

Simple non-empirical calculations of the zero-field splitting in bis(aquo) bis(malonato) nickel(II)

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Summary. A simple non-empirical method is applied to calculate the splittings of the ground state triplet, caused by the spin-orbit coupling, in bis(aquo) bis(malonato) nickel(II), allowing for a certain geometry variation. The calculations yield splittings on the order of $10\text{--}20\text{ cm}^{-1}$. The comparison of exact (within model) and second-order perturbation theory calculations indicate that the spin Hamiltonian formalism is valid. The implications of the results for the theory of nuclear spin relaxation in paramagnetic complexes in solution are discussed.

Key words: Bis(aquo) bis(malonato) nickel(II) – Ground state triplet – Splittings – Spin-orbit coupling

1 Introduction

The spin Hamiltonian formalism is a useful tool for the interpretation of magnetic, thermodynamic and spectroscopic properties of transition metal complexes. For systems with $S \geq 1$, the spin Hamiltonian contains a term of the form $\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$, denoted the zero-field splitting (ZFS) interaction [1]. The ZFS interaction vanishes for ideal octahedral symmetry around the metal ion. In the case of axial symmetry, the zero-field splitting tensor \mathbf{D} is fully characterized by a single parameter D , while two energy parameters (D and E) and the orientation of the principal frame of the tensor are required in a general case.

For Ni(II) ($S = 1$) complexes with distorted octahedral symmetry, experimental determinations of the ZFS parameters can be done in solid state at low temperatures. The methods are optical polarization spectroscopy, ESR and measurements of magnetic susceptibility and heat capacity.

In isotropic liquids, the ZFS interaction cannot be observed directly because of the zero-trace property of the ZFS tensor. However, the ZFS can act as an efficient and often dominant relaxation mechanism for the electron spin [2, 3]. The ESR signal of Ni(II) complexes in solution has, to the best of our knowledge, never been observed, because of extensive line broadening. However, the electron spin relaxation processes can be monitored indirectly by measurements of the relaxation rate

for nuclear spins residing in the ligands. It is in principle possible to use the nuclear relaxation data to estimate the magnitude of the ZFS parameter D in a complex in solution (in particular if the measurements are carried out over a wide range of the magnetic fields, the so-called nuclear magnetic relaxation dispersion (NMRD) experiment). The difficulty lies in the fact that the determination of D in this way is dependent on the model used to describe the electronic and nuclear spin relaxation [2, 4]. The state-of-the-art as far as such models are concerned is not really satisfactory, in particular for systems with symmetry lower than octahedral.

Some time ago, an NMR relaxation study for amine protons and nitrogen-15 in aniline in the presence of bis(2,2,6,6-tetramethyl-heptanedionato) nickel(II) (often called Ni(dpm)₂) was reported from this laboratory [5]. The measurements were made at two magnetic fields over a wide range of temperatures. The results were interpreted using a model considering the electron spin to be coupled to the molecular rotations through the ZFS interaction (static in the molecular frame) and neglecting any other modulation of the ZFS. The fitting of the data gave a D value of about 85 cm⁻¹ for the bis(aniline) complex of Ni(dpm)₂. Subsequently, we performed proton NMRD measurements (over the proton Larmor frequency range 0.01–500 MHz) on the same system [6] and were not able to interpret this extended data set using the same model. We find it therefore motivated to estimate the ZFS in a similar but somewhat simpler compound, bis(aquo) bis(malonato) nickel(II) (1), by means of quantum chemical calculations, following a non-empirical scheme recently developed at our laboratory [7, 8, 9].

2 Computational details

The calculations closely follow the earlier approach [7, 8, 9]. Briefly, molecular orbitals optimized for the triplet ground state of the Ni(II) complex are obtained in an open-shell SCF calculation, using the MOLECULE program package [10]. The atomic basis sets for hydrogen, carbon, oxygen and nickel atoms are the same as in our previous studies, i.e. those of Huzinaga [11].

In the next step, the molecular orbitals are used to construct a suitable Slater determinant basis set for a limited CI expansion including single and some double excitations with respect to the SCF ground state. The selection of the core, the valence and the active orbitals used in the CI is based on the orbital energies. Then, the eigenfunctions from the CI calculation are used to define a new basis set $|\gamma, s, M_s, E_n\rangle$, where γ denotes the irreducible representation of the molecular point group and E_n the energy. s and M_s are the spin quantum numbers. In the third step, the spin-orbit coupling is included using an effective operator of the form:

$$H = \sum_i \hat{A}^{(i)} \cdot \hat{S}^{(i)}$$

$$\hat{A}^{(i)} = \frac{\alpha^2 Z_{\text{eff}}^{K,l}}{2 \hat{r}_{K,i}^3} (\hat{\mathbf{r}}_{K,i} \times \hat{\mathbf{p}}_i)$$

$Z_{\text{eff}}^{K,l}$ is the effective charge for the subshell with azimuthal quantum number l of the valence shell ($3d$ for Ni in this case) of the atomic center K . In analogy with the previous study [8], the effective charge was set to 16.0 atomic units. The spin-orbit coupling causes mixing of states with different spin and spatial symmetries. Therefore, the double group symmetry becomes a useful tool in the analysis of the results

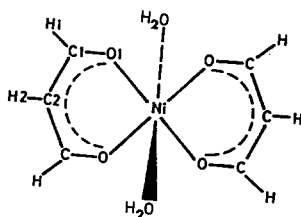
Table 1. The nickel-aqueous oxygen distances (R_{NiO}), the orientation of the HH vector in the water molecules with respect to the C2–H2 bond (θ) and the corresponding total energies

Geom. no.	R_{NiO} [pm]	θ	E_{SCF} [a.u.]
1a	200	0	– 2186.793499
2a	214	0	– 2186.799105
2b	214	90°	– 2186.806422
3a	230	0	– 2186.796356

[8]. The effects of the spin-orbit coupling are calculated at two levels of approximation: by using second order perturbation theory and by diagonalizing the total Hamiltonian matrix set up in the $|\gamma, s, M_s, E_n\rangle$ basis.

3 Results and discussion

The geometry of the bis(malonato) nickel(II) unit in complex 1, based on the crystal structure of bis(aquo) bis(acetylacetonato) nickel(II) [12], was taken from an earlier theoretical study from this laboratory [13, 14]. The unit is placed in the xy plane of the coordinate system, with the C2–H2 bond coincident with the x -axis. The water oxygens were located on the z -axis of the coordinate frame. The position and orientation of the water ligands was subject to a certain variation, cf. Table 1, consistent with the D_{2h} symmetry of the bis(aquo) bis(malonato) nickel(II). All the calculations have been performed for a state with singly-occupied $d_{x^2-y^2}$ and d_{xy} orbitals. This state has earlier been found to be the ground state at the nickel-aqueous oxygen distance of 214 pm (which corresponds to the crystal structure [12]) and the wave function, as far as space symmetry is concerned, belongs to the irreducible representation B_{1g} of D_{2h} . As can be seen in Table 1, the



Scheme 1

distance $R = 214$ pm gives the lowest total energy.

The calculated splittings of the triplet ground state are collected in Table 2. Results from two sets of CI calculations are reported. The smaller CI expansion, denoted CI(1), includes the excitations from occupied orbitals with orbital energies higher than -0.7 a.u. to the virtual orbitals with orbital energies lower than

Table 2. The spin-orbit splittings of the triplet ground state obtained at different levels of approximation. The energy levels are shifted to zero trace. All values are in cm^{-1}

Geom. no.	Double group symmetry	CI(1)		CI(2)	
		CI	PT 2nd order	CI	PT 2nd order
1a	<i>A</i>	-1.6	-2.4	-1.5	-2.3
	<i>B</i> ₃	-1.2	-0.9	-1.2	-1.0
	<i>B</i> ₂	2.8	3.4	2.7	3.3
2a	<i>A</i>	-5.2	-6.8	-9.0	-11.5
	<i>B</i> ₃	-3.1	-2.8	2.7	3.6
	<i>B</i> ₂	8.3	9.6	6.3	7.9
2b	<i>A</i>	-5.6	-7.4	-9.3	-11.8
	<i>B</i> ₂	-4.2	-3.9	1.1	2.1
	<i>B</i> ₃	9.8	11.2	8.1	9.7
3a	<i>A</i>	-14.2	-19.1	-17.8	-24.3
	<i>B</i> ₃	0.7	2.4	7.3	10.2
	<i>B</i> ₂	13.5	16.7	10.5	14.2

0.5 a.u. The total number of configurations in CI(1) is about 1000, divided into blocks according to spatial and spin symmetry. In the larger CI expansion, denoted CI(2) and including about 5000 configurations, the lower limit of the occupied orbital energies is decreased to -1.2 a.u. For each of the expansions, we report the results of the "exact" calculation (involving the diagonalization of the spin-orbit coupled CI matrix), denoted "CI" in Table 2, as well as a second-order perturbation theory estimate.

It can be seen in Table 2 that the splitting pattern is rather sensitive to the size of the CI expansion. In particular the relative position of the middle state, *B*₃ for geometry (a) and *B*₂ for geometry (b), with respect to the other two changes substantially between CI(2) and CI(1). This change originates mainly from the variation of the energy of three lowest excited states. Further, it can be seen in the table that the second order perturbation theory provides reasonable estimates of the SOCI splittings. This is in agreement with our earlier experience [7, 8] for systems moderately distorted from octahedral symmetry. The spin-orbit coupling thus mixes a very small contribution from excited states into the three lowest levels, which can consequently be described in terms of components of the ground state multiplet. This gives justification for the use of the spin Hamiltonian formalism. The triplet splitting for geometries 1a, 2a and 2b, and its relation to the spin Hamiltonian parameters *D* and *E*, is also sketched in Fig. 1.

The geometry variation of the ZFS in Table 2 is similar to what could be seen in earlier work from our laboratory [7, 8, 9]. The variation of the NiO distance has clearly a major effect on the ZFS pattern. In fact, we found earlier that this type of geometry variation had an effect similar to the replacement of a ligand by another one [8]. We can note that elongating the nickel-water distance increases the splitting between the *A* level on one hand and the average of the two *B* levels. This splitting corresponds to the *D* parameter of the spin Hamiltonian (cf. Fig. 1). During this geometry variation, the splitting between the *B*₃ and *B*₂ levels (the *E* parameter) is almost constant. The rotation of the water ligands (transforming geometry 2a into 2b) gives rise to a level crossing between the *B*₃ and *B*₂ (the sign

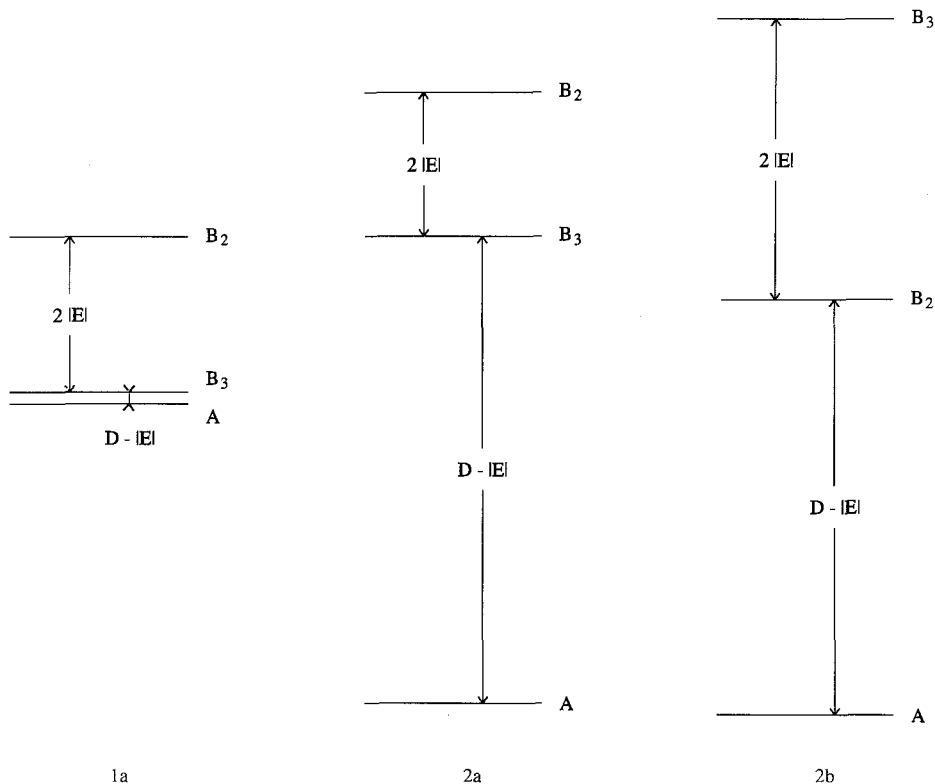


Fig. 1. The relation between the energy level splitting and the zero-field splitting parameters D and E . The state denoted A in the double-group symmetry notation corresponds to $M_s = 0$ and the calculated D is thus always positive [1]. The labels 1a, 2a and 2b refer to the geometries given in Table 1

change of the parameter E), while the parameter D as defined in Fig. 1 remains essentially constant. This is interesting and shows that both the orientation of the axes of the principal coordinate system and the rhombicity of the ZFS tensor are closely connected to the orientation of the water molecules.

The main reason for performing the calculations described in this work was to attempt to answer certain questions arising in the theory of nuclear spin relaxation, and it is therefore important to discuss the results in Table 2 from this point of view. The first such issue is the absolute value of the D parameter. According to our earlier experience [8], the zero-field splittings calculated by the present approach are likely to overestimate the real splittings by a factor of about two. Thus, the present work indicates that in bis(β -diketonato) nickel(II) complexes with axial oxygen (or nitrogen) ligands one should expect D values of at most $10\text{--}20\text{ cm}^{-1}$. The D value of 85 cm^{-1} reported by Benetis et al. [5] therefore seems grossly overestimated and indicates strongly, along with spectroscopic evidence [6], that the model for nuclear relaxation used in that paper was not correct. The second issue is that of the rhombicity of the ZFS tensor. The calculations clearly indicate that even though the complex appears to deviate only little from cylindrical symmetry, the ZFS pattern can display very significant rhombicity (large E parameter). The rhombicity of the ZFS has not been discussed as a possible source of

relaxation until recently [15]. The final issue is the modulation of the ZFS by motions other than the overall reorientation of the complex. The results of this work, along with earlier studies [7, 8], indeed point to the possibility of energetically easily accessible ligand rotations as a possible source of fast modulation of the ZFS pattern.

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