Exact Spin-Pairing Energies at the Crossovers in Octahedral d^4, d^5, d^6, and d^7 Transition Metal Complexes

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Exact spin-pairing energies Π are calculated by direct diagonalization of the relevant ligand field plus interelectronic repulsion matrices for the configurations d^4, d^5, d^6, and d^7 of octahedral transition metal ions. The results are presented in terms of Π/B as function of $\gamma = C/B$ for the range of values $\gamma = 3.0$ to 8.0. Comparison with the quantity π resulting from a simplified approach in which configuration interaction is neglected or considered on an approximate basis only reveals significant differences. Useful estimates of spin-pairing energies are provided, in addition, on the basis of empirical magnetic and electronic spectral data.

Exakte Spinpaarungsenergien Π für die Konfigurationen d^4, d^5, d^6 und d^7 oktaedrischer Übergangsmetallionen werden durch direkte Diagonalisierung der entsprechenden Matrizen des Ligandenfeldes sowie der Elektronenwechselwirkung berechnet. Die Ergebnisse für Π/B werden in Abhängigkeit von $\gamma = C/B$ für den Wertebereich $\gamma = 3.0$ bis 8.0 angegeben. Ein Vergleich mit der Größe π, die bei einer vereinfachten Behandlung unter Vernachlässigung oder näherungsweiser Berücksichtigung der Konfigurationswechselwirkung erhalten wird, zeigt auffallende Unterschiede. Nützliche Abschätzungen der Spinpaarungsenergie werden außerdem unter Benutzung empirischer magnetischer und elektronenspektroskopischer Daten erhalten.

Les énergies exactes de couplage de spin Π sont calculées par diagonalisation directe du champ de ligand correspondant en plus des matrices de répulsion électronique pour les configurations d^4, d^5, d^6 et d^7 des ions octaédriques des métaux de transition. Les résultats sont présentés en termes de Π/B en fonction de $\gamma = C/B$ dan l'intervalle $\gamma = 3,0$ à $8,0$. On trouve des différences significatives par comparaison de π avec les valeurs résultant d'une approche simplifiée sans interaction de configuration ou avec interaction de configuration approchée. De plus, des estimations des énergies de couplage de spin sont obtenues à partir de données empiriques magnétiques et spectrales.

1. Introduction

The concept of spin-pairing energy has been introduced independently by Griffith [1, 2] and Orgel [3] as the value of the ligand field splitting parameter $\Delta = 10\,Dq$ at the crossover in certain octahedral transition metal ions (*viz.* those of d^4, d^5, d^6, and d^7 electron configurations). The well-known approximate expressions for this quantity (*cf.* section below) were obtained simply by equating the energy of the terms involved in the crossover neglecting configuration interaction with terms of higher energy. We have shown recently [4] that the value of $10\,Dq$ at which the actual energies cross may be significantly different from that resulting from the approximate expression. However, the exact value may always be obtained by a direct diagonalization of the relevant ligand field plus interelectronic repulsion matrices with or without taking account of spin-orbit interaction. It seems that explicit calculations of this quantity have never been attempted on an extended scale.

Therefore, in this study, we will report the results of calculations of the exact spin-pairing energies in the octahedral d^4, d^5, d^6, and d^7 electron configurations. The results will be compared with values of the approximate formulae as well as with those values which were corrected for off-diagonal matrix elements of configuration interaction employing a method suggested by Jørgensen [5]. The results are of particular interest since, within the last few years numerous compounds of the d^5, d^6, and d^7 configurations were synthesized which are close to the crossover [6, 7] and, no doubt, similarly behaving compounds of the d^4 electron system will soon be obtained.

2. Approximate Treatment of the Mean Pairing Energy

In each of the aforementioned configurations, one of two possible ground terms may be stabilized, depending on the strength of the ligand field. These states are characterized by a different symmetry transformation property and a different value of the total spin S. The possible terms and the strong-field configurations from which they derive are in d^4: $^5E_g(t_{2g}^3e_g)$ and $^3T_{1g}(t_{2g}^4)$; in d^5: $^6A_{1g}(t_{2g}^3e_g^2)$ and $^2T_{2g}(t_{2g}^5)$; in d^6: $^5T_{2g}(t_{2g}^4e_g^2)$ and $^1A_{1g}(t_{2g}^6)$; in d^7: $^4T_{1g}(t_{2g}^5e_g^2)$ and $^2E_g(t_{2g}^6e_g)$. Terms with the maximum value of S (high-spin behavior) are associated with weak ligand fields, those with the minimum value of S (low-spin behavior) arise in strong ligand fields. The point at which the spin of the ground term changes is called a crossover point.

At the crossover, the energies of the two terms involved are equal. From this condition, the value of $10\,Dq$ at the crossover may be derived. If configuration interaction with higher energy terms is disregarded, the resulting quantity is refered to as the 'mean pairing energy' which will be denoted here by π. The expressions for π thus derived are as follows

$$d^4: \quad \pi = 6B + 5C$$
$$d^5: \quad \pi = 7\tfrac{1}{2}B + 5C$$
$$d^6: \quad \pi = 2\tfrac{1}{2}B + 4C \tag{1}$$
$$d^7: \quad \pi = 4B + 4C.$$

In Eq. (1), B and C are the Racah parameters of electrostatic electron-electron repulsion.

In a slightly modified approach, we may introduce the spin-pairing energy as the difference in interelectronic repulsion energy between the low-spin and the high-spin state,

$$P = E(\text{low-spin})_{Dq=0} - E(\text{high-spin})_{Dq=0} \tag{2}$$

and, accordingly, the ligand field stabilization energy as

$$Q = E(\text{low-spin})_{B,C=0} - E(\text{high-spin})_{B,C=0}. \tag{3}$$

Here we have assumed the same approximation to be valid as above. Also, the quantity P is always positive, whereas Q may be negative if Hund's rule is to be violated. Now if P is greater than the absolute value of Q, the high-spin state

will be stabilized, if it is less, the low-spin state will be lower in energy, *i.e.*,

$$P + Q > 0 \quad \text{high-spin complex}$$
$$P + Q < 0 \quad \text{low-spin complex} \tag{4}$$

and, consequently, $P + Q = 0$ at the crossover point. In the particular case of the d^6 configuration, *e.g.*, we obtain

$$E(^5T_{2g}) = -4Dq + 15A - 35B + 7C$$
$$E(^1A_{1g}) = -24Dq + 15A - 30B + 15C \tag{5}$$

and, therefore,

$$P = 5B + 8C$$
$$Q = -20Dq \tag{6}$$

so that Eq. (4) becomes, is or is not $20Dq > 5B + 8C$. Since, at the crossover, the transfer of *two* electrons is effected between the t_{2g} and e_g orbitals, one half of P may be regarded as the mean pairing energy per electron transfered, π (*viz.* Eq. (1)). Numerical values of this quantity for bivalent and tervalent transition metal ions of the iron series which were estimated previously [2, 3] are listed in Table 1 together with the relevant expressions for π.

The crossover conditions for tetrahedral complexes and for the situation where all ligands are arranged at the corners of a cube may be easily obtained from those of the octahedral case, *cf*. Eq. (1), if the expressions of the conjugate hole configuration are employed and the theoretical Dq values are reduced by 4/9 and 8/9, respectively.

It has been pointed out by Griffith [8] that refinements of the simplified theory of mean pairing energies may be required. A possible approach which has been followed [8, 9] introduces correction terms which should take approximate account of the non-diagonal matrix elements of configuration interaction. The procedure is based on second-order perturbation theory and is outlined by Jørgensen [5]. The same author [10] has tabulated the required corrections to numerous low energy terms within the configurations d^2 to d^8. If these corrections are introduced into Eq. (1), expressions for the mean pairing energy result which are listed below.

$$d^4: \quad \pi = 6B + 5C - 64B^2/10Dq$$
$$d^5: \quad \pi = 7\tfrac{1}{2}B + 5C - 70B^2/10Dq$$
$$d^6: \quad \pi = 2\tfrac{1}{2}B + 4C - 60B^2/10Dq \tag{7}$$
$$d^7: \quad \pi = 4B + 4C - 60B^2/10Dq + x$$

where

$$x = -4.5B - 5Dq \pm \tfrac{1}{2}\{225B^2 + 100Dq^2 + 180Dq \cdot B\}^{1/2}.$$

According to a particular example within the d^6 configuration (*viz.* $B = 917\,\text{cm}^{-1}$, $C = 4040\,\text{cm}^{-1}$, the Fe^{2+} free ion values), Eq. (1) gives $\pi = 18{,}452.5\,\text{cm}^{-1}$, whereas from Eq. (7) $\pi = 15{,}114.4\,\text{cm}^{-1}$ was obtained [4]. However, the actual terms cross at $17{,}006.8\,\text{cm}^{-1}$ or at $17{,}100\,\text{cm}^{-1}$, respectively, depending on spin-orbit coupling

Table 1. *Values of the mean pairing energy* π *estimated on the basis of* Eq. (1) *for octahedral ions of the iron series*

Configuration	π	M^{2+}, cm^{-1}	M^{3+}, cm^{-1}
d^4	$6F_2 + 145F_4 = 6B + 5C$	23,500	28,000
d^5	$7\frac{1}{2}F_2 + 137\frac{1}{2}F_4 = 7\frac{1}{2}B + 5C$	25,500	30,000
d^6	$2\frac{1}{2}F_2 + 127\frac{1}{2}F_4 = 2\frac{1}{2}B + 4C$	17,600	21,000
d^7	$4F_2 + 120F_4 = 4B + 4C$	19,500	23,500

having not or having been taken into account explicitly [4]. Thus it seems that the correction term included in Eq. (7) may exceed by far the deviation of Eq. (1) from the exact value of the crossover energy.

3. Calculation of the Exact Spin-Pairing Energy

From the foregoing it is apparent that the spin-pairing energy is considerably influenced by configuration interaction of the terms directly involved in the crossover with higher energy terms of the same irreducible representation. In fact, in the d^4 configuration, the $^3T_{1g}(t_{2g}^4)$ term interacts with six higher $^3T_{1g}$ terms, whereas the $^5E_g(t_{2g}^3 e_g)$ is pure. In d^5, $^6A_{1g}(t_{2g}^3 e_g^2)$ also is pure, whereas $^2T_{2g}(t_{2g}^5)$ mixes with altogether nine different $^2T_{2g}$ terms. In d^6, $^1A_{1g}(t_{2g}^6)$ interacts with four higher energy $^1A_{1g}$ terms and $^5T_{2g}(t_{2g}^4 e_g^2)$ again is pure. Finally, in d^7, $^4T_{1g}(t_{2g}^5 e_g^2)$ mixes with another single $^4T_{1g}$ and $^2E_g(t_{2g}^6 e_g)$ with three different ^2E_g terms. Direct diagonalization of the secular equations for the terms of interest is thus required in order to obtain reasonably accurate values of the energies. By this means we calculated exact spin-pairing energies which will be denoted here by Π. The required matrix elements have been taken from Tanabe and Sugano [11]. The numerical values of Π were obtained by an iterative procedure. It has been shown recently [12, 13] that considerable variation in the ratio of Racah parameters $\gamma = C/B$ may occur, this inference being in sharp contrast to the usually assumed fixed value of $\gamma = 4.0$ or $\gamma = 4.5$. Therefore, we have obtained Π (in units of B) as function of γ for a reasonably large range of values of this quantity ($\gamma = 3.0$ to 8.0), *cf.* Fig. 1. Numerical values of the function Π/B are listed in Appendix 1. It is easily seen that Π/B is a linear function of γ which may be well approximated as

$$d^4: \quad \Pi/B = 0.4878\,\gamma + 0.4840$$
$$d^5: \quad \Pi/B = 0.4897\,\gamma + 0.6347$$
$$d^6: \quad \Pi/B = 0.3708\,\gamma + 0.2195 \tag{8}$$
$$d^7: \quad \Pi/B = 0.3594\,\gamma + 0.5051\,.$$

The expressions Eq. (8) were obtained by a least square procedure. The deviation between original and calculated Π/B-values was limited to 0.0025, the mean square deviations range between 0.0019 and 0.0069. Fig. 2 shows the lowest range of energies ($E/B < 10$) in the Tanabe-Sugano diagrams of the d^4, d^5, d^6, and d^7 configurations as calculated for the present purpose. In these plots, $\gamma = 4.0$ has
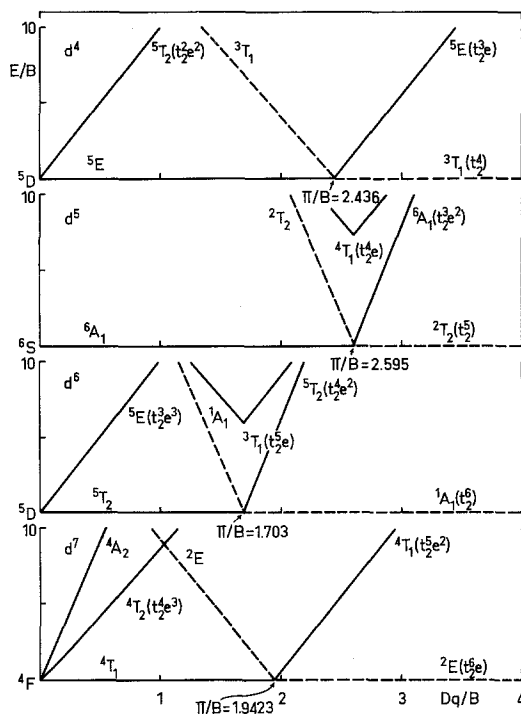
Fig. 1. Energies of the lowest terms (in units of B) in the configurations octahedral d^4, d^5, d^6, and d^7 as function of Dq/B ($\gamma = 4.0$)
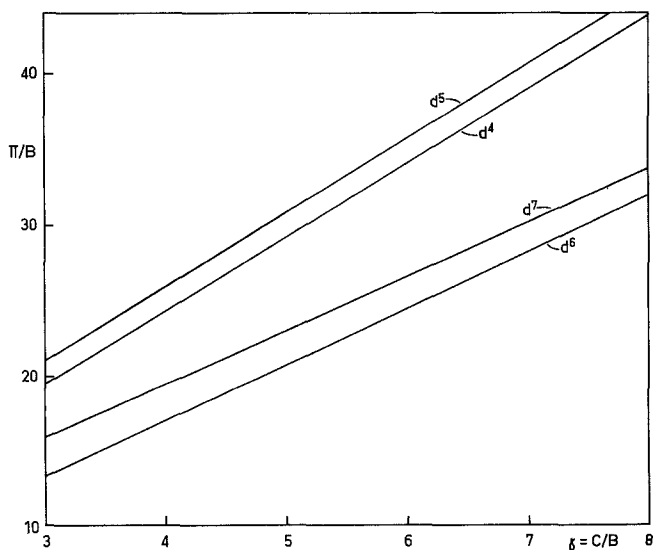

Fig. 2. Exact spin-pairing energy Π (in units of B) as function of $\gamma = C/B$ in the configurations octahedral d^4, d^5, d^6, and d^7
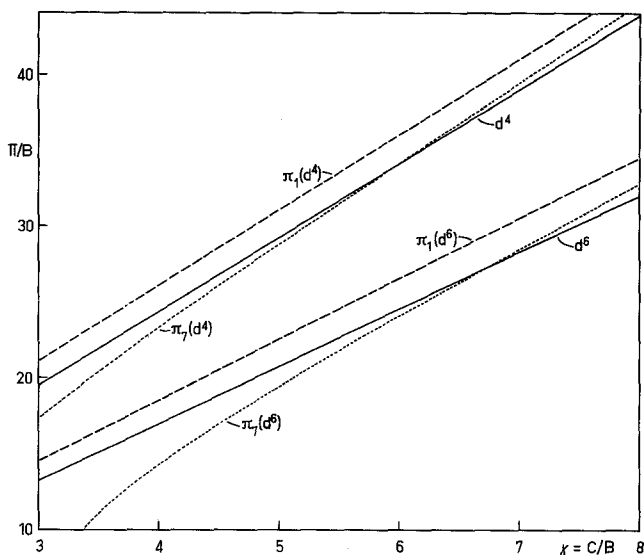
Fig. 3. Comparison of the exact spin-pairing energy Π and the approximate quantities π_1 and π_7 resulting respectively from Eq. (1) and Eq. (7) (all in units of B). The quantities are plotted for the configurations d^4 and d^6 as functions of $\gamma = C/B$

been assumed for convenience. The resulting values of the exact spin-pairing energy are displayed in terms of Π/B. In addition, we list in Appendix 2 the eigenvectors of those terms which are directly involved in the crossover for the particular value of Π/B resulting from Fig. 2. These eigenvectors indicate the amount of mixing that actually occured. Finally, plots of the exact spin-pairing energy Π and of the approximate quantities π resulting from Eq. (1) and Eq. (7) (all three in units of B) are shown in Fig. 3 for the configurations d^4 and d^6 as an example.

4. Discussion

Although there is now a considerable number of complexes available which are close to the crossover, reliable spectral data for comparison with the present results are rare. Thus $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ (phen = 1,10-phenanthroline) exhibit $^5T_2 - {}^1A_1$ crossover behavior combined with a second-order phase change at $T_c = 174\ °K$ and $232\ °K$, respectively [14]. Since normal temperature shifts of electronic bands are rather small, the $298\ °K$ spectrum should be practically identical to the spectrum at the crossover temperature. From the $^5T_{2g} \rightarrow {}^5E_g$ band in the spectra of both compounds $10 Dq(^5T_{2g}) = 11,900\ cm^{-1}$ was determined. Unfortunatelly, values of B and C are unknown. If $\gamma = 4.0$ is assumed, the plot for d^6 in Fig. 1 yields $B = 700\ cm^{-1}$ (nephelauxetic ratio $\beta = 0.76$) in reasonable agreement with the value expected. Similarly, in the six-coordinate iron(II)-poly(1-pyrazolyl)borate termed "compound I" [15, 16] $10 Dq(^5T_{2g}) = 12,500\ cm^{-1}$ was obtained from the electronic spectrum. In conjunction with Fig. 1 this value gives $B = 735\ cm^{-1}$ ($\beta = 0.80$) if $\gamma = 4.0$ is assumed.

Some N,N-dialkyldithiocarbamates of iron(III) show $^6A_1 - {}^2T_2$ crossover effects over a range of temperatures. Previously, $10 Dq \sim 12,800\ cm^{-1}$ has been

estimated in $Fe(S_2CNMe_2)_3$ [17]. However, according to a more recent study [18], the reliability of this value is questionable. From the analysis of the spectrum of the iron(III) pyrrolidyl dithiocarbamates $10\,Dq \sim 19{,}000\,cm^{-1}$ has now been suggested. Assuming again $\gamma = 4.0$, the d^5 curve of Fig. 1 gives $B = 732\,cm^{-1}$ in good agreement with the reported value of $B \sim 750\,cm^{-1}$ [18].

A number of N-bonded ligands produce cobalt(II) complexes which are believed to be thermal mixtures of high-spin and low-spin states. In these, the electronic spectrum of $Co(pvdh)_3Br_2$ (pvdh = pyruvaldihydrazone) [19] gives $10\,Dq = 13{,}800\,cm^{-1}$ and therefrom and using Fig. 1 we obtained $B = 711\,cm^{-1}$ ($\beta = 0.73$) if again $\gamma = 4.0$ is assumed.

Of course, the limited data discussed here provide a first qualitative orientation only. The usefulness of the results presented in this study will become apparent as more accurate spectroscopic studies of crossover systems become available.

In addition, estimates of the spin-pairing energies which are expected in complexes of the electronic configurations d^4, d^5, d^6, and d^7 may be obtained on an empirical basis. To this end we employed the tabulated magnetic [20] and spectroscopic [5, 10] data of transition metal complexes. The resulting values of the quantity Π which should replace the outdated estimates of Table 1 are presented in Table 2. These estimates may prove helpful in the design and synthesis of novel complex compounds which are expected to show crossover behavior.

The use of corrections according to Eq. (7) does not seem to be a reasonable alternative as demonstrated by the results of Fig. 3. Comparable results were obtained for the d^5 and d^7 configurations as well.

The correction to the spin-pairing energy arising as a consequence of spin-orbit interaction has been shown [4] to be, in the d^6 configuration, of the order of $100\,cm^{-1}$ if the parameters B and C of the free ion are employed. We believe that, likewise, in the d^4, d^5, and d^7 configurations, the values of Π will be only slightly altered if spin-orbit coupling is taken into account. An investigation to this end is in progress.

Table 2. *Values of the spin-pairing energy estimated on the basis of empirical magnetic and electronic spectral data*

Configuration	M^{2+}, cm^{-1}	M^{3+}, cm^{-1}
d^4	$> 17{,}500$[a]	$> 20{,}100$[b]
d^5	$> 10{,}100$[c]	$\sim 19{,}000$
d^6	$12{,}000$	$> 13{,}100$[d]
d^7	$13{,}800$	$< 16{,}200$[e]

[a] Estimated from the $^5E \to {}^5T_2$ band of $Cr(en)_3^{2+}$ which has a ^5E ground term, whereas that of $Cr(bipy)_3^{2+}$ is $^3T_1$ [5].

[b] The only well characterized Mn^{3+} complex having a $^3T_1$ ground state being $Mn(CN)_6^{3-}$, this estimate follows from $10\,Dq$ of $Mn(ox)_3^{3-}$ with a ^5E ground term [5].

[c] From $10\,Dq$ of $Mn(en)_3^{2+}$ with $^6A_1$ ground term.

[d] Estimated from $^5T_2 \to {}^5E$ of CoF_6^{3-} after allowance for the Jahn-Teller effect, *cf.* Cotton, F. A., Meyers, M. D.: J. Amer. Chem. Soc. **82**, 5023 (1960).

[e] Estimated from the spectrum of NiF_6^{3-}, the ground state being ^2E, *cf.* Allen, G. C., Warren, K. D.: Inorg. Chem. **8**, 1895 (1969).

Appendix 1

Values of the Exact Spin-Pairing Energy Π Calculated by Direct Diagonalization

1. Configuration d^4:

γ	3.0	4.0	4.611	5.0	5.833	6.5	7.666
Π/B	19.44	24.36	27.35	29.25	33.30	36.55	42.21

2. Configuration d^5:

γ	3.0	4.0	4.5	6.0	8.0
Π/B	21.00	25.95	28.41	35.75	45.50

3. Configuration d^6:

γ	3.2	4.0	4.404	5.0	6.0	7.0	8.0
Π/B	14.04	17.03	18.55	20.76	24.49	28.00	31.94

4. Configuration d^7:

γ	3.0	4.0	4.5	5.0	6.0	7.0	8.0
Π/B	15.87	19.42	21.21	23.00	26.60	30.21	33.83

Appendix 2

Eigenvectors at the Crossover for the Two Lowest Terms Assuming $\gamma = 4.0$

1. Configuration d^4 ($\Pi/B = 2.436$)

$$|^3T_1\rangle = 0.9861\,|t_2^4\rangle + 0.0779\,|t_2^3(^2T_1)\,e\rangle + 0.0815\,|t_2^3(^2T_2)\,e\rangle$$
$$- 0.1153\,|t_2^2(^3T_1)\,e^2(^1A_1)\rangle + 0.0373\,|t_2^2(^3T_1)\,e^2(^1E)\rangle$$
$$- 0.0160\,|t_2^2(^1T_2)\,e^2(^3A_2)\rangle - 0.0011\,|t_2e^3\rangle$$
$$|^5E\rangle = |t_2^3e\rangle$$

2. Configuration d^5 ($\Pi/B = 2.595$).

$$|^2T_2\rangle = 0.9744\,|t_2^5\rangle - 0.1771\,|t_2^4(^3T_1)\,e\rangle - 0.0438\,|t_2^4(^1T_2)\,e\rangle$$
$$+ 0.0061\,|t_2^3(^2T_1)\,e^2(^3A_2)\rangle + 0.0135\,|t_2^3(^2T_1)\,e^2(^1E)\rangle$$
$$- 0.1262\,|t_2^3(^2T_2)\,e^2(^1A_1)\rangle - 0.0238\,|t_2^3(^2T_2)\,e^2(^1E)\rangle$$
$$- 0.0095\,|t_2^3(^1T_2)\,e^3\rangle + 0.0130\,|t_2^2(^3T_1)\,e^3(^2E)\rangle + 0.0148\,|t_2e^4\rangle$$
$$|^6A_1\rangle = |t_2^3e^2\rangle$$

3. Configuration d^6 ($\Pi/B = 1.703$).

$$|^1A_1\rangle = 0.9813\,|t_2^6\rangle - 0.0327\,|t_2^4(^1E)\,e^2(^1E)\rangle - 0.1851\,|t_2^4(^1A_1)\,e^2(^1A_1)\rangle$$
$$- 0.0312\,|t_2^3(^2E)\,e^3\rangle + 0.0285\,|t_2^2e^4\rangle$$
$$|^5T_2\rangle = |t_2^4e^2\rangle$$

4. Configuration d^7 ($\Pi/B = 1.9423$).

$$|^2E\rangle = 0.9865\,|t_2^6e\rangle - 0.0453\,|t_2^4(^1E)\,e^3\rangle - 0.1550\,|t_2^4(^1A_1)\,e^3\rangle$$
$$- 0.0260\,|t_2^3(^2E)e^4\rangle$$
$$|^4T_1\rangle = 0.9801\,|t_2^5e^2(^3A_2)\rangle - 0.1984\,|t_2^4(^3T_1)\,e^3\rangle$$

References

1. Griffith, J. S.: J. inorg. nuclear Chem. **2**, 1 (1956).
2. — J. inorg. nuclear Chem. **2**, 229 (1956).
3. Orgel, L. E.: J. chem. Physics **23**, 1819 (1955).
4. König, E., Kremer, S.: Theoret. chim. Acta (Berl.) **22**, 45 (1971).
5. Jørgensen, C. K.: Absorption spectra and chemical bonding in complexes. London: Pergamon Press 1962.
6. Martin, R. L., White, A. H.: Transition metal Chem. **4**, 113 (1968).
7. Barefield, E. Kent, Busch, D. H., Nelson, S. M.: Quart. Rev. **22**, 457 (1968).
8. Griffith, J. S.: The theory of transition metal ions. Cambridge: University Press 1961.
9. König, E., Schläfer, H. L.: Z. physik. Chem. (Frankfurt) **34**, 355 (1962).
10. Jørgensen, C. K.: Adv. Chem. Physics **5**, 33 (1963).
11. Tanabe, Y., Sugano, S.: J. physic. Soc. Japan **9**, 753 (1954).
12. Witzke, H.: Theoret. chim. Acta (Berl.) **20**, 171 (1971).
13. Ferguson, J.: Progr. inorg. Chem. **12**, 159 (1970).
14. König, E., Madeja, K.: Inorg. Chem. **6**, 48 (1967); **7**, 2677 (1968).
15. Jesson, J. P., Weiher, J. F., Trofimenko, S.: J. chem. Physics **48**, 2058 (1968).
16. — Trofimenko, S., Eaton, D. R.: J. Amer. chem. Soc. **89**, 3158 (1967).
17. Ewald, A. H., Martin, R. L., Ross, I. G., White, A. H.: Proc. Roy. Soc. (London) A **280**, 235 (1964).
18. — — Sinn, E., White, A. H.: Inorg. Chem. **9**, 1837 (1969).
19. Fisher, H. M., Stoufer, R. C.: Inorg. Chem. **5**, 1172 (1966).
20. König, E.: Magnetic properties of coordination and organo-metallic transition metal compounds, Landolt-Börnstein, New Series, Vol. II/2, Hellwege, K. H. and Hellwege, A. M., Eds. Berlin: Springer 1966.

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