

# Applicability of the Solomon–Bloembergen Equation to the Study of Paramagnetic Transition-Metal–Water Complexes. An ab Initio SCF-MO Study

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**Abstract:** Nonempirical SCF-MO calculations of the effective distances between the ligand nuclei and the unpaired electron spins are presented for the ground states of paramagnetic hexaaquo complexes of the divalent transition-metal cations  $M(\text{H}_2\text{O})_6^{2+}$  with  $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Cu}$ . The validity of the point dipole approximation in the Solomon–Bloembergen equation is discussed. The calculations show that the point dipole approximation functions very satisfactorily for the hydrogen atoms. On the other hand, the effective distance between the oxygen atoms and the unpaired electron spin is shorter than the intermolecular oxygen–metal distances, and the extent of the deviation varies significantly throughout the series. Calculations of hyperfine coupling constants are also reported and the relation between  $^{17}\text{O}$  hyperfine couplings and deviations from the point dipole approximation is investigated. The errors caused by approximations to the rigorous treatment are discussed.

It is generally believed that the nuclear spin–lattice relaxation of the ligand nuclei in paramagnetic metal complexes arises primarily via dipolar interaction between the nuclear spin and the unpaired electron spin. If the electron spin is assumed to act as a point dipole located at the metal, the nuclear spin–lattice relaxation rate ( $T_{11}^{-1}$ ) is found to be proportional to the inverse sixth power of the distance between the nucleus of interest and the metal (the Solomon–Bloembergen equation).<sup>1,2</sup> This assumption forms the basis of numerous experimental investigations of geometries of metal complexes in solution, determinations of coordination numbers, and calculations of correlation times.<sup>3–5</sup> However, it has been noted that some of the experimental results<sup>6,7</sup> could not be explained with the framework of the point dipole approximation and new theoretical formulations have been proposed.<sup>8–12</sup> Basically, the  $R^{-6}$  term in the Solomon–Bloembergen equation is replaced by the inverse sixth power of the “effective distance”,  $r_{\text{eff}}$ , expressed as a kind of expectation value calculated by using the electronic wave function of the system. In this way, deviations from the point dipole approximation which are due to the finite size of the atomic orbitals and to spin delocalization and spin polarization can explicitly be taken into account. Very recently, we have reported the first test of the validity of the point dipole approximation based on nonempirical calculations using  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  in its triplet ground state as a model system.<sup>13</sup> It was found that the effective distance between the oxygen atom and the unpaired electron spin is significantly shorter than the internuclear nickel–oxygen distance, while the deviations from the point dipole approximation are minor for the case of the hydrogen atoms.

The aim of the present investigation is to extend the calculations to other high-spin hexaaquo complexes of divalent cations of the first transition series, i.e.,  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ , and  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ , and to investigate whether similar conclusions

hold for these systems. Furthermore, we study the effects that approximations to the rigorous treatment have on the computed  $r_{\text{eff}}$ . We also discuss the relation between the magnitude of hyperfine coupling constants and the deviations from the point dipole approximation. In section 2 of this paper, we present briefly the theoretical model used and the computational details. In section 3, the calculated energy data, effective distances, and hyperfine coupling constants are reported. The results are discussed in section 4.

## Method of Calculation

We follow the approach of Gottlieb et al.,<sup>8</sup> based on the spin density matrix formalism. The equation for the dipolar part of the relaxation rate  $T_{11}^{-1}$  is in this formalism written as:

$$T_{11}^{-1} = \frac{4\pi}{75} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \cdot \sum_{m=-2}^2 \sum_{st} |D_{st}(s|F_2^m|t)|^2 J(\omega_i, \tau_j) \quad (1)$$

Here,  $\gamma_I$  and  $\gamma_S$  are the magnetogyric ratios of the nucleus under consideration and of the electron, respectively,  $S$  is the total electron spin quantum number, and  $D_{st}$  is the spin density matrix element for atomic orbitals  $\phi_s$  and  $\phi_t$ . The matrix is defined so that  $D_{st}\phi_s\phi_t$  integrates to unity.  $J(\omega_i, \tau_j)$  denotes a linear combination of various spectral densities, influenced by different correlation times  $\tau_j$  and evaluated at different angular frequencies  $\omega_j$ .  $F_2^m$  are products of the inverse third power of the distance between the electron and the nucleus  $I$  and  $l = 2$  spherical harmonics.  $F_2^m$  may easily be related to the Cartesian components of the field gradient operators,  $\hat{q}_{\alpha\beta}$ , and eq 1 takes the form of eq 2, where the elements  $\langle q_{\alpha\beta} \rangle$  of the so-called spin-differential

$$T_{11}^{-1} = \frac{1}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{1}{4} \left[ \langle q_{zz} \rangle^2 + \frac{1}{3} (\langle q_{xx} \rangle - \langle q_{yy} \rangle)^2 + \frac{4}{3} \langle q_{xy} \rangle^2 + \frac{4}{3} \langle q_{xz} \rangle^2 + \frac{4}{3} \langle q_{yz} \rangle^2 \right] J(\omega_i, \tau_j) \quad (2)$$

field gradient tensor<sup>13</sup> are given by eq 3.

$$\langle q_{\alpha\beta} \rangle = \sum_{st} D_{st}(s|\hat{q}_{\alpha\beta}|t) \quad (3)$$

The point dipole approximation implies that the distribution of spin density,  $\sum_{st} D_{st}\phi_s\phi_t$  in eq 3, is replaced by a Dirac delta function at the site of the metal ion. Equation 2 is then reduced to eq 4, i.e., to the Solomon–Bloembergen equation mentioned in the introduction. The comparison of eq 2 and 4 provides the

$$T_{11}^{-1} = \frac{1}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) R^{-6} J(\omega_i, \tau_j) \quad (4)$$

definition of  $r_{\text{eff}}$ : The quantum chemical calculation of the spin-differential field gradient tensor is a two-step procedure. In the first step, the wave function and the spin-density matrix are

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$$r_{\text{eff}}^{-6} = \frac{1}{4} \left[ \frac{1}{3} (\langle q_{xx} \rangle - \langle q_{yy} \rangle)^2 + \langle q_{zz} \rangle^2 + \frac{4}{3} \langle q_{xy} \rangle^2 + \frac{4}{3} \langle q_{xz} \rangle^2 + \frac{4}{3} \langle q_{yz} \rangle^2 \right] \quad (5)$$

evaluated. For this purpose, we use the spin-unrestricted Hartree-Fock (UHF) method. Earlier work<sup>13,14</sup> indicated that this approach should be more reliable for the properties at hand than the restricted Hartree-Fock (RHF) procedure. The second step involves calculation of the matrix elements of the field gradient operators and evaluation of  $\langle q_{\alpha\beta} \rangle$  according to eq 3. This step is computationally much simpler, and for the nonempirical calculations using Gaussian type functions (GTFs), there is no need to invoke any approximations at this stage. However, in order to provide a bench mark for semiempirical work (in which the calculation of the field gradient integrals may be the difficult part) we also report the results of two more approximate approaches to eq 3. In the first approximation, denoted as pseudo-one-center, we neglect the integrals  $\langle s|\hat{q}_{\alpha\beta}|t \rangle$  unless the atomic orbitals  $\phi_s$  and  $\phi_t$  have their origin at the same center. In the second approximation, denoted one-center, we further neglect the integrals in which  $\phi_s$  and  $\phi_t$  are not centered at the point at which  $\langle q_{\alpha\beta} \rangle$  is evaluated.

All calculations have been carried out using the metal-oxygen distances suggested by Drakin.<sup>15</sup> For the water molecules, we used  $R_{\text{OH}} = 0.957 \text{ \AA}$  and  $\angle\text{HOH} = 104.52^\circ$ . The water molecules were placed around the nickel atom so that the six oxygens formed a regular octahedron. The two water molecules trans to each other were placed in one plane, and the planes defined by the three pairs of water molecules were perpendicular to each other. The resulting symmetry of the complexes was thus  $D_{2h}$ . The calculations were carried out using the program system MOLEUCLE.<sup>16</sup> The atomic basis sets for metals were chosen in analogy with the work of the hexaaquonickel ion;<sup>13</sup> it consisted of 10s, 7p, and 5d GTFs (with the exponents of other than diffuse functions taken from Roos et al.;<sup>17</sup> the set of diffuse functions suggested for nickel by Åkermark et al.<sup>18</sup> has been used throughout), contracted to 3s, 4p, and 2d. For the oxygens we used the 7s3p basis set of Roos and Siegbahn<sup>19</sup> contracted to 3s2p. Four s functions of van Duijneveldt,<sup>20</sup> contracted to two, were used on each hydrogen atom. With this choice of basis set, consisting of totally 105 contracted functions, we were able to retain the flexibility of the split valence shell, while at the same time reducing costs by using the minimal basis of the inner-shell orbitals.

## Results

The results of the calculations of total energies and gross atomic populations in the  $\text{M}(\text{H}_2\text{O})_6^{2+}$  and  $\text{M}^{2+}$  systems are collected in Table I. The results for  $\text{M} = \text{Ni}$  are taken from ref 13 and included for comparison. The hydration energies calculated for the  $\text{M}(\text{H}_2\text{O})_6^{2+}$  complexes are around 60% of the experimental values.<sup>21</sup> When considering these results, it should be borne in mind that the second and further hydration spheres, absent in our calculations, contribute to the systems under consideration a substantial part of the total measured hydration energy.<sup>22,23</sup> In all complexes, the metal carries a formal charge of about +1.5

e and the water molecules are slightly polarized, i.e., the negative charge on oxygen in the complexes is somewhat higher than for free water (8.640 e with the same basis set). The table also contains the calculated spin populations (normalized to unity) obtained by replacing the ordinary density matrices in the Mulliken population analysis by the spin-density matrices  $\mathbf{D}$ .

The metal-oxygen distances ( $R_{\text{MO}}$ ), as assumed in the calculations, are compared in Table II with  $r_{\text{eff}}$  calculated in eq 5 without any approximation in eq 3 (ab initio) and using the two approximations mentioned above. In the last row of Table II, we list  $r_{\text{eff}}$  calculated using the wave functions for free metal ions and evaluating  $\langle q_{\alpha\beta} \rangle$  at the point where the oxygen atoms are positioned in the complexes. These values correspond closely to the calculations reported by Waysbort and Navon<sup>9,10</sup> with the covalency parameter  $\lambda$  set to zero. Analogous data for the metal-hydrogen distances are displayed in Table III.

For the complexes with orbitally degenerate ground state ( $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ), the  $r_{\text{eff}}$  quoted in Tables II and III are average values of the water molecules located on the three perpendicular planes. The  $r_{\text{eff}}$  calculated for individual atoms are not identical because the UHF calculations are performed for a given set of populations of d orbitals of different symmetries. This method of averaging is equivalent to the averages taken for one particular atom over various UHF determinants corresponding to the same degenerate manifold.

Another type of property of interest that can easily be computed for the complexes under consideration is the isotropic hyperfine coupling. The hyperfine coupling constants for  $^{17}\text{O}$  and  $^1\text{H}$  are also known experimentally<sup>24-30</sup> and can provide a test of the accuracy of the calculations. The calculated and experimental hyperfine coupling constants are compared to each other in Table IV. Here, also, the earlier reported results for the hexaaquonickel<sup>13</sup> ion are included for the sake of completeness.

## Discussion

The most noteworthy feature of the results presented in Table II is the wide variation of the deviation from the point dipole approximation for the oxygen atom in  $\text{M}(\text{H}_2\text{O})_6^{2+}$  as a function of  $\text{M}$ . The difference between  $r_{\text{eff}}$  and  $R_{\text{MO}}$  is only 1% for the manganese complex at one end of the scale but 14-15% for copper and nickel at the other end. Iron and cobalt hold intermediate positions. The complexes with smaller deviations from the point dipole approximation also have longer  $R_{\text{MO}}$ . This is, however, unlikely to be the reason for the variation;  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  shows a substantially larger difference between  $r_{\text{eff}}$  and  $R_{\text{MO}}$  than does  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  for exactly the same assumed internuclear distance. Calculations using the free ion wave functions show the extent of the shortening of  $r_{\text{eff}}$  due to finite spatial extension of the d orbitals. This effect, directly related to the metal-oxygen distance, is practically negligible.

The magnitude of the deviations from the point dipole approximation in the series of hexaaquo transition-metal ions is thus a specific property of the metal ion. It is therefore of interest to compare the calculated  $r_{\text{eff}}/R_{\text{MO}}$  ratios with other measures of the extent of spin delocalization and spin polarization in the complexes. The spin populations listed in Table I are one such measure and a rough correlation between the spin population at the oxygen atoms and the  $r_{\text{eff}}/R_{\text{MO}}$  ratio can be noted. It is more interesting to compare the ratio with a measurable quantity such as the  $^{17}\text{O}$  hyperfine coupling constant,  $a_0$ . We may first note that the calculated  $^{17}\text{O}$  hyperfine coupling constants agree well with the experiments, providing a good indication of the reliability of the wave functions. It can also be seen that the relative shortening of  $r_{\text{eff}}$  compared to  $R_{\text{MO}}$  in the series of  $\text{M}(\text{H}_2\text{O})_6^{2+}$  complexes follows the same trend as  $a_0$ , i.e., a large difference between  $r_{\text{eff}}$  and  $R_{\text{MO}}$  is accompanied by a large hyperfine coupling

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Table I. Energetics and Gross Atomic Populations for Ground States of  $M(H_2O)_6^{2+}$  and  $M^{2+}$ 

property	Mn	Fe	Co	Ni <sup>d</sup>	Cu
ground state: <sup>a</sup>					
$M(H_2O)_6^{2+}$	<sup>6</sup> A <sub>1g</sub>	<sup>3</sup> T <sub>2g</sub>	<sup>4</sup> T <sub>1g</sub>	<sup>3</sup> A <sub>2g</sub>	<sup>2</sup> E <sub>g</sub>
$M^{2+}$	<sup>6</sup> S	<sup>5</sup> D	<sup>4</sup> F	<sup>3</sup> F	<sup>2</sup> D
total energy, au					
$M(H_2O)_6^{2+}$	-1602.4073	-1714.7489	-1833.4486	-1958.6962	-2090.4404
$M^{2+}$	-1146.8942	-1259.2096	-1377.8780	-1503.1050	-1634.8589
hydration energy, <sup>b</sup> kJ mol <sup>-1</sup>					
calcd	1553	1622	1704	1754	1733
exptl <sup>c</sup>	2519	2757	2849	2933	3064
gross atomic population in hexaaquo ion					
M	23.469	24.502	25.485	26.485	27.459
O	8.720	8.716	8.724	8.731	8.732
H	0.596	0.597	0.600	0.594	0.601
spin population (normalized to unity)					
M	0.9894	0.9855	0.9702	0.9502	0.9392
O	0.0011	0.0019	0.0042	0.0073	0.0093
H	0.0003	0.0003	0.0004	0.0005	0.0004

<sup>a</sup>  $O_h$  point group notation is used for  $M(H_2O)_6^{2+}$ . <sup>b</sup>  $E_{tot}(H_2O) = -75.8202$ . <sup>c</sup> From ref 21. <sup>d</sup> From ref 13.

Table II. Internuclear Metal-Oxygen Distances,  $R_{MO}$ , and the Corresponding  $r_{eff}$  Calculated with Different Approximations for  $M(H_2O)_6^{2+}$ 

approximation	Mn	Fe	Co	Ni	Cu
$R_{MO}$	4.195	4.195	3.949	3.894	3.798
$r_{eff}$ , ab initio	4.153 (1%)	4.000 (5%)	3.599 (9%)	3.306 (15%)	3.256 (14%)
$r_{eff}$ , pseudo-one-center	4.111 (2%)	3.967 (5%)	3.540 (10%)	3.233 (17%)	3.192 (16%)
$r_{eff}$ , one-center	3.852 (8%)	3.669 (13%)	3.277 (17%)	2.933 (25%)	2.877 (24%)
$r_{eff}$ , free ion wave function	4.195	4.186	3.927	3.852	3.771

<sup>a</sup> All distances are in atomic units (1 au = 0.5292 Å). The values in parentheses are the relative reductions of  $r_{eff}$  compared to  $R$ .

Table III. Internuclear Metal-Hydrogen Distances,  $R_{MH}$ , and the Corresponding  $r_{eff}$  Calculated with Different Approximations for  $M(H_2O)_6^{2+}$ 

approximation	Mn	Fe	Co	Ni	Cu
$R_{MH}$	5.492	5.492	5.255	5.206	5.110
$r_{eff}$ , ab initio	5.481 (0%)	5.471 (0%)	5.221 (1%)	5.160 (1%)	5.071 (1%)
$r_{eff}$ , pseudo-one-center	5.407 (2%)	5.396 (2%)	5.081 (3%)	4.939 (3%)	4.866 (5%)
$r_{eff}$ , one-center	5.061 (8%)	4.982 (9%)	4.626 (12%)	4.384 (16%)	4.303 (16%)
$r_{eff}$ , free ion wave function	5.492	5.489	5.249	5.194	5.102

<sup>a</sup> All distances are in atomic units (1 au = 0.5292 Å). The values in parentheses are the relative reductions of  $r_{eff}$  compared to  $R$ .

Table IV. Calculated and Experimental Hyperfine Coupling Constants  $a_O$  and  $a_H$  in  $M(H_2O)_6^{2+}$  (All Values in MHz)

hyperfine coupling constant	Mn	Fe	Co	Ni	Cu
<sup>17</sup> O, calcd	-8.08	-10.1	-19.4	-31.3	-33.8
<sup>17</sup> O, exptl	$\pm 7^{24}$	-11 <sup>25</sup>	-17 <sup>26</sup>	-28 <sup>25</sup>	-33 <sup>27</sup>
<sup>1</sup> H, calcd	0.612	0.453	0.647	0.804	0.770
<sup>1</sup> H, exptl	0.62 <sup>28</sup>	0.50 <sup>29</sup>	0.37 <sup>30</sup>	0.13 <sup>28</sup>	0.15 <sup>29</sup>

constant. In Figure 1, we plot the  $r_{eff}/R_{MO}$  ratio versus  $a_0$ . No clear quantitative relationship can be seen in the figure. We thus conclude that qualitative arguments relating the magnitude of the deviation from the Solomon-Bloembergen equation<sup>31</sup> to hyperfine coupling constant are reasonable. Further, the qualitative explanations of the origin of the variation of  $a_0$  as a function of the metal ion<sup>32,33</sup> (based on ligand field theory argument) may probably also be employed to rationalize the dependence of the  $r_{eff}/R_{MO}$  ratio on the metal. On the other hand, the attempts to use the measured hyperfine coupling constants to provide a quantitative measure of the deviations from the point dipole approximation<sup>7,12,34</sup> seem to lack a sound foundation.

The ab initio calculated  $r_{eff}$  for hydrogen, given in Table III, are in all cases within 1% of the  $R_{MH}$  values, thus in agreement

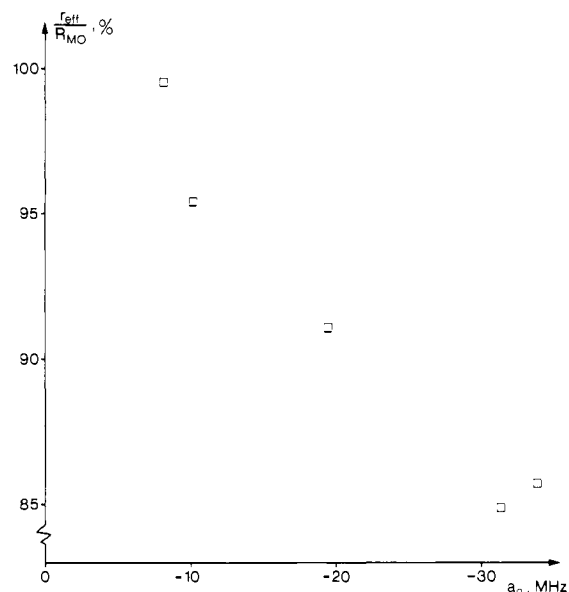


Figure 1. Plot of calculated  $r_{eff}/R_{MO}$  ratio vs. calculated oxygen-17 hyperfine coupling constants.

with the semiempirical calculations of Waysbort and Navon<sup>10</sup> for  $Mn(H_2O)_6^{2+}$ . The smallness of the effects is gratifying in view of the wide application of the Solomon-Bloembergen equation to the interpretation of proton relaxation enhancement data for water coordinated to the metal site in biological macromolecules.<sup>5</sup>

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The correlation of the small differences between  $R_{MH}$  and  $r_{eff}$  with oxygen and proton hyperfine coupling constants does not seem meaningful. On the other hand, it is of interest to comment on the calculated proton hyperfine coupling constants themselves. They show no clear trend in the series of the  $M(H_2O)_6^{2+}$  complexes. The good agreement with the experiment for  $Mn(H_2O)_6^{2+}$  and  $Fe(H_2O)_6^{2+}$  may therefore be fortuitous. It should, in this connection, be borne in mind that the absolute values of the calculated spin densities at the sites of the protons are very small, two orders of magnitude smaller than their counterpart at the sites of the oxygen atoms.

The next point to discuss concerns the effects of neglecting certain integrals in eq 3. It can be seen in Tables II and III that the pseudo-one-center approximation is reasonable for the case of oxygen, but that the errors in the calculated  $r_{eff}$  for the hydrogen atoms are not quite negligible. The use of the real one-center approximation, i.e., the neglect of the effect of the electron-spin distribution on one atom on the spin-differential field gradient on another center, should on the other hand definitely be avoided, because it gives a very substantial underestimation of  $r_{eff}$ . It is in this connection interesting to note a correlation between the type of field gradient integral treatment and the conclusions about the validity of the point dipole approximation reached by different authors. Thus, Waysbort and Navon,<sup>9,10</sup> who postulated small deviations from the point dipole approximation for protons in simple inorganic ligands, seem to have included all the integrals. On the other hand, Doddrell, Gottlieb, and co-workers<sup>7,8</sup> make approximations similar to our one-center or pseudo-one-center and suggest much larger deviations from the Solomon-Bloembergen equation in the case of acetylacetonate complexes.

In conclusion, the calculations performed in this work show that the point dipole approximation inherent in the Solomon-Bloembergen equation is well motivated for the water protons in the series  $M(H_2O)_6^{2+}$ . For the oxygen atoms the deviations vary strongly with metal ion. It is considerable for copper(II) and nickel(II), whereas for manganese(II) it is practically negligible. In biological

applications where manganese(II) is often used, the symmetry of the complexes will be different than for the hexaquo complexes. All ligands will not be the same and tetrahedral coordination may also occur. However, we believe that for the case of water protons coordinated to  $Mn^{2+}$  which is bound to an enzyme, the above conclusion will still hold. This must of course be tested by further calculations on other complexes. These calculations are currently in progress at this laboratory.

The above discussion does however not imply that the application of the Solomon-Bloembergen expression for  $T_{11}^{-1}$  (given in eq 4) to the study of water binding to metal enzymes in general is straightforward. The explicit form of the spectral density term  $J(\omega_i, \tau_j)$  in eq 4 which is usually applied<sup>3-5</sup> is valid only under the condition that the electron spin relaxation times are longer than the relevant correlation time (the Redfield limit). For the case of  $S > 1/2$  ions bound to macromolecules as well as in some other situations, this condition may not be fulfilled. Various attempts to generalize the form of the spectra density term to cover the non-Redfield limit have been presented,<sup>11,35-40</sup> but none of the suggested treatments is completely general.

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**Registry No.**  $Mn(H_2O)_6^{2+}$ , 15365-82-9;  $Fe(H_2O)_6^{2+}$ , 15365-81-8;  $Co(H_2O)_6^{2+}$ , 15276-47-8;  $Cu(H_2O)_6^{2+}$ , 14946-74-8.

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## Nuclear Magnetic Resonance Studies of Terpenes with Chiral and Achiral Lanthanide(III)-Silver(I) Binuclear Shift Reagents

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**Abstract:** Certain binuclear metal  $\beta$ -diketonate complexes consisting of a lanthanide(III) tetrakis chelate anion with a silver(I) counterion are effective NMR shift reagents for olefinic and aromatic substrates. The silver in the ion pair forms a bond with the olefinic or aromatic, and shifts are observed in the NMR spectrum of the substrate because of the proximity of the paramagnetic lanthanide. Significant alterations are produced in the complex NMR spectra of terpenes such as  $\alpha$ - and  $\beta$ -pinene, camphene, and  $\Delta$ -3-carene in the presence of these shift reagents. In contrast with the excellent shifts in the spectra of olefins and aromatic compounds observed with fluorinated  $\beta$ -diketonate complexes of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione or (trifluoroacetyl)-*d*-camphor, shifts with 2,2,6,6-tetramethyl-3,5-heptanedione chelates are much smaller. In addition, through proper choice of a chiral lanthanide chelate and silver  $\beta$ -diketonate, it is possible to distinguish certain dextro and levo resonances of enantiomers.

We have recently reported the development of new silver-containing NMR shift reagents that are effective for aromatics, olefins, halogenated compounds, and phosphines.<sup>1,2</sup> The shift

reagents are binuclear complexes formed in solution from a lanthanide(III)  $\beta$ -diketonate and silver(I)  $\beta$ -diketonate. We believe that an ion pair involving a tetrakis lanthanide chelate anion is formed. The silver cation is capable of bonding to a soft Lewis

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