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Density Functional Calculation of the Electric Field Gradient in Cadmium Complexes: Comparison with Hartree−Fock, Second-Order Møller−Plesset, and Experimental Results

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Density functional B3LYP calculations of the electric field gradient at the metal site in small linear cadmium model complexes and two larger structures are presented. The results are compared to those by Hartree−Fock, second-order Møller−Plesset, and experiment. The quality of the cadmium basis set is tested by augmenting the uncontracted basis set of Kellö and Sadlej with additional basis functions. B3LYP generally gives an electric field gradient which is smaller in magnitude than Hartree−Fock with a reduction of the electric field gradient in the range 0.1−1.4 atomic units (au) or 15−30% for the examined complexes. This reduction of the electric field gradient seems to be caused by a larger cancellation of p- and d-contributions from the Cd atomic orbitals than for the other methods. The second-order Møller−Plesset result for the electric field gradient lies between B3LYP and Hartree−Fock, except for the complex chloroglycylglycinato(imidazole)-cadmium. The changes of the electric field gradient between tested basis sets are up to 0.2 au or 6% and smaller than the variations between different methods. The addition of tight functions to the cadmium basis set has a smaller effect than extra basis functions in the range already spanned. Comparing to experiment, B3LYP gives the best result for dimethylcadmium. For the two larger cadmium complexes Hartree−Fock and second-order Møller−Plesset are closer to the measured values, but crystal effects are neglected making the comparison with experiment more uncertain than for dimethylcadmium.

1. Introduction

The electric field gradient (EFG) is a sensitive probe of the local charge distribution, because of its r^{-3} dependence. The EFG is influenced by the number and type of ligands of the probe nucleus and the coordination geometry. Determining the EFG via measurement of its nuclear quadrupole interaction (NQI) with the nuclear quadrupole moment by nuclear quadrupole resonance (NQR), Mössbauer, or perturbed angular correlation (PAC) of γ-rays spectroscopies therefore provides valuable information about the structure in the vicinity of the probe.

Especially PAC spectroscopy of ^{111m}Cd has been successfully applied to give information about the local environment and the flexibility of the metal site in Cd-substituted copper and zinc ion containing proteins.[1−9] Usually the coordination geometry and the number and types of ligands bound to the metal ion are derived from the measured NQI frequencies with the angular overlap model.[10] This method is based on empirical NQI frequencies assigned to each ligand.

Alternatively electronic structure calculations are used to interpret PAC spectra without prior reference to experimental data by calculating the EFG at the site of the cadmium nucleus.[11−17] However, it is necessary to include all electrons in the calculation if the electric field gradient is calculated from first principles. Furthermore, correlation effects play an important role in obtaining an exact estimate of the EFG.[13,l8,19] Therefore ab initio calculations of the EFG in molecules are in general limited to lighter (first and second row) elements so far.[18−26]

Density functional theory (DFT) is an alternative approach to include exchange and correlation effects.[27,28] DFT has been very successfully applied to determine the structure and properties of molecular systems in recent years. Especially the calculation of electric field gradients in heavy elements has become feasible by density functional methods.[29−33] Similar to computational effort such as Hartree−Fock calculations, DFT often competes with the accuracy of correlated methods.

Here the performance of the density functional B3LYP method[34] for the calculation of electric field gradients in cadmium complexes is tested. We examine small linear cadmium model complexes and compare the results to Hartree−Fock (HF) and second-order Møller−Plesset (MP2) calculations. The influence of the basis set on the computed EFG is studied in detail with emphasis on the choice of cadmium functions. The results on $CdCl_2$ are compared to high level ab initio[13] and density functional calculations,[29] those on $Cd(CH_3)_2$ to experiment.[35] Two larger cadmium complexes with biologically relevant ligands which have been studied both experimentally[10] and theoretically[13] are examined, too.

2. Methods

The calculations have been performed with the Gaussian98 program[36] on a 400 MHz PentiumII PC with 512 MB of memory, an SGI R10000 workstation, and an SGI Origin 2000 system. If not otherwise stated, the uncontracted basis set of Kellö and Sadlej[37] is used on cadmium and the standard basis set 6-31G(d)[38−42] on ligand atoms. In MP2 calculations the core orbitals on the ligand and the 1s- through 3d-orbitals on cadmium are frozen;[13,15] i.e., determinants with excitations out of these shells are excluded from the perturbation expansion.

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For CdF_2 and $CdCl_2$ the same linear structures as in ref 13 are used to allow comparison of the results. d(Cd−F) = 2.16 Å and d(Cd−Cl) = 2.51 Å are the sums of the covalent radii of cadmium and ligand atoms. Experimentally the upper limit for the $CdCl_2$ bond distance in gas phase is d(Cd−Cl) = 2.284 Å.[43−45] For $Cd(CH_3)_2$, the experimental geometry is[46] d(Cd−C) = 2.112 Å, d(C−H) = 1.09 Å, and θ(H−C−H) = 108.4°.

All other linear cadmium model complexes are constructed as described in ref 15. The cadmium−ligand bond distances are the average of the bond lengths found in the model complexes constituting the experimental basis of the angular overlap model:[10] d(Cd−O) = 2.35 Å for $Cd(H_2O)_2^{2+}$, d(Cd−O) = 2.39 Å for $Cd(CH_3COO)_2$ with the carboxylate coordinating monodentately, d(Cd−S) = 2.61 Å for $Cd(CH_3S)_2$, and d(Cd−N) = 2.26 Å for $Cd(Im)_2^{2+}$. The geometries of water and imidazole are taken from experiment.[47,48] The structures of carboxylate and thiolate are taken from the fragment library of the InsightII program[49] as geometries of aspartate and cysteinate side chains, respectively.

Calculations on the two larger complexes chloroglycylglycinato(imidazole) (CGI) cadmium and 1,5,9,13-tetrathiacyclohexadecane (TTC) cadmium are done on their crystal structure geometries.[50,51] The dimeric unit in CGI cadmium is truncated to the third coordination shell of cadmium. Broken bonds are saturated with hydrogen atoms in standard bond lengths[52] d(C−H) = 1.09 Å and d(N−H) = 1.01 Å.

The electronic contribution to the electric field gradient is the expectation value of

$$V_{ij} = \frac{3r_i r_j - r^2\delta_{ij}}{r^5}$$

The total EFG includes the nuclear contribution of the surrounding ligands. The EFG is reported in diagonal form with V_{xx}, V_{yy}, and V_{zz} in the usual notation $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ or as V_{zz} and $\eta = (V_{xx} - V_{yy})/V_{zz}$. The computed electric field gradient V_{zz} is compared to the measured nuclear quadrupole interaction frequency ν_Q with the relation[53]

$$\nu_Q = |eQV_{zz}|/h$$

While the electronic charge e and the Planck constant h are known very accurately, the experimental uncertainty of the nuclear quadrupole moment Q of ^{111m}Cd gives a range of EFG values even when extracting the EFG from precisely measured NQI frequencies: 1 atomic unit (au) = 195 MHz/s for Q = 0.83 b and 172 MHz/s for Q = 0.73 b. This is the range of published values[54−56] for Q.

3. Results

3.1. Choice of Numerical Parameters. In density functional theory the exchange correlation potential has to be integrated numerically during each self-consistent field (SCF) iteration, even if Gaussian basis functions are used. This introduces a numerical error into the calculation. We tested how this error affects the field gradient calculation for two small complexes $CdCl_2$ and $Cd(CH_3)_2$. It was seen that in these two complexes the field gradient is changed by the order of 10^{-3} au for different integration grids: 75 302, 87 434, 99 590, 111 770, and 123 974, where the first two or three digits give the number of radial shells around each atom and the last three digits the number of angular points in each shell. We choose the so-called fine grid with 75 radial shells and 302 angular points for all subsequent DFT calculations. This choice of grid also leads to the lowest energy among the tested grids. The energy does not necessarily decrease with increasing grid size.

Another numerical parameter that might influence the accuracy of the result is the convergence criterion in the SCF procedure. We examined the B3LYP result for the field gradient, when the root-mean-square deviation of the density matrix elements is converged to 10^{-N} au and the maximum deviation is converged to $10^{-(N-2)}$ au. For values of $N \geq 6$ the change of the field gradient is below 10^{-4} au and therefore even smaller than the error obtained by numerical integration. We choose $N = 6$ for all further calculations, but $N = 5$ and probably also $N = 4$ seem to be sufficient to get the EFG within 5×10^{-3} au.

3.2. Comparing B3LYP, Hartree−Fock, and MP2. Table 1 shows the calculated electric field gradients at the site of the cadmium nucleus in a series of small linear two-coordinate model complexes given by Gaussian/B3LYP, HF, and MP2. At the MP2 level of theory, the correlation effect shown by the linear complexes consists in the reduction of the absolute value of the electric field gradient of about 9%, ranging from 0.05 au or 2% in $Cd(H_2O)_2^{2+}$ to 0.58 au or 15% in $Cd(CH_3S)_2$. The influence of inner-shell excitations on the MP2 result was tested for CdF_2, $CdCl_2$, and $Cd(CH_3)_2$. A full MP2 calculation results in $V_{zz} = -3.439$, -3.126, and -6.055 au, i.e., a further reduction of the EFG by 16 (0.5%) and 9×10^{-3} au (0.3%) for the two polar molecules and a change less than 10^{-3} au for $Cd(CH_3)_2$ (see also ref 13).

The magnitude of the electric field gradient calculated by B3LYP density functional theory is in all cases smaller than both HF and MP2 results. The magnitude of the B3LYP value for the electric field gradient is about 25% smaller than the HF value, the difference ranging from 0.39 au or 18% of the HF value in $Cd(H_2O)_2^{2+}$ to 1.16 au or 30% in $Cd(CH_3S)_2$ and 1.42 au or 18% in $Cd(CH_3)_2$. Compared to MP2, B3LYP also reduces the EFG, but the reduction is about 17% and smaller than that of the HF result. The discrepancy between the reduction of the MP2 and the HF results by B3LYP is least pronounced in $Cd(H_2O)_2^{2+}$, where the HF and the MP2 values are very similar. For $Cd(CH_3)_2$, on the other hand, the B3LYP reduction of the MP2 result amounts to one-third the B3LYP reduction of the HF result. Here the MP2 value for the electric field gradient is closer to the B3LYP than to the HF result.

B3LYP calculations are performed at about the same cost as HF calculations. The MP2 calculations, on the other hand, require significantly more computing time, ranging from a factor of 2 for the small linear model complexes in Table 1 to a factor of about 15 (see Table 6 below) for larger complexes, where disk space and memory requirements restrict to the use of a supercomputer.

According to density functional theory the electronic ground state density is given by minimizing an existing functional.[27,28] The relation of the functional to the Hamiltonian of the system, however, is unknown. For practical applications exchange-correlation potentials are determined by fitting numerical or experimental results on a representative set of molecules.[57−60] Table 2 shows how the choice of the exchange-correlation potential influences the value of the electric field gradient for the different hybrid potentials that are implemented in Gaussian98. The variation of the computed electric field gradients is 0.44 au or 17% for $CdCl_2$ and 0.59 au or 11% for $Cd(CH_3)_2$. The B3LYP result is always at the lower end of the range of the absolute values and all absolute values are smaller than the MP2 result for $CdCl_2$, while for $Cd(CH_3)_2$ BHandH and BHandHLYP give larger values than MP2.

TABLE 1: Comparison of B3LYP with HF and MP2 for Small Linear Cadmium Complexes (Structures Described in the Text)[a]

	Cd−L		B3LYP	HF	MP2	nuclear EFG
CdF_2	2.16	E	−5667.2151	−5663.9377	−5664.9306	
		V_{zz}	−2.685	−3.824	−3.455	0.529
		CPU	21:35.9	24:31.5	50:23.7	
$CdCl_2$	2.51	E	−6388.0002	−6384.1218	−6385.0119	
		V_{zz}	−2.516	−3.483	−3.135	0.637
		CPU	18:35.0	27:26.5	1:4:55.6	
$Cd(CH_3)_2$[b]	2.112	E	−5547.3171	−5544.2280	−5545.1673	
		V_{zz}	−5.585	−7.004	−6.054	0.449
		CPU	16:54.0	27:55.0	59:57.1	
$Cd(H_2O)_2^{2+}$[c]	2.35	E	−5619.6624	−5616.4770	−5617.4370	
		V_{zz}	−1.771	−2.163	−2.114	0.404
		CPU	22:3.9	24:18.4	1:0:24.2	
$Cd(CH_3COO)_2$[d]	2.39	E	−5924.4865	−5919.5035	−5921.3563	
		V_{zz}	−2.227	−2.985	−2.827	0.560
		η	0.09	0.08	0.06	0.18
		CPU	2:2:19.3	1:20:9.0	4:21:3.8	
$Cd(CH_3S)_2$	2.61	E	−6343.7504	−6339.3277	−6340.4830	
		V_{zz}	−2.742	−3.901	−3.323	0.609
		η	0.34	0.20	0.27	0.09
		CPU	59:6.7	51:56.0	2:1:32.3	
$Cd(Im)_2^{2+}$[e]	2.26	E	−5919.4207	−5914.2190	−5916.2291	
		V_{zz}	−3.037	−3.967	−3.575	0.639
		CPU	2:59:34.9	1:42:51.8	6:36:17.6	

[a] Bond length in Å, E and V_{zz} in au, CPU time in h:min:s. $\eta = 0$ if not otherwise mentioned. Calculations performed on a 400 MHz PentiumII PC with 512 MB of memory. MP2 read the converged HF wave function as initial guess. The last column gives the nuclear contribution in the total EFG reported. [b] Experimental geometry (ref 46). [c] $H_2O \perp H_2O$. [d] COO coordinates monodentately. [e] Im ⊥ Im.

TABLE 2: Test of Different Hybrid Functionals[a]

	$CdCl_2$		$Cd(CH_3)_2$	
	E	V_{zz}	E	V_{zz}
B3LYP	−6388.0002	−2.516	−5547.3171	−5.585
B3P86	−6389.8609	−2.597	−5548.8617	−5.654
B3PW91	−6387.9565	−2.621	−5547.3521	−5.671
B1LYP	−6387.9536	−2.587	−5547.2351	−5.673
MPW1PW91	−6388.3612	−2.702	−5547.6423	−5.771
BHandH	−6382.1493	−2.940	−5542.9118	−6.161
BHandHLYP	−6387.9497	−2.951	−5547.2220	−6.172

[a] E and V_{zz} in au.

3.3. Basis Set Effects. In order to determine the quality of our basis set for field gradient calculation, we performed a basis set study including tight functions on cadmium, but also diffuse functions and tests of different basis sets on the ligands. Table 3 shows for $CdCl_2$ and $Cd(CH_3)_2$ the effect on the calculated electric field gradient at the cadmium nucleus when Dunning's correlation consistent basis sets[61−66] are used on the ligand instead of 6-31G(d). Going from 6-31G(d) to cc-pVDZ, the magnitude of the electric field gradient is reduced by 28×10^{-3} au or 1% for $CdCl_2$ and by 54×10^{-3} au or 1% for $Cd(CH_3)_2$. Changing to triple, quadruple, and quintuple zeta functions on the ligand, the magnitude of the field gradient increases to a value closer to the 6-31G(d) result.

Adding diffuse functions to the ligand basis set in most cases increases the magnitude of the electric field gradient at Cd between 1% and 2% or 50×10^{-3} au. For $Cd(CH_3)_2$ exceptions are the 6-31+G(d) basis set, which results in a slightly smaller EFG at Cd than 6-31G(d), and AUG-cc-pV5Z, which gives a 50×10^{-3} au or 1% smaller electric field gradient than cc-pV5Z. Altogether the changes introduced by different ligand basis sets are about 1−2% for the two complexes under consideration. Increasing the ligand basis set size leads to a 987 and 523×10^{-3} au lower total energy for $CdCl_2$ and $Cd(CH_3)_2$, respectively.

To improve Kellö and Sadlej's uncontracted basis set on cadmium[37] for field gradient calculation, we follow the idea suggested in ref 19 and add tight basis functions by choosing the largest exponent for every angular momentum and multiplying it by 3. As can be seen from Table 4, the most pronounced effect arises from the additional d-functions, which increase the magnitude of the electric field gradient by 30×10^{-3} au, while the additional tight f-functions decrease the magnitude of the EFG by 10×10^{-3} au. Additional tight s- and p-functions change the EFG by about 10^{-3} au, so that the composite effect of one set of additional tight functions for each angular momentum increases the magnitude of the EFG by 20×10^{-3} au compared to the original basis set.

An analoguous way to add diffuse basis functions is to divide the smallest exponent for each angular momentum by 3. This decreases the magnitude of the EFG except for additional p- and f-functions on $CdCl_2$. The total reduction introduced by all additional diffuse functions is 10^{-3} au for $CdCl_2$ and 14×10^{-3} au for $Cd(CH_3)_2$. The effects of additional tight and diffuse functions on the electric field gradient as well as on the total energy are almost additive when included simultaneouosly into the cadmium basis set.

Repeating this procedure results in an additional increase of the electric field gradient when two, three, four, and five sets of tight s-, p-, d-, and f-functions are added to the uncontracted cadmium basis set of Kellö and Sadlej (Table 5). The decreasing variation of the electric field gradient with increasing number of additional tight functions—from four to five additional tight functions the change of the electric field gradient is less than 10^{-3} au for $CdCl_2$ and slightly larger than 10^{-3} au for $Cd(CH_3)_2$—suggests that the electric field gradient converges by this procedure. Its absolute value is 32×10^{-3} au or about 1% larger than the value for the uncontracted basis set of Kellö and Sadlej without additions for $CdCl_2$ and 47×10^{-3} au or less than 1% larger for $Cd(CH_3)_2$. Additional sets of diffuse basis functions on cadmium do not cause a change larger than 10^{-3} au.

We added several different basis functions with exponents in the range already spanned, too. The largest effect was found by adding one single p-function to the uncontracted basis set

TABLE 3: Influence of Ligand Basis Set on B3LYP Result[a]

		$CdCl_2$		$Cd(CH_3)_2$	
			+ diffuse		+ diffuse
6-31G(d)	E	−6388.0002	−6388.0049	−5547.3171	−5547.3216
	V_{zz}	−2.516	−2.517	−5.585	−5.560
cc-pVDZ	E	−6388.0511	−6388.0583	−5547.3203	−5547.3280
	V_{zz}	−2.488	−2.531	−5.531	−5.584
cc-pVTZ	E	−6388.0819	−6388.0845	−5547.3559	−5547.3585
	V_{zz}	−2.526	−2.569	−5.526	−5.593
cc-pVQZ	E	−6388.0905	−6388.0921	−5547.3631	−5537.3657
	V_{zz}	−2.535	−2.570	−5.549	−5.580
cc-pV5Z	E	−6388.0974	−6488.0989	−5547.3667	−5547.3694
	V_{zz}	−2.541	−2.578	−5.564	−5.515
expt[b] $\lvert V_{zz}\rvert$					
	$Q = 0.73$ b			5.515	
	$Q = 0.83$ b			4.851	

[a] E and V_{zz} in au. [b] Reference 53.

TABLE 4: Effect of One Set of Additional Tight and Diffuse Cadmium Basis Functions for Each Angular Momentum on B3LYP Result[a]

		$CdCl_2$			$Cd(CH_3)_2$		
		+ tight		+ diffuse	+ tight		+ diffuse
none	E		−6388.0002			−5537.3171	
	V_{zz}		−2.516			−5.585	
s	E	−6388.0011		−6388.0002	−5547.3180		−5547.3172
	V_{zz}	−2.517		−2.516	−5.585		−5.585
p	E	−6388.0006		−6388.0003	−5547.3175		−5547.3173
	V_{zz}	−2.517		−2.517	−5.587		−5.583
d	E	−6388.0019		−6388.0026	−5547.3188		−5547.3188
	V_{zz}	−2.546		−2.510	−5.616		−5.580
f	E	−6388.0002		−6388.0017	−5547.3172		−5547.3190
	V_{zz}	−2.507		−2.521	−5.573		−5.576
all	E	−6388.0032		−6388.0041	−5547.3201		−5547.3208
	V_{zz}	−2.538		−2.516	−5.607		−5.571
tight + diffuse	E		−6388.0071			−5547.3237	
	V_{zz}		−2.538			−5.594	

[a] E and V_{zz} in au.

TABLE 5: Effect of *n* Sets of Additional Tight and Diffuse Cadmium Basis Functions for All Angular Momenta on B3LYP Result[a]

		$CdCl_2$			$Cd(CH_3)_2$		
n		+ tight		+ diffuse	+tight		+ diffuse
0	E		−6388.0002			−5547.3171	
			(−6387.9906)			(−5547.3093)	
	V_{zz}		−2.516			−5.585	
			(−2.368)			(−5.400)	
1	E	−6388.0032		−6388.0041	−5547.3201		−5547.3208
	V_{zz}	−2.538		−2.516	−5.607		−5.571
2	E	−6388.0046		−6388.0043	−5547.3215		−5547.3209
	V_{zz}	−2.550		−2.516	−5.624		−5.572
3	E	−6388.0046		−6388.0043	−5547.3215		−5547.3209
	V_{zz}	−2.543		−2.516	−5.624		−5.573
4	E	−6388.0046		−6388.0044	−5547.3216		−5547.3209
	V_{zz}	−2.548		−2.516	−5.633		−5.573
5	E	−6388.0047		−6388.0044	−5547.3216		−5547.3209
	V_{zz}	−2.548		−2.516	−5.632		−5.573
5 tight + 5 diffuse	E		−6388.0088			−5547.3254	
	V_{zz}		−2.548			−5.620	

[a] E and V_{zz} in au. The results for the contracted basis set of Kellö and Sadlej[37] are given in parentheses.

of Kellö and Sadlej with the exponent 0.2952 au It increases the magnitude of the electric field gradient on cadmium in $CdCl_2$ by 75 × 10^{-3} au (3%) and in $Cd(CH_3)_2$ by 126 × 10^{-3} au (2.5%).

Additional g-functions are included in the cadmium basis with the exponent chosen to minimize the total energy among a given discrete set of considered values. The value of the g-exponent with the lowest energy depends on the complex as well as the on the ligand basis set, probably also on the cadmium basis: 0.4185 au for $CdCl_2$ with cc-pVDZ on the ligand, 0.1310 au for $CdCl_2$ with cc-pVTZ on the ligand and $Cd(CH_3)_2$ with cc-pVDZ or cc-pVTZ on the ligand. In all four cases the cadmium basis set was augmented with p- (0.2952 au), d- (0.04088 au), and f-functions (0.04088 au). The g-exponent with the largest effect on the electric field gradient, 1.337 au in all cases, does not have lowest energy. The total change of the EFG is 15 and 16 × 10^{-3} au for $CdCl_2$ and $Cd(CH_3)_2$, respectively, and far below 1%.

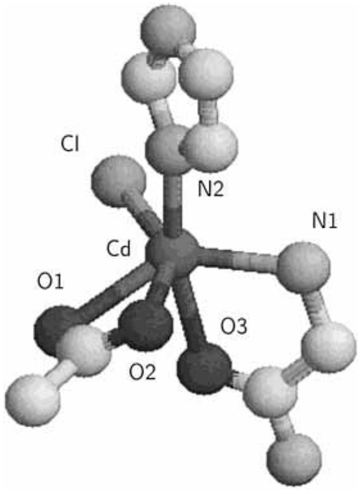

Figure 1. Structure of chloroglycylglycinato(imidazole) (CGI) cadmium[50] truncated to the third coordination shell of cadmium. d(Cd−Cl) = 2.47 Å, d(Cd−N1) = 2.31 Å, d(Cd−N2) = 2.30 Å, d(Cd−O1) = 2.41 Å, d(Cd−O2) = 2.42 Å, d(Cd−O3) = 2.42 Å. The image was generated with RasMol.[72]

The largest observed change of the electric field gradient obtained by adding extra basis functions to the uncontracted basis set of Kellö and Sadlej on cadmium amounts to an increase of 141 × 10^{-3} au or 5.7% for $CdCl_2$ and an increase of 165 × 10^{-3} au or 3.2% for $Cd(CH_3)_2$. The magnitude of this change is similar to the difference between the EFGs for the contracted and the uncontracted cadmium basis: 148 and 185 × 10^{-3} au for $CdCl_2$ and $Cd(CH_3)_2$, respectively (see Table 5). The largest variation of the total energy is about 10 × 10^{-3} au and smaller than the energy gain due to uncontraction (96 × 10^{-3} au for $CdCl_2$ and 78 × 10^{-3} au for $Cd(CH_3)_2$). In general, additional tighter functions on cadmium lead to slightly larger field gradients than additional more diffuse functions, whereas additional more diffuse functions on cadmium lead to slightly lower total energy than additional tighter functions.

3.4. The Complexes Chloroglycylglycinato(imidazole)-cadmium and 1,5,9,13-Tetrathiacyclohexadecanecadmium. In cadmium-substituted zinc enzymes the coordination number of the metal ion is larger than 2. Therefore two six-coordinate complexes with biologically relevant ligands are examined by B3LYP density functional theory, too. In chloroglycylglycinato-(imidazole) (CGI) cadmium each cadmium ion is coordinated to a chloride ion, the imino nitrogen of an imidazole, the terminal amino nitrogen and carbonyl oxygen of one glycylglycine, and the two carboxylate oxygens of a second glycylglycine, in a distorted octahedral geometry[50] (Figure 1). 1,5,9,13-Tetrathiacyclohexadecane (TTC) cadmium is involving a nearly square-planar array of thioether sulfur atoms around the cadmium provided by an encircling tetradentate macrocyclic ligand and two perchlorate anions that occupy apical positions to complete an elongated octahedral geometry[51] (Figure 2).

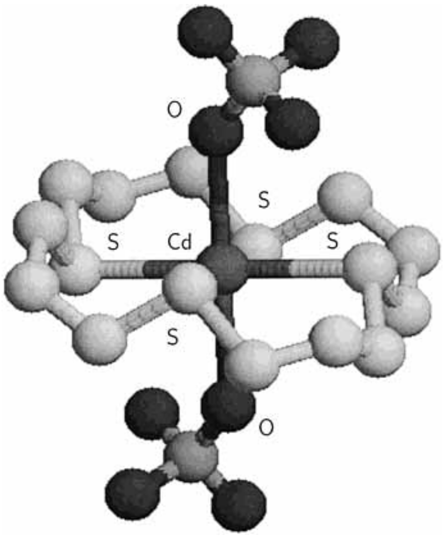

Figure 2. Structure of 1,5,9,13-tetrathiacyclohexadecane (TTC) cadmium.[51] d(Cd−S) = 2.62 Å, d(Cd−O) = 2.43 Å. The image was generated with RasMol.[72]

In TTC cadmium the calculated (Table 6) and measured EFGs are almost axial ($\eta \approx 0.1$). The computation shows the same tendency as observed in the linear complexes. The Hartree−Fock calculation results in the EFG with the largest absolute value. Correlation effects at the MP2 level of theory reduce the electric field gradient by 0.19 au or 15%. V_{zz} calculated with B3LYP is smaller than the HF value by 0.36 au or 28% and smaller than the MP2 value by 0.17 au or 15%. The asymmetry parameter is $\eta = 0.12$ in B3LYP and 0.11 in MP2, whereas HF gives a value of $\eta = 0.06$. As for $CdCl_2$ and $Cd(CH_3)_2$ (Table 3) changing to cc-pVDZ as ligand basis set further decreases the EFG by 0.04 au or 5%. Comparison with ref 13 shows that the effect of uncontraction on the calculated electric field gradient is to increase the Hartree−Fock result by 0.08 au or 6%.

In CGI cadmium a larger asymmetry of the EFG is estimated ($\eta \approx 0.6$) and measured ($\eta \approx 0.4$). Here the MP2 calculation increases V_{zz} by 0.02 au or 4% and decreases the asymmetry from $\eta = 0.61$ to 0.36 compared to the HF result. In contrast B3LYP density functional theory reduces the HF estimate of the electric field gradient by 0.08 au or 15% and the MP2 result by 0.10 au or 18% and gives $\eta = 0.51$. The crystal of CGI cadmium contains a dimer as unit. The EFG calculation on the dimer shows that the Hartree−Fock and the B3LYP results are reduced by 0.02 au or 3% and 0.03 au or 6%, respectively, compared to the situation when only half the dimer is included in the calculation, and the asymmetry is increased by 0.11 and 0.07 in each case. Changing the ligand basis set from 6-31G(d) to cc-pVDZ merely has an effect on the result of the EFG calculation.

4. Discussion

4.1. Variation of the Electric Field Gradient with Method and Basis Set.

To determine the accuracy and efficiency of density functional methods for electric field gradient calculation, we performed a series of B3LYP calculations on small linear Cd complexes and two larger structures. Employing default convergence criteria and integration grid sizes in Gaussian98,[36] the numerical errors are of the magnitude 10^{-3} au and do not significantly affect the results. Uncertainty of structure determinations and methodological limitations such as inadequate treatment of electron correlation, basis set truncation, and neglect of relativistic effects cause much larger errors than the numerical inaccuracy.

The largest differences for the calculated EFG values are found in application of different levels of theory. The HF result of the electric field gradient is reduced when including electron correlation by a second-order Møller−Plesset calculation. A similar observation is made in refs 13 and 19. Density functional B3LYP calculations lead to a further reduction of the MP2 estimate. The six-coordinate TTC cadmium complex with an almost axial electric field gradient shows this behavior like the linear cadmium complexes.

TABLE 6: Comparison of B3LYP with HF and MP2 for Two Larger Complexes[a]

	E	V_{xx}	V_{yy}	V_{zz}	η	CPU
			CGI Cadmium			
HF/6-31G(d)[b]	−6639.4655	0.110	0.447	−0.556	0.61	2:48:49.2
HF/6-31G(d)[c]	−13276.628	0.076	0.462	−0.538	0.72	1:10:11:12.4
MP2/6-31G(d)[b]	−6642.2856	0.185	0.392	−0.577	0.36	20:25:21.1
B3LYP/6-31G(d)[b]	−6646.8191	0.116	0.359	−0.474	0.51	4:46:14.1
B3LYP/6-31G(d)[c]	−13291.249	0.093	0.352	−0.445	0.58	12:17:55.5
B3LYP/cc-pVDZ[c]	−13291.414	0.088	0.356	−0.444	0.60	1:12:17:59.4[e]
nuclear EFG[b]		−0.016	−0.125	0.141	0.77	
nuclear EFG[c]		−0.078	−0.164	0.242	0.36	
expt[d]						
$Q = 0.73$ b		0.26	0.56	−0.81	0.37	
$Q = 0.83$ b		0.23	0.49	−0.71		
			TTC Cadmium			
HF/6-31G(d)	−9040.2835	−0.602	−0.683	1.285	0.06	4:53:44.7
MP2/6-31G(d)	−9044.7280	−0.485	−0.609	1.094	0.11	4:3:3:29.1
B3LYP/6-31G(d)	−9053.1150	−0.410	−0.519	0.929	0.12	7:49:29.7
B3LYP/cc-pVDZ	−9053.2370	−0.390	−0.496	0.886	0.12	22:0:55.3[e]
nuclear EFG		0.015	0.058	−0.073	0.59	
expt[d]						
$Q = 0.73$ b		−0.62	−0.74	1.36	0.09	
$Q = 0.83$ b		−0.55	−0.65	1.19		

[a] 6-31G(d) or cc-pVDZ on ligand atoms. E, V_{xx}, V_{yy}, and V_{zz} in au, CPU time in d:h:min:s. Calculations performed on an SGI Origin 2000 system. MP2 read the converged HF wave function as initial guess. The last lines give the nuclear contribution in the total EFG reported. [b] Half dimer. [c] Dimer. [d] Reference 13, sign has been chosen in accord with computation. [e] Performed on an IBM RS6K SP supercomputer.

TABLE 7: Anisotropy of the *l*th Subshell on Cadmium in $CdCl_2$ and $Cd(CH_3)_2$[a]

	$CdCl_2$				$Cd(CH_3)_2$			
	Δn_p		Δn_d		Δn_p		Δn_d	
n	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF
2	0.0	0.0			0.0	0.0		
3	−0.0	−0.0	0.0	0.0	−0.001	−0.0	0.0	0.0
4	−0.003	−0.002	0.021	0.018	−0.002	0.001	0.058	0.046
5	0.002	−0.011	0.053	0.037	−0.066	−0.076	0.016	0.005
6	−0.172	−0.189	−0.002	−0.002	−0.279	−0.316	−0.0	−0.003
7	−0.162	−0.167	0.0	−0.0	−0.215	−0.261	0.0	0.0
8	0.002	0.0	−0.0	0.0	0.002	0.001	0.0	0.0
9	−0.0	0.0	0.0	0.0	−0.0	0.0	0.0	0.0

[a] $\Delta n_p = (n_x + n_y)/2 - n_z$, $\Delta n_d = n_{xy} + n_{x^2-y^2} - n_{z^2} - (n_{xz} + n_{yz})/2$, where n_i is the Mulliken population of the ith cadmium-centered basis orbital. 6-31G(d) on ligand atoms; the cadmium basis functions are transformed to the HF orbitals from a calculation on the Cd atom. For main quantum numbers $n > 4$, the p- and d-orbitals are unoccupied in the atom. Therefore these orbitals are not the 5p, 5d, ... atomic orbitals.

There is a general trend that B3LYP gives smaller electric field gradients than HF and MP2. Assuming that the EFG can be written approximately $\propto \sum \langle r^{-3} \rangle_l \Delta n_l$ with Δn_l being the anisotropy of the lth subshell,[67] we tested whether the difference between HF and B3LYP is due to the anisotropy or the r^{-3} expectation value. Following the idea of ref 68, we perform a calculation on the neutral Cd atom and print out the contributions of each occupied orbital. Since the contribution of an orbital in the lth shell is proportional to $\langle r^{-3} \rangle_l$, the ratio of the B3LYP and HF contributions is proportional to the ratio of the B3LYP and HF r^{-3} expectation values. They amount to 1.002, 0.994, 1.000, 1.057, and 1.032 for 2p, 3p, 3d, 4p, and 4d, respectively, using Kellö and Sadlej's uncontracted basis set. In ref 68 it is shown that a HF calculation with Gaussian basis functions (the contracted basis set of Kellö and Sadlej is used) underestimates numerical r^{-3} expectation values[69] only by 0.1%.

The estimation of $\langle r^{-3} \rangle$ for the 5p orbital is difficult, since it is unoccupied in Cd at usual oxidation states. In ref 68 the EFG of a doubly occupied 5p orbital in Cd*($5s^0 5p^2$) is calculated at the HF level. However, the B3LYP calculation converges to a $5s^2 5p^0$ ground state. Therefore we performed a calculation on the Cd^{2-} anion. The ratio between $\langle r^{-3} \rangle$ calculated by B3LYP and that by HF is 1.334. That is, the B3LYP result is significantly larger than the HF estimate. It should be mentioned that the HF r^{-3} expectation value for the 5p orbital in Cd^{2-} is only 11% of the result for the excited determinant Cd*($5s^0 5p^2$).

In order to determine the anisotropy of the atomic subshells, we "contract" the Cd basis set to the atomic orbitals of a HF calculation on the Cd atom. Using this contracted basis set, we compare the Mulliken populations of the B3LYP with those of the HF calculation on $CdCl_2$ and $Cd(CH_3)_2$ with the 6-31G(d) basis set on ligands (Table 7). The anisotropies derived by the two methods, though not identical, appear very similar. The anisotropies of the p-shells, which are occupied in the Cd atom, and of the d-shells are slightly larger in the B3LYP than in the HF calculation. The B3LYP calculated anisotropies of the 5th, 6th, and 7th p-type basis functions, which are unoccupied for the atom, are smaller than those of HF. These basis orbitals, which predominantly make up the Cd 5p orbital of the complexes, have the largest anisotropies and consequently make the largest contribution to the EFG. Multiplying their Δn values with the EFGs of the 5th, 6th, and 7th p-type basis functions, a decrease of their contribution by 0.4 au for $CdCl_2$ and 0.65 au for $Cd(CH_3)_2$ is obtained when going from the HF to the B3LYP result. This decrease, however, is almost compensated by an increase of the contribution due to the other shells, and by far does not explain the decrease of the total EFGs by 1 au for $CdCl_2$ and 1.4 au for $Cd(CH_3)_2$ (Table 1).

Altogether the general trend of smaller electric field gradients computed with B3LYP than HF is probably caused by an enhanced cancellation of contributions with opposite sign from the p- and the d-shells, rather than by changes of the r^{-3} expectation value or the anisotropy alone. The effects of changes in the anisotropies seem to compensate each other. Surprisingly, $\langle r^{-3}\rangle$ for the atomic cadmium orbitals has the tendency to be larger for B3LYP than for HF. We note, that despite the formal similarity between the HF and Kohn−Sham equations, orbitals in density functional theory have a different meaning than HF orbitals.[70] Furthermore, ligand contributions to the EFG have to be considered, too. Analysis of the Mulliken charges indicate a smaller polarity of the cadmium−ligand bonds in B3LYP than in HF. Hybrid functionals other than B3LYP, however, result in larger electric field gradients than the B3LYP estimate.

The changes in the EFG when using different basis sets are up to 0.2 au and larger than the inaccuracy introduced by numerical errors, but smaller than the differences between different applied methods. The changes of the EFG at the cadmium nucleus introduced by different ligand basis sets are less pronounced than those caused by additional basis functions centered on cadmium. Adding basis functions to the uncontracted basis set of Kellö and Sadlej on cadmium results in an increase of the electric field gradient similar to that caused by uncontraction of the cadmium basis set. The effect of additional diffuse cadmium basis functions on the calculated electric field gradient is smaller than that of additional tight basis functions. The largest effect is not obtained by additional tight or diffuse functions, but by a p-function with an exponent in the range already spanned. A more systematic method to estimate the basis set truncation error within a particular level of theory which eventually provides a converged value of the electric field gradient in the basis set limit is therefore desirable. In the work of Halkier et al.[19] it is shown that calculations using Gaussian basis functions can come closer than 10×10^{-3} au to numerical Hartree−Fock values of the EFG in diatomic molecules of first row atoms. It should be noted that the variation of the EFG with different basis sets could be an underestimate of the basis set truncation error.

The nuclear EFG is about 1 order of magnitude smaller than the total EFG and has the opposite sign (Tables 1 and 6). Therefore the accuracy of EFG calculation depends primarily on the quality of the computed electronic charge density. That inclusion of inner-shell excitations in MP2 calculation changes the result of the EFG calculation in $CdCl_2$ and CdF_2 by a maximal 0.5% confirms the result of ref 13 that their impact on this level of accuracy is minor. These polar molecules are hard test cases for the ability of the basis set to model polarization of the cadmium core. In ref 68, a detailed analysis of the contributions to the EFG from individual orbitals in Cd^{2+}, Cd, and $CdCl_2$ is presented, using Kellö and Sadlej's contracted basis set.[37] It is shown that 35% of the total EFG in $CdCl_2$ is due to polarization of Cd 1s through 4p. A detailed study of the decomposition of the EFG for the two larger complexes along the line of ref 68 is under way and will be presented in a seperate work.

4.2. Comparison with Other Work. In view of the significant variation of the computed electric field gradients when different methods like MP2 or B3LYP are used, the question arises, which of the different results are the best? For $CdCl_2$ the electric field gradient is measured in the crystalline state and no molecular EFG is available for comparison to date. In ref 13 Hemmingsen and Ryde calculate the molecular EFG for $CdCl_2$ to −3.115 au at the coupled cluster CCSD(T) level of theory with the same geometry and basis set as here. For CdF_2 their result is −3.411 au. Both values are close to the MP2 results (Table 1), about halfway between HF and B3LYP. In ref 29 another DFT method (LAPW) is used to calculate the EFG of crystalline $CdCl_2$ in 18×10^{-3} au or 9% agreement with experiment. By artificially enlarging the unit cell, the authors estimate a gas phase molecular EFG of -35.0×10^{21} V/m^2 = −3.228 au at the equilibrium bond length of 4.22 au = 2.233 Å. Our values of the EFG at this geometry amount to −3.533, −4.834, and −4.213 au for B3LYP, HF, and MP2, respectively. The LAPW estimate is smaller than all these values and closest to the B3LYP result, where the difference is about 0.3 au.

The variation of experimental NQI values for $Cd(CH_3)_2$ determined with PAC measurements is small and nearly independent of the solvent.[35] Therefore, in $Cd(CH_3)_2$ the electric field gradient at the cadmium nucleus is almost entirely of molecular origin, and the results of a gas phase calculation are assumed to be directly comparable to experiment. At 77 K an interaction frequency for the nuclear quadrupole interaction of the cadmium nucleus of $\nu_Q = 946$ MHz is measured.[35] This corresponds to a field gradient of 4.851 au if a quadrupole moment $Q = 0.83$ b is assumed, or 5.515 au for $Q = 0.73$ b. The B3LYP value for $Cd(CH_3)_2$ with the AUG-cc-pV5Z basis set on the methyl groups and the uncontracted basis set of Kellö and Sadlej on cadmium exactly matches the experimental value if a quadrupole moment of $Q = 0.73$ b is assumed (Table 3). The theoretical values for the field gradient in $Cd(CH_3)_2$ in Table 1 with basis 6-31G(d) on ligand do not fall into the experimental range. Compared to HF and MP2, the agreement with experiment using B3LYP is best here.

While for the small complexes $CdCl_2$ and $Cd(CH_3)_2$ B3LYP provides better results than MP2 and HF, in TTC cadmium the HF estimate of the electric field gradient almost exactly matches experiment for the average of $Q = 0.73$ b and $Q = 0.83$ b (Table 6). Both MP2 and B3LYP levels of theory worsen the result. In CGI cadmium all calculated EFGs are smaller than experiment and MP2 gives the result closest to the measured value with almost the exact experimental asymmetry. Again B3LYP shows the worst performance.

It is known from transition metal compounds that the metal orbitals become more contracted with increasing coordination number. Perhaps B3LYP performs worse for the six-coordinate complexes due to overemphasized orbital delocalization characteristic for the majority of density functional methods, while HF wave functions are often too localized. Furthermore, the relativistic effects may be different than in the linear complexes (see also below). However, most important is probably the fact that the experiments were performed on polycrystalline samples, and it is shown in ref 13 that the polarizing effect of the surrounding molecules can change the result by 10−25%. Therefore, calculation and experiment are not directly comparable.

4.3. Relativistic Effects. Relativistic effects have not been treated in these calculations, although they are known to be quite important in the 4d transition series. In ref 69 numerical relativistic Dirac−Fock calculations for the ground states of neutral atoms are presented. The ratio of relativistic values to nonrelativistic ones vary from 0.977 61 (4D) to 1.079 02 (4P) for the r^{-3} expectation values, where D and P stand for the shells with $j = 2 + 1/2$ and $1 + 1/2$, respectively. The correction of $\langle r^{-3}\rangle$ for the 5P orbital in indium falls into this range: 1.074 06. Full relativistic calculations on Cd-containing molecules have not yet been reported to our knowledge. In ref 16 the LAPW method is used to calculate the energy band structure of crystalline Cd(OH)$_2$. The influence of spin−orbit coupling on the electric field gradient was investigated and found to be of little importance (about 1%). In ref 13 relativistic effects are treated using the scalar approximation, i.e., the mass-velocity and the Darwin terms. The mean absolute correction to the CCSD(T) result in CdF$_2$, CdCl$_2$, and CdF$_2$Cl$_2^{2-}$ is found to be 0.07 au or 3% of the largest element of the diagonalized EFG; the maximal correction is 0.25 au. However, in ref 71 the relativistic correction to the EFG from electrons in 5p orbitals is 17%. An examination of the full relativistic effect in Cd-containing complexes therefore remains highly desirable.

5. Summary and Conclusions

According to our study the accuracy of the B3LYP density functional method for electric field gradient calculation is comparable to that of HF and MP2. For dimethylcadmium with the basis set used and neglecting relativistic effects, B3LYP shows the best agreement with experiment. For the two larger complexes the performance of B3LYP is less convincing, but for a rigorous comparison with experiment the polarizing effect of the crystalline environment should be included here. The trend is that B3LYP gives the smallest electric field gradients among the methods examined, which is most likely caused by a larger cancellation of p- and d-contributions from the Cd atomic orbitals than in the other methods.

To estimate the overall accuracy of the computed EFGs is difficult. For dimethylcadmium the estimated B3LYP value is in the experimental range, while for the two larger complexes a discrepancy of 0.4 au between computation and measurement is obtained. The spread of results due to different basis sets is about 0.2 au in our case. The largest effect does not arise from additional tight functions. Therefore, it is not the shape of the Gaussian functions but the incompleteness of the basis set that causes the inaccuracy.

Alltogether, it is likely that despite the absolute error of each individual calculation trends are represented with a higher accuracy when examining a series of related systems with one method of choice. Here it is important that B3LYP and HF can be performed at a cost much smaller than MP2 or other correlated methods.

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