J. Braz. Chem. Soc., Vol. 9, No. 3, 243-247, 1998.
Printed in Brazil.

Article

A Description of Ligand Field Effects in the Di-μ-Azido-Bis [{Azido(N,N-Diethylethylenediamine)}Copper(II)] Compound by the Simple Overlap Model

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Received: June 30, 1997

Apresentamos uma descrição teórica de efeitos de campo ligante no composto di-μ-azido-bis[{azido(N,N-dietiletilenodiamina)}cobre(II)] através do Modelo Simples de Recobrimento. O Hamiltoniano do campo ligante é expresso em termos de operadores tensoriais irredutíveis, assumindo-se um sítio de simetria D_{3h} ocupado pelo íon cobre (II). Os parâmetros de campo ligante, calculados a partir de dados estruturais disponíveis, indicam que o íon cobre(II) encontra-se sob a influência de um campo ligante muito forte.A energia da absorção d-d é bem reproduzida fenomenologicamente pelo modelo.

We present a theoretical description of ligand field effects in the di-μ-azido- bis[{azido(N,N-diethylethylenediamine)} copper(II)] compound by the Simple Overlap Model. The ligand field Hamiltonian is expressed in terms of irreducible tensor operators for an assumed D_{3h} site symmetry occupied by the copper ion. The ligand field parameters, calculated from the available structural data, indicate that the copper ion is under the influence of a very strong ligand field. The energy of the d-d absorption band is well reproduced phenomenologically by the model.

Keywords: *copper(II), complexes, amine ligands, ligand field*

Introduction

One of our research interests has been the synthesis and solid state structural characterization of copper complexes with bidentate amine ligands[1-3]. Structural and spectroscopic data concerning these complexes with pseudo-halides, mainly the azido-group, have a great importance since they may be related to those of important biological systems such as copper-containing proteins[4-6].

The d^9 ion is characteristically stereochemically flexible and, as a consequence, it may form distorted stereochemistries of difficult description. The spectroscopy of these systems turns out to be rather difficult and, in some cases, uncertain. Thus, electronic spectroscopy alone is not a definitive tool for identifying structure or corroborating X-ray structural data. In several instances a theoretical analysis of ligand field effects and spectral intensities in these complexes may be very useful.

In this work we apply the simple overlap model (SOM)[7,8] to describe ligand field effects in the complex $[Cu(N_3)_2(N,N\text{-diEten})]_2$ (N_3 = azide; N,N-diEten = N,N-diethylethylenediamine), for which crystallographic data are available[3]. The aim is to describe theoretically the d-d transition energies and to get information on the ligand field strength in the complex.

Experimental

The complex was prepared as described previously in the literature, together with a full X-ray crystallographic analysis[3]. Electronic spectra of ethanolic or acetone solutions of the compound were obtained in a HP-8425 dyode array spectrophotometer.

As described previously in the X-ray crystallographic analysis[3], the structure of the complex consists of a centrosymmetric Cu_2N_2 unit whose N atoms belong to the azido bridges. Each copper atom is also surrounded by three nitrogen atoms, two from one N,N-diEten and one from the terminal azide. The five nitrogen atoms altogether occupy the vertices of a slightly distorded trigonal bipyramid and the azido bridge leads to a rather short Cu … Cu distance of 3.37 Å. If the slight distortions are not considered we may assume a D_{3h} site symmetry occupied by the copper. The molecular structure is shown in Fig. 1.

The UV electronic absorption spectrum of the compound in ethanolic solution, Fig. 2, shows two bands at 276 nm (ε = 581 $M^{-1}cm^{-1}$) and 384 nm (ε = 525 $M^{-1}cm^{-1}$), assigned to internal $\pi \rightarrow \pi^*$ transitions in the N_3^- anion[9-11], or to charge transfer transitions between the azide and copper ion ($N_{3,\pi} \rightarrow Cu_d$). As can be seen in the acetone solution absorption spectrum shown in Fig. 3, in the visible region, one broad band is observed. By using a simulation program with gaussian line shapes[12], only one component was identified in the d-d transition region, at 670 nm.

The Simple Overlap Model

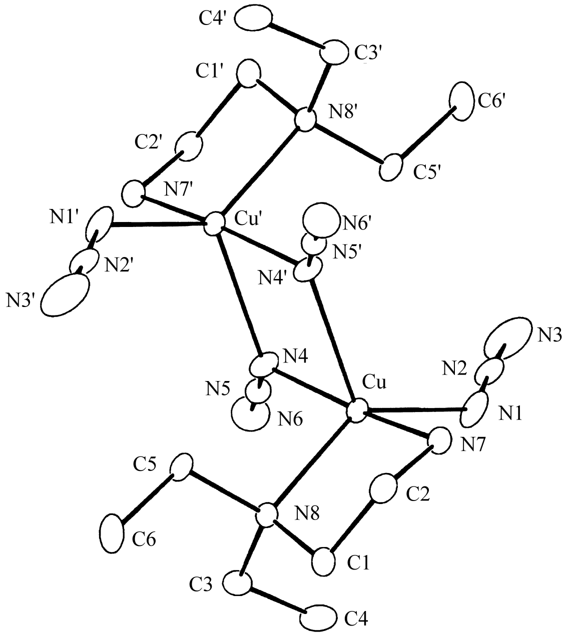

Figure 1. The molecular structure of $[Cu(N_3)_2(N,N\text{-diEten})]_2$.

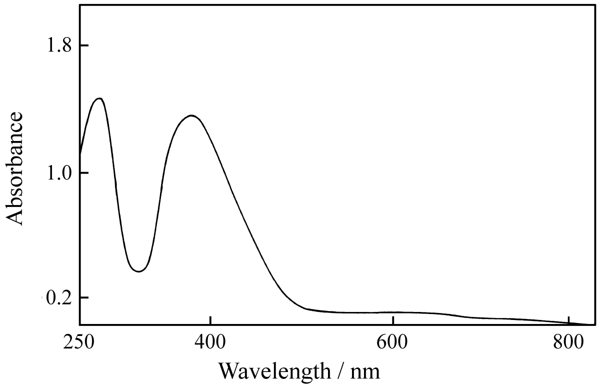

Figure 2. Electronic absorption spectrum of the compound $[Cu(N_3)_2(N,N\text{-diEten})]_2$ in ethanolic solution (2.53 10^{-4} mol L^{-1}).

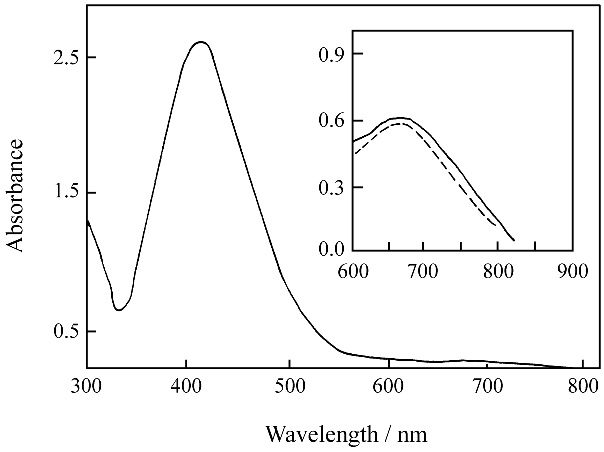

Figure 3. Absorption spectrum of the compound $[Cu(N_3)_2(N,N\text{-diEten})]_2$ in acetone solution (3.13 10^{-4} mol L^{-1}) (main figure); the visible region component (inset): experimental (—) and obtained (---) using a simulation program.

The splitting of the d levels in ligand fields have been successfully described by the angular overlap model (AOM) in terms of the anti-bonding character acquired by d orbitals in a chemical environment[13].

In this section we briefly outline the alternative approach based on the SOM.This model has been introduced and has been applied to the case of lanthanide compounds[7,8]. The general form of the one-particle ligand field Hamiltonian for a metal ion in a chemical environment is given by[7,8,14]:

$$V = \sum_{k,q,i} B_q^k C_q^{(k)}(\mathbf{i}) \qquad (1)$$

where $C_q^{(k)}$ is a Racah tensor operator of rank k and i labels the electrons in the open shell of the metal ion. In the point charge electrostatic model (PCEM) the so-called ligand field parameters, B_q^k, are given by:

$$B_q^k(\text{PCEM}) = \langle r^k \rangle \gamma_q^k(\text{PCEM}) \qquad (2)$$

where $\langle r^k \rangle$ is the radial expectation value of $\mathbf{r}^k$ and the sum over ligand atoms, γ_q^k (PCEM), is given by

$$\gamma^k_q\,(\mathrm{PCEM}) = \left(\frac{4\pi}{2k+1}\right)^{1/2} \sum_j \frac{g_j\, e^2}{R_j^{k+1}}\, Y^{k*}_q\,(\Omega_j) \qquad (3)$$

The sum runs over point charges $g_j e$ at the ligand positions $\vec{R_j}$ with respect to a coordinate system centered at the nucleus of the metal ion and Y_q^k is a spherical harmonic of rank k.

In the SOM it is assumed that[7,8]:

1) the interaction energy of Eq. 1 is produced by effective charges uniformly distributed over small regions centered around the mid-point of the metal ion-ligand distance.

2) the total charge in each region is equal to $g_j e \rho_j$, where ρ_j is the magnitude of the total overlap integral between the metal ion and the j-th ligand wavefunctions.

Then, a general radial matrix element of the interaction V involving equivalent *nl* electrons is given by:

$$< n1 \,|\, V \,|\, n1 > = e^2 \sum_{k,q,i,j} g_j\, \rho_j \left(\frac{4\pi}{2k+1}\right)^{1/2} Y^{k*}_q\,(\Omega_j)$$

$$C^{(k)}_q\,(\mathbf{i}) \left(\frac{1}{r_j^{k+1}} \int_0^{r_j} r^k\, \phi^2_{n1}\, r^2\, dr + r_j^k \int_{r_j}^{\infty} \frac{\phi^2_{n1}}{r^{k+1}}\, r^2\, dr \right) \qquad (4)$$

where $r_j = R_j/2\beta_j$, with β_j being a dimensionless quantity introduced to account for the fact that the barycenters of the charge distributions are not necessarily situated at the middle distances $R_j/2$. It has been shown that an approximate expression for β_j can be given by[8]:

$$\beta_j = \frac{1}{1 \pm \rho_j} \qquad (5)$$

where the plus and minus signs are somewhat arbitrarily associated with the size and the hardness/softness character of the ligand in the complex. Thus, the minus sign has been used in the case of sizable ligands such as chlorine, while the plus sign has been used in the case of oxygen and fluorine ligands. If the second integral in the right-hand side of Eq. 4 can be neglected, then for each ligand we have:

$$\gamma^k_q\,(\mathrm{SOM}, j) = \rho_j\, (2\beta_j)^{k+1}\, \gamma^k_q\,(\mathrm{PCEM}, j) \qquad (6)$$

From the above equations it may be noted that an advantage of the SOM lies in a much more simple scheme to be used in practical estimations of ligand field effects. Ligand field parameters can be obtained directly from structural data without going through the construction of monoelectronic molecular orbitals, which requires a further transformation in order to express the ligand field interaction in terms of Racah's tensor operators. On the other hand it is clear that detail on the characteristics of the chemical bonding cannot be accounted for by the model.

It is well known[14] that in the PCEM the higher rank B_q^k (k > 2) are in general underestimated, suggesting that chemical bonding effects are more important for these parameters, while the B_q^2 parameters are in general considerably overestimated. These tendencies of the PCEM are modified, in the correct sense, by the SOM factors $\rho_j(2\beta_j)^{k+1}$, producing a significant improvement in the theoretical B_q^k values. This is a consequence of assuming effective charges, proportional to the magnitude of the total overlap between metal and ligand orbitals, at around the metal-ligand half distances. Aspects of chemical bonding are, therefore, taken into account in this model.

Results and Discussion

We assume a coordinate system centered on a copper ion in a D_{3h} site symmetry, with the z-axis passing through nitrogens N_4 and N_7. The set of spherical coordinates used in our analysis is shown in Table 1.

The ground term ^2D is split according to the irreducible representations A'_1, E' and E" of the D_{3h} point group, and electric dipole transitions are allowed between the states E' and E", in σ polarization, and the states A'_1 and E' in π polarization.

In this point symmetry the ligand field Hamiltonian, for d elements, reduces to

$$V = B^2_0\, C^{(2)}_0 + B^4_0\, C^{(4)}_0 \qquad (7)$$

In the |LM> basis, where L is the total orbital angular momentum (L = 2 and M = 0, ±1, ±2, in our case), the secular determinant, restricted to the ^2D ground term, gives the following roots:

$$\varepsilon_0 = -0.2856\,(B^2_0 + B^4_0) \qquad (8)$$

$$\varepsilon_1 = -0.1428\, B^2_0 + 0.1905\, B^4_0 \qquad (9)$$

$$\varepsilon_2 = 0.2856\, B^2_0 - 0.0476\, B^4_0 \qquad (10)$$

where the matrix elements $<LM \,|\, C_o^{(k)} \,|\, LM>$ have been calculated by usual tensor operator techniques[15,16]. From the symmetry properties of the states |LM> one may find that the roots ε_0, ε_1, and ε_2 correspond, respectively, to the ligand field states A'_1, E", and E'. We now proceed with the evaluation of B_0^2 and B_0^4 as given by the SOM.

Table 1. Spherical coordinates, R (in Å), θ and φ (in degree), for the ligand nitrogens in the $[Cu(N_3)_2(N,N\text{-diEten})]_2$ compound.

	R	θ	φ
N_1	2.157	90	330
N_4	1.984	0	0
N_7	1.984	180	0
N_8	2.157	90	210
N'_4	2.157	90	90

The corresponding expressions for these ligand field parameters are given by:

$$B_0^2 = e^2 < r^2 > \sum_j g_j \rho_j (2\beta_j)^3 \frac{1}{R_j^3} \frac{1}{2} (3\cos^2 \theta_j - 1) \qquad (11)$$

and

$$B_0^4 = e^2 < r^4 > \sum_j g_j \rho_j (2\beta_j)^5 \frac{1}{R_j^5} \frac{1}{8} (35\cos^4 \theta_j - 30\cos^2 \theta_j + 3) \qquad (12)$$

The overlap ρ in the case of lanthanide compounds is typically of the order of 0.05[7,8,17,18]. In the case of d elements it may assume values typically between 0.1 and 0.2[13]. In the SOM the dependence of the overlap with the distance ligand-metal has been expressed as[19]:

$$\rho = \rho_0 \left(\frac{R_0}{R} \right)^{3.5} \qquad (13)$$

where R_0 is the smallest among the distances ligand-metal and, for d elements, we will assume $\rho_0 = 0.15$. The radial integrals appearing in Eqs. 11 and 12 were taken from Ref. 20; $<r^2> = 1.043$ a.u. and $<r^4> = 2.682$ a.u. . For the factors β_j, in Eq. 5 the minus sign was taken since the nitrogen ligand atoms are bonded also to rather sizable groups of atoms, from the diEten and azide ligands, and are expected to present a rather soft character. In the SOM this means that the effective charges producing the ligand field are slightly displaced towards the central ion. In fact, we have noticed that if the plus sign in Eq. 5 is taken no satisfactory description of the d-d transition energy in the complex can be obtained. The charge factors g_j and the overlap integrals ρ_j define these effective charges, with the condition that g_j be smaller or at most equal to the valence of the ligand atom. In our case we found that an excellent fitting of the d-d transition energy (~14900 cm^{-1}, λ_{abs} ~670 nm) is obtained by considering all g_j's equal to 1.3. This corresponds to ligand field parameters $B_0^2 = 13620$ cm^{-1} and $B_0^4 = 27239$ cm^{-1}. A diagram of ligand field energy levels is shown in Fig. 4.

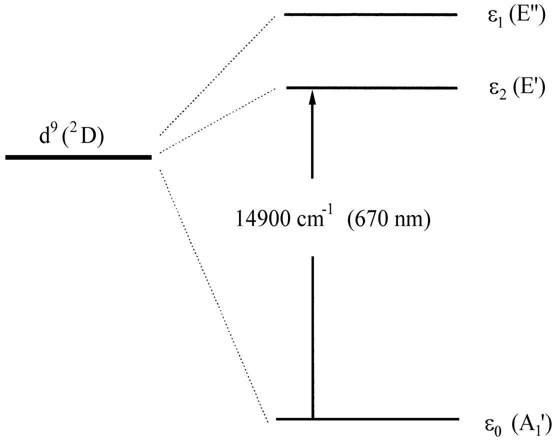

Figure 4. Diagram of ligand energy levels calculated, with the experimental transition assigned.

The ligand field strength in the complex can be analyzed in terms of the so-called ligand field strength parameter, N_v, introduced by Auzel[21,22]

$$N_v = \left[\sum_{k,q} \frac{4\pi}{2k+1} | B_q^k |^2 \right]^{½} \qquad (14)$$

Thus, from the values of the ligand field parameters given above we find $N_v = 38760$ cm^{-1}. Values of N_v for lanthanide compounds are typically of the order of 2500 cm^{-1}, while for d elements N_v is greater[23] by a factor of ~10. Therefore, for the present compound we may conclude that copper is under the influence of a very strong ligand field.

Finally, we emphasize that the above theoretical results provide strong support for the assumption that the site symmetry occupied by the copper is very close to a D_{3h} one, as indeed indicated by the crystallographic data.

Acknowledgments

The authors acknowledge the financial support from CNPq, CAPES, FAPESP and FACEPE (Brazilian Agencies).

References

1. Schpector, J.Z.; Castellano, E.E.; Oliva, G.; Mauro, A.E.; Roveri, M.R. *Acta Crystallogr.* **1985**, C41, 204.
2. Schpector, J.Z.; Castellano, E.E.; Oliva, G.; Mauro, A.E.; Roveri, M.R. *Acta Crystallogr.* **1986**, C42, 302.
3. Casagrande-Jr., O.L.; Klein, S.I.; Mauro, A.E.; Tomita, K. *Trans. Met. Chem.* **1989**, *14*, 45.
4. Casella, I.; Carugo, O.; Gullotti, M.; Garofani, S.; Zanello, P. *Inorg. Chem.* **1993**, *32*, 2056.
5. Wilkinson, G.; Gillard, R.D.; Meeleverty, J.A. In *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties and Applications of Coordination Compounds,* V.6, Pergamon Press, N.York, 1987.
6. Norris, G.E.; Anderson, B.G.; Baker, E.N. *J. Am. Chem. Soc.* **1986**, *108*, 2784.
7. Malta, O.L. *Chem. Phys. Lett.* **1982**, *87*, 27.
8. Malta, O.L. *Chem. Phys. Lett.* **1982**, *88*, 353.
9. Meglynn, C.; Azumi, T.; Kuman, D. *Chem. Rev.* **1981**, *81*, 475.
10. Rabalais, J.W.; McDonald, J.R.; Meglynn, S.P. *J. Chem. Phys.* **1969**, *51*, 5103.
11. McDonald, J.R.; Rabalais, J.W.; Meglynn, S.P. *J. Chem. Phys.* **1970**, *52*, 1332.
12. Melo, W.I.; Nascimento, O.R. *Quimica Nova* **1992**, *15*, 77.

13. Jorgensen, C.K. *Modern Aspects of Ligand Field Theory*, North-Holland, Amsterdam, 1971.
14. Newman, D.J. *Adv. Phys*. **1971**, *20*, 197.
15. Edmonds, A.R. *Angular Momentum in Quantum Mechanics*, Princeton University Press, Princeton, 1957.
16. Condon, E.U.; Odabasi, H. *Atomic Structure*, Cambridge University Press, N.York, 1980.
17. Axe, J.D.; Burns, G. *Phys. Rev*. **1966**, *152*, 331.
18. Garcia, D.; Faucher, M. *J. Chem. Phys.***1985**, *82*, 5554.
19. Malta, O.L.; dos Santos, M.A.C.; Thompson, L.C.; Ito, K. *J. Luminescence* **1996**, *69*, 77.
20. Fraga, S.; Karwowski, J.; Saxena, K.M.S. *Atomic Energy Levels*, Elsevier Scientific Publishing Company, Amsterdam, 1979.
21. Auzel, F. *Mater. Res. Bull*. **1979**, *14*, 223.
22. Auzel, F.; Malta, O.L. *J. Physique* **1983**, *44*, 201.
23. Auzel, F. In *Spectroscopy of Solid-State Laser-Type Materials*, Ed.Baldassare Di Bartolo, Plenum Publishing Corporation, 1987.

FAPESP helped in meeting the publication costs of this article