TETRAGONALLY DISTORTED TETRAHEDRAL ML_4-COMPLEXES. II
Splitting of the d^3-Configuration in Strong Ligand Field of D_{2d} Symmetry

By

M. I. BÁN

Institute of General and Physical Chemistry, Attila József University, Szeged

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The energies of spectroscopic levels arising from the splittings, in ligand field of D_{2d} symmetry, of strong field configurations deduced from the electronic system d^3 have been given in terms of the interelectronic repulsion parameters B and C, the three ligand field parameters K, L, and M and the distortion angle β.

GILDE and BÁN qualitatively described [1] the orbital splittings of configurations d^n ($n=2, 3, \ldots, 8$) in strong ligand field of D_{2d} symmetry, using the determinantal functions [2] valid in the subspaces corresponding to the splittings. FURLANI *et al.* [3] calculated, by the weak field approximation, the orbital splittings of pseudotetrahedral CoA_2B_2 (C_{2v} symmetry) and CoA_3B (C_{3v} symmetry) complexes (both types containing Co^{II}-ion; d^7-configuration) and gave the energy matrices for the quartet levels.

In the present paper—using the procedure described in the earlier publication [4] and employing the functions mentioned—the strong field matrices for the d^3-configuration in D_{2d} symmetry have been given.

Energy matrices

On the basis of the perturbation method, using the assumptions made and the procedure described in the first paper of this series [4], the energy matrix elements[1] related with the electron-electron and ligand-electron interactions have been calculated.

The complete energy matrices[2] are as follow:

$$(b_2)(e)^2 \quad {}^4B_1: \quad -12K-12L+6M \tag{1}$$

$$(b_1)(e)^2 \quad {}^4B_2: \quad -12K-24L+6M \tag{2}$$

${}^4A_2$:

	$(a_1)(e)^2$	$(a_1)(b_1)(b_2)$
	$12B-6K-18L+10M$	$-6B$
		$3B+6K-18L+4M$

(3)

${}^4E$:

$(a_1)(b_1)(e)$	$(a_1)(b_2)(e)$	$(b_1)(b_2)(e)$
$3B-24L+7M$	$3B$	$-\sqrt{27}B$
	$3B-12L+7M$	$-\sqrt{27}B$
		$9B-18L+3M$

(4)

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[1] The corresponding integrals are written up with the the determinantal funcions [2] and the operators [3] end [8] of Paper I [4].

[2] The matrix elements below the diagonals are the mirror images of those above them.

$^2A_1$:	$(a_1)(b_1)^2$	$(a_1)(b_2)^2$	$(a_1)(e)^2$	$(b_1)(e)^2$	$(b_2)(e)^2$	
	$7B+4C+6K-30L+4M$	C	$\sqrt{2}(3B+C)$	$\sqrt{6}B$	0	
		$7B+4C+6K-6L+4M$	$\sqrt{2}(3B+C)$	0	$-\sqrt{6}B$	
			$25B+5C-6K-18L+10M$	$\sqrt{75}B$	$-\sqrt{75}B$	(5)
				$9B+3C-12K-24L+6M$	$-3B$	
					$9B+3C-12K-12L+6M$	

$^2A_2$:	$(a_1)(e)^2$	$(b_1)(e)^2$	$(b_2)(e)^2$	$(a_1)(b_1)(b_2)$	$(a_1)(b_1)(b_2)$	
	$15B+3C-6K-18L+10M$	$-3B$	$-3B$	$-3B$	$\sqrt{27}B$	
		$9B+3C-12K-24L+6M$	$3B$	$3B$	$-\sqrt{3}B$	
			$9B+3C-12K-12L+6M$	0	$-\sqrt{12}B$	(6)
				$9B+3C+6K-18L+4M$	$-\sqrt{12}B$	
					$13B+3C+6K-18L+4M$	

$^2B_1$:	$(a_1)^2(b_1)$	$(b_1)(b_2)^2$	$(a_1)(e)^2$	$(b_1)(e)^2$	$(b_2)(e)^2$	
	$7B+4C+12K-24L+6M$	$4B+C$	$\sqrt{6}B$	$\sqrt{2}(B+C)$	0	
		$27B+4C-12L$	0	$\sqrt{2}(3B+C)$	$-\sqrt{54}B$	
			$19B+3C-6K-18L+10M$	$\sqrt{75}B$	$-3B$	(7)
				$15B+5C-12K-24L+6M$	$-\sqrt{27}B$	
					$9B+3C-12K-12L+6M$	

$^2B_2$:	$(a_1)^2(b_2)$	$(b_1)^2(b_2)$	$(a_1)(e)^2$	$(b_1)(e)^2$	$(b_2)(e)^2$	
	$7B+4C+12K-12L+8M$	$4B+C$	$-\sqrt{6}B$	0	$\sqrt{2}(B+C)$	
		$27B+4C-24L$	0	$\sqrt{54}B$	$\sqrt{2}(3B+C)$	
			$19B+3C-6K-18L+10M$	$-3B$	$-\sqrt{75}B$	(8)
				$9B+3C-12K-24L+6M$	$\sqrt{27}B$	
					$15B+5C-12K-12L+6M$	

^2E:

$(e)^3$	$(a_1)^2(e)$	$(b_1)^2(e)$	$(b_2)^2(e)$	$(a_1)(b_1)(e)\ldots$
$12B+4C-18K-18L+9M$	$B+C$	$3B+C$	$3B+C$	$\sqrt{6}B$
	$22B+4C+6K-18L+11M$	$4B+C$	$4B+C$	$\sqrt{\frac{75}{2}}B$
		$12B+4C-6K-30L+3M$	C	$\sqrt{\frac{75}{2}}B$
			$12B+4C-6K-6L+3M$	0
				$13B+3C-24L+7M$

$\ldots(a_1)(b_1)(e)$	$(a_1)(b_2)(e)$	$(a_1)(b_2)(e)$	$(b_1)(b_2)(e)$	$(b_1)(b_2)(e)$
0	$-\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{3}{2}}B$	$-\sqrt{\frac{27}{2}}B$	$-\sqrt{\frac{81}{2}}B$
$-\sqrt{\frac{9}{2}}B$	$-\sqrt{\frac{81}{2}}B$	$\sqrt{\frac{3}{2}}B$	0	0
$\sqrt{\frac{9}{2}}B$	0	0	$-\sqrt{\frac{27}{2}}B$	$-\sqrt{\frac{9}{2}}B$
0	$-\sqrt{18}B$	$\sqrt{24}B$	0	$-\sqrt{18}B$
$\sqrt{3}B$	$-\sqrt{\frac{27}{4}}B$	$-\frac{3}{2}B$	$-\frac{9}{2}B$	$\sqrt{\frac{3}{4}}B$
$9B+3C-24L+7M$	$\frac{3}{2}B$	$-\sqrt{\frac{27}{4}}B$	$-\sqrt{\frac{27}{4}}B$	$-\frac{3}{2}B$
	$\frac{21}{2}B+3C-12L+7M$	$-\sqrt{\frac{27}{4}}B$	$-\sqrt{\frac{27}{4}}B$	$\frac{3}{2}B$
		$\frac{23}{2}B+3C-12L+7M$	$\frac{3}{2}B$	$-\sqrt{\frac{75}{4}}B$
			$\frac{27}{2}B+3C-18L+3M$	$\sqrt{\frac{27}{4}}B$
				$\frac{33}{2}B+3C-18L+3M$

(9)

In the matrices, B and C are Racah's parameters and

$$K = \frac{5}{42} D_4(35\cos^4\beta - 30\cos^2\beta + 3),$$

$$L = \frac{5}{6} D_4(1-\cos^2\beta)^2,$$

$$M = D_2(3\cos^2\beta - 1),$$

where D_2 and D_4 denote—apart from numerical factors—the integrals related to second-order spherical harmonics and fourth-order ones, respectively.

The expressions (1)—(9) can easily be transcribed for the case of configuration d^7. Then—apart from a constant energy term contributing to all diagonal elements—the elements related with interelectronic repulsions remain unchanged and the ligand field energies—apart from another additive constant—are found by reversing the signs of those for d^3-configuration.

The energy matrices can be utilized—as was shown *e.g.* in [5, 6]—for the interpretation of such properties of d^3- or d^7-complexes which can be attributed to changes in the electronic energies.

References

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ТЕТРАГОНАЛЬНО ДЕФОРМИРОВАННЫЕ ТЕТРАЭДРИЧЕСКИЕ КОМПЛЕКСЫ ML_4. II
РАСЩЕПЛЕНИЕ d^3-КОНФИГУРАЦИЙ В СИЛЬНЫХ ПОЛЯХ ЛИГАНДОВ D_{2d} СИММЕТРИЙ

М. И. Бан

Используя приближение сильного поля, рассчитали энергетическое состояние электронов, происходящих из расщепления конфигураций создаваемых из d^3 электронных структур в лигандных полях D_{2d} (деформированные тетраэдрические) симметрии в зависимости от параметров B электростатического и лигандных полей, а также угла деформации.