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INVESTIGATIONS OF THE EPR PARAMETERS FOR  $\text{Cu}^{2+}$  IN  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$ 

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The electron paramagnetic resonance (EPR) parameters ( $g$  factors and hyperfine structure constants) for  $\text{Cu}^{2+}$  in  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  (ipt is isophthalic acid, dap — 1,3-diaminopropane) are theoretically investigated from the high order perturbation formulas of these parameters for a  $3d^9$  ion in a rhombically elongated octahedron. The ligand orbital and spin-orbit coupling contributions are included from the cluster approach because of strong covalency of the system. The nearly axial anisotropies of the  $g$  factors and hyperfine structure constants are correlated to the significant elongation distortion of the five-fold coordinated  $\text{Cu}^{2+}$  (in a distorted square pyramidal  $[\text{CuN}_2\text{O}_3]$  group). Nevertheless, the perpendicular anisotropies arising from the nonequivalent planar ligands are largely concealed by the experimental uncertainties. The theoretical analysis of the EPR behaviours for  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  would be helpful to understand the local structures and properties of this and relevant systems.

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**Keywords:** electron paramagnetic resonance (EPR),  $\text{Cu}^{2+}$ ,  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$ .

## INTRODUCTION

Inorganic-organic hybrid complexes formed by transition-metal ions and various organic bridging ligands (especially those containing nitrogen and oxygen) [1–4] have been the hot subjects in inorganic and coordination chemistry [1, 2] due to structural diversity (e.g., single, dual and multi-core complexes) [5–9] and novel exotic catalytic, absorption, magnetic, electrical conductive, nonlinear optical properties and self-assembled structural designing performance [7–13]. Normally, the above properties can be sensitively connected with the local environments around the transition-metal ions, which play an important role in the functions of these materials. Among these materials, 1,3-diaminopropane (dap) isophthalate (ipt) copper(II) complex  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  containing transition-metal  $\text{Cu}^{2+}$  ( $3d^9$ , equivalent to one hole) may be regarded as a model system because of the relatively simpler  $3d$  energy level structure with at most five orbital levels under low symmetrical (e.g., rhombic) environments. It is known that the local structural properties and behaviour of transition-metal ions can be conveniently investigated by electron paramagnetic resonance (EPR) technique, and experimental EPR spectra are usually described as the EPR parameters (e.g., anisotropic  $g$  factors and hyperfine structure constants). For example, the EPR experiments were employed for  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$ , and the EPR parameters were measured for the  $[\text{CuN}_2\text{O}_3]$  group [14].

Up to now, however, the above EPR experimental results have not been theoretically interpreted. As for the quantitative analysis of EPR spectra for  $3d^9$  systems, the previous treatments were largely based on the simple second-order perturbation formulas of the EPR parameters by using various

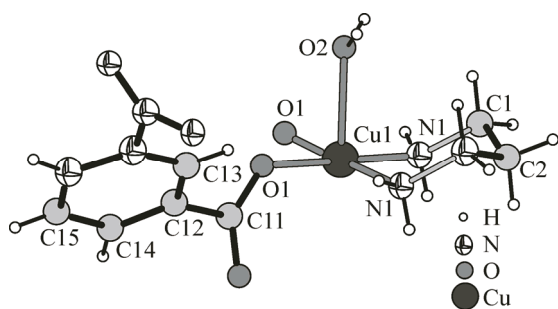


Fig 1. Structure of the distorted square pyramidal  $[\text{CuN}_2\text{O}_3]$  in  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$

Table 1

The anisotropic  $g$  factors and the hyperfine structure constants (in  $10^{-4} \text{ cm}^{-1}$ ) for  $\text{Cu}^{2+}$  in  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$

	$g_x$	$g_y$	$g_z$	$A_x$	$A_y$	$A_z$
Cal. <sup>a</sup>	2.129	2.116	2.221	-24.03	-28.50	-34.60
Cal. <sup>b</sup>	2.079	2.072	2.150	-35.16	-37.83	-60.12
Exp. [ 14 ]	2.074	2.074	2.158	-37.36	-37.36	-59.12

<sup>a</sup> Calculations based on omission of the ligand orbital and spin-orbit coupling contributions (i.e., similar to the treatments of the conventional crystal-field model).

<sup>b</sup> Calculations based on inclusion of the ligand contributions from the cluster approach.

adjustable low symmetrical distortion parameters [ 15—17 ]. Meanwhile, despite of the strong covalency of these systems, only the central ion orbital and spin-orbit coupling contributions were taken into account, while those from the ligand orbital and spin-orbit coupling interactions were neglected [ 15—18 ]. Since further quantitative analysis of the spectroscopic behaviours for  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  can reveal profound microscopic mechanisms helpful for understanding the properties of the relevant systems, theoretical investigations on the experimental EPR parameters are of scientific and practical significance. In this work, the fourth-order perturbation formulas of the EPR parameters for a  $3d^9$  ion under rhombically elongated octahedra are applied in the EPR analysis for  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$ . The influences of the ligand orbitals and spin-orbit coupling interactions are included in the calculations from the cluster approach in view of significant covalency of the system.

### CALCULATIONS

The experimental  $g$  factors  $g_x \approx g_y \approx 2.074$  and  $g_z \approx 2.158$  and hyperfine structure constants  $|A_x| \approx |A_y| \approx 37.36 \times 10^{-4} \text{ cm}^{-1}$  and  $|A_z| \approx 59.12 \times 10^{-4} \text{ cm}^{-1}$  [ 14 ] for  $\text{Cu}^{2+}$  in  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  are given in Table 1. The theoretical analysis can be performed as follows. Having isophthalate (ipt) as bridging moieties and chelating 1,3-diaminopropane (dap) as structure modulating units,  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  exhibits an overall one-dimensional zig-zag nature but with a distorted square pyramidal  $[\text{CuN}_2\text{O}_3]$  chromophore [ 14 ] (Fig. 1). The five-fold coordinated  $\text{Cu}^{2+}$  in the  $[\text{CuN}_2\text{O}_3]$  group is surrounded by one apical oxygen and four nearly coplanar (two oxygen and two nitrogen) ions. In this square pyramidal  $[\text{CuN}_2\text{O}_3]$  group, one absent apical oxygen of a regular octahedron can be regarded as escaping to infinity, and the planar  $\text{Cu—O}$  and  $\text{Cu—N}$  bond lengths are shorter than the axial  $\text{Cu—O}$  distance. So, the paramagnetic  $\text{Cu}^{2+}$  actually resides in a rhombically elongated octahedron. For a  $3d^9(\text{Cu}^{2+})$  ion in rhombically elongated octahedra, the original cubic ground state  ${}^2E_g$  may split into two orbital singlets  ${}^2A'_{1g}(\varepsilon)$  and  ${}^2A_{1g}(\theta)$ , with the former being lowest. The original cubic excited state  ${}^2T_{2g}$  can be separated into three orbital singlets  ${}^2B_{1g}(\zeta)$ ,  ${}^2B_{2g}(\eta)$  and  ${}^2B_{3g}(\xi)$  [ 17, 18 ]. Since the  $\text{Cu—N}$  bonds with shorter bond lengths have stronger covalency than the  $\text{Cu—O}$  ones with longer bond lengths, the system shows obvious covalency and copper-ligand orbital admixtures. Then, the ligand orbital and spin-orbit coupling contributions should be taken into account in the EPR analysis of the  $[\text{CuN}_2\text{O}_3]$  group, and the perturbation formulae of the EPR parameters based on the cluster approach containing the ligand contributions are adopted here. Thus, we have [ 19 ]:

$$g_x = g_s + 2k\zeta'/E_2 - 4k\zeta\zeta'/(E_1E_3) + k'\zeta\zeta'[2/(E_1E_2) - 1/(E_2E_3)] + g_s\zeta\zeta'[2/E_1^2 - (1/E_2^2 - 1/E_3^2)/2] + k\zeta\zeta'^2\{(1/E_2 - 1/E_3)(1/E_3 + 1/E_2)/(2E_1) + (2/E_1 - 1/E_2)(2/E_1 + 1/E_2)/(2E_3) -$$

$$\begin{aligned}
& - (1/E_2 - 1/E_3)/(2E_2E_4) \} + (g_s \zeta \zeta'^2/4)[(1/E_3 - 2/E_1)/E_2^2 + (2/E_3 - 1/E_2)/E_3^2 + \\
& + 2(1/E_2 - 1/E_3)/E_1^2 + 2(1/E_2^2 - 1/E_3^2)/E_1], \\
g_y = g_s & + 2k\zeta'/E_3 - 4k\zeta\zeta'/(E_1E_2) + k'\zeta\zeta'[2/(E_1E_3) - 1/(E_2E_3)] + g_s\zeta\zeta'[2/E_1^2 + (1/E_2^2 - 1/E_3^2)/2] + \\
& + k\zeta\zeta'^2\{(1/E_3 - 1/E_2)(1/E_3 + 1/E_2)/(2E_1) + (2/E_1 - 1/E_3)(2/E_1 + 1/E_3)/(2E_2) + \\
& + (1/E_2 - 1/E_3)/(2E_3E_4)\} + (g_s\zeta\zeta'^2/4)[(1/E_2 - 2/E_1)/E_3^2 + (2/E_2 - 1/E_3)/E_2^2 + \\
& + 2(1/E_3 - 1/E_2)/E_1^2 + 2(1/E_3^2 - 1/E_2^2)/E_1], \\
g_z = g_s & + 8k'\zeta'/E_1 + k\zeta'^2/(E_3E_2) + 2k'\zeta'^2[(1/E_1E_2 + 1/E_1E_3)] - g_s\zeta\zeta'[1/E_1^2 - (1/E_2^2 + 1/E_3^2)/4] + \\
& + k'\zeta\zeta'^2[8/E_1 - (1/E_2 + 1/E_3)]/(2E_2E_3) - 2k'\zeta\zeta'^2[1/(E_1E_2) + 1/(E_1E_3) - 1/(E_2E_3)]/E_1 + \\
& + (g_s\zeta\zeta'^2/4)[2(1/E_2^2 + 1/E_3^2)/E_1 - (1/E_2 + 1/E_3)/(E_2E_3)], \\
A_x & = -P\kappa + P'[2N/7 + (g_x - g_s) - 3(g_y - g_s)/14], \\
A_y & = -P\kappa + P'[2N/7 + (g_y - g_s) - 3(g_x - g_s)/14], \\
A_z & = -P\kappa + P'[-4N/7 + (g_z - g_s) + 3(g_y - g_s)/14 + 3(g_x - g_s)/14]. \tag{1}
\end{aligned}$$

Here  $g_s$  ( $\approx 2.0023$ ) is the spin-only value, and  $\kappa$  is the core polarization constant. The denominators  $E_i$  ( $i = 1-4$ ) denote the energy separations between the excited  ${}^2A_{1g}(\theta)$ ,  ${}^2B_{1g}(\zeta)$ ,  ${}^2B_{2g}(\eta)$  and  ${}^2B_{3g}(\xi)$  and the ground  ${}^2A_{1g}(\varepsilon)$  states. They can be obtained from the energy matrices for a  $3d^9$  ion under rhombic symmetry in terms of the cubic field parameter  $D_q$  and the rhombic field parameters  $D_s$ ,  $D_t$ ,  $D_\xi$  and  $D_\eta$ :

$$\begin{aligned}
E_1 & \approx 10D_q, \\
E_2 & \approx 10D_q - 3D_s + 5D_t - 3D_\xi + 4D_\eta, \\
E_3 & \approx 10D_q - 3D_s + 5D_t + 3D_\xi - 4D_\eta, \\
E_4 & \approx -4D_s + 5D_t. \tag{2}
\end{aligned}$$

In Eq. (1),  $k$  (and  $k'$ ),  $\zeta$  (and  $\zeta'$ ) and  $P$  (and  $P'$ ) are the orbital reduction factors, the spin-orbit coupling coefficients and the dipolar hyperfine structural parameters, respectively, for an octahedral  $3d^9$  center. The above quantities and those in the round brackets denote the diagonal (and off-diagonal) matrix elements for the orbital angular momentum, the spin-orbit coupling and hyperfine interaction operators within the cubic ( $O_h$ ) irreducible representations  $\gamma$  ( $= T_{2g}$  and  $E_g$ ). They are determined from the cluster approach [20]:

$$\begin{aligned}
\zeta & = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), & \zeta' & = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\
k & = N_t(1 + \lambda_t^2/2), & k' & = (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_sA)/2], \\
P & = P_0N_t, & P' & = P_0(N_tN_e)^{1/2}, \tag{3}
\end{aligned}$$

where  $\zeta_d^0$  and  $\zeta_p^0$  are the spin-orbit coupling coefficients of a free  $3d^9$  and ligand ions, respectively.  $P_0$  is the dipolar hyperfine structure parameter for the free  $3d^9$  ion.  $A$  denotes the integral  $R\langle ns|\partial/\partial y|np_y\rangle$ , with the reference copper-ligand distance  $R$ .  $N_\gamma$  and  $\lambda_\gamma$  (or  $\lambda_s$ ) are, respectively, the normalization factors and the orbital admixture coefficients. By adopting the cluster approach [20], these molecular orbital coefficients can be determined from the normalization conditions

$$\begin{aligned}
N_t(1 - 2\lambda_tS_{dpt} + \lambda_t^2) & = 1, \\
N_e(1 - 2\lambda_eS_{dpe} - 2\lambda_sS_{ds} + \lambda_e^2 + \lambda_s^2) & = 1, \tag{4}
\end{aligned}$$

and the approximate relationships

$$\begin{aligned}
N^2 & = N_t^2[1 + \lambda_t^2S_{dpt}^2 - 2\lambda_tS_{dpt}], \\
N^2 & = N_e^2[1 + \lambda_e^2S_{dpe}^2 + \lambda_s^2S_{ds}^2 - 2\lambda_eS_{dpe} - 2\lambda_sS_{ds}]. \tag{5}
\end{aligned}$$

Here  $S_{dpy}$  (and  $S_{ds}$ ) are the group overlap integrals.  $N$  is the covalency factor, characteristic of the covalency of the system. Since orbital admixture and overlap between the central ion and ligands have consistent dependence on the bond length, one may reasonably adopt the proportionality relationship  $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$  for the same irreducible representation  $E_g$ . Based on omission of the ligand orbital and spin-orbit coupling contributions by taking  $k = k' = N$ ,  $\zeta = \zeta' = k\zeta_d^0$  and  $P = P' = P_0N$ , the expressions

in Eq.(1) are reduced to the conventional crystal-field model ones containing only the central ion contributions.

In the square pyramidal  $[\text{CuO}_4\text{N}_2]$  group (Fig. 1), the two planar nitrogen ligands are labeled as  $\text{N}_1$ , and the two planar and one axial oxygen ions are labeled as  $\text{O}_1$  and  $\text{O}_2$ , respectively. The angles of  $\text{Cu}-\text{L}_1$  ( $\text{L} = \text{N}$  and  $\text{O}$ ) bonds related to  $Z$  and  $X$  axes are defined as  $\theta_{\text{L}}$  and  $\Phi_{\text{L}}$ . Thus, there are three groups of structural data for the  $\text{Cu}^{2+}$  site:  $R_{\text{O}_1} \approx 1.9949 \text{ \AA}$ ,  $\theta_{\text{O}} \approx 87.18^\circ$ ,  $\Phi_{\text{O}} \approx 90.21^\circ$ ;  $R_{\text{N}} \approx 2.004 \text{ \AA}$ ,  $\theta_{\text{N}} \approx 94.20^\circ$ ,  $\Phi_{\text{N}} \approx 91.58^\circ$ ;  $R_{\text{O}_2} \approx 2.292 \text{ \AA}$  [ 14 ].

From the superposition model [ 21—24 ] and the local geometry of  $\text{Cu}^{2+}$  site in the  $[\text{CuO}_4\text{N}_2]$  group, the rhombic field parameters can be expressed as follows:

$$\begin{aligned} D_s &= (2/7)\bar{A}_2(\bar{R}_{\text{O}_1})(3\cos^2\theta_{\text{O}}-1)(\bar{R}_{\text{O}_1}/R_{\text{O}_1})^{t_2} + (2/7)\bar{A}_2(\bar{R}_{\text{N}})(3\cos^2\theta_{\text{N}}-1)(\bar{R}_{\text{N}}/R_{\text{N}})^{t_2} + \\ &\quad + (2/7)\bar{A}_2(\bar{R}_{\text{O}_2})(\bar{R}_{\text{O}_2}/R_{\text{O}_2})^{t_2}, \\ D_t &= (2/21)\bar{A}_4(\bar{R}_{\text{O}})(7\sin^4\theta_{\text{O}}\cos 2\Phi_{\text{O}} + 35\cos^4\theta_{\text{O}} - 30\cos^2\theta_{\text{O}} + 3)(\bar{R}_{\text{O}}/R_{\text{O}})^{t_4} + (2/21)\bar{A}_4(\bar{R}_{\text{N}}) \times \\ &\quad \times (7\sin^4\theta_{\text{N}}\cos 2\Phi_{\text{N}} + 35\cos^4\theta_{\text{N}} - 30\cos^2\theta_{\text{N}} + 3)(\bar{R}_{\text{N}}/R_{\text{N}})^{t_4} + (8/21)\bar{A}_4(\bar{R}_{\text{O}_2})(\bar{R}_{\text{O}_2}/R_{\text{O}_2})^{t_4}, \\ D_\xi &= (1/7)\bar{A}_2(\bar{R}_{\text{O}_1})(\bar{R}_{\text{O}_1}/R_{\text{O}_1})^{t_2}\sin^2\theta_{\text{O}}\cos\Phi_{\text{O}} + (1/7)\bar{A}_2(\bar{R}_{\text{N}})(\bar{R}_{\text{N}}/R_{\text{N}})^{t_2}\sin^2\theta_{\text{N}}\cos\Phi_{\text{N}}, \\ D_{\eta_1} &= (10/21)\bar{A}_4(\bar{R}_{\text{O}})(\bar{R}_{\text{O}}/R_{\text{O}})^{t_4}\sin^2\theta_{\text{O}}(1-7\cos^2\theta_{\text{O}})\cos\Phi_{\text{O}} + \\ &\quad + (10/21)\bar{A}_4(\bar{R}_{\text{N}})(\bar{R}_{\text{N}}/R_{\text{N}})^{t_4}\sin^2\theta_{\text{N}}(1-7\cos^2\theta_{\text{N}})\cos\Phi_{\text{N}}. \end{aligned} \quad (6)$$

Here  $t_2$  ( $\approx 3$ ) and  $t_4$  ( $\approx 5$ ) are the power-law exponents [ 21 ].  $\bar{A}_2(\bar{R}_{\text{L}})$  and  $\bar{A}_4(\bar{R}_{\text{L}})$  are the rank-2 and rank-4 intrinsic parameters for ligand  $\text{L}$ , with the reference distance  $\bar{R}_{\text{L}}$  taken as the average of the  $\text{Cu}-\text{L}$  distances, i.e.,  $\bar{R}_{\text{O}} \approx (2R_{\text{O}_1} + R_{\text{O}_2})/3$  and  $\bar{R}_{\text{N}} \approx R_{\text{N}}$ . For  $3d^n$  ions in octahedra, the relationships  $\bar{A}_4(\bar{R}_{\text{L}}) \approx (3/4)D_q(\text{L})$  and  $\bar{A}_2(\bar{R}_{\text{L}}) \approx 10.8\bar{A}_4(\bar{R}_{\text{L}})$  [ 25—27 ] have been proved valid in many systems and are reasonably employed here. Thus, the local structure of the system is quantitatively correlated to the rhombic field parameters and hence to the EPR parameters, especially axial and perpendicular anisotropies  $\Delta g$  ( $= g_z - (g_x + g_y)/2$ ) and  $\delta g$  ( $= g_x - g_y$ ).

From the total average copper-ligand distance  $\bar{R} = (2R_{\text{O}_1} + R_{\text{O}_2} + 2R_{\text{N}})/5 \approx 2.058 \text{ \AA}$ , the group overlap integrals  $S_{dpt} \approx 0.0140$ ,  $S_{dpe} \approx 0.0394$ ,  $S_s \approx 0.0320$  and  $A \approx 1.126$  are calculated using the self-consistent field (SCF) functions [ 28, 29 ]. The cubic field parameter  $D_q \approx 1552 \text{ cm}^{-1}$  and the covalency factor  $N \approx 0.681$  can be obtained from the optical spectral measurements for  $\text{Cu}^{2+}$  in  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  [ 14 ]. From the relationship of total  $D_q$  ( $\approx [2D_q(\text{N}) + 3D_q(\text{O})]/5$ ) and the optical spectral studies for the  $[\text{CuO}_6]$  and  $[\text{CuN}_6]$  groups in oxides and nitrides [ 16, 30 ], the values  $D_q(\text{O}^{2-}) \approx 1510 \text{ cm}^{-1}$  and  $D_q(\text{N}^{3-}) \approx 1620 \text{ cm}^{-1}$  are reasonably estimated for the  $\text{Cu}-\text{O}$  and  $\text{Cu}-\text{N}$  bonds in the studied system. Thus, the normalization factors and the orbital admixture coefficients are calculated from Eqs.(4) and (5):  $N_t \approx 0.689$ ,  $N_e \approx 0.708$ ,  $\lambda_t \approx 0.685$ ,  $\lambda_e \approx 0.539$ ,  $\lambda_s \approx 0.438$ . Then the quantities  $\zeta \approx 596 \text{ cm}^{-1}$ ,  $\zeta' \approx 559 \text{ cm}^{-1}$ ,  $k \approx 0.851$ ,  $k' \approx 0.451$ ,  $P' \approx 277 \times 10^{-4} \text{ cm}^{-1}$  and  $P \approx 280 \times 10^{-4} \text{ cm}^{-1}$  are determined from Eq. (3) and the free-ion values  $\zeta_d^0 \approx 829 \text{ cm}^{-1}$  [ 31 ] and  $P_0 \approx 402 \times 10^{-4} \text{ cm}^{-1}$  [ 32 ] for  $\text{Cu}^{2+}$  and  $\zeta_p^0 \approx 151 \text{ cm}^{-1}$  [ 33 ] for  $\text{O}^{2-}$  (note that the spin-orbit coupling contributions of  $\text{N}^{3-}$  are neglected here due to the much smaller  $\zeta_p^0 \approx 75 \text{ cm}^{-1}$  [ 34 ]). In the formulas of hyperfine structure constants, the core polarization constant is taken as  $\kappa \approx 0.26$ , which is close to that ( $\approx 0.23-0.26$ ) for  $\text{Cu}^{2+}$  in Tutton salts [ 15 ], and can be regarded as suitable.

Substituting the above values into Eq.(1), the EPR parameters are calculated and shown in Table 1. To clarify relative importance of covalency and ligand orbital and spin-orbit coupling contributions, the results (Cal.<sup>a</sup>) based on the conventional crystal-field model formulae (i.e., taking  $\zeta = \zeta' = N\zeta_d^0$ ,  $k = k' = N$  and  $P = P' = P_0N$ ) are also listed in Table 1.

## DISCUSSION

Table 1 reveals that the calculated EPR parameters (Cal.<sup>b</sup>) based on the ligand contributions show better agreement with the observed values than those (Cal.<sup>a</sup>) in the absence of these contributions. Thus, the EPR spectra for Cu<sup>2+</sup> in the [CuO<sub>3</sub>N<sub>2</sub>] group of [Cu(ipt)(dap)H<sub>2</sub>O]<sub>*n*</sub>·*n*H<sub>2</sub>O are satisfactorily interpreted.

1. The experimental EPR spectra of [Cu(ipt)(dap)H<sub>2</sub>O]<sub>*n*</sub>·*n*H<sub>2</sub>O may be illustrated as the axial and perpendicular anisotropies Δ*g* and δ*g*, which originate largely from the axial (relevant to *D<sub>s</sub>* and *D<sub>t</sub>* due to the axial elongation) and perpendicular (relevant to *D<sub>ξ</sub>* and *D<sub>η</sub>* due to the nonequivalent planar ligands nitrogen and oxygen) rhombic distortions, respectively. The above *g* anisotropies are thus connected with the local structure around Cu<sup>2+</sup> in the rhombically elongated square pyramidal [CuN<sub>2</sub>O<sub>3</sub>] group. Therefore, the observed moderate axial anisotropy Δ*g* (≈ 0.074) can be ascribed to the local elongation of the [CuN<sub>2</sub>O<sub>3</sub>] group, characterized by the stronger crystal-fields arising from the mixed planar ligands than those from the merely apical oxygen. On the other hand, the much smaller calculated perpendicular anisotropy δ*g* (≈ *g<sub>x</sub>* – *g<sub>y</sub>*, ≈ 0.008) is qualitatively in agreement with the measured approximately axial (i.e., *g<sub>x</sub>* ≈ *g<sub>y</sub>* ≈ *g<sub>⊥</sub>* or δ*g* ≈ 0) EPR signals [ 14 ]. This point can be illustrated by the fact that the anisotropic contributions to the EPR parameters along the *X* and *Y* axes from nonequivalent planar ligands N and O with distinct bond lengths and angles may largely cancel one another, resulting in the nearly axial *g* and *A* factors within the experimental uncertainties [ 14 ].

2. The system exhibits strong covalency and copper-ligand orbital admixtures due to the strongly covalent Cu—N bonds with small bond lengths. This can be described as the small covalency factor *N* (≈ 0.683 << 1) and the obvious orbital admixture coefficients (≈ 0.4—0.7). Further, the significant relative deviations (or anisotropies) (*k'* – *k*)/*k* (≈ 47 %), (*ζ'* – *ζ*)/*ζ* (≈ 6 %) and (*P'* – *P*)/*P* (≈ 1 %) can be obtained from the cluster approach for the orbital reduction factors, the spin-orbit coupling coefficients and the dipolar hyperfine structure parameters, respectively. The theoretical *g* factors and hyperfine structure constants (Cal.<sup>a</sup>) without the ligand contributions are much larger and smaller, respectively, in magnitude, than the experimental data. Moreover, the above discrepancies cannot be removed by modifying the relevant spectral parameters, suggesting that the experimental Cu<sup>2+</sup> EPR spectra for [Cu(ipt)(dap)H<sub>2</sub>O]<sub>*n*</sub>·*n*H<sub>2</sub>O could not be analyzed by the conventional crystal-field model formulae containing only the central ion orbital and spin-orbit coupling contributions. Therefore, the ligand orbital and spin-orbit coupling contributions should be taken into account in the EPR studies of Cu<sup>2+</sup> in [Cu(ipt)(dap)H<sub>2</sub>O]<sub>*n*</sub>·*n*H<sub>2</sub>O and similar systems with significant covalency.

3. The signs of the hyperfine structure constants were not experimentally determined in [ 14 ]. Based on the present calculations, both signs of *A<sub>∥</sub>* and *A<sub>⊥</sub>* are negative. From Eq. (1), *A* factors depend mainly upon the negative isotropic terms related to the core polarization constant, while the positive anisotropic terms related to the *g* anisotropies are usually smaller in magnitude. Second, the magnitude or average (*|A|* = *|A<sub>∥</sub>* + 3*A<sub>⊥</sub>* ≈ 45 × 10<sup>–4</sup> cm<sup>–1</sup> [ 14 ]) of the hyperfine structure constants is much smaller than those (≈ 80 – 120 × 10<sup>–4</sup> cm<sup>–1</sup> [ 35, 36 ]) for the conventional elongated octahedral Cu<sup>2+</sup> centers. This can be illustrated by the much stronger covalency for the studied [CuN<sub>2</sub>O<sub>3</sub>] group in [Cu(ipt)(dap)H<sub>2</sub>O]<sub>*n*</sub>·*n*H<sub>2</sub>O, since the magnitudes of hyperfine structure constants decrease with increasing covalency of the systems [ 35 ]. Third, the anisotropy Δ*A* (= *|A<sub>z</sub>* – (*A<sub>x</sub>* + *A<sub>y</sub>*)/2) ≈ 22 × 10<sup>–4</sup> cm<sup>–1</sup> [ 14 ]) of the hyperfine structure constants is also much smaller than those (≈ 100 – 180 × 10<sup>–4</sup> cm<sup>–1</sup> [ 35 ]) for common elongated octahedral Cu<sup>2+</sup> centers. The above anomaly may reveal dissimilar local distortion around Cu<sup>2+</sup> in the studied [CuN<sub>2</sub>O<sub>3</sub>] group. This point can be further illustrated by the very large ratio *g<sub>z</sub>*/*A<sub>z</sub>* (≈ 365 (cm<sup>–1</sup>)<sup>–1</sup> [ 14 ], which reflects considerable local low symmetrical (rhombic) distortion [ 35, 37 ].

## CONCLUSIONS

The EPR parameters for Cu<sup>2+</sup> in [Cu(ipt)(dap)H<sub>2</sub>O]<sub>*n*</sub>·*n*H<sub>2</sub>O are theoretically investigated from the perturbation calculations based on the cluster approach. The nearly axial anisotropies of the *g* factors and hyperfine structure constants correlate with the significant elongation distortion of the five-fold



coordinated  $\text{Cu}^{2+}$  in the square pyramidal  $[\text{CuN}_2\text{O}_3]$  group. The perpendicular anisotropic contributions to the EPR parameters from nonequivalent planar ligands N and O may largely cancel one another and thus lead to the nearly axial EPR signals within the experimental uncertainties. The present EPR analysis for  $[\text{Cu}(\text{ipt})(\text{dap})\text{H}_2\text{O}]_n \cdot n\text{H}_2\text{O}$  would be useful to the understanding of the local structures and properties of this and relevant systems.

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