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Performance of the Effective Core Potentials of Ca, Hg, and Pb in Complexes with Ligands Containing N and O Donor Atoms

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Abstract: This paper presents a systematic study of the performance of the relativistic effective core potentials (RECPs) proposed by Dolg-Stoll-Preuss, Christiansen-Ermler, and Hay-Wadt for Ca^{2+}, Hg^{2+}, and Pb^{2+}. The RECPs performance is studied when these cations are combined with ethyleneglycol, 2-aminoethanol, and ethylenediamine to form bidentate complexes. First, the description of the bidentate ligands is analyzed with the Kohn−Sham method by using SVWN, BLYP, and B3LYP exchange-correlation functionals, and they are compared with the Møller−Plesset perturbation theory (MP2); for all these methods the TZVP basis set was used. We found that the BLYP exchange-correlation functional gives similar results like those obtained by the B3LYP and MP2 methods. Thus, the bidentate metal complexes were studied with the BLYP method combined with the RECPs. To compare RECPs performance, all the systems considered in this work were studied with the relativistic all-electron Douglas-Kroll (DK3) method. We observed that the Christiansen-Ermler and Dolg-Stoll-Preuss RECPs give the best energetic and geometrical description for Ca and Hg complexes when compared with the all-electron method. For Pb complexes the spin−orbit effect and the basis set superposition error must be taken into account in the RECP calculations. In general, the trend showed in the complexation energies with the all-electron method is followed by the complexation energies computed with all the pseudopotentials tested in this work.

I. Introduction

Coordination chemistry plays a crucial role in chemical science. Aqueous solvation, liquid−liquid partitioning, binding to proteins and other biomolecules, and catalysis are just a few of many examples. The study of the interactions that occur between ligands and metal ions is useful to establish the relationship between structure and the stability of a complex and the selectivity of a sequestering agent.[1] It is well-known that ligands with many donor atoms give thermodynamically more stable complexes than their analogous containing unidentate ligands.[2]

It is common to find neutral nitrogen and oxygen atoms as donor binding sites in multidentate ligands interacting with metal ions.[3] Nucleic acids, crown ethers, and macrocycles with antibiotic action are all examples where this kind of interaction is observed. From a quantum chemistry point of view, many of these systems have sizes that are prohibitive for an all-electron ab initio treatment. Additionally, some metal cations show relativistic effects, which make the calculations more expensive computationally.

These characteristics have motivated many authors to combine ab initio calculations with effective core potentials (ECPs) for modeling inner electrons in an atom.[4] For methods based on localized basis set functions, different ECPs approaches have been developed to describe the interaction between metal cations and several ligands. Two different

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groups of ECPs may be distinguished in the literature according to the procedure to obtain them. One group considers that the atomic ECP should reproduce physical properties such as the first ionization potentials, the first excitation energies, and electron affinities. This approach has been proposed by the Stuttgart-Dresden group.[5] The second type of ECPs comes from the shape-consistent extraction method; in this, the ECP should give a nodeless pseudo-orbital, and it is constructed in such a way that the pseudo-orbital has the same shape of the valence part as the atomic orbital and its energy must be the same as that obtained from the all-electron atomic calculation. To this second group of ECPs belong Christiansen-Ermler[6] and Hay-Wadt ECPs,[7] for example. In the design of all these ECPs the Hartree—Fock method is used, and they are represented in terms of Gaussian functions. Dolg-Stoll-Preuss,[5] Christiansen-Ermler,[6] and Hay-Wadt[7] approaches are available in electronic structure codes and commonly used for the description of ligand—metal ion interactions. Some of these ECPs have been used in combination with Hartree—Fock and Møller—Plesset methods[8] for theoretical studies of organometallic compounds,[9] photochemical reactions,[10] metalation reactions in organic chemistry,[11] etc. Even when, in our knowledge, these ECPs have not been optimized or designed in the density functional theory (DFT)[12] context, DFT calculations have been combined with these ECPs to study adsorption phenomena onto catalyst surfaces,[13] defects in semiconductors,[14] metal—ligand bonding[15] and bonding energetics of zerovalent and cationic metals,[16] the O[17] and C[13] NMR chemical shifts in metal complexes,[17] and so on. All these cited examples solve a particular problem on a particular system, and there have been no systematic studies to show the performance of these ECPs on the structural and energetic of complexes where, specifically, neutral oxygen and nitrogen donor atoms interact with cations.

The aim of this paper is to study the performance of relativistic standard ECPs in combination with DFT, in the description of complexes between the metal ions Ca^{2+}, Hg^{2+}, and Pb^{2+} with ligands where neutral nitrogen and oxygen are donor atoms (ethyleneglycol, 2-aminoethanol, and ethylenediamine). We chose these ligands for our research because they are analogues of common structural elements that occur in multidentate ligands. Thus, our conclusions regarding the performance of the models on these systems may be extrapolated to more complex ligands interacting with divalent cations. We have divided our work into four sections. In section II, the methodology applied in this study is described, in section III the results and discussion are presented, and in section IV the conclusions of this work are pointed out.

II. Methodology

To choose the appropriate level of theory to describe the structure and conformational changes of free bidentate ligands ethyleneglycol (EG), 2-aminoethanol (AE), and ethylenediamine (EDA), within the Kohn—Sham (KS) model,[12] which is the most popular DFT implementation, three exchange-correlation functionals were tested. These include a local density approximation (SVWN),[18] a generalized gradient approximation (BLYP),[19] and a hybrid approach

(B3LYP).[20] We use, in all of these calculations, the polarized triple-ζ basis set (TZVP).[21] For comparison we carried out second-order Møller—Plesset (MP2) calculations with the same basis set on EG, AE, and EDA conformations. The results of both methodologies (DFT and MP2) for the most stable conformer of each molecule are contrasted with experimental data and previous results reported in the literature. From this comparison, we have selected the method to describe free bidentate ligands with the best ratio between the structural and energetic description and a reasonable computational effort.

To determine the ECPs performance on the energetic description of Ca, Hg, and Pb atoms, the first and second ionization potentials were estimated using each type of relativistic pseudopotentials tested in this work. For Ca, 10 core electrons were replaced with a relativistic effective core potential (RECP). We used three RECPs approaches: Dolg-Stoll-Preuss (Stuttgart),[5] Christiansen-Ermler (CRENBL),[6] and Hay-Wadt (LANL2DZ).[7] For the Hg case, 60 core electrons were replaced in Stuttgart, CRENBL and 68 for LANL2DZ RECPs. And for Pb, 60 core electrons were replaced with Stuttgart RECP, 68 with the CRENBL approach, and 78 with LANL2DZ. To determine the effect of using a different valence on the description of the energetics, Stuttgart RECPs with a different number of electrons in the core (large core, LC) were used: 18 core electrons were replaced in calcium, 78 for Hg, and 78 for Pb. To estimate spin—orbit effects in the Pb, we used the CRENBL RECP corrected by spin—orbit (CRENBL+SO) as was proposed by Christiansen[6] and that designed by Dolg-Stoll-Preuss for the Stuttgart RECPs (Stuttgart+SO and Stuttgart+SO+LC).[5] In all of them, we are using the coefficients of primitive Gaussians of RECPs and basis sets as were reported in the references.

The RECP results for ionization potentials were compared with experimental values. To provide additional points for comparison, ionization potentials were determined with relativistic all-electron (Douglas-Kroll, DK3)[22a] calculations in combination with the BLYP exchange correlation functional. The DK3 method is a higher-order scheme of the DK transformation extensively studied by Hess and co-workers.[23] The basis sets used in all calculations done with this method are as follows: (20s15p)/[4s2p] for Ca, (23s23p15d10f)/[6s4p3d1f] for Hg, and (23s23p15d10f)/[6s5p3d1f] for Pb; these were optimized for the DK3 method.[22b] However, this number of functions represents a minimal basis set for these metals. This is important because, for example, the basis set for Ca does not contain *d* orbitals that are important if we want to describe a bond in the complexes. For comparison, the performance of the DK3 method using a TZVP basis set (DK3/TZVP method) was tested, due to the size, just for Ca.[21] It is important to mention that the authors of the DK3 basis set functions suggest spherical coordinates for the calculations with this kind of functions.[22c] Thus, in this work we used this representation for all the calculations for metals, ligands, and complexes.

Complexes between EG, AE, and EDA and the metal cations (Ca^{2+}, Hg^{2+}, and Pb^{2+}) were fully optimized with BLYP/TZVP for the ligands and each RECP described above
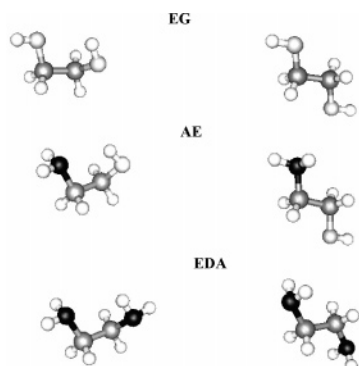
Figure 1. The most stable gauche, G_{min}, and trans, T_{min}, conformers for ethylenediamine (EDA), ethyleneglycol (EG), and 2-aminoethanol (AE), optimized at the BLYP/TZVP level. The black color is for N, gray for C, and white for O atoms; the H atoms are the smallest white spheres.

Table 1. Relative Energies (kcal mol^{-1}) between the Most Stable Gauche and Trans Conformers of Ethyleneglycol (EG), 2-Aminoethanol (AE), and Ethylenediamine (EDA)[a]

ab initio level	EG	AE	EDA
SVWN.	3.85	4.13	2.42
BLYP	2.78	2.71	1.54
B3LYP	2.79	2.73	1.57
MP2	2.84	2.89	1.67

[a] All computations were made with the TZVP basis set.

for metals. Also, the relativistic all-electron DK3 method was used in the optimization of the complexes to contrast with the RECP results, as in the case of ionization potentials; also the TZVP combined with DK3 for calcium complexes was tested. The complexation energies were calculated with each RECP as $\Delta E = E(\text{complex}) - E(\text{ligand}) - E(\text{metal})$. Again, these energies were compared with the relativistic all-electron (DK3) energies. Additionally, correction to the formation energies due to the basis set superposition error (BSSE) using the counterpoise method proposed by Boys and Bernardi are presented.[24] All the calculations were done with the NWChem v4.5 code.[25]

III. Results and Discussion

IIIa. Free Ligands. The most stable gauche and trans conformers for EG, AE, and EDA are showed in Figure 1. From this figure we can see that the gauche conformers present an intramolecular hydrogen bond (structures at the left in Figure 1), which make this conformer more stable than the corresponding trans conformer. This observation is consistent with other studies in the literature.[26]

The relative energies between gauche and trans conformers are reported in Table 1 for each method tested in this work. From this table it is clear that the SVWN method gives the largest relative energy, suggesting that the hydrogen bond in the gauche conformer is overestimated. This is consistent with prior reports showing that SVWN overestimates intermolecular hydrogen bonds.[27] The BLYP and B3LYP results are similar to one another, and the largest deviation from the MP2 calculations is of 6.2% for AE. The MP2 relative energies are always higher than the BLYP and B3LYP ones.

The structural parameters for the hydrogen bonds in the gauche conformers are reported in Table 2. Consistent with

Table 2. Structural Parameters of the Hydrogen Bond in the Most Stable Gauche Conformers of Ethyleneglycol (EG), 2-Aminoethanol (AE), and Ethylenediamine (EDA)[a]

structural parameter	SVWN	BLYP	B3LYP	MP2
		EG		
D O−H ⋯ O	2.11	2.42	2.39	2.31
D O - - - O	2.67	2.87	2.83	2.79
< O−H ⋯ O	114.1	107.5	107.1	109.6
		AE		
D O−H ⋯ N	1.97	2.27	2.26	2.19
D O - - - N	2.64	2.84	2.82	2.78
< O−H ⋯ N	122.7	115.9	115.2	117.6
		EDA		
D N−H ⋯ N	2.27	2.53	2.50	2.43
D N - - - N	2.79	2.96	2.92	2.88
< N−H ⋯ N	109.2	104.2	104.3	106.2

[a] Distances are in angstroms and angles in degrees. All computations were made with the TZVP basis set.

Table 3. Comparison of the Relative Energies (kcal mol^{-1}) for Some Gauche and Trans Conformers of Ethyleneglycol (EG), 2-Aminoethanol (AE), and Ethylenediamine (EDA) Calculated in This Paper (BLYP/TZVP) and Previous Results

	EG		
	G_{min}	T_{min}	T_1
this work	0.00	2.78	2.85
MP2/cc-pVTZ//MP2/cc-pVDZ[a]	0.00	2.80	2.85
	AE		
	G_{min}	T_{min}	G_1
this work	0.00	2.71	2.05
B3LYP/6-311++G(2p,2d)[b]	0.00	2.85	1.90
	EDA		
	G_{min}	T_{min}	T_1
this work	0.00	1.54	1.64
MP2/6-31++G**//HF/6-31++G** [c]	0.00	1.66	1.75

[a] Reference 28. [b] Reference 29. [c] Reference 30.

the relative energies, the structural parameters from the SVWN method suggest an overestimation of the hydrogen bond strength, the donor−acceptor angles of this method are the most linear, and the hydrogen−acceptor and donor−acceptor distances are the shortest, while the BLYP and B3LYP methods give a similar description of the hydrogen bond structural parameters. This result is very important because calculations with the B3LYP exchange correlation functional are computationally more expensive than those with BLYP, and this can be significant when bigger systems are treated. The distances and angles of both methods (BLYP and B3LYP) are close to those calculated with the MP2 method. In accord with the relative energies, MP2 predicts slightly more linear angles and shorter hydrogen bond distances in comparison to the BLYP and B3LYP methods.

Because the performance of BLYP and B3LYP is very similar in the description of structural parameters and relative energies, we present in Table 3 only the relative energies of three conformers of each molecule calculated with the BLYP/TZVP method for comparison to results obtained from prior

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Table 4. Comparison of Geometrical Parameters for the Most Stable Gauche Conformer of Ethylenglycol (EG) Predicted by the BLYP/TZVP Method and Experimental Parameters[a]

geometrical parameter	this work	experimental[b]
D O−H	0.978	0.961 ± 0.008
D C−O	1.457	1.424 ± 0.001
D C−C	1.525	1.517 ± 0.005
D O - - - O	2.868	2.813 ± 0.006
D O−H ⋯ O	2.419	2.365 ± 0.045
< C−C−O	106.7	109.3 ± 0.4
< C−C−H	108.7	105.8 ± 2.7
< O−C−C−O	62.7	60.7 ± 1.8
< C−C−O1−H	−52.4	−54.0 ± 2.1
< C−C−O2−H	−165.8	−169.7 ± 2.0

[a] Distances are in angstroms and angles in degrees. [b] Reference 31.

Table 5. Comparison of Geometrical Parameters for the Most Stable Gauche Conformer of Ethylendiamine (EDA) Predicted by the BLYP/TZVP Method and Experimental Parameters[a]

geometrical parameter	this work	experimental[b]
D C−C	1.536	1.545 ± 0.008
D C1−N1	1.489	1.469 ± 0.004
D C2−N2	1.481	1.469 ± 0.004
D N−H	1.024	0.995 ± 0.005
< C2−C1−N1	110.3	110.2 ± 0.7
< C1−C2−N2	110.0	110.2 ± 0.7
< N−C−C−N	64.0	64.0 ± 0.4

[a] Distances are in angstroms and angles in degrees. [b] Reference 32.

Table 6. Comparison of Geometrical Parameters for the Most Stable Gauche Conformer of 2-Aminoethanol (AE) Predicted by the BLYP/TZVP Method and Experimental Parameters[a]

geometrical parameter	this work	experimental[b]
D C−C	1.537	1.526 ± 0.016
D C−O	1.441	1.396 ± 0.010
D C−N	1.489	1.475 ± 0.023
D O−H	0.982	1.000 ± 0.020
D N−H1	1.022	1.017 ± 0.003
D N−H2	1.024	1.017 ± 0.005
D O - - - N	2.839	2.808 ± 0.005
D O−H ⋯ N	2.269	2.300 ± 0.040
< C−C−O	111.2	112.1 ± 1.0
< C−C−N	108.8	108.1 ± 2.0
< C−O−H	104.5	108.0 ± 2.0
< C−N−H1	111.2	111.3 ± 0.8
< C−N−H2	110.8	110.4 ± 0.8
< H−N−H	107.1	109.9 ± 0.5
< O−C−C−N	55.0	55.4 ± 2.0
< C−C−O−H	−40.3	−27.0 ± 6.0
< C−C−N−H1	31.2	32.3 ± 1.0
< C−C−N−H2	−110.5	−110.5 ± 1.0

[a] Distances are in angstroms and angles in degrees. [b] Reference 33.

Table 7. First and Second Ionization Potentials in eV for Ca[a]

method	first	second
Stuttgart	6.12	12.03
Stuttgart-LC	6.02	11.34
CRENBL	6.10	12.11
LANL2DZ	6.36	11.72
DK3	6.37	11.74
experimental[b]	6.11	11.86

[a] All methods were combined with BLYP. [b] Reference 34.

Table 8. First and Second Ionization Potentials in eV for Hg[a]

method	first	second
Stuttgart	10.46	19.14
Stuttgart-LC	9.39	17.30
CRENBL	10.42	19.07
LANL2DZ	9.32	17.37
DK3	10.59	19.00
experimental[b]	10.43	18.74

[a] All methods were combined with BLYP. [b] Reference 34.

studies. We found that the relative deviations do not exceed 5%. We note that prior results obtained from a B3LYP calculation with the 6-311++G(2p,2d) basis set is very similar to that obtained by us with the BLYP/TZVP method.

Finally in Tables 4−6, the comparison between some available gas-phase experimental structural parameters of the most stable conformer of each molecule with the BLYP/TZVP results is shown. As it can be seen, only the C−C−O−H angle for the AE has a big deviation from the experimental value. In the paper where these results were reported, the authors mentioned they had doubts about this angle.[33] The angle of −27.0 degrees proposed in that work is not favorable for the hydrogen bond, and we found that this geometry to be unstable.

The results presented here on the ligand conformations allow us to conclude that the BLYP functional with the TZVP basis set properly describes the structural and energetic behavior of these bidentate ligands, and this method will be used in the following sections.

IIIb. ECP Performance in the Ionization Potentials for Ca, Hg, and Pb. To explore the energetic description of Ca, Hg, and Pb, the first and second ionization potentials (IP) were estimated by each type of RECP and the relativistic all-electron DK3 method at the BLYP ab initio level. The results are reported in Tables 7−9. To investigate the influence of a more extended valence on the energetic description, we used two RECPS from the Stuttgart group (named Stuttgart and Stuttgart-LC in the tables) that have

different numbers of core electrons. Additional RECPs reported in the tables have been described in the methodology section.

Comparing relativistic all-electron calculations using the DK3 method and experimental values, we found good agreement for the first and second ionization potentials for Ca, and they differ just in 4.3% and 1.0%, respectively. The test of the basis set TZVP with DK3 in this atom improves only the first IP since the relative error with this basis set is 0.7% (the first IP is 6.07 and the second 12.07 eV with the DK3/TZVP method), and for the second IP the relative error is 1.8%. For the Hg ionization potentials predicted by the DK3 method, a better agreement is observed; their results differ only about 1.5% from the experimental values, using just

Table 9. First and Second Ionization Potentials in eV for Pb[a]

method	first ionization potential	second ionization potential
Stuttgart	6.83	13.66
Stuttgart + SO	7.13	14.76
Stuttgart-LC	6.99	13.70
Stuttgart + SO-LC	7.29	14.41
CRENBL	6.36	12.81
CRENBL + SO	6.60	13.87
LANL2DZ	6.89	13.90
DK3	7.13	13.88
experimental[b]	7.41	15.01

[a] All methods were combined with BLYP. [b] Reference 34.

the basis set optimized for the DK3 described in the methodology. We can see that the DK3-BLYP performance is good for these systems. However, the DK3 method shows a different behavior for the IPs in the Pb than that observed for Ca and Hg atoms, since the first IP has a 3.8% relative error with respect to the experimental value, and the second IP 7.5%. The Ca and Hg results suggest that these deviations can be attributed to spin−orbit effects that are not considered in the implementation of the DK3 method in the code used in this work. We will come back in this issue later when the RECPs results for Pb are discussed. But in general, we may say that the energetic description of DK3 method for the metals and their ions is reasonably good, even when the basis sets optimized for this method are limited. We may increase the basis set, or test different exchange-correlation functionals, or explore the spin−orbit effects to assess the DK3 performance in the metals considered here; however, such a study is not the target of this work.

It is also observed in Tables 7−9 that Stuttgart-LC, for Ca and Hg, gives larger relative errors than Stuttgart (one magnitude order for the first IP), with respect to experimental IPs. While for Pb, the error of LC is almost the same than the more expanded valence. The Dolg-Stoll-Preuss more expanded valence RECP results are in better agreement with respect to experimental values, for calcium where the largest relative error is 1.4% for the second IP. For Hg, we found 0.3 and 2.1% deviations from the first and second IPs, respectively. As it was mentioned before, the bigger deviations are found for Pb, where the largest difference is observed in the second ionization potential, 9.0% for the more expanded valence; however, when this RECP in the corrected spin−orbit version is used, the difference with the experimental value goes to 1.7% and 3.8% for the first IP. For the first IP the Stuttgart large core corrected by the spin−orbit effect shows the lowest difference, 1.6% and 4.0% for the second IP.

Comparing all computed RECPs results for Ca and Hg with the experimental values (Tables 7 and 8), the smaller relative errors are observed in CRENBL and Stuttgart ECPs, and the relative errors are not over 2%. Contrary to Ca and Hg, the CRENBL RECP results for Pb show the largest deviations with respect to experimental IPs, 14.2 and 14.7% for the first and second IP, respectively. When the SO effect is included in the RECP, the errors diminish to 10.9 and 7.6%. It is important to say that we tested the spin−orbit

Figure 2. Complexes between Pb(II) and ethyleneglycol (EG), 2-aminoethanol (AE), and ethylenediamine (EDA), optimized at the BLYP/TZVP level combined with CRENBL RECP for the metal. The black color is for N, gray for C, and white for O atoms; the H atoms were suppressed for simplicity.

Table 10. Structural Parameters for Ca^{2+} with Ethylenediamine (EDA)[a]

method	D N−Ca	D N---N	< N−Ca−N	< N−C−C−N
Stuttgart	2.40	2.99	77.09	60.50
Stuttgart-LC	2.57	3.09	73.88	64.30
CRENBL	2.53	3.08	74.75	63.60
LANL2DZ	2.51	3.07	74.87	63.40
DK3	2.52	3.06	74.85	62.35

[a] All RECPs were combined with BLYP/TZVP. Distances are in angstroms and angles in degrees.

effect in the Hg IPs, using the Christiansen RECPs, and there was not a difference when this effect is not considered.

With respect to relativistic all-electron DK3 calculations, the largest deviations are obtained for LANL2DZ RECP, 12.2% for the first ionization potential and 8.6% for the second of the Hg atom.

IIIc. Bidentate Ligand Complexes. The metal complexes with dications of Ca, Hg, and Pb were fully optimized, using each RECP tested in this work for metals combined with the BLYP/TZVP for ligands. For comparison, relativistic all-electron DK3 calculations for all complexes also were computed. For the Ca complexes two basis sets were tested, TZVP and the minimal basis set for the DK3 method described in the methodology, although for consistency, in the correspondent tables just the results obtained with the latter basis set are reported. The optimized geometries for Pb complexes at the BLYP/TZVP level combined with CRENBL RECP are presented in Figure 2. Structural parameters for complexes with EDA ligand are reported in Tables 10−12. We decided to report just the complexes with EDA since the differences between RECPs and the DK3 method are similar in the other complexes. However, structural parameters for complexes with EG and AE are given in the Supporting Information.

Structural parameters in these tables (11 and 12) show that the geometries from the Stuttgart RECPs are in good agreement with the DK3 geometries, with the exception of the Hg^{2+} complex, where relative errors reach around 15.5% for the N−Hg distance and 19.8% in the N−Hg−N angle when less expanded valence (Stuttgart-LC) RECP is used; it predicts a shorter donor−metal distance. For the Ca^{2+}−EDA complex (Table 10), all RECPs predict structural parameters with a deviation less than 5% with respect to the DK3 method, for this case when the DK3/TZVP method is used the geometrical parameters are almost the same, just the N−Ca distance (2.49 Å) and the N−Ca−N (75.81 degrees) show a small change. For the same ligand with Hg^{2+}, the largest relative error, after Stuttgart-LC, with respect to DK3 was found for Hay-Wadt RECP, 7.2% for the N−C−C−N angle (see Table 11). Curiously, better agreement is found

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Table 11. Structural Parameters for Hg^{2+} with Ethylenediamine (EDA)[a]

method	D N − Hg	D N - - - N	< N−Hg−N	< N−C−C−N
Stuttgart	2.40	3.09	80.34	58.40
Stuttgart-LC	2.12	3.03	91.26	55.90
CRENBL	2.38	3.09	80.89	58.90
LANL2DZ	2.44	3.09	78.54	60.40
DK3	2.51	3.10	76.20	56.33

[a] All RECPs were combined with BLYP/TZVP. Distances are in angstroms and angles in degrees.

Table 12. Structural Parameters for Pb^{2+} with Ethylenediamine (EDA)[a]

method	D N − Pb	D N - - - N	< N−Pb−N	< N−C−C−N
Stuttgart	2.46	2.95	73.58	58.40
Stuttgart+SO	2.46	2.95	73.62	58.40
Stuttgart-LC	2.47	2.95	73.34	58.10
Stuttgart+SO-LC	2.47	2.95	73.39	58.10
CRENBL	2.58	2.99	70.85	60.40
CRENBL+SO	2.58	2.99	70.88	60.50
LANL2DZ	2.41	2.92	74.67	56.40
DK3	2.51	2.97	72.57	58.79

[a] All RECPs were combined with BLYP/TZVP. Distances are in angstroms and angles in degrees.

Table 13. Formation Energy in kcal/mol for Ca^{2+} Complexes, without (wo) Considering BSSE Correction and with (w) This Correction[a]

Ca^{2+} − EG	wo/BSSE	w/BSSE
Stuttgart	−110.46	−109.56
Stuttgart-LC	−87.01	−86.54
CRENBL	−92.19	−91.89
LANL2DZ	−92.36	−91.37
DK3	−91.46	−90.90

Ca^{2+} − AE	wo/BSSE	w/BSSE
Stuttgart	−116.33	−115.21
Stuttgart-LC	−91.64	−91.22
CRENBL	−97.80	−97.34
LANL2DZ	−97.56	−96.60
DK3	−96.65	−96.06

Ca^{2+} − EDA	wo/BSSE	w/BSSE
Stuttgart	−123.61	−122.29
Stuttgart-LC	−98.25	−97.90
CRENBL	−105.45	−104.82
LANL2DZ	−104.77	−103.93
DK3	−103.90	−103.28

[a] The BLYP exchange correlation functional was used in all calculations.

Table 14. Formation Energy in kcal/mol for Hg^{2+} Complexes, without (wo) Considering BSSE Correction and with (w) This Correction[a]

Hg^{2+} − EG	wo/BSSE	w/BSSE
Stuttgart	−172.27	−170.49
Stuttgart-LC	−169.14	−168.01
CRENBL	−171.17	−170.09
LANL2DZ	−139.36	−138.29
DK3	−164.80	−162.04

Hg^{2+} − AE	wo/BSSE	w/BSSE
Stuttgart	−202.45	−200.67
Stuttgart-LC	−190.34	−189.34
CRENBL	−201.10	−199.84
LANL2DZ	−162.71	−161.54
DK3	−193.56	−190.52

Hg^{2+} − EDA	wo/BSSE	w/BSSE
Stuttgart	−229.74	−227.62
Stuttgart-LC	−212.43	−211.52
CRENBL	−228.49	−226.83
LANL2DZ	−186.35	−185.00
DK3	−221.80	−218.60

[a] The BLYP exchange correlation functional was used in all calculations.

tions are small for Ca^{2+} and Hg^{2+}, they are important for Pb^{2+} complexes. In the latter case, application of the BSSE correction results in about 7% change to the complexation energy when using the DK3 method. As expected, the RECP results are not as affected as the all-electron calculations, with the largest correction found in LANL2DZ and Stuttgart-LC RECPs for Pb^{2+} complexes where the BSSE is around 4.6%.

Comparing the computed complexation energies using RECPs versus the DK3 method, we found that the worst deviation occurs with the Stuttgart RECP in Ca^{2+} complexes, which gives about 20% of relative error in all Ca−ligand complexes. This behavior is observed due to the limited basis set optimized for the DK3 method. However, when the DK3/TZVP method is applied, the binding energies corrected by the BSSE are as follows: −98.39 kcal/mol for the EG, −103.42 kcal/mol for the AE and, −110.23 kcal/mol for the EDA calcium complexes; in all cases when the basis set of calcium has polarization functions the binding energy is increased in about 7.5%. This makes that the relative errors of Stuttgart RECP with respect to the DK3 method diminish around 10%. With respect to the DK3/TZVP method, Stuttgart-LC RECP shows the largest error (about 12%), and for the other RECPs the relative error is increased from less than 2% to around 6%. It means that when the basis set includes polarization functions in this atom, the DK3/TZVP and Stuttgart RECP methods give similar results.

An additional test was made for the DK3 method, and just for the Ca^{2+} complexes we performed a conventional DFT calculations BLYP/TZVP; these results were compared with those obtained with DK3/TZVP. Geometrical parameters for all complexes are very similar; the bigger difference in distances is 0.06 Å and in angles 1.2 degrees. With respect to the complexes binding energies they differ by less than

for the Pb^{2+}−ligand, where the largest deviation was 4.2% for the same angle as the Hg^{2+} complex and also for LANL2DZ RECP, as it is shown in Table 12. For all metal−ligand complexes, there is no significant change in angles and distances for the inclusion of spin−orbit correction in the CRENBL and Stuttgart RECPs.

The complexation energies for all metals, ligands, and methods explored in this work are reported in Tables 13−15. These complexation energies were computed both with and without BSSE corrections. Although the BSSE correc-

Table 15. Formation Energy in kcal/mol for Pb^{2+} Complexes, without (wo) Considering BSSE Correction and with (w) This Correction

$Pb^{2+} - EG$	wo/BSSE	w/BSSE
Stuttgart	−118.10	−116.39
Stuttgart+SO	−120.88	−118.20
Stuttgart-LC	−116.36	−110.97
Stuttgart+SO-LC	−117.41	−112.01
CRENBL	−101.65	−100.36
CRENBL+SO	−103.15	−101.84
LANL2DZ	−126.79	−120.96
DK3	−118.73	−110.23
$Pb^{2+} - AE$	wo/BSSE	w/BSSE
Stuttgart	−130.83	−128.91
Stuttgart+SO	−134.34	−131.54
Stuttgart-LC	−130.09	−124.28
Stuttgart+SO-LC	−131.57	−125.75
CRENBL	−112.74	−111.17
CRENBL+SO	−114.94	−113.35
LANL2DZ	−139.66	−133.40
DK3	−132.37	−123.39
$Pb^{2+} - EDA$	wo/BSSE	w/BSSE
Stuttgart	−144.90	−142.78
Stuttgart+SO	−149.12	−146.16
Stuttgart-LC	−145.22	−138.90
Stuttgart+SO-LC	−147.12	−140.79
CRENBL	−125.35	−123.49
CRENBL+SO	−128.20	−126.33
LANL2DZ	−153.64	−146.83
DK3	−147.21	−137.81

[a] The BLYP exchange correlation functional was used in all calculations.

1%. It means that the errors of the DK3 method occur, mainly due to the minimal basis set optimized for this method, more than the relativistic DK treatment.

With the LANL2DZ RECPs, the largest deviations with respect to DK3 were observed for the Hg^{2+} complexes, where the relative error is around 15.0%. Finally the CRENBL

Figure 3. Calculated structures for (a) $[Hg(EDA)_2]^{2+}$ and (b) $[Ca(EDA)_4]^{2+}$ complexes, optimized at the BLYP/TZVP level combined with CRENBL RECP for the metal. The black color is for N and gray for C; the H atoms were suppressed for simplicity.

RECPs give the largest differences with the Pb^{2+} complexes, but when the spin−orbit effect is considered in the binding energies for these complexes the relative error diminishes from 9.7% to 8% on average, after the BSSE correction.

In general, Sttutgart RECP binding energies are the values closest to the DK3 results, with the exception of the calcium complexes. It is important to note that just the Stuttgart RECPs (small core) are comparable in size to the TZVP basis set.

Regardless of the RECP, the complexation energies follow the same trend as the DK3 calculations. For all metal cations the most stable complex is that built with the EDA ligand, where two nitrogen atoms are acting as donor atoms, followed by the AE ligand, and the least stable complexes are formed with EG. It has been observed that in the gas phase the neutral nitrogen donor shows stronger metal coordinating properties than the neutral oxygen donor,[1] and our results agree with this observation. For a given ligand, always the complexes with Hg^{2+} are more stable than those with Pb^{2+}, and the latter more stable than complexes where Ca^{2+} is the metal ion. Thus, the most stable complex is the $Hg^{2+}−EDA$ complex.

It is important to note that there are no experimental values to compare with our theoretical results for the simple 1:1 M:L complexes. Although there are crystal structures that contain bidentate ligands (EG, EDA, or AE) bound to the metal ion, additional bound ligands are also present. To benchmark the ability of the methodologies to describe experimental geometries, we carried out the same calculations with all RECPs in the $[Hg(EDA)_2]^{2+}$ and $[Ca(EDA)_4]^{2+}$ complexes where experimental structures are reported.[35,36] In Figure 3, the calculated structures of these complexes are depicted. The root-mean-square errors (RMS) of all RECPs geometries with respect to the experimental structural are on average 0.37 Å for the calcium complex and 0.31 Å for the $[Hg(EDA)_2]^{2+}$. These errors show that all RECPs give a close description of the experimental structures, even when the calculations are performed in a vacuum.

In Tables 16 and 17 some structural parameters are listed to obtain a more detailed comparison between experimental and theoretical data. Relative errors with respect to experimental values are also given for $[Ca(EDA)_4]^{2+}$ and $[Hg(EDA)_2]^{2+}$ complexes in Tables 16 and 17. As we can see for the Ca complex all RECPs relative errors with respect to the experimental are less than 9%, the lowest errors are found when the Stuttgart more expanded valence RECP is used, and Stuttgart-LC, LANL2DZ, and CRENBL give similar errors. In the case of the Hg complex (Table 17) the lower relative errors, in general, are found with the Stuttgart and CRENBL RECPs. For this complex, the bigger relative error is found in one of the N−C−C−N dihedral angles; the cause of this difference is due to the presence of a ClO_4^- ion that appears in the experimental crystal structure, and it is close enough to interact with the CH_2 group of one of the EDA molecules in the Hg complex. The ligand that does not show that this interaction has a better agreement with the calculated dihedral angle.

In Tables 16 and 17 also DK3 structural parameters are given; in the calcium complex case the basis set used for
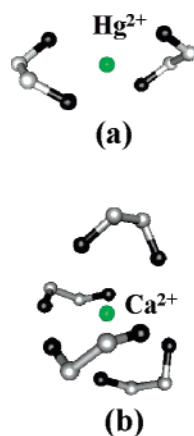
Effective Core Potentials of Ca, Hg, and Pb

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Table 16. Structural Parameters for the [Ca(EDA)$_4$]$^{2+}$ Complex[a]

geometrical parameter	Stuttgart	Stuttgart-LC	CRENBL	LANL2DZ	DK3	exp[b]
D N−Ca	2.70	2.79	2.78	2.77	2.76	2.56
	(5.47)	(8.98)	(8.59)	(8.20)	(7.81)	
D N−Ca	2.73	2.82	2.80	2.80	2.79	2.61
	(4.60)	(8.05)	(7.28)	(7.28)	(6.90)	
D N - - - N	2.94	2.98	2.97	2.97	2.97	2.84
	(3.52)	(4.93)	(4.58)	(4.58)	(4.58)	
< N−Ca−N	65.51	64.18	64.45	64.45	64.70	66.60
	(1.64)	(3.63)	(3.23)	(3.23)	(2.85)	
< N−C−C−N	−59.40	−61.10	−60.90	−60.90	−60.50	−57.39
	(3.50)	(6.46)	(6.12)	(6.12)	(5.40)	

[a] All RECPs were combined with BLYP/TZVP. Relative errors are reported in parentheses. Distances are in angstroms and angles in degrees.
[b] Reference 35.

Table 17. Structural Parameters for the [Hg(EDA)$_2$]$^{2+}$ Complex[a]

geometrical parameter	Stuttgart	Stuttgart-LC	CRENBL	LANL2DZ	DK3	exp[b]
D N−Hg	2.41	2.20	2.40	2.48	2.43	2.29
	(5.24)	(3.93)	(4.80)	(8.30)	(6.11)	
D N−Hg	2.41	2.20	2.40	2.48	2.43	2.32
	(3.88)	(5.17)	(3.45)	(6.90)	(4.74)	
D N - - - N	2.97	2.92	2.97	3.02	2.96	2.89
	(2.77)	(1.04)	(2.77)	(4.50)	(2.42)	
D N - - - N	2.97	2.92	2.97	3.02	2.96	2.94
	(1.02)	(0.68)	(1.02)	(2.72)	(0.68)	
< N−Hg−N	76.14	83.09	76.35	74.83	75.07	77.23
	(1.41)	(7.59)	(1.14)	(3.11)	(2.80)	
< N−Hg−N	76.14	83.09	76.35	74.83	75.07	78.48
	(2.98)	(5.87)	(2.71)	(4.65)	(4.35)	
< N−C−C−N	−58.50	−55.90	−57.80	−60.70	−57.60	−58.77
	(0.46)	(4.88)	(1.65)	(3.28)	(1.99)	
< N−C−C−N	−58.50	−55.90	−58.10	−60.70	−57.60	−64.92
	(9.89)	(13.89)	(10.51)	(6.50)	(11.28)	

[a] All RECPs were combined with BLYP/TZVP. Relative errors are reported in parentheses. Distances are in angstroms and angles in degrees.
[b] Reference 36.

Table 18. Structural Parameters for the [Pb(EDA)$_2$]$^{2+}$ Complex[a]

geometrical parameter	Stuttgart	Stuttgart-LC	CRENBL	LANL2DZ	DK3
D N−Pb	2.55	2.56	2.66	2.49	2.58
	(1.16)	(0.78)	(3.10)	(3.49)	
D N−Pb	2.66	2.70	2.75	2.63	2.68
	(0.75)	(0.75)	(2.61)	(1.87)	
D N - - - N	2.96	2.97	3.00	2.94	2.97
	(0.34)	(0.00)	(1.01)	(1.01)	
< N−Pb−N	69.23	68.59	67.42	70.01	68.76
	(0.68)	(0.25)	(1.95)	(1.82)	
< N−C−C−N	−59.50	−59.80	−61.50	−58.40	−60.20
	(1.16)	(0.66)	(2.16)	(2.99)	

[a] All RECPs were combined with BLYP/TZVP; numbers in parentheses are relative errors. Distances are in angstroms and angles in degrees.

the DK3 calculation was TZVP although there is not a big difference with the results obtained for structural parameters when the small basis set optimized for DK3 is used, as it was observed in the bidentate ligand complexes.

We also found a report of X-ray structure for a complex of Pb with EDA ([Pb(EDA)$_2$]$^{2+}$), but coordinates are not available. In this case we made the comparison only with respect to a DK3 all-electron calculation. For this Pb complex the RMS is 0.07 Å on average for RECPS with respect to the DK3 computation, and the largest RMS was 0.l2 Å given for the overimposition with the LANL2DZ RECP. In

Table 18 a more detailed comparison between some RECPs and DK3 geometrical parameters is shown. As it can be seen, relative errors are not over 3.5%. For this complex it is important to mention that we took as a starting point, the geometry of the [Hg(EDA)$_2$]$^{2+}$ replacing the Hg by Pb. However all calculations give a structure where the metal ion is not at the middle of both ligands as in the Hg case; instead, the Pb is found above the center of the ligands as it is shown in Figure 4, and a similar behavior was observed previously for halogenated lead hydrides and methyl lead compounds.[37]
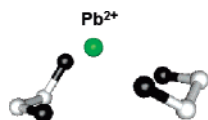
Figure 4. Calculated structure for the $[Pb(EDA)_2]^{2+}$ complex optimized with the relativistic all-electron DK3 method combined with BLYP/TZVP. The black color is for N and gray for C; the H atoms were suppressed for simplicity.

IV. Concluding Remarks

For the free ligands, both BLYP and B3LYP with the TZVP basis set reproduce experimental geometries as well as the geometries and relative energies calculated with other methods using bigger basis sets. Since BLYP and B3LYP exchange-correlation functionals both yield similar results, the BLYP method was selected for this study because it is computationally cheaper. As expected from earlier studies of intermolecular hydrogen bonds, the local SVWN exchange correlation functional overestimates hydrogen bond strength within the ligands, yielding shorter hydrogen bond distances and more linear hydrogen bonds.

The best results for Ca and Hg ionization potentials come from Dolg-Stoll-Preuss and Christiansen-Ermler RECPs. The Pb ionization potentials predicted by the RECPs show important differences with respect to the experimental ones. To obtain better results in Pb ionization potentials, it is important to use the version where spin−orbit effects are incorporated. However, a detailed study is required in this system to see which is the impact of a different exchange-correlation functional or different basis sets in the computation of IPs.

The basis sets optimized for the DK3 method reported in the literature, which were used here, are minimal for all metals. When the TZVP basis set is tested in combination with DK3 for the calcium atom, the first ionization potential improves with respect to the experimental value. However, in the description of complexes, the role of the basis set on the calcium atom is more relevant in small systems since in bigger systems the basis set functions of the ligands compensate for the limitations of the DK3 basis set of this atom. These problems are not observed for Hg and Pb complexes since, even when these metals have associated a minimal basis set, there are *d* and *f* functions involved.

For the complexes, Dolg-Stoll-Preuss RECPs show that it is necessary to use extended valence, even for Ca, to obtain geometrical parameters that are comparable to those obtained from relativistic all-electron calculations. The comparison between the Christiansen and Dolg-Stoll-Preuss RECPs with and without spin−orbit effects reveals that this correction does not significantly impact the geometrical parameters for any of the metal complexes. However, this correction is important to predict binding energies since it contributes at least 2 kcal/mol, depending on the complex.

All complexation energies calculated with RECPs follow qualitatively the same trend as those obtained from relativistic all-electron calculations. For all metal cations the most stable complex is formed with EDA. For each ligand, the complexes formed with Hg^{2+} are always more stable than those formed with Pb^{2+}, and these are always more stable than complexes with Ca^{2+}.

The Dolg-Stoll-Preuss more expanded valence and Christiansen-Ermler RECPs combined with BLYP/TZVP for the ligand are always closer to the all-electron DK3 method; we may recommend both methods since in the systems tested here the performance with bidentate ligands is good in all cases except for Pb^{2+}. In this case, the poor results can be notably improved if the BSSE is considered.

Supporting Information Available: Cartesians coordinates of optimized structures in angstroms of all free bidentate ligands and complexes and tables of structural parameters for 2-aminoethanol and ethyleneglycol complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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