–d* transition. This makes J (Coulomic integral) small and the excitation energy large.

The results of *ab initio* MO calculations show that in the ammine complex, $^1T_{2g}$ is calculated to be greater than that of the experimental value, although the calculated $^1T_{1g}$ is in good agreement with experiment. On the other hand in cyanide complexes both $^1T_{1g}$ and $^1T_{2g}$ levels are calculated to be smaller than those of experimental ones. In order to improve these results it seems necessary to use a large basis set and carry out large CI calculation.

As seen from Table I, the transition energies of $^1T_{1g}$ and $^1T_{2g}$ calculated by INDO method are in good agreement with experiment. Accordingly, the INDO method is the useful tool for the theoretical study of empirical rules because we can carry out systematic calculation of a series of various transition metal complexes with an economical rate. Furthermore, the INDO method provides simple and clear chemical pictures of the electronic structure of transition metal complexes.

When the calculated excitation energies are plotted against experimental ones (Fig. 1), a linear relation is obtained. This suggests that our parameters are useful for the comparative study of d–d* transitions of various transition metal complexes. From this figure, it is found that the order of these excitation energies is in accord with that of spectrochemical series. In Table II, the calculated orbital energies and AO coefficients are shown. Our calculation shows that the d–d* transition is related closely to the participation of d-orbital of the central metal in the metal–ligand bond. The order of $\Delta\epsilon$ (the difference of t_{2g} (HOMO) and e_{g*} (LUMO)) among these complexes is not coincident with that of the spectrochemical series. However, the order of $A(=1 - C_{t_{2g}}^2 C_{e_g*}^2)$ which measures the extent of the participation of d-orbital in the metal–ligand bond is in accord with that of excitation energy. Namely, the large A causes the increase of the excitation energy. Figure 2 shows the plots of A against the nephelauxetic parameter (h) of the ligands. The linearity between A and h shows that our calculation explains the nephelauxetic series.

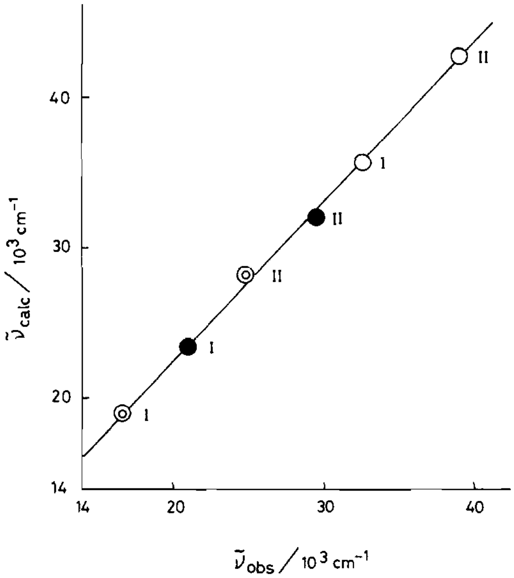

Fig. 1. Plots of calculated d–d* transition energies *vs.* observed ones for six coordinate compounds. I, $^1T_{1g}$; II, $^1T_{2g}$. ◎, $[Co(OH_2)_6]^{3+}$; ●, $[Co(NH_3)_6]^{3+}$; ○, $[Co(CN)_6]^{3-}$.

The CNDO scheme such as CNDO/S method which has been used for the study of the electronic spectra is useful for delocalized systems such as the conjugated compounds [19, 20]. However, it is not

TABLE II. Calculated Orbital Energies (in a.u.) of HOMO and LUMO and AO Coefficients.

	$[Co(OH_2)_6]^{3+}$	$[Co(NH_3)_6]^{3+}$	$[Co(CN)_6]^{3-}$
ϵ_{e_g*}(LOMO)	−0.591	−0.498	0.787
$\epsilon_{t_{2g}}$(HOMO)	−1.219	−1.167	0.138
$\Delta\epsilon$	0.628	0.668	0.649
C_{e_g*}(LUMO)	0.902	0.867	0.781
$C_{t_{2g}}$(HOMO)	0.950	0.957	0.938
$(C_{e_g*})^2(C_{t_{2g}})^2$	0.734	0.688	0.537

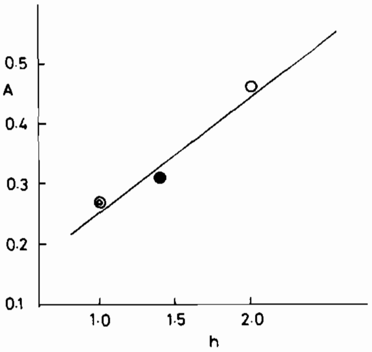

Fig. 2. Plots of A(=1 − $C^2_{e_g*}C^2_{t_{2g}}$) *vs.* nephelauxetic parameter (h). ◎, $[Co(OH_2)_6]^{3+}$; ●, $[Co(NH_3)_6]^{3+}$; ○, $[Co(CN)_6]^{3-}$.

appropriate to study the localized excitation such as d–d* transition. Therefore, in such systems it is necessary to use a scheme which takes account of all types of one-center exchange integrals. As the INDO calculation using our parameter set explains the experimental d–d* transition energies satisfactorily, we are investigating other empirical rules such as averaged potential field rule with the present scheme.

Acknowledgements

We would like to express our gratitude to the Computer Center of Institute for Molecular Science for the use of the HITAC M-200H computer and the Data Processing Center of Kyoto University for the use of the FACOM M-200 Computer.

References

1 For example, A. F. Williams, 'Inorganic Chemistry', Springer-Verlag, New York (1979).
2 For example, C. J. Ballhausen, 'Introduction to Ligand Field Theory', McGraw–Hill, New York (1962).
3 E. Kai and K. Nishimoto, *Int. J. Quant. Chem., XVIII,* 403 (1980).
4 E. Kai, T. Misawa, and K. Nishimoto, *Bull. Chem. Soc. Jpn., 53,* 2481 (1980).
5 E. Kai and K. Nishimoto, *Bull. Chem. Soc. Jpn., 55,* 1242 (1982).
6 A. D. Bacon and M. C. Zerner, *Theoret. Chim. Acta Berl.), 53,* 21 (1979).
7 G. H. Loew, Z. S. Herman, and M. C. Zerner, *Int. J. Quant. Chem., XVIII,* 481 (1980).
8 M. C. Zerner, G. H. Loew, R. F. Kirchner, and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc., 102,* 589 (1980).
9 D. R. Armstrong, R. Fortune, and P. G. Perkins, *J. Chem. Soc. Dalton,* 753 (1976).
10 D. W. Clack, *Mol. Phys.,* 1513 (1974).
11 D. W. Clack and W. Smith, *J. Chem. Soc. Dalton,* 2015 (1974).
12 T. Anno and H. Teruya, *J. Chem. Phys., 52,* 2480 (1970).
13 M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Comm.,* 307 (1966).
14 M. Iwata and Y. Saito, *Acta Crystallogr., B29,* 822 (1973).
15 B. L. Kalman and J. W. Richardson, *J. Chem. Phys., 55,* 4443 (1971).
16 M. Sano, Y. Hatano, H. Kashiwagi, and H. Yamatera, *Bull. Chem. Soc. Jpn., 54,* 1523 (1981).
17 C. E. Schaffer, Private Communication.
18 K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem., 7,* 1165 (1968).
19 J. Del Bene and H. H. Jaffe, *J. Chem. Phys., 48,* 1807 (1968).
20 J. Del Bene and H. H. Jaffe, *ibid. 48,* 4050 (1968).