Density Functional Theory Study of Transition-Metal Compounds Containing Metal−Metal Bonds. 1. Molecular Structures of Dinuclear Compounds by Complete Geometry Optimization

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Received February 19, 1997[⊗]

Abstract: Complete geometry optimizations were carried out by methods of density functional theory to study molecular structures of dinuclear transition-metal compounds containing metal−metal bonds of various orders. It is shown that the structures of the dinuclear compounds can be accurately predicted by DFT methods. In particular, we show that accurate geometry optimization can be performed efficiently by using small basis sets in the calculations. Furthermore, an effective core potential approximation may be incorporated into the DFT calculations for computational effectiveness without losing much accuracy. The molecules included in this study were $M_2(O_2CH)_4$ (M = Nb, Mo, Tc), $M_2(HNCHNH)_4$ (M = Nb, Mo, Tc, Ru, Rh), $M_2(HNNNH)_4$ (M = Mo, Ru, Rh), and $M_2Cl_4(PH_3)_4$ (M = Nb, Mo, Tc).

Introduction

Theoretical and computational studies of transition-metal compounds with metal−metal bonds have attracted great attention ever since the discovery of the first Re−Re quadruple bond.[1] In a continuing effort to explore the nature of metal−metal bonding in the past three decades,[2] the metal−metal bonded molecular systems of different structural types have been the subjects of numerous quantum chemical calculations,[3] employing theoretical models ranging from, for example, Xα-SW molecular orbital methods[4] to various *ab initio* techniques.[5−8] The results of these calculations provide excellent, qualitative accounts for a large range of experimentally observed properties. In many cases, quantitative explanations and predictions are found to be very reliable. In fact, we have gained a great deal of insight into the complex nature of electronic structures of these complicated molecular systems, and we have a good understanding of chemical, spectroscopic, and structural properties of a variety of such compounds.[2]

Despite all these successes, however, the complicated electronic and molecular structures of the metal−metal bonded compounds have always been a challenge to the traditional *ab initio* models. This is particularly true, for example, in cases when a quantitative calculation of high accuracy becomes desirable or when a complete geometry optimization is necessary to predict a new structure. It may be stressed that the systems we are dealing with here contain at least two transition-metal atoms. The number of ligand atoms varies but normally can be very large. Thus, the total number of electrons involved in a calculation may easily add up to a few hundred. It has also long been known that electron correlation in these metal systems[9] is enormously strong so that the effects have to be taken into account in every case even for a qualitative *ab initio* treatment. Therefore, the number of basis functions and the number of configurations that must be included to achieve the desired results can easily make it a formidable or simply an impractical task to perform a conventional *ab initio* calculation that uses a multiconfigurational wave function.

Recent development in density function theory (DFT)[10] has shown that DFT may become a powerful computational alternative to the conventional quantum chemical methods. The computational efficiency and accuracy of the DFT methods have been very well documented by their applications to a variety of chemical problems and chemical systems including transition-metal complexes.[11] DFT calculations are much less computationally demanding and yet have the important feature of including electron correlation. Therefore, the methods have a high potential for treating large molecular systems with strong

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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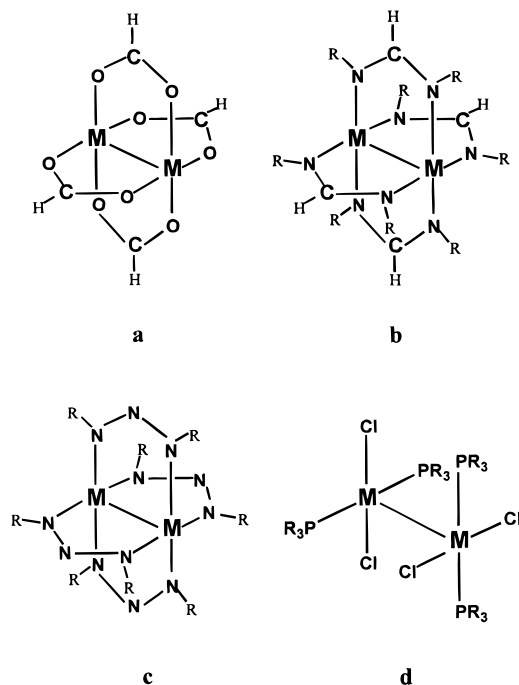
Figure 1. Structures of dinuclear compounds to be studied in this work. The R groups in all cases were replaced by hydrogen atoms in the calculations.

electron correlation such as the compounds with metal−metal bonds. In this respect, we note the pioneering DFT study by Ziegler[12] on electronic and molecular structures of the metal−metal bonded species using the approximate, exchange-only Hartree−Fock−Slater method. Recent progress in this field,[13] though very limited, has shown clearly that the new generation of gradient-corrected DFT methods[11b] is very promising for making accurate calculations on the transition-metal complexes which are very difficult or even impossible by the conventional methods.

In this laboratory we have also been exploring the application of DFT methods to the study of electronic and structural properties of transition-metal compounds with metal−metal bonds. In this first paper of a series we plan to publish, we report results of complete geometry optimizations by DFT methods for a number of second-row dinuclear compounds which contain metal−metal bonds of different orders and which belong to a few representative and most commonly seen structural types (Figure 1). Specifically, these are the tetra-bridged compounds with a paddle-wheel structure, namely, $M_2(O_2CH)_4$, $M_2(HNCHNH)_4$, and $M_2(HNNNH)_4$, and the compounds with unsupported metal−metal bonds, namely, $M_2Cl_4(PH_3)_4$. We felt that success with these compounds would justify confidence in the DFT method in other less straightforward cases.

Complete geometry optimization of dinuclear transition-metal complexes is almost impossible by the conventional ab initio methods of high accuracy for the reasons stated earlier. There

was only one such attempt made for quadruply bonded dichromium compounds by the generalized valence bond method,[5c] although metal−metal distances were optimized in a fixed ligand framework in a few occasions.[6,7,9b] Because of the size of the metal complexes, it can be anticipated that it may not be a trivial computational task even for the cost-effective DFT methods. We started our investigation with the dinuclear compounds which are of moderate size and most of which have known structures to compare with. We hope to find accurate and yet economical ways to predict molecular structures, which may be very valuable in our future study for larger and more complex compounds with metal−metal bonds. We have been particularly interested in the possibility of employing very small basis functions for metal atoms in the DFT geometry optimizations. We have also incorporated the effective core potential (ECP) approximation into the DFT calculations.

As we will see below, the results are very encouraging and promising. The DFT calculations not only accurately reproduced the structure of each known compound, but also predicted in a group of compounds the same structural trends as those observed experimentally. Therefore, we are also confident that the predicted structures for a few compounds which are yet to be characterized ought to be reliable and accurate.

Computational Details

The DFT calculations were carried out with the Becke−Lee−Yang−Parr (BLYP) gradient-corrected density functional[14] method and with the hybrid functional B3LYP[15] method by using the Gaussian 94 program.[16]

Three types of basis functions were employed in the calculations of molecular structures through geometry optimization. In the calculations on quadruply bonded dimolybdenum compounds, the Mo basis set is a [6s5p3d] contraction of the (17s11p8d) primitive set by Huzinaga[17] plus two diffuse p functions to describe the 5p orbitals. Raffenetti's general contraction scheme[18] was used. The 6-31G basis sets[19a] were used for all ligand atoms in this case. We will refer to this first type of basis set as LARGE in the following discussion.

The second type of basis set, which is much smaller, consists of the 3-21G sets[19a] for metal atoms and the 3-21G or 3-21G plus a polarization function, namely, 3-21G(d), sets for the ligand atoms. In the calculations of the $M_2Cl_4(PH_3)_4$ type of compounds, one set of basis functions, labeled as 3-21Gd1, includes 3-21G(d) for Cl atoms only and 3-21G for all other atoms, while the 3-21Gd2 basis set uses 3-21G-(d) for both Cl and P atoms.

In addition to the all-electron (AE) calculations, we also tested use of effective core potentials (ECP) in the DFT calculations for geometry optimization. The ECPs and associated basis functions (LANL2DZ) are those developed by Hay and Wadt[20] from atomic Hartree−Fock (HF) calculations, which includes all-electron valence double-ζ basis sets[19b] for the first-row and hydrogen atoms. A polarization d function has been added to the LANL2DZ basis sets for Cl and P atoms in some calculations. The exponents of the d function are 0.37 and 0.60 for P and Cl atoms, respectively. Such basis functions will be referred to as LANL2DZd in the following discussion.

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Table 1. Calculated and Experimental Structural Parameters and Harmonic Mo−Mo Stretching Frequency for $Mo_2(O_2CH)_4$

	ECP		AE			
	LANL2DZ		LARGE	3-21G		
	BLYP	B3LYP	B3LYP	BLYP	B3LYP	exptl[a]
Distance (Å)						
Mo−Mo	2.188	2.150	2.126	2.142	2.108	2.091
Mo−O	2.131	2.118	2.135	2.122	2.107	2.11
O−C	1.318	1.300	1.294	1.313	1.295	1.29
C−H	1.099	1.091	1.088	1.096	1.087	0.97
Angle (deg)						
Mo−Mo−O	91.46	91.51	91.77	92.10	92.11	92.0
Mo−O−C	117.95	118.05	117.49	116.84	117.02	117.0
O−Mo−O	89.96	89.96	89.95	89.92	89.92	90.0
H−C−O	119.41	119.56	119.25	118.93	119.13	119.0
Frequency (cm^{-1})						
ν(Mo−Mo)			450		472	406[b]

[a] Average bond distances and angles from crystal structure data of $Mo_2(O_2CH)_4$ (see ref 22). [b] See ref 2.

Results and Discussion

Molecular Structures of Tetrabridged Compounds of the Paddle-Wheel Type. This is one of most commonly seen structural types in dinuclear compounds containing metal−metal bonds.[2] Compounds of this type, $M_2(L-L)_4$, have virtual D_{4h} or at least D_4 symmetry, in which the two metal atoms are bridged by four L-L groups such as carboxylato, formamidinato, or triazenato ligands, as shown schematically in Figure 1 (a, b, and c).

$Mo_2(O_2CH)_4$. Table 1 shows the results of the geometry optimizations for $Mo_2(O_2CH)_4$ in D_{4h} symmetry by different DFT methods employing different basis functions. This compound may already be one of most studied, both experimentally and theoretically, of all dinuclear compounds with metal−metal quadruple bonds.[2] It is clear from Table 1 that all calculated structural parameters are in good to excellent agreement with the experimental values, except that the Mo−Mo distance obtained from ECP calculation by the BLYP method is about 0.1 Å too long. The C−H distance (0.97 Å) from the crystal structure data for $Mo_2(O_2CH)_4$[21] is only apparently too short, as is normal for X-ray structures. The calculated C−H distances, on the other hand, are nearly correct.

The best results, surprisingly, are from the AE B3LYP calculation with the very small 3-21G basis sets, which almost identically reproduces the experimental structural data, rather than those by a similar calculation but employing the much larger basis sets (LARGE).

It may be noted that the possibility of incorporating an effective core potential approximation into DFT calculations has been explored only recently.[22] DFT-ECP calculations using ECPs derived from atomic HF calculations can be as accurate as DFT-AE calculations when common AE basis functions are used.[22] In our DFT-ECP calculations, however, both ECPs and the associated basis functions (LANL2DZ) are those obtained from atomic HF-ECP calculations.[20] This is the only choice in the Gaussian 94 program. It was mentioned but not discussed in detail in ref 22 that such calculations could lead to large error. However, we found that such an approach is totally acceptable in the geometry optimization of the dinuclear compounds with the hybrid density functional method. As can be seen in Table 1, the Mo−Mo distance (2.150 Å) from the ECP B3LYP

calculation is about 0.04 Å longer than the 3-21G B3LYP distance (2.108 Å) and 0.06 Å longer than the experimental value (2.091 Å). For the other bond distances and all bond angles so calculated, the agreement is simply excellent.

We have already seen that DFT-ECP calculations tend to produce metal−metal distances longer than those from the DFT-AE calculations. It may also be noted that, in both ECP and AE calculations, the bond distances obtained by the BLYP method are always a little longer than the same distances given by the hybrid B3LYP method, and the latter are closer to the experimental results. As we will see shortly, this generalization applies to all calculations on the bridged compounds carried out in this work. Therefore, we shall not repeat it every time in the following discussion of other bridged compounds. Furthermore, only the results obtained with the hybrid B3LYP method will be presented.

Also listed in Table 1 are the harmonic Mo−Mo stretching frequencies for $Mo_2(O_2CH)_4$ from the DFT-AE calculations and from measurements. Again, the two different basis sets give rise to very similar results, both of which agree satisfactorily with the measured result.

$Mo_2(HNCHNH)_4$ and $Mo_2(HNNNH)_4$. These two quadruply bonded compounds can be regarded as models for crystallographically characterized $Mo_2(RNCHNR)_4$[23] (R = p-$CH_3C_6H_4$) and $Mo_2(PhNNNPh)_4$[24] compounds, respectively. Calculations similar to those for $Mo_2(O_2CH)_4$ were carried out, and very similar results are obtained. The fully optimized geometry parameters for the two Mo compounds are listed in Table 2 together with comparison to the average bond distances and angles of $Mo_2(RNCHNR)_4$[23] and $Mo_2(PhNNNPh)_4$.[24]

The calculations were carried out in D_4 symmetry, in which the dihedral angles, N−Mo−Mo−N, are allowed to change. As can be seen in Table 2, both compounds prefer an eclipsed configuration with the angle N−Mo−Mo−N almost equal to zero. The observed angle of 10.5° in $Mo_2(PhNNNPh)_4$ may be caused by crystal packing rather than steric effects due to the phenyl groups, since the same angle is only about 3° in $Mo_2(RNCHNR)_4$ (R = p-$CH_3C_6H_4$).

Again, all major bond parameters for the real compounds are well reproduced from the model calculations, particularly, from that using the 3-21G basis sets. The results strongly suggest that the most important features of the electronic and structural properties of $Mo_2(RNCHNR)_4$ (R = p-$CH_3C_6H_4$) and Mo_2-$(PhNNNPh)_4$ should be obtainable from model calculations on $Mo_2(HNCHNH)_4$ and $Mo_2(HNNNH)_4$, respectively. Finally, It may be pointed out that the calculated Mo−Mo distances by ECP B3LYP methods in Table 2 are both longer than the corresponding experimental values by about 0.06 Å, which is exactly the same case as in $Mo_2(O_2CH)_4$ (Table 1).

Triply Bonded $M_2(O_2CH)_4$ and $M_2(HNCHNH)_4$ (M = Nb, Tc) Compounds. These Nb(II) and Tc(II) compounds are yet to be synthesized and structurally characterized. DFT geometry optimizations were thus performed to predict their molecular structures. Because of the excellent performance of the DFT methods so far seen, it is reasonable to believe that the calculated results in Table 3 should be very close to the true picture of these tetrabridged, triply bonded dinuclear compounds.

The calculations were carried out in D_4 symmetry, but all four of these compounds adopt an eclipsed configuration as shown by the calculated dihedral angles, O−M−M−O or N−M−M−N, in Table 3 which are all nearly zero, even though there does not exist any δ bond between the metal atoms. The optimized bond distances and angles all appear to be reasonable.

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Table 2. Calculated Molecular Structures for $Mo_2(HNCHNH)_4$ and $Mo_2(HNNNH)_4$ with Comparison to $Mo_2(RNCHNR)_4$ and $Mo_2(PhNNNPh)_4$

	Mo₂(HNCHNH)₄						Mo₂(HNNNH)₄			
	ECP		AE				ECP	AE		
	LANL2DZ		LARGE 3-21G				LANL2DZ	LARGE 3-21G		
	B3LYP	BLYP	B3LYP		exptl[a]		B3LYP	B3LYP		exptl[b]
			Distance (Å)							
Mo−Mo	2.14	2.176	2.116	2.093	2.085	Mo−Mo	2.135	2.112	2.090	2.083
Mo−N	2.152	2.163	2.170	2.157	2.17	Mo−N	2.137	2.153	2.134	2.14
N−C	1.344	1.358	1.336	1.335	1.30	N−N	1.336	1.321	1.343	1.31
N−H	1.019	1.029	1.016	1.023		N−H	1.021	1.017	1.026	
C−H	1.097	1.104	1.095	1.094						
			Angle (deg)							
Mo−Mo−N	92.33	92.12	92.50	92.82	92.3	Mo−Mo−N	91.10	91.17	91.68	91.4
Mo−N−C	118.24	118.60	117.83	117.53	117.0	Mo−N−N	122.82	122.44	122.77	121.0
N−C−N	118.86	118.56	119.34	119.30	121.0	N−N−N	112.16	112.76	111.10	112.5
N−Mo−Mo−N	0.04	0.0	0.02	0.0	3.2	N−Mo−Mo−N	0.02	0.0	0.01	105
			Frequency (cm⁻¹)							
ν(Mo−Mo)			474			ν(Mo−MO)			485	

[a] Average bond distances and angles from crystal structure data of $Mo_2(RNCHNR)_4$ (R = p-$CH_3C_6H_4$). See ref 23. [b] Average bond distances and angles from crystal structure data of $Mo_2(PhNNNPh)_4$. See ref 24.

Table 3. Predicted Molecular Structures for $M_2(O_2CH)_4$ and $M_2(HNCHNH)_4$ (M = Nb, Tc)[a]

	Nb₂(O₂CH)₄		Tc₂(O₂CH)₄			Nb₂(HNCHNH)₄		Tc₂(HNCHNH)₄	
	ECP	AE	ECP	AE		ECP	AE	ECP	AE
			Distance (Å)						
M−M	2.293	2.238	2.146	2.110	M−M	2.286	2.225	2.123	2.083
M−O	2.202	2.180	2.125	2.116	M−N	2.237	2.231	2.161	2.172
O−C	1.298	1.293	1.295	1.291	N−C	1.342	1.333	1.339	1.330
C−H	1.094	1.091	1.092	1.089	N−H	1.020	1.024	1.017	1.021
					C−H	1.101	1.098	1.097	1.096
			Angle (deg)						
M−M−O	89.93	90.65	91.65	92.15	M−M−N	90.74	91.38	92.63	93.00
M−O−C	118.33	117.84	117.23	116.37	M−N−C	118.44	117.63	117.27	116.68
O−C−O	123.49	124.33	122.25	122.97	N−C−N	121.63	121.99	120.20	120.64
H−C−O	118.25	117.84	118.88	118.52	H−C−N	119.18	119.01	119.90	119.68
O−M−M−O	0.02	0.0	0.03	0.0	N−M−M−N	0.0	0.03	0.09	0.16
			Frequency (cm⁻¹)						
ν(M−M)		439			ν(M−M)		433		

[a] ECP calculations used LANL2DZ basis sets, and AE calculations used 3-21G basis sets. All calculations were performed with the B3LYP functional.

It is interesting to see that the calculations have predicted a very short electron-rich Tc−Tc triple bond. The Tc−Tc triple bond is 0.1 Å shorter than the Nb−Nb triple bond in both formate and formamidinate compounds and, therefore, is very close in length to the Mo−Mo quadruple bond (see also Tables 1 and 2). While there are no technetium compounds that exactly correspond to the Tc_2^{4+} ones for which we have carried out our calculations, there are similar ones with Tc_2^{5+} cores. For $Tc_2(O_2CCH_3)_4Cl$ and $K[Tc_2(O_2CCH_3)_4Cl_2]$ the reported Tc−Tc distances[25a] are both about 2.13 Å, and the value in the neutral $Tc_2(O_2CCH_3)_4$ molecule should not differ by more than 0.01−0.03 Å from this. Similarly, the $Tc_2(PhNCHNPh)_4Cl$ compound has Tc−Tc = 2.12 Å.[25b]

Ruthenium and Rhodium Compounds, $M_2(HNCHNH)_4$ and $M_2(HNNNH)_4$. As in the case of analogous Mo compounds, the actual Ru and Rh compounds exist as M_2-$(RNCHNR)_4$ and $M_2(RNNNR)_4$ with R = Ph or p-$CH_3C_6H_4$,[26−29] but the simpler compounds with R = H can be used as

satisfactory models for the real compounds. This is shown by the excellent agreement between the optimized and observed structures in Table 4 for the Ru compounds and in Table 5 for the Rh compounds. Once again, it is the AE calculations using the 3-21G basis sets that give the best fit, but the results from the ECP calculations are certainly acceptable. As in the previous calculations on the Mo compounds, the metal−metal distances given by the ECP calculations are again about 0.06 Å longer than the observed distances in all compounds.

Crystal structure data show that the Ru−Ru distance in either $Ru_2(RNCHNR)_4$ or $Ru_2(RNNNR)_4$ is 0.04 Å longer than the Rh−Rh distance in a corresponding Rh compound, even though the Ru−Ru bond is formally a double bond (a σ and a δ bond) whereas the Rh compounds have only a single σ bond. It is satisfying that these differences in the metal−metal distances are exactly reproduced by the DFT calculations on the model compounds.

It is also an experimental observation that, in both Ru and Rh compounds and in other similar systems[30] of low bond order, the length of a M−M bond bridged by the formamidinate ligands

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Table 4. Calculated Molecular Structural Parameters for $Ru_2(HNCHNH)_4$ and $Ru_2(HNNNH)_4$ with Comparison to $Ru_2(RNCHNR)_4$ and $Ru_2(RNNNR)_4$

	$Ru_2(HNCHNH)_4$[a]				$Ru_2(HNNNH)_4$[a]		
	ECP	AE	exptl[b]		ECP	AE	exptl[c]
			Distance (Å)				
Ru–Ru	2.540	2.494	2.475	Ru–Ru	2.478	2.434	2.417
Ru–N	2.049	2.057	2.04	Ru–N	2.038	2.039	2.04
N–C	1.341	1.333	1.32	N–N	1.331	1.338	1.31
N–H	1.021	1.025		N–H	1.022	1.027	
C–H	1.096	1.095					
			Angle (deg)				
Ru–Ru–N	87.23	87.72	87.	Ru–Ru–N	86.69	87.26	87.2
Ru–N–C	121.97	121.37	121.	Ru–N–N	125.88	125.97	125.0
N–C–N	121.60	121.83	122.	N–N–N	114.86	113.53	115.5
N–Ru–Ru–N	0.01	0.03	9	N–Ru–Ru–N	0.03	0.02	0.0
			Frequency (cm^{-1})				
ν(Ru–Ru)		296		ν(Ru–Ru)		331	

[a] All calculations used B3LYP functionals. ECP calculations used LANL2DZ basis sets, and AE calculations used 3-21G basis sets. [b] Averge bond distances and angles from crystal structure data of $Ru_2(RNCHNR)_4$ (R = p-$CH_3C_6H_4$). See ref 26. [c] Averge bond distances and angles from crystal structure data of $Ru_2(RNNNR))_4$ (R = p-$CH_3C_6H_4$). See ref 27.

Table 5. Calculated Structural Parameters for $Rh_2(HNCHNH)_4$ and $Rh_2(HNNNH)_4$ with Comparison to $Rh_2(RNCHNR)_4$ and $Rh_2(PhNNNPh)_4$

	$Rh_2(HNCHNH)_4$[a]				$Rh_2(HNNNH)_4$[a]		
	ECP	AE	exptl[b]		ECP	AE	exptl[c]
			Distance (Å)				
Rh–Rh	2.498	2.457	2.434	Rh–Rh	2.447	2.396	2.377
Rh–N	2.071	2.082	2.05	Rh–N	2.067	2.069	2.05
N–C	1.335	1.326	1.33	N–N	1.319	1.325	1.30
N–H	1.017	1.021		N–H	1.019	1.023	
C–H	1.096	1.096					
			Angle (deg)				
Rh–Rh–N	87.80	88.08	87.7	Rh–Rh–N	87.01	87.21	86.0
Rh–N–C	120.96	120.20		Rh–N–N	124.89	124.23	
N–C–N	122.46	122.74	123.7	N–N–N	116.01	114.64	
N–Rh–Rh–N	0.70	6.12	16.7	N–Rh–Rh–N	0.32	11.10	
			Frequency (cm^{-1})				
ν(Rh–Rh)		296		ν(Rh–Rh)		332	

[a] All calculations used B3LYP functionals. ECP calculations used LANL2DZ basis sets, and AE calculations used 3-21G basis sets. [b] Averge bond distances and angles from crystal structure data of $Rh_2(RNCHNR)_4$ (R = p-$CH_3C_6H_4$). See ref 28. [c] Averge bond distances and angles from crystal structure data of $Rh_2(PhNNNPh))_4$ See ref 29.

Table 6. Comparison of Optimized and Observed Metal–Metal Distances (Å) in $M_2(RNCHNR)_4$ and $M_2(RNNNR)_4$

	observed[a]			calculated (AE)[b]			calculated (ECP)[c]		
	R_{M-M}			R_{M-M}			R_{M-M}		
	$(RNCHNR)_4$	$(RNNNR)_4$	ΔR	$(HNCHNH)_4$	$(HNNNH)_4$	ΔR	$(HNCHNH)_4$	$(HNNNH)_4$	ΔR
Ru_2	2.475	2.417	0.06	2.494	2.434	0.060	2.540	2.478	0.062
Rh_2	2.434	2.377	0.06	2.457	2.396	0.061	2.498	2.447	0.051
Mo_2	2.085	2.083	0.00	2.093	2.090	0.003	2.140	2.135	0.005

[a] For reference, see Tables 2, 4, and 5. [b] Results in Tables 2, 4, and 5 by B3LYP 3-21G calculations. [c] Results in Tables 2, 4, and 5 by B3LYP LANL2DZ calculations.

is almost always longer by 0.06 Å than the same bond bridged by the triazenate ligands. We have argued[30] that steric effects may be the main cause for the change in the metal–metal distances. Interestingly, such a trend in M–M distances has been exactly predicted by the DFT geometry optimizations.

To give a clear view of these interesting and important results, relevant metal–metal distances, both observed and optimized, are collected in Table 6. Included in the table are also the quadruply bonded Mo–Mo distances in the analogous compounds. The Mo–Mo distances are essentially unchanged with the ligands as shown by both calculated and measured results.

M–M Stretching Frequencies. In principle, the results of a DFT geometry optimization should allow the calculation of the vibrational spectrum of the molecule. In molecules with metal–metal bonds the value of ν_{MM} is always of interest. In general the degree to which any one normal vibration can be

associated with the specific internal coordinate defined by the M–M bond distance is very uncertain. However, for the paddle-wheel structures treated here, the degree of kinetic (**G**-matrix) mixing of M–M stretching with the totally symmetric mode of M–O or M–N stretching should be negligible, although mixing through electronic coupling (**F**-matrix) cannot be ruled out. On balance, it seemed worthwhile to calculate values of ν_{MM}, and they are presented in the tables.

In the dimolybdenum compounds, the results are 15–20% too high.[31] For the niobium compounds we have no experimental results with which to compare. (See Note Added in Proof.) For the ruthenium compounds direct comparisons are not possible, but in compounds of the same type with carboxylate ligands the values[31] are 330 ± 10 cm^{-1}. Thus, the agreement is quite good.

(31) See ref 2, pp 735–737.

Table 7. Calculated Molecular Structure for $Mo_2Cl_4(PH_3)_4$ with Comparison to $Mo_2Cl_4(PMe_3)_4{}^a$

	ECP			AE[b]				
	BLYP	B3LYP	B3LYP	B3LYP				
	LANL2DZ		LANL2DZd	LARGE	3-21G	3-21Gd1	3-21Gd2	exptl[a]
Distance (Å)								
Mo−Mo	2.192	2.151	2.173	2.130	2.101	2.107	2.149	2.13
Mo−Cl	2.492	2.475	2.425	2.482	2.463	2.436	2.409	2.41
Mo−P	2.611	2.595	2.558	2.602	2.580	2.581	2.435	2.55
P−H	1.442	1.431	1.425	1.432	1.427	1.428	1.411	
	1.425	1.425	1.419	1.426	1.421	1.421	1.408	
Angle (deg)								
Mo−Mo−Cl	109.89	109.96	110.21	110.35	108.37	109.03	111.33	112.2
Mo−Mo−P	98.29	98.28	96.94	98.86	99.06	98.58	97.31	102.3
Cl−Mo−P	87.19	87.18	87.61	86.93	87.15	87.21	87.35	85.4

[a] Average bond distances and angles from crystal structure data of $Mo_2Cl_4(PMe_3)_4$. See ref 35. *[b]* 3-21Gd1: using 3-21G(d) basis set for Cl atoms only. 3-21Gd2: using 3-21G(d) basis sets for both P and Cl atoms.

Table 8. Calculated Molecular Structures for $Nb_2Cl_4(PH_3)_4$ and $Tc_2Cl_4(PH_3)_4{}^a$

	$Nb_2Cl_4(PH_3)_4$				$Tc_2Cl_4(PH_3)_4$				
	ECP		AE		ECP		AE		
	LANL2DZ	LANL2DZd	3-21Gd1	3-21Gd2	LANL2DZ	LANL2DZd	3-21Gd1	3-21Gd2	exptl[b]
Distance (Å)									
M−M	2.361	2.392	2.279	2.287	2.181	2.202	2.142	2.149	2.138
M−Cl	2.478	2.428	2.447	2.439	2.454	2.401	2.413	2.409	2.37
M−P	2.713	2.679	2.692	2.659	2.490	2.447	2.490	2.435	2.48
P−H	1.433	1.427	1.429	1.413	1.430	1.423	1.427	1.411	
	1.426	1.419	1.422	1.406	1.425	1.419	1.421	1.406	
Angle (deg)									
M−M−Cl	106.63	107.10	105.43	105.52	111.70	112.25	111.52	111.33	111.7
M−M−P	97.63	95.98	98.57	97.77	97.81	96.90	97.78	97.31	102.6
Cl−M−P	87.82	88.24	87.73	87.93	87.12	87.40	87.15	87.35	85.0

[a] All calculations used B3LYP functionals. *[b]* Average bond parameters from the crystal structure of $Tc_2Cl_4(PMePh_2)_4$ (see ref 36).

The results for the two rhodium compounds are also in harmony with results for the related carboxylato and amidato compounds, for which values in the range 285−314 cm^{-1} have been reported.[31] The fact that the values calculated here support the experiment values is of additional interest because in the past there was some dispute about the latter. Given the observed Raman spectra of $Rh_2(O_2CR)_4$ compounds, ν_{RhRh} could have been assigned as low as 170−180 cm^{-1}, with the lines in the region of 300 cm^{-1} then being attributed to ν_{RhO} modes. The lower values were at one time preferred[32] because they appeared to be in better accord with vibrational structure found in one of the electronic absorption bonds. Ultimately, however, the assignment of this electronic absorption band was changed[33] so that the higher frequency assignment was required for ν_{RhRh}. The DFT results, by confirming the higher values for ν_{RhRh}, therefore indirectly also support the assignment of the UV−vis spectrum according to which the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition is in the 500−600 nm range.[34] More studies on the M−M stretching vibrations are still in progress and will be reported later.

Molecular Structures of Dinuclear Compounds with Unsupported Metal-Metal Bonds. $M_2Cl_4(PH_3)_4$. We now turn to dinuclear compounds with unbridged multiple metal−metal bonds. We start with the quadruply bonded $M_2Cl_4(PH_3)_4$ compound which has been extensively used as a theoretical model for a class of structurally characterized compounds, Mo_2-$Cl_4(PR_3)_4$, with different phosphine ligands,[2] for example, Mo_2-$Cl_4(PMe_3)_4$.[35] All compounds of this type have a similar eclipsed structure of virtual D_{2d} symmetry as shown in Figure 1d. *Ab initio* CASSCF calculations[7a] on $Mo_2Cl_4(PH_3)_4$ indicate that any departure from the eclipsed conformation would lead to a rapid increase in the ground state energy.

Table 7 shows the results of DFT geometry optimizations and their comparison to the average bond parameters of Mo_2-$Cl_4(PMe_3)_4$.[35] The calculations were performed assuming the eclipsed conformation of D_{2d} symmetry for the above reasons. As can be seen, the calculated structural parameters are quantitatively comparable to those of the actual trimethylphosphine compound. The results in Table 7 also display trends very similar to those in the calculations for the bridged compounds. The bond distances given by the BLYP optimizations are generally longer than the B3LYP results, and the ECP calculations tend to predict longer bond lengths, both metal−metal and metal−ligand, than the corresponding AE calculations do.

The results in Table 7 for $Mo_2Cl_4(PH_3)_4$ reveal the importance of using polarization basis functions for heavier main group atoms in the DFT geometry optimizations. As shown in Table 7, a long Mo−P distance and, in particular, a very long Mo−Cl distance have been predicted by the calculations using a basis set (LANL2DZ, LARGE, or 3-21G) without the polarization function. By adding a polarization function of the d type, for example, to the LANL2DZ basis sets for both P and Cl in the ECP B3LYP calculation, the resultant LANL2DZd sets improve the metal−ligand distances significantly while there is only a small change in the metal−metal distance.

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The situation is a little different in the AE calculations. Using the 3-21G(d) sets for both P and Cl atoms (see the results under 3-21Gd2 in Table 7) results in excellent agreement between the optimized and observed Mo−Cl distances, but also leads to overcorrection of the Mo−P distance which has become too short, namely, 2.435 Å in comparison with 2.580 and 2.55 Å from the 3-21G calculation and the experiment, respectively. On the other hand, overall better results may be obtained by adding the d polarization function only to the Cl atoms, as shown by the results in the column under 3-21Gd1 in Table 7. More studies are surely needed concerning this aspect of the work.

Two other compounds, $Nb_2Cl_4(PH_3)_4$ and $Tc_2Cl_4(PH_3)_4$, of similar structure but having a metal−metal triple bond were also calculated by using the hybrid B3LYP method, and the results are given in Table 8. The optimized structure for $Tc_2Cl_4(PH_3)_4$ is compared in the table with the $Tc_2Cl_4(PMePh_2)_4$ compound[36] of known structure. Again, the 3-21Gd1 basis set which includes 3-21G(d) only for Cl atoms shows an overall good performance, while the use of a d function for P atoms (3-21Gd2 and LANL2DZd) leads to a much shorter Tc−P distance. No $Nb_2Cl_4(PR_3)_4$ compounds have yet been made, but efforts are underway to do so. On the basis of the performance of various DFT calculations on compounds of this type that we have seen so far, we may foresee their structure from the optimized results for $Nb_2Cl_4(PH_3)_4$ using the 3-21Gd1 basis set.

Concluding Remarks

We have found that DFT methods can be a powerful and effective computational tool to predict structural properties of the second-row metal complexes that contain metal−metal bonds. It is particularly interesting to see the excellent performance of the B3LYP method together with the 3-21G basis sets in the geometry optimization of these systems. We have also shown that satisfactory results could be obtained by incorporating an ECP approximation into the DFT calculations.

It has to be pointed out, however, that the same computational procedures may not be automatically applied to the similar compounds of the first-row metal atoms, particularly in cases where the electron correlation effects are exceptionally strong. One well-known example is the dichromium tetracarboxylate compound, $Cr_2(O_2CR)_4$.[8] Various DFT calculations[8] failed, just as did many conventional *ab initio* attempts, to provide a correct estimate of the length of the Cr−Cr quadruple bond. We have attempted geometry optimization of a dichromium tetraformamidinate compound, $Cr_2(HNCHNH)_4$, by DFT procedures similar to those used in this work. Preliminary results showed that a satisfactory Cr−Cr distance could not be obtained. On the other hand, however, a BLYP calculation on $V_2(HNCHNH)_4$ correctly predicted the length of the V−V triple bond in V_2-$(RNCHNR)_4$ (R = *p*-$CH_3C_6H_4$)[37] which does not have a δ bond. This result suggests that one may have to find a different form of the correlation functional in the DFT treatment to handle the extreme case of electron correlation created by the very weak δ bonding between a pair of first-row metal atoms. Work in this direction, among other DFT studies, is also underway in this laboratory.

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