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The contribution from spin–orbit coupling of ligand ions to g-factors in VCl_2 and VBr_2

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Abstract. This paper presents a two-SO-coupling-parameter model, in which not only the contribution due to the SO coupling of the central TM ions but also that of the ligand ions are included, for the calculation of the g-factors and the anisotropy $\Delta g(= g_z - g_x)$ of the trigonal d^3 cluster. The calculated results for VCl_2 and VBr_2 show that the contribution to both g and Δg due to the SO coupling of the ligand ions is small in VCl_2 but is sufficiently important in VBr_2, about 85% for g and 40% for Δg. It suggests that in the calculation of g and Δg the two-SO-coupling-parameter model should be preferred in the case of heavy-element ligand ions such as Br^- ions.

1. Introduction

The role of covalence in explaining the microscopic origin of the g-factors of transition-metal (TM) ions has often been neglected because of the complexity of the problem. However, since both the spin–orbit (SO) coupling and covalence increase with increasing atomic number of the ligand ions, contributions to the g-factors from the SO coupling of the ligand electrons are expected to increase with increasing covalence. There have been many experimental investigations of the g-factors of TM ions in covalent crystals, and there has been much interest in the theoretical investigation of the g-factors. Aramburu and Moreno (1985) and Misra and Wang (1989) investigated the g-factors of d^1–d^9 clusters. Viccaro *et al* (1982) investigated the g-factors of d^4–d^6 clusters. Our previous work (Du 1992, Du and Rudowicz 1992, Du *et al* 1992, Chen *et al* 1992a, b) investigated the g-factors of d^3–d^7 and d^2–d^8 clusters. These studies focused attention on the g-shift $g - g_s$, where g_s is the spin-only value and investigated the contribution due to the SO coupling of both TM ions and ligand ions. In this paper we focus our attention on the anisotropy of the g-factors due to the SO coupling of ligand ions.

The classical crystal-field approach can give expressions for the g-factors of the TM clusters. For a d^3 cluster with octahedral symmetry, Abragam and Bleaney (1970) gave a formula for the g-factor involving only the energy difference between the ground state and the $^4T_2(t_2^3)$ state and the SO coupling parameter of the TM ions in the crystal. For a d^3 cluster with trigonal symmetry, Macfarlane (1970) gave a third-order perturbation expression for the g-factors using a strong-field perturbation-loop method. In Macfarlane's work, a contribution due to the spin doublets is included, and the contributions to the anisotropy of the g-factors from the trigonal distortion (represented by two crystal-field parameters v and v') and the SO coupling of TM ions (represented by parameter ξ) are considered. In the case of ionic crystals containing TM ions, it is a good approximation. Our previous studies (Du 1992, Du and Rudowicz 1992, Du *et al* 1992, Chen *et al* 1992b) show that the contribution to the g-shift $g - g_s$ from SO coupling of the ligand ions is smaller than that from SO coupling of the TM ions in the case of the light-element ligand ions, e.g. Cl^- ions, but it is larger in the case of heavy-element ligand ions, e.g. Br^- and I^- ions. In this paper we investigate the effect on the anisotropy $\Delta g (= g_\parallel - g_\perp = g_z - g_x)$ due to the SO coupling of the ligand ions.

2. Theoretical model

In the classical crystal-field approach, the one-electron irreducible representation basis function can be written as

$$|\gamma\rangle = |d_\gamma\rangle \tag{1}$$

and the SO coupling interaction Hamiltonian as

$$\hat{H}_{\mathrm{so}} = \sum_i \xi_{\mathrm{c}}(r_i)\hat{l}_i \cdot \hat{s}_i \tag{2}$$

where the subscript c denotes the central TM ion and $|d_\gamma\rangle$ is a d function transforming as the irreducible representation γ. For the heavy-element ligand ions, the SO coupling of ligand electrons should be considered. Using the LCAO method, the one-electron basis function can be written as (Du 1992)

$$|\gamma\rangle = \sqrt{N}_\gamma(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle) \tag{3}$$

and the SO coupling interaction Hamiltonian as

$$\hat{H}_{\mathrm{so}} = \hat{H}_{\mathrm{so}}(\mathrm{d}) + \hat{H}_{\mathrm{so}}(\mathrm{p}) \tag{4a}$$

$$\hat{H}_{\mathrm{so}}(\mathrm{d}) = \sum_i \xi_{\mathrm{d}}(r_{i\mathrm{d}})\hat{l}_i \cdot \hat{s}_i \tag{4b}$$

$$\hat{H}_{\mathrm{so}}(\mathrm{p}) = \sum_i \xi_{\mathrm{p}}(r_{i\mathrm{p}})\hat{l}_i \cdot \hat{s}_i \tag{4c}$$

where N_γ and λ_γ are renormalization and orbital mixing coefficients, respectively, and $1 > N_\gamma > 0$ and $1 > \lambda_\gamma > 0$ for the antibonding orbital; the subscript $\gamma \equiv \mathrm{t}_{2\mathrm{g}}$ or e_g denotes the irreducible representation of the $\mathrm{O_h}$ group; the subscripts d and p denote the d electron of the central TM ion and the p electron of ligand ion, respectively.

Using equations (3) and (4), the SO coupling interaction matrices within the trigonal basis (Sugano *et al* 1970) are obtained as

$$\begin{array}{c} \\ x_+^+ \\ x_-^- \\ u_+^+ \\ u_-^- \end{array}
\begin{array}{c}
\begin{array}{cccc} \quad x_+^+ \quad & \quad x_-^- \quad & \quad u_+^+ \quad & \quad u_-^- \quad \end{array} \\
\left(\begin{array}{cccc}
-\xi_{\mathrm{d}}^{\mathrm{t}}/2 - \xi_{\mathrm{p}}^{\mathrm{t}}/2 & 0 & -\sqrt{2}\xi_{\mathrm{d}}^{\mathrm{te}}/2 + \sqrt{2}\xi_{\mathrm{p}}^{\mathrm{te}}/2 & -\xi_{\mathrm{d}}^{\mathrm{te}} + \xi_{\mathrm{p}}^{\mathrm{te}} \\
0 & -\xi_{\mathrm{d}}^{\mathrm{t}}/2 - \xi_{\mathrm{p}}^{\mathrm{t}}/2 & \xi_{\mathrm{d}}^{\mathrm{te}} - \xi_{\mathrm{p}}^{\mathrm{te}} & -\sqrt{2}\xi_{\mathrm{d}}^{\mathrm{te}}/2 + \sqrt{2}\xi_{\mathrm{p}}^{\mathrm{te}}/2 \\
-\sqrt{2}\xi_{\mathrm{d}}^{\mathrm{te}}/2 + \sqrt{2}\xi_{\mathrm{p}}^{\mathrm{te}}/2 & \xi_{\mathrm{d}}^{\mathrm{te}} - \xi_{\mathrm{p}}^{\mathrm{te}} & 0 & 0 \\
-\xi_{\mathrm{d}}^{\mathrm{te}} + \xi_{\mathrm{p}}^{\mathrm{te}} & -\sqrt{2}\xi_{\mathrm{d}}^{\mathrm{te}}/2 + \sqrt{2}\xi_{\mathrm{p}}^{\mathrm{te}}/2 & 0 & 0
\end{array}\right)
\end{array} \tag{5a}$$

and

$$\begin{array}{c|ccc} & x_+^-(x_-^+) & x_0^+(x_0^-) & u_+^-(u_-^+) \\ \hline x_+^-(x_-^+) & \xi_d^t/2+\xi_p^t/2 & -\sqrt{2}\xi_d^t/2-\sqrt{2}\xi_p^t/2 & \sqrt{2}\xi_d^{te}/2-\sqrt{2}\xi_p^{te}/2 \\ x_0^+(x_0^-) & -\sqrt{2}\xi_d^t/2-\sqrt{2}\xi_p^t/2 & 0 & \xi_d^{te}-\xi_p^{te} \\ u_+^-(u_-^+) & \sqrt{2}\xi_d^{te}/2-\sqrt{2}\xi_p^{te}/2 & \xi_d^{te}-\xi_p^{te} & 0 \end{array} \qquad (5b)$$

and

$$\begin{aligned} \xi_d^t &= N_t\xi_d & \xi_d^{te} &= \sqrt{N_tN_e}\,\xi_d \\ \xi_p^t &= N_t\lambda_t^2\xi_p/2 & \xi_p^{te} &= \sqrt{N_tN_e}\,\lambda_t\lambda_e\xi_p/2 \end{aligned} \qquad (6)$$

where x_i^j and u_i^j are the components of the t_{2g} and e_g terms, respectively; ξ_d and ξ_p are the SO coupling parameters of the d electron of the TM ions and the p electron of the ligand ions in free ions, respectively. Misetich and Buch (1964) and Misetich and Watson (1966) estimated the magnitude of the matrix elements between the central TM ions and ligand ions for KNiF$_3$ with the assumptions that near the TM ions the ligand functions and r_{ip}^{-3} are small and near the ligand ions the d functions and r_{id}^{-3} are small. They came to the conclusion that the elements are very small and can be neglected. In our case, the ligand ions Cl$^-$ in VCl$_2$ and Br$^-$ in VBr$_2$ as well as F$^-$ in KNiF$_3$ are all halogen ions and there are larger TM ion–ligand distances in VCl$_2$ and VBr$_2$ than in KNiF$_3$. So one can consider that the assumptions are valid. The matrix elements between the d and p orbitals hence are neglected in equation (5). Equation (5) includes the SO coupling interaction of the ligand ions and hence can be used as a basis to calculate the contribution of the SO coupling of the ligand ions.

For a d^3 cluster with a trigonal field, the Hamiltonian can be written as

$$\hat{H} = \hat{H}(10Dq) + \hat{H}(B, C) + \hat{H}(v, v') + \hat{H}_{so} + \hat{H}_Z \qquad (7)$$

where $\hat{H}(10Dq)$ is the octahedral field, $\hat{H}(B, C)$ is the electrostatic interaction, $\hat{H}(v, v')$ is the trigonal distortion field, $\hat{H}_{so}$ is the SO coupling as in equation (4) and $\hat{H}_Z$ is the Zeeman interaction. For a distortion octahedral field, $\hat{H}(10Dq)$ and $\hat{H}(B, C)$ are the dominant terms in equation (7), and usually the cubic parameter $10Dq$ is larger than the Racah electrostatic parameter B. The diagonal elements $\langle n|\hat{H}(10Dq) + \hat{H}(B, C)|n\rangle$ in the strong-field scheme equal approximately the eigenvalues of $\hat{H}(10Dq) + \hat{H}(B, C)$. Hence we can use Macfarlane's (1970) strong-field perturbation-loop method and take

$$\hat{H}_0 = \hat{H}(10Dq) + \hat{H}_a(B, C) \qquad (8a)$$

$$\hat{H}' = \hat{H}_b(B, C) + \hat{H}(v, v') + \hat{H}_{so} + \hat{H}_Z \qquad (8b)$$

where $\hat{H}_a(B, C)$ and $\hat{H}_b(B, C)$ are the diagonal and off-diagonal parts of $\hat{H}(B, C)$, respectively. The zero-order wavefunctions transforming as the irreducible representations of the octahedron group (Sugano *et al* 1970) are combined with the one-electron wavefunctions possessing the form of equation (3). Using equation (8), we obtain analytical perturbation formulae for the g-factors of the d^3 cluster with trigonal symmetry as follows:

$$g_z = g_s + g_z(\xi_d) + g_z(\xi_p) + g_z(\xi_d, \xi_p) \tag{9a}$$

$$\begin{aligned} g_z(\xi_d) = {} & -8k'\xi_d^{te}/3D_1 - 2\xi_d^{te}(2k'\xi_d^{t} - k\xi_d^{te} + 2g_s\xi_d^{te})/9D_1^2 + 4\xi_d^{te^2}(k - 2g_s)/9D_3^2 \\ & - 2\xi_d^{t^2}(k + g_s)/3D_2^2 + 4k'\xi_d^{te}\xi_d^{t}/9D_1D_3 - 4k'\xi_d^{te}\xi_d^{t}/3D_1D_2 + 4k'\xi_d^{te}\xi_d^{t}/3D_2D_3 \\ & + 8k'\xi_d^{te}v/9D_1^2 - 4\sqrt{2}(k\xi_d^{te} + k'\xi_d^{t})v'/3D_1D_4 \end{aligned} \tag{9b}$$

$$\begin{aligned} g_z(\xi_d, \xi_p) = {} & 4(2g_s - k)\xi_d^{te}\xi_p^{te}/9D_1^2 - 8\xi_d^{te}\xi_p^{te}(k - 2g_s)/9D_3^2 - 4(k + g_s)\xi_d^{t}\xi_p^{t}/3D_2^2 \\ & + 4k'(-1/9D_1^2 + 1/9D_1D_3 - 1/3D_1D_2 + 1/3D_2D_3)(\xi_d^{te}\xi_p^{t} - \xi_d^{t}\xi_p^{te}) \end{aligned} \tag{9c}$$

$$\begin{aligned} g_z(\xi_p) = {} & 8k'\xi_p^{te}/3D_1 + 2\xi_p^{te}(2k'\xi_p^{t} + k\xi_p^{te} - 2g_s\xi_p^{te})/9D_1^2 + 4\xi_p^{te^2}(k - 2g_s)/9D_3^2 \\ & - 2\xi_p^{t^2}(k + g_s)/3D_2^2 - 4k'\xi_p^{te}\xi_p^{t}/9D_1D_3 + 4k'\xi_p^{te}\xi_p^{t}/3D_1D_2 - 4k'\xi_p^{te}\xi_p^{t}/3D_2D_3 \\ & - 8k'\xi_p^{te}v/9D_1^2 - 4\sqrt{2}(k'\xi_p^{t} - k\xi_p^{te})v'/3D_1D_4 \end{aligned} \tag{9d}$$

and

$$\Delta g = \Delta g(\xi_d) + \Delta g(\xi_p) \tag{10a}$$

$$\Delta g(\xi_d) = 4k'\xi_d^{te}v/3D_1^2 - 4\sqrt{2}(2k\xi_d^{te} + k'\xi_d^{t})/3D_1D_4 \tag{10b}$$

$$\Delta g(\xi_p) = -4k'\xi_p^{te}v/3D_1^2 - 4\sqrt{2}(k'\xi_p^{t} - 2k\xi_p^{te})/3D_1D_4 \tag{10c}$$

where

$$\begin{aligned} k &= N_t(1 + \lambda_t^2/2) \\ k' &= \sqrt{N_t N_e}(1 - \lambda_t\lambda_e/2) \end{aligned} \tag{11}$$

and $\Delta g = g_z - g_x$ is the anisotropy of the g-factor; $g_s = 2.0023$ is the spin-only value; v and v' are the trigonal distortion parameters. The energy denominators D_1, D_2, D_3 and D_4 are the differences between the ground level $^4A_2(t_2^3)$ and the excited levels $^4T_2(t_2^2e)$, $^2T_{2a}(t_2^3)$, $^2T_{2b}(t_2^2e)$ and $^4T_{1a}(t_2^2e)$, respectively, which either can be extracted from experimental data or can be calculated from following equations:

$$\begin{aligned} D_1 &= 10Dq \\ D_2 &= 15B + 5C \\ D_3 &= 9B + 3C + 10Dq \\ D_4 &= 12B + 10Dq \end{aligned} \tag{12}$$

In equations (9) and (10), equations 9(c), (9d) and (10c) are due to the contribution of the SO coupling of ligand p electrons. It has not been included in the classical crystal model formulae. Taking $\lambda_t = \lambda_e = 0$ and $N_t = N_e = N$, $g_z(\xi_p) = 0$, $g_z(\xi_d, \xi_p) = 0$ and $\Delta g(\xi_p) = 0$. Then equations (9) and (10) become Macfarlane's (1970) formulae. For some heavy-element ligand ions, there are larger ξ_p and larger λ_t, λ_e than for light-element ligand ions, for example $\xi_p = 2460\ \mathrm{cm}^{-1}$ and $(\lambda_t, \lambda_e) \simeq 0.33$ for Br^- ligand ions but $\xi_p = 587\ \mathrm{cm}^{-1}$ and $(\lambda_t, \lambda_e) \simeq 0.31$ for Cl^- ligand ions (Du 1992). Obviously, in this case, $g_z(\xi_p)$ and $\Delta g_z(\xi_p)$ cannot be neglected in an investigation of the g-factors and their anisotropy.

3. Application to VCl$_2$ and VBr$_2$

In VCl$_2$ and VBr$_2$ crystals, V^{2+}–6Cl$^-$ and V^{2+}–6Br$^-$ clusters possess trigonal symmetry. In this paper, we investigate g and Δg in VCl$_2$ and VBr$_2$ crystals by using equations (9) and (10). For the clusters, the SO coupling parameters are $\xi_d(V^{2+}) = 167$ cm^{-1} (Griffith 1964), $\xi_p(\mathrm{Cl}^-) = 587$ cm^{-1} and $\xi_p(\mathrm{Br}^-) = 2460$ cm^{-1} (McPherson *et al* 1974). One can see that ξ_p^t and ξ_p^{te} are smaller than ξ_d^t and ξ_d^{te} for the V^{2+}–6Cl$^-$ cluster but ξ_p^t and ξ_p^{te} are larger than ξ_d^t and ξ_d^{te} for the V^{2+}–6Br$^-$ cluster. The contribution from ξ_p^t and ξ_p^{te} to g and Δg are more important for VBr$_2$.

Using the approximate relation (Du 1992, Du and Rudowicz 1992)

$$f_\gamma = N_\gamma^2[1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma)] \tag{13}$$

and the normalization relation

$$N_\gamma[1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2] = 1 \tag{14}$$

the LCAO coefficients N_γ and λ_γ in equation (3) are related to $S_{dp}(\gamma)$ and f_γ, where $S_{dp}(\gamma)$ is the group overlap integral of d_γ and p_γ orbitals:

$$S_{dp}(\gamma) = \int d_\gamma^*(1) p_\gamma(2)\, d\tau_1\, d\tau_2 \tag{15}$$

and f_γ is the ratio of the electrostatic repulsion in the crystal to that in the free ion. f_γ can be obtained from the ratio of the Racah electrostatic parameter in the crystal to that in the free ion (Du and Rudowicz 1992) as

$$f_\gamma = B/B_0. \tag{16}$$

The Racah parameters B in VCl$_2$ and VBr$_2$ crystals have been obtained from the theoretical investigation of the spectra (Li and Li 1987) and B_0 in the free ion can be taken from the paper by Griffiths (1964). As is well known, it is often convenient to use the Slater orbital in the computation of the overlap integral, but a reasonable SO coupling coefficient cannot be obtained from this orbital. On the contrary, the self-consistent field (SCF) orbital is capable of yielding a reasonable SO coupling coefficient. Clementi and Raimondi (1963) and Clementi *et al* (1967) gave Slater-type SCF orbitals (which are simple to apply) to obtain the SCF energy. We hence use the Slater-type SCF function to calculate the group overlap integral $S_{dp}(\gamma)$. The results calculated for f_γ, $S_{dp}(\gamma)$ and N_γ, λ_γ for VCl$_2$ and VBr$_2$ are listed in table 1. Then we obtain from equation (6) that

$$\xi_d^t = 156 \text{ cm}^{-1} \qquad \xi_d^{te} = 157 \text{ cm}^{-1}$$
$$\xi_p^t = 25 \text{ cm}^{-1} \qquad \xi_p^{te} = 28 \text{ cm}^{-1}$$

for VCl$_2$, and

$$\xi_d^t = 153 \text{ cm}^{-1} \qquad \xi_d^{te} = 154 \text{ cm}^{-1}$$
$$\xi_p^t = 139 \text{ cm}^{-1} \qquad \xi_p^{te} = 150 \text{ cm}^{-1}$$

for VBr$_2$. Obviously, $(\xi_p^t, \xi_p^{te}) \ll (\xi_d^t, \xi_d^{te})$ for VCl$_2$, but (ξ_p^t, ξ_p^{te}) are close to (ξ_d^t, ξ_d^{te}) for VBr$_2$. So the contribution from the SO coupling of the ligand p electron to the g-factor and

Table 1. The group overlap integrals and the LCAO coefficients for VCl_2 and VBr_2.

	f_γ	$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	λ_t	λ_e	N_t	N_e
VCl_2	0.8577	0.0258	0.0763	0.2945	0.3191	0.9332	0.9495
VBr_2	0.8198	0.0295	0.0864	0.3366	0.3633	0.9145	0.9353

Table 2. The g-factors for VCl_2 and VBr_2.

	VCl_2^a	VBr_2^b
$g_z(\xi_d)$	−0.0429	−0.0458
$g_z(\xi_p)$	0.0068	0.0392
$g_z(\xi_d, \xi_p)$	0.00006	0.0004
$g_z - g_s$(total)	−0.0363	−0.0062
$g_z - g_s$(experiment)^c	-0.032 ± 0.002	-0.010 ± 0.002
$g_x(\xi_d)$	−0.0410	−0.0429
$g_x(\xi_p)$	0.0067	0.0380
$g_x(\xi_d, \xi_p)$	0.00006	0.0004
$g_x - g_s$ (total)	−0.0343	−0.0043
$g_x - g_s$ (experiment)^c	-0.028 ± 0.002	-0.007 ± 0.002

[a] Calculated using the parameters $B = 657$, $C = 2402$, $Dq = 914$, $v = -114$ (Li and Li 1987) and $v' = 300\ \mathrm{cm}^{-1}$.

[b] Calculated using the parameters $B = 628$, $C = 2294$, $Dq = 825$, $v = -148$ (Li and Li 1987) and $v' = 400\ \mathrm{cm}^{-1}$.

[c] From Yamada *et al* (1984).

Table 3. The anisotropy $\Delta g = g_z - g_x$ for VCl_2 and VBr_2.

	VCl_2^a	VBr_2^b
$\Delta g(\xi_d)$	−0.0019	−0.0029
$\Delta g(\xi_p)$	0.0001	0.0012
Δg (total)	−0.0018	−0.0017
Δg (experiment)^c	-0.004 ± 0.002	-0.003 ± 0.002

[a] For the parameters, see footnote a in table 2.

[b] For the parameters, see footnote b in table 2.

[c] From Yamada *et al* (1984).

the anisotropy Δg is not negligible for VBr_2. The results calculated for g and Δg, using equations (9) and (10), are listed in tables 2 and 3.

From table 2, one can find that $g_z(\xi_d, \xi_p)$ is very small for both VCl_2 and VBr_2; $g_z(\xi_p)$ is smaller than $g_z(\xi_d)$ for VCl_2, but close to $g_z(\xi_d)$ for VBr_2. Here $|g_z(\xi_p)/g_z(\xi_d)|$ is 85% for VBr_2. This means that neglecting the contribution from the SO coupling of ligand ions results in a large error and hence is unreasonable for the theoretical investigation of the g-factors, in the case of heavy-element ligand ions such as Br^-. The contribution from ξ_p to g_x is similar.

From table 3, one can find that $\Delta g(\xi_p)$ is very small and can be neglected reasonably for VCl_2 but is important for VBr_2. $|\Delta g(\xi_p)/\Delta g(\xi_d)|$ is about 40%. The calculated $|\Delta g(\xi_d)|$ for VCl_2 is smaller than $|\Delta g(\xi_d)|$ for VBr_2. It is contrary to the experimental result. The large $\Delta g(\xi_p)$ for VCr_2, which has the opposite sign from $\Delta g(\xi_d)$, changes the value of Δg for VBr_2 and gives a consistent theoretical result with experiment.

4. Conclusion

The theoretical investigation of the g-factors currently uses the one-SO-coupling-parameter formulae. Our work presents a two-SO-coupling-parameter model, in which the contributions from the SO coupling parameters of both the TM ions and the ligand ions to the g-factors are included. For VCl_2 and VBr_2, the theoretical calculation shows that $|g(\xi_p)/g(\xi_d)|$ is about 15% and $|\Delta g(\xi_p)/\Delta g(\xi_d)|$ is about 5% for VCl_2 but $|g(\xi_p)/g(\xi_d)|$ is about 85% and $|\Delta g(\xi_p)/\Delta g(\xi_d)|$ is about 40% for VBr_2. It shows that the contribution due to the SO coupling of ligand ions is important for the g-factors and the anisotropy of the g-factors in the case of Br^- ligand ions.

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