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## Assessment of density functional approximations for calculation of exchange coupling constants in thiocyanato and cyanato double bridged binuclear Ni(II) complexes

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**Abstract:** In the present work, we examine the magnetic properties of 8 “end-to-end” thiocyanato, and 3 “end-to-end” cyanato double bridged Ni(II) binuclear complexes. Thiocyanato complexes are weakly ferromagnetic. Cyanato bridged complexes exhibit weak antiferromagnetic coupling. Therefore, it is a challenge for computational chemistry to calculate the exchange coupling constant in these systems accurately. 17 different density functional approximations with different flavours are used to find the method of choice to study magnetic properties in binuclear Ni(II) complexes within the broken-symmetry approach. It is found that M06-2X and PWPB95 performed the best compared to the experimental values for the entire set of examined complexes. Furthermore, the magneto-structural correlation rationalizes the results.

**Keywords:** BS-DFT; ferromagnetic coupling; antiferromagnetic coupling; magneto-structural correlations; double-hybrid functionals.

### INTRODUCTION

Due to important and versatile applications in industry, medicine, and technology, various bi- and poly-nuclear transition metal (TM) based magnetic materials have been investigated.<sup>1–5</sup> These kinds of complexes are characterized by two or more paramagnetic metal centers, often bridged through one or more small ligands. The partially filled *d*-orbitals of TM centers lead to ferromagnetic (FM) or antiferromagnetic (AF) exchange coupling.<sup>6,7</sup> Various symmetrical<sup>8,9</sup> and unsymmetrical<sup>10,11</sup> polydentate ligands are responsible for promoting the

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formation of polynuclear core. However, bridging units have a more critical influence on the electronic structure. The thiocyanato ( $\text{SCN}^-$ ) and cyanato ( $\text{OCN}^-$ ) ions are ambidentate ligands that can coordinate *via* nitrogen or chalcogen (sulfur or oxygen) as monodentate or bridging ligands.<sup>12</sup> As bridging ligands, like their well-examined azide ( $\text{N}_3^-$ ) ion analog, they predominantly coordinate in “end-on” ( $\mu$ -1,1) and “end-to-end” ( $\mu$ -1,3) fashion (Fig. 1).<sup>13,14</sup> This additionally enriches the structural versatility of these molecules. The bridging mode strongly influences the magnetic interactions between TM ions and the magnetic characteristics of a molecule.

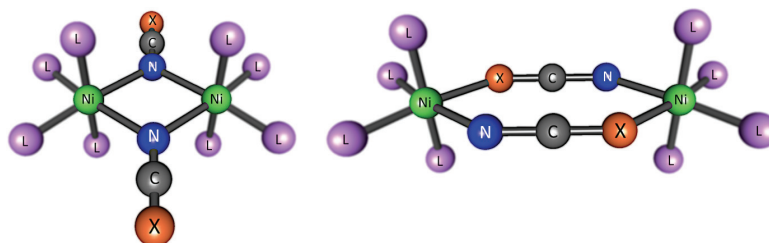


Fig. 1. Possible double bridging modes of cyanato and thiocyanato ions in binuclear nickel(II) complexes; “end-on” on the left and “end-to-end” mode on the right; X= O or S; L – spectator ligands.

In contrast to thiocyanato-bridged polynuclear complexes of some other metals (like, for example, Cu(II)<sup>15–20</sup>), the number of Ni(II) complexes is considerably smaller, whereby only a few binuclear cyanato-bridged complexes have been synthesized and characterized. “End-to-end” thiocyanato double bridged complexes are weakly FM,<sup>7,14,21</sup> while “end-to-end” cyanato double bridged complexes exhibit weak AF coupling.<sup>22,23</sup>

Although much has been explained and learned in the field of electronic structure, a clear understanding of magnetization phenomena remains a challenge. From a quantum chemical point of view, the accurate description of this fundamental characteristic requires precise modeling of magnetic energy levels associated with the magnetic interaction between two open-shell centers. Although density functional theory (DFT)<sup>24,25</sup> has evolved into a method that can be used to describe and even predict various molecular properties, due to its single-determinantal nature, the determination of exchange coupling (constants) may seem out of reach. Exchange coupling constant ( $J$ ) is a measure of the energy differences between the electronic states with different spin multiplicity.<sup>26</sup> If the state of the highest spin multiplicity is the ground state, the coupling is FM (positive  $J$  value). If the low-spin state is the ground state, AF coupling occurs (negative  $J$  value). Since only the FM states can be described with a single determinant and hence directly computed, in all other cases, broken-symmetry DFT (BS-DFT)<sup>27–30</sup> approach is commonly utilized.

In the present work, we examine the magnetic properties of 8 “end-to-end” thiocyanato (Fig. 2) and 3 “end-to-end” cyanato (Fig. 3) double bridged Ni(II) binuclear complexes by calculating the  $J$  constants within the framework of BS-DFT. DFT is, in principle, the exact theory, however, in practical computational work requires approximations (density functional approximations – DFAs) on its path to solutions. The choice of the DFA strongly influences the accuracy of calculations. It was usually found that for magnetic systems, hybrid DFAs and range-separated hybrid DFAs provide much better agreement with experimental data than semi-local DFAs.<sup>31–35</sup> However, this does not need to be true always. For example, in the case of double “end-on” azido bridged binuclear Ni(II) complexes, it was found that hybrid DFAs did not improve the results compared to general gradient approximations (GGA).<sup>36</sup> In that study, it was shown<sup>36</sup> that only double-hybrid functionals<sup>37,38</sup> (MP2 correlation energy added to the hybrid or meta-hybrid energy) give acceptable accuracy. Even more importantly, only double-hybrids predicted the sign of  $J$  correctly in all complexes.<sup>36</sup> It is noteworthy to mention that double-hybrids do not always give better results than the hybrid functionals.<sup>35,39</sup> This implies that the choice of DFAs for the calculation of magnetic coupling is firmly system dependent. Here we address the question of DFAs’ influence on the overall DFT accuracy for calculation of  $J$  constant in double bridged “end-to-end” thiocyanato and cyanato Ni(II) binuclear complexes. These systems are challenging because the weak FM or AF coupling is observed ( $J$  value ranges from  $-4.8$  to  $+6.3$   $\text{cm}^{-1}$ ). 17 different DFAs, with different flavors, are used: GGAs, meta-GGAs, hybrid functionals, meta-hybrid functionals, long-range corrected and double-hybrid functionals. Furthermore, the magneto-structural correlations in these systems will be examined.

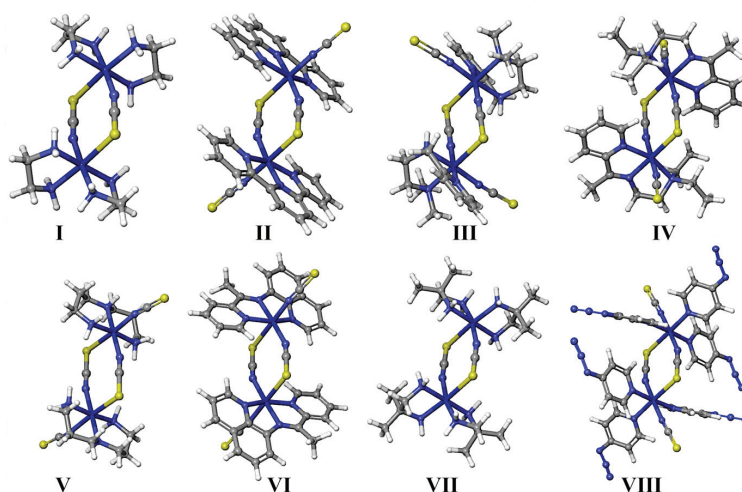


Fig. 2. “End-to-end” thiocyanato double bridged Ni(II) binuclear complexes.

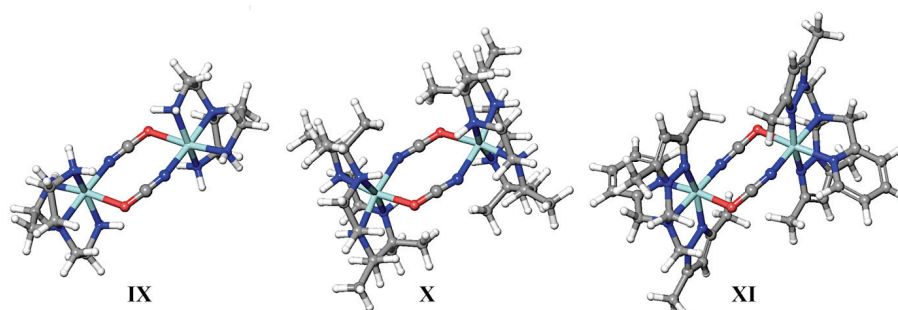


Fig. 3. “End-to-end” cyanato double bridged Ni(II) binuclear complexes.

### METHODOLOGY

All DFT calculations have been performed with the ORCA program package (version 4.1.2)<sup>40,41</sup> with ZORA-def2-TZVP(-f)<sup>42,43</sup> basis set for all atoms. Zero-order-regular-approximation (ZORA)<sup>44</sup> has been used to account for scalar-relativistic effects. For GGA and meta-GGA functionals, RI approximation in the Split-RI-J variant was used. The scalar relativistically recontracted SARC/J<sup>43,45,46</sup> auxiliary basis sets have been used to fit the Coulomb integrals in the resolution of the identity (RI) approximation.<sup>47</sup> The chain-of-spheres approximation to the exact exchange (COSX)<sup>48</sup> was employed for hybrid, meta-hybrid, long-range corrected, and double hybrid DFAs. The RI approach was used in the MP2 part of the calculation for double-hybrid functionals, combined with def2-TZVP/C<sup>49</sup> correlation fitting basis sets.

#### Choice of DFAs

The choice of DFAs used in this work include: i) GGA functionals in the form of BP86,<sup>50–52</sup> BLYP,<sup>50,53–55</sup> OLYP<sup>53–56</sup> and OPBE<sup>56,57</sup> ii) meta-GGA in the form of M06-L<sup>58,59</sup> and TPSS<sup>60,61</sup> iii) hybrid functionals B3LYP,<sup>62</sup> B3LYP\*<sup>63</sup> and BHandHLYP iv) meta-hybrid TPSSh,<sup>60,61</sup> M06<sup>58,59</sup> and M06-2X<sup>58,59</sup> v) double-hybrid B2PLYP<sup>37</sup> and PWPB95<sup>64</sup> vi) long-range corrected<sup>65</sup> LC-BLYP,<sup>66</sup> cam-B3LYP,<sup>67</sup> and wB97X.<sup>68</sup> DFAs used have different amount of the exact exchange: 0 % (GGAs and meta-GGAs), 10 % (TPSSh), 15 % (B3LYP\*), 20 % (B3LYP), 27 % (M06), 50 % (BHandHLYP and PWPB95), 53 % (B2PLYP), 54 % (M06-2X). LC-BLYP has 0 % exact exchange in the short-range, while 100% in the long-range; cam-B3LYP has 19 % in the short-range and 65 % in the long-range; wB97X has 16 % in the short-range and 100 % in the long-range. B2PYLP is the standard double-hybrid functional with the perturbative treatment of correlation on top of the DF energy. PWPB95 is double-hybrid, which accounts for the correlation of opposite-spin electron pairs solely.

#### Binuclear Ni(II) complexes

Binuclear Ni(II) complexes analyzed in this work are:  $[\{\text{Ni}(\text{en})_2\}_2(\mu_{1,3}\text{-NCS})_2]^{2+}$  (en = ethylenediamine) **I**,  $[\{\text{Ni}(\text{terpy})(\text{NCS})\}_2(\mu_{1,3}\text{-NCS})_2]$  (terpy = 2,2',6',2''-terpyridine) **II**,  $[\{\text{NiL}^1\text{-(NCS)}\}_2(\mu_{1,3}\text{-NCS})_2]$  ( $\text{L}^1 = N,N$ -dimethyl- $N'$ -(pyrid-2-ylmethyl)-ethylenediamine) **III**,  $[\{\text{NiL}^2\text{-(NCS)}\}_2(\mu_{1,3}\text{-NCS})_2]$  ( $\text{L}^2 = N,N$ -diethyl- $N'$ -(1-pyridin-2-yl-ethylidene)-ethylenediamine) **IV**,  $[\{\text{NiL}^3\text{-(NCS)}\}_2(\mu_{1,3}\text{-NCS})_2]$  ( $\text{L}^3 = \text{bis}(3\text{-aminopropyl})\text{amine}$ ) **V**,  $[\{\text{NiL}^4\text{-(NCS)}\}_2(\mu_{1,3}\text{-NCS})_2]$  ( $\text{L}^4 = 1\text{-(pyridin-2-yl)-N-(quinolin-8-yl)ethan-1-imine}$ ) **VI**,  $[\{\text{NiL}^5\}_2(\mu_{1,3}\text{-NCS})_2]^{2+}$  ( $\text{L}^5 = 1,2\text{-diamino-2-methylpropane}$ ) **VII**,  $[\{\text{Ni}(4\text{-azpy})_6\}_2(\mu_{1,3}\text{-NCS})_2]$  (4-azpy = 4-azidopyridine) **VIII**,  $[\{\text{Ni}(\text{tren})\}_2(\mu_{1,3}\text{-OCN})_2]^{2+}$  (tren = tris(2-aminoethyl)amine) **IX**,  $[\{\text{Ni}(\text{Me}_6[14]\text{aneN}_4)\}_2(\mu\text{-OCN})_2]^{2+}$  ( $\text{Me}_6[14]\text{aneN}_4 = \text{DL-5,5,7,12,12,14-hexamethyl-}$

-1,4,8,11-tetraazacyclotetradecane) **X**,  $[\{\text{NiL}^6\}_2(\mu_{1,3}\text{-OCN})_2]^{2+}$  ( $\text{L}^6 = N,N\text{-bis}(3,5\text{-dimethylpyrazol-1-ylmethyl})\text{aminomethylpyridine}$ ). Complexes **I–VIII** are bridged with two “end-to-end” thiocyanato ligands and complexes **IX–XI** with two “end-to-end” cyanato ligands. Each Ni(II) center is hexacoordinated in distorted octahedral environment with two bridging ligands, one bonded *via* nitrogen donor atom and other *via* chalcogen (sulfur or oxygen donor atoms). Remaining coordination places around Ni(II) centers are occupied by two bidentate ligands (**I**, **VII**), one tridentate ligand and monodentate  $\text{NCS}^-$  (coordination *via* N atom; **II–V**), one tetradentate ligand (**VI**, **IX–XI**), or six monodentate ligands (**VIII**). Therefore, the first coordination sphere around each Ni(II) is  $\text{NiN}_5\text{X}$  ( $\text{X} = \text{S/O}$ ). All the calculations were performed on the complexes from the experimental X-ray structures: **I** (CCDC 1219660),<sup>69</sup> **II** (CCDC 1261119),<sup>21</sup> **III** (CCDC 263465),<sup>70</sup> **IV** (CCDC 772821),<sup>14</sup> **V** (CCDC 180314),<sup>71</sup> **VI** (CCDC 1918388),<sup>7</sup> **VII** (CCDC 1206993),<sup>72</sup> **VIII** (CCDC 1010020),<sup>73</sup> **IX** (CCDC 1275667),<sup>22</sup> **X** (CCDC 1245877),<sup>74</sup> **XI** (CCDC 782334).<sup>75</sup> Solvent molecules (complex **III**) and counterions (complexes **I**, **VII**, **IX–XI**) were removed, missing hydrogen atoms were added to complex **I**. Positions of hydrogen atoms were optimized in all structures, assuming the high-spin state, using BP86 functional with Grimme’s third-generation dispersion energy correction<sup>76</sup> and Becke-Johnson damping,<sup>77</sup> *i.e.*, BP86-D3. In the X-ray structure of **V**, both the binuclear and central part of tetranuclear units are considered. Terminal Ni(II) units of tetranuclear structure in **V** are removed because they are connected with a single NCS bridge to the central part (coordination to the central part *via* S atom, *i.e.*, *trans*- $\text{NiN}_4\text{S}_2$  coordination sphere).<sup>71</sup>

#### Exchange coupling

The exchange coupling constant  $J$  of the Heisenberg–Dirac–van Vleck spin-Hamiltonian ( $H = -2JS_1S_2$ ) was calculated with BS-DFT formalism<sup>27–30</sup> according to the Yamaguchi:<sup>40,78</sup>  $J = (E_{\text{HS}} - E_{\text{BS}}) / (\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}})$ .  $\langle S^2 \rangle_{\text{HS}}$  and  $\langle S^2 \rangle_{\text{BS}}$  are the spin expectation values of the high-spin and broken-symmetry states, respectively.  $E_{\text{HS}}$  and  $E_{\text{BS}}$  are corresponding energies. When the Hamiltonian is in the form  $H = -JS_1S_2$  (complexes **IV**, **X**, **XI**), the reported  $J$  values from the literature are divided by two to compare calculated and experimental values. In the case of **V**, the average of the two computed  $J$  values is compared with the experiment because only one  $J$  is reported for double-bridged pathways.<sup>71</sup>

## RESULTS AND DISCUSSION

Results for calculation of  $J$  constants in complexes **I–XI** with GGAs and meta-GGAs are presented in Table I. On the same complexes, results of calculations with three hybrid and three meta-hybrid DFAs are summarized in Table II. Finally, Table III shows the results obtained with double-hybrid and long-range corrected DFAs. In Table II, DFT only values of double-hybrids are given as well. In all tables, mean error ( $ME$ ), mean absolute error ( $MAE$ ), minimal absolute error (Min  $AE$ ), and maximal absolute error (Max  $AE$ ) with respect to the experimental values are given. The results indicate the accuracy of a given functional for the investigated set of complexes. Generally speaking, GGAs do not perform well, as indicated by the largest MAE (more than  $10 \text{ cm}^{-1}$ ). Meta-GGAs do not improve the results comparing to GGAs. In some cases, there is an overestimation of FM coupling (**II**, **III**, **VI**, **VII**), while in other cases AF coupling is more pronounced. This is different than in double “end-on” azido bridged binuclear Ni(II) complexes where all GGAs largely overestimated FM coupling.<sup>36</sup> BP86,

TABLE I. Exchange coupling constants ( $J / \text{cm}^{-1}$ ), calculated with selected GGAs and meta-GGAs for 8 “end-to-end” thiocyanato (Fig. 2, **I–VIII**) and 3 “end-to-end” cyanato (Fig. 3, **IX–XI**) double bridged Ni(II) binuclear complexes and comparison with experimentally determined values. Mean error ( $ME$ ), mean absolute error ( $MAE$ ), minimal absolute error (Min  $AE$ ) and maximal absolute error (Max  $AE$ )

Complex	Exp.	GGA					
		BP86	BLYP	OLYP	OPBE	M06-L	TPSS
<b>I</b>	4.50 <sup>69</sup>	0.38	1.77	8.41	11.07	6.48	2.04
<b>II</b>	4.90 <sup>21</sup>	19.49	18.6	25.59	27.15	16.33	16.37
<b>III</b>	3.90 <sup>70</sup>	7.49	6.46	13.98	16.48	9.68	6.54
<b>IV</b>	0.34 <sup>14</sup>	-12.12	-13.33	-4.12	-2.01	0.29	-8.39
<b>V</b>	2.73 <sup>71</sup>	-5.38	-6.61	0.65	3.25	2.11	-3.80
<b>VI</b>	4.71 <sup>7</sup>	17.96	17.43	23.14	22.65	13.31	14.11
<b>VII</b>	6.33 <sup>72</sup>	28.48	27.35	45.24	46.17	21.98	21.30
<b>VIII</b>	1.56 <sup>73</sup>	-1.98	-3.07	5.60	7.58	4.62	-1.19
<b>IX</b>	-4.41 <sup>23</sup>	-12.46	-12.93	-9.15	-7.88	-4.73	-10.30
<b>X</b>	-4.80 <sup>74</sup>	-31.55	-32.05	-28.89	-15.41	-15.98	-25.86
<b>XI</b>	-3.10 <sup>75</sup>	-21.65	-22.42	-17.71	-15.41	-9.58	-17.86
$ME$		-2.54	-3.22	4.19	7.00	2.53	-2.15
$MAE$		12.29	12.32	13.28	12.23	5.93	9.16
Min $AE$		3.54	2.56	2.085	0.52	0.05	2.46
Max $AE$		26.75	27.25	38.94	39.87	15.68	21.06

BLYP, and TPSS, predict the wrong sign of  $J$  constant in cases **IV**, **V** and **VIII**. OLYP and OPBE revealed the opposite sign only in the case of **IV**. This complex is also problematic for B3LYP\* and TPSSh (Table II). M06-L is the only DFA from these functionals that qualitatively gives correct results (Table I). As expected, hybrid functionals performed much better giving MAE in the range 2.2-3.8  $\text{cm}^{-1}$ . DFAs with a higher percentage of the exact exchange (50% in BHandHLYP and 54 % in M06-2X) give somewhat better results. Meta-hybrid M06-2X has the lowest MAE (1.4  $\text{cm}^{-1}$ ) among chosen “standard DFAs” (Tables I and II) and Max  $AE$  of 3.6  $\text{cm}^{-1}$ . Long-range corrected functionals do not perform better than standard hybrid functionals for herein studied complexes (Table III). Double-hybrid DFAs give good agreement with experimental values. PWPB95, double-hybrid with only opposite-spin correlation, is the best of all 17 selected functionals with MAE of 1.1  $\text{cm}^{-1}$  and Max  $AE = 2.8 \text{ cm}^{-1}$ . DFT only values of double-hybrids (without perturbational corrections) are similar to the results obtained with BHandHLYP and M06-2X. Considering the high computational cost of double-hybrids, the use of M06-2X is recommended for double-bridged NCS/NCO binuclear Ni(II) complexes.

#### Magneto-structural correlations

Herein analyzed thiocyanato “end-to-end” double-bridged binuclear Ni(II) complexes show weak FM coupling ( $J$  value from 0.3 to 6.3  $\text{cm}^{-1}$ ), while rare cya-



TABLE II. Exchange coupling constants ( $J / \text{cm}^{-1}$ ), calculated with selected hybrid and meta-hybrid DFAs for 8 “end-to-end” thiocyanato (Fig. 2, **I–VIII**) and 3 “end-to-end” cyanato (Fig. 3, **IX–XI**) double bridged Ni(II) binuclear complexes and comparison with experimentally determined values. Mean error ( $ME$ ), mean absolute error ( $MAE$ ), minimal absolute error ( $\text{Min } AE$ ), and maximal absolute error ( $\text{Max } AE$ )

Complex	Exp.	DFA					
		B3LYP	B3LYP*	BHandHLYP	TPSSh	M06	M06-2X
<b>I</b>	4.50 <sup>69</sup>	4.37	3.79	4.06	6.4	6.95	3.25
<b>II</b>	4.90 <sup>21</sup>	11	12.7	7.37	10.99	13.8	5.97
<b>III</b>	3.90 <sup>70</sup>	5.97	7.15	5.59	7.09	8.21	3.93
<b>IV</b>	0.34 <sup>14</sup>	1.6	-0.42	3.49	-2.53	1.43	1.83
<b>V</b>	2.73 <sup>71</sup>	1.54	2.13	3.22	0.115	2.39	1.345
<b>VI</b>	4.71 <sup>7</sup>	8.83	8.89	5.71	8.63	11.63	4.88
<b>VII</b>	6.33 <sup>72</sup>	13.00	15.94	12.01	15.89	17.41	9.74
<b>VIII</b>	1.56 <sup>73</sup>	1.11	1.00	3.60	3.86	4.47	2.32
<b>IX</b>	-4.41 <sup>23</sup>	-4.06	-4.02	-0.26	-3.57	-1.54	-0.77
<b>X</b>	-4.80 <sup>74</sup>	-9.78	-12.58	-2.9	-14.32	-8.65	-3.51
<b>XI</b>	-3.10 <sup>75</sup>	-6.69	-8.75	-1.79	-7.69	-5.19	-2.19
$ME$		0.93	0.84	2.13	0.75	3.12	0.92
$MAE$		2.81	3.76	2.21	4.31	4.26	1.40
$\text{Min } AE$		0.13	0.38	0.44	0.83	0.34	0.03
$\text{Max } AE$		6.7	9.64	5.71	9.59	11.11	3.63

TABLE III. Exchange coupling constants ( $J / \text{cm}^{-1}$ ), calculated with selected double-hybrid and long-range corrected DFAs for 8 “end-to-end” thiocyanato (Fig. 2, **I–VIII**) and 3 “end-to-end” cyanato (Fig. 3, **IX–XI**) double bridged Ni(II) binuclear complexes and comparison with experimentally determined values. Mean error ( $ME$ ), mean absolute error ( $MAE$ ), minimal absolute error ( $\text{Min } AE$ ), and maximal absolute error ( $\text{Max } AE$ ) in  $\text{cm}^{-1}$ . DFT only values for double-hybrids is given

Complex	Exp.	DFA						
		B2PLYP (DFT)	B2LYP	PWPB95 (DFT)	PWPB95	LC-BLYP	Cam-B3LYP	wB97X
<b>I</b>	4.50 <sup>69</sup>	4.49	4.75	3.7	2.92	5.25	4.63	4.88
<b>II</b>	4.90 <sup>21</sup>	7.62	8.10	6.36	6.43	13.18	9.64	9.29
<b>III</b>	3.90 <sup>70</sup>	5.86	5.89	4.45	4.23	6.07	6.4	5.98
<b>IV</b>	0.34 <sup>14</sup>	3.72	1.81	2.34	0.73	0.46	3.16	3.78
<b>V</b>	2.73 <sup>71</sup>	3.16	3.03	1.7	0.93	1.08	1.82	2.49
<b>VI</b>	4.71 <sup>7</sup>	6.12	6.96	4.63	5.16	9.30	8.44	8.03
<b>VII</b>	6.33 <sup>72</sup>	12.33	6.14	10.17	4.57	15.20	13.73	12.23
<b>VIII</b>	1.56 <sup>73</sup>	4.28	4.17	2.92	2.29	4.57	3.69	4.78
<b>IX</b>	-4.41 <sup>23</sup>	-0.09	-0.33	-0.74	-1.55	-4.22	-2.14	-0.45
<b>X</b>	-4.80 <sup>74</sup>	-2.91	-4.85	-3.23	-5.36	-10.53	-6.86	-5.24
<b>XI</b>	-3.10 <sup>75</sup>	-0.32	-2.87	-1.89	-3.29	-6.03	-4.73	-4.8
$ME$		2.51	1.47	1.25	0.04	1.61	1.92	2.21
$MAE$		2.51	1.51	1.60	1.10	3.48	2.76	2.65
$\text{Min } AE$		0.01	0.05	0.07	0.19	0.12	0.13	0.24
$\text{Max } AE$		6.03	4.07	3.87	2.85	8.9	7.43	5.93

nato ones show weak AF coupling (from  $-3.1$  to  $-4.8$   $\text{cm}^{-1}$ ). All complexes have similar coordination around Ni(II) centers and similar Ni–Ni distances (thiocyanato in the range  $5.5$ – $5.7$  Å, and cyanato in the range  $5.1$ – $5.5$  Å). The correlation between the magnetic properties of these complexes with their geometries reveals the importance of symmetry of the bridging unit.<sup>7,23,74,79</sup> The more symmetric the bridge is, the more AF coupling is pronounced. The measure of symmetry/asymmetry of a bridge,  $\delta$ , is defined as a difference between Ni–X ( $X = \text{O/S}$ ) and Ni–N bond lengths.<sup>7</sup> In Fig. 4, where experimental  $J$  values are plotted vs.  $\delta$  (from corresponding X-ray structures), linear dependence is observed ( $R^2 = 0.89$ ). The AF coupled cyanate bridged complexes have smaller  $\delta$  ( $0.1$ – $0.3$  Å) than FM coupled thiocyanato bridged complexes. The same trend is observed with DFT calculated  $J$  coupling, Fig. 5 ( $R^2 = 0.96$  and  $R^2 = 0.87$  for M06-2X and PWPB95, respectively). The symmetry of the double pseudohalide bridges is known to be important for other binuclear complexes as well.<sup>80</sup>

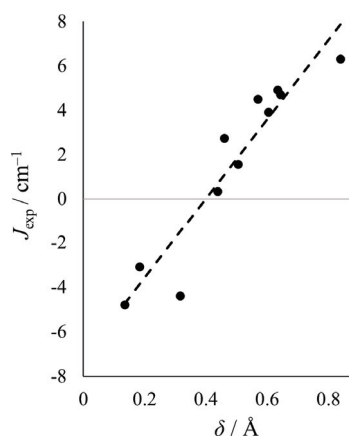


Fig. 4. Relationship between experimental exchange coupling constant  $J_{\text{exp}}$  and symmetry of the bridge  $\delta$  (from corresponding X-ray structures).

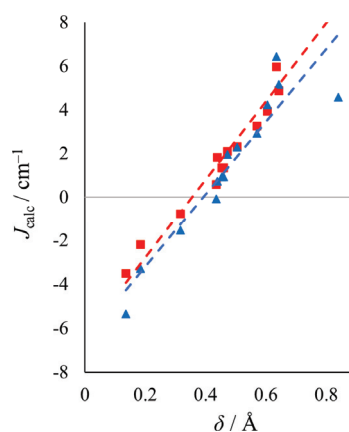


Fig. 5. Relationship between calculated exchange coupling constant  $J_{\text{calc}}$  and symmetry of the bridge  $\delta$  (from corresponding X-ray structures);  $J_{\text{calc}}$  by M06-2X – squares and PWPB95 – triangles.



Interestingly, there exists a linear relationship between the error of GGAs ( $J_{\text{calc}} - J_{\text{exp}}$ ) and  $\delta$  ( $R^2 = 0.88$  and  $R^2 = 0.92$  for BP86 and OPBE, respectively). In Fig. 6 relationship between  $J_{\text{calc}} - J_{\text{exp}}$  and  $\delta$  for BP86, OPBE, and PWPB95 are shown.

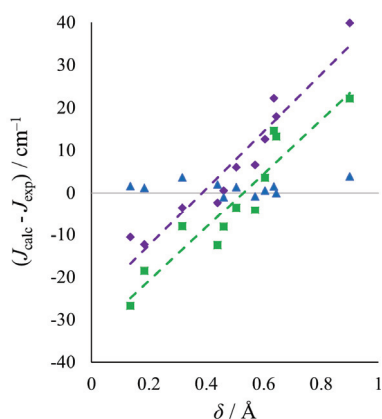


Fig. 6. Relationship between  $J_{\text{calc}} - J_{\text{exp}}$  and  $\delta$  (from corresponding X-ray structures) –  $J_{\text{calc}}$  by BP86 (squares), OPBE (diamonds) and PWPB95 (triangles).

When  $\delta$  is small, GGAs tend to overestimate AF coupling. This is in line with the known tendency of GGAs to stabilize the low-spin states.<sup>81</sup> OPBE, which is suitable for spin-state energetics of mononuclear complexes<sup>81</sup> corrects this behavior, albeit not sufficiently. As  $\delta$  is increasing, AF coupling becomes less critical, as discussed above (Fig. 4). When  $\delta$  is larger, FM coupling, dominated by the high-spin state's spin-delocalization, becomes more important. In these cases, GGAs enlarge FM coupling because of its nature to overestimate electron spin delocalization.<sup>82</sup> On the other hand, DFAs with exact exchange tend to stabilize the high-spin state and to localize the spin density.<sup>81,83</sup> Therefore, hybrid and meta-hybrid DFAs showed better performance (Table II). Double hybrids improve the results because MP2 correlation corrects the over-stabilization of the high-spin states, and there is no correlation between the  $J_{\text{calc}} - J_{\text{exp}}$  and  $\delta$  (ME for PWPB95 is  $0.04 \text{ cm}^{-1}$ ).

#### CONCLUSION

In this study, the performance of 17 DFAs with different flavors for the calculation of the magnetic coupling in 11 binuclear Ni(II) complexes have been presented. These results are compared to experimentally determined  $J$  values. Furthermore, the magneto-structural correlation between the  $J$  constant and symmetry of the bridging unit has been examined. This study shows that M06-2X and PWPB95 are the methods of choice for studying magnetic coupling in binuclear Ni(II) complexes, which can be used for predictive analyses. It is noteworthy that these results are somewhat different from double “end-on” azido bridged binuclear Ni(II) complexes,<sup>36</sup> where M06-2X gave the wrong sign of  $J$  in one

case, showing the importance of bridging ligands. Magneto-structural correlation delved deeper into the origin of various DFAs' behavior and gave a rational explanation of their tendencies.

Although most polynuclear complexes are obtained accidentally, this study will guide the smart choice of polydentate and bridging ligands. This can open a door for rational tuning of the electronic structure, magnetic interactions, and thus all general properties of a binuclear complex.

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## ИЗВОД

ИСПИТИВАЊЕ АПРОКСИМАТИВНИХ ФУНКЦИОНАЛА ГУСТИНЕ ЗА  
ИЗРАЧУНАВАЊЕ КОНСТАНТИ КУПЛОВАЊА У ДВОСТРУКО ПРЕМОШЋЕНИМ  
ТИОЦИЈАНАТО И ЦИЈАНАТО БИНУКЛЕАРНИМ Ni(II) КОМПЛЕКСИМА

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Проучавана су магнетна својства 8 „end-to-end“ тиоцијанато, и 3 „end-to-end“ цијанато двоструко премошћених Ni(II) бинуклеарних комплекса. Тиоцијанато премошћени комплекси су слабо феромагнетни. Комплекси премошћени цијанато лигандима показују слабо антиферомагнетно купловање. Због тога је прецизно израчунавање константи купловања у овим системима изазов за рачунарску хемију. Константе купловања у овим системима су израчунате *Broken-Symmetry* приступом у оквиру теорије функционала густине. Седамнаест апроксимативних функционала густине су коришћени како би се пронашао најпоузданији ниво теорије за проучавање магнетних својстава бинуклеарних Ni(II) комплекса. Утврђено је да су M06-2X и PWPB95 показали најбоље слагање са експерименталним вредностима за цео скуп испитиваних комплекса. Напослетку, резултати су рационализовани магнетно-структурном корелацијом.

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## REFERENCES

1. G. Li, D. Zhu, X. Wang, Z. Su, M. R. Bryce, *Chem. Soc. Rev.* **49** (2020) 765 (<https://doi.org/10.1039/c8cs00660a>)
2. D. M. Zink, M. Bächle, T. Baumann, M. Nieger, M. Kühn, C. Wang, W. Klopffer, U. Monkowius, T. Hofbeck, H. Yersin, S. Bräse, *Inorg. Chem.* **52** (2013) 2292 (<https://doi.org/10.1021/ic300979c>)
3. J. He, M. Zeng, H. Cheng, Z. Chen, F. Liang, *Zeitschrift Anorg. Allg. Chem.* **639** (2013) 1834 (<https://doi.org/10.1002/zaac.201300153>)
4. N. Xiong, G. Zhang, X. Sun, R. Zeng, *Chinese J. Chem.* **38** (2020) 185 (<https://doi.org/10.1002/cjoc.201900371>)
5. M. Jarenmark, H. Carlsson, E. Nordlander, *Comptes Rendus Chim.* **10** (2007) 433 (<https://doi.org/10.1016/j.crci.2007.02.015>)

6. D. Venegas-Yazigi, D. Aravena, E. Spodine, E. Ruiz, S. Alvarez, *Coord. Chem. Rev.* **254** (2010) 2086 (<https://doi.org/10.1016/j.ccr.2010.04.003>)
7. P. Ghorai, P. Brandão, S. Benmansour, C. J. G. García, A. Saha, *Polyhedron* **188** (2020) 114708 (<https://doi.org/10.1016/j.poly.2020.114708>)
8. A. L. Gavrilova, C. J. Qin, R. D. Sommer, A. L. Rheingold, B. Bosnich, *J. Am. Chem. Soc.* **124** (2002) 1714 (<https://doi.org/10.1021/ja012386z>)
9. C. Incarvito, A. L. Rheingold, C. J. Qin, A. L. Gavrilova, B. Bosnich, *Inorg. Chem.* **40** (2001) 1386 (<https://doi.org/10.1021/ic0012773>)
10. K. Shanmuga Bharathi, S. Sreedaran, A. Kalilur Rahiman, V. Narayanan, *Spectrochim. Acta, A* **105** (2013) 245 (<https://doi.org/10.1016/j.saa.2012.12.031>)
11. D. Ghosh, S. Mukhopadhyay, S. Samanta, K.-Y. Choi, A. Endo, M. Chaudhury, *Inorg. Chem.* **42** (2003) 7189 (<https://doi.org/10.1021/ic034314>)
12. J. Burmeister, *Coord. Chem. Rev.* **105** (1990) 77 ([https://doi.org/10.1016/0010-8545\(90\)80019-P](https://doi.org/10.1016/0010-8545(90)80019-P))
13. T. S. Mahapatra, S. Chaudhury, S. Dasgupta, V. Bertolasi, D. Ray, *New J. Chem.* **40** (2016) 2268 (<https://doi.org/10.1039/c5nj02410b>)
14. P. Bhowmik, S. Chattopadhyay, M. G. B. Drew, C. Diaz, A. Ghosh, *Polyhedron* **29** (2010) 2637 (<https://doi.org/10.1016/j.poly.2010.06.014>)
15. T. Mallah, M. L. Boillot, O. Kahn, J. Gouteron, S. Jeannin, Y. Jeannin, *Inorg. Chem.* **25** (1986) 3058 (<https://doi.org/10.1021/ic00237a027>)
16. O. Kahn, T. Mallah, J. Gouteron, S. Jeannin, Y. Jeannin, *J. Chem. Soc. Dalt. Trans.* (1989) 1117 (<https://doi.org/10.1039/DT9890001117>)
17. J. Carranza, J. Sletten, F. Lloret, M. Julve, *J. Mol. Struct.* **890** (2008) 31 (<https://doi.org/10.1016/j.molstruc.2007.11.034>)
18. A. E. Mauro, S. I. Klein, J. S. Saldaña, C. A. De Simone, J. Zukerman-Schpector, E. E. Castellano, *Polyhedron* **9** (1990) 2937 ([https://doi.org/10.1016/S0277-5387\(00\)84204-7](https://doi.org/10.1016/S0277-5387(00)84204-7))
19. S. Youngme, J. Phatchimkun, U. Suksangpanya, C. Pakawatchai, G. A. Van Albada, J. Reedijk, *Inorg. Chem. Commun.* **8** (2005) 882 (<https://doi.org/10.1016/j.inoche.2005.06.024>)
20. C. Diaz, J. Ribas, M. Salah El Fallah, X. Solans, M. Font-Bardía, *Inorg. Chim. Acta* **312** (2001) 1 ([https://doi.org/10.1016/S0020-1693\(00\)00281-4](https://doi.org/10.1016/S0020-1693(00)00281-4))
21. T. Rojo, R. Cortés, L. Lezama, M. I. Arriortua, K. Urriaga, G. Villeneuve, *J. Chem. Soc. Dalt. Trans.* (1991) 1779 (<https://doi.org/10.1039/DT9910001779>)
22. D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* **13** (1974) 2056 (<https://doi.org/10.1021/ic50139a003>)
23. D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* **13** (1974) 2929 (<https://doi.org/10.1021/ic50142a031>)
24. W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH Verlag GmbH, Weinheim, 2001 (<https://doi.org/10.1002/3527600043>)
25. R. G. Parr, *Density Functional Theory of Atoms and Molecules*, in *Horizons Quantum Chem.*, Springer, Amsterdam, 1980, pp. 5–15 ([https://doi.org/10.1007/978-94-009-9027-2\\_2](https://doi.org/10.1007/978-94-009-9027-2_2))
26. O. Kahn, *Molecular magnetism*, VCH-Verlag, Weinheim, 1993 (ISBN 3-527-89566-3)
27. L. Noodleman, *J. Chem. Phys.* **74** (1981) 5737 (<https://doi.org/10.1063/1.440939>)
28. L. Noodleman, E. R. Davidson, *Chem. Phys.* **109** (1986) 131 ([https://doi.org/10.1016/0301-0104\(86\)80192-6](https://doi.org/10.1016/0301-0104(86)80192-6))
29. F. Neese, *Coord. Chem. Rev.* **253** (2009) 526 (<https://doi.org/10.1016/j.ccr.2008.05.014>)

30. A. Bencini, F. Totti, *J. Chem. Theory Comput.* **5** (2009) 144 (<https://doi.org/10.1021/ct800361x>)
31. G. David, N. Guihéry, N. Ferré, *J. Chem. Theory Comput.* **13** (2017) 6253 (<https://doi.org/10.1021/acs.jctc.7b00976>)
32. S. Ninova, V. Lanzilotto, L. Malavolti, L. Rigamonti, B. Cortigiani, M. Mannini, F. Totti, R. Sessoli, *J. Mater. Chem., C* **2** (2014) 9599 (<https://doi.org/10.1039/c4tc01647e>)
33. J. E. Peralta, J. I. Melo, *J. Chem. Theory Comput.* **6** (2010) 1894 (<https://doi.org/10.1021/ct100104v>)
34. J. J. Phillips, J. E. Peralta, *J. Chem. Phys.* **138** (2013) 174115 (<https://doi.org/10.1063/1.4802776>)
35. N. A. G. Bandeira, B. Le Guennic, *J. Phys. Chem., A* **116** (2012) 3465 (<https://doi.org/10.1021/jp300618v>)
36. T. Keškić, Z. Jagličić, A. Pevec, B. Čobeljić, D. Radanović, M. Gruden, I. Turel, K. Anđelković, I. Brčeski, M. Zlatar, *Polyhedron* **191** (2020) 114802 (<https://doi.org/10.1016/j.poly.2020.114802>)
37. S. Grimme, *J. Chem. Phys.* **124** (2006) 034108 (<https://doi.org/10.1063/1.2148954>)
38. L. Goerigk, S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **4** (2014) 576 (<https://doi.org/10.1002/wcms.1193>)
39. D. A. Pantazis, *Inorganics* **7** (2019) 57 (<https://doi.org/10.3390/inorganics7050057>)
40. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2** (2012) 73 (<https://doi.org/10.1002/wcms.81>)
41. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **8** (2018) e1327 (<https://doi.org/10.1002/wcms.1327>)
42. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7** (2005) 3297 (<https://doi.org/10.1039/b508541a>)
43. D. A. Pantazis, X.-Y. Chen, C. R. Landis, F. Neese, *J. Chem. Theory Comput.* **4** (2008) 908 (<https://doi.org/10.1021/ct800047t>)
44. C. van Wüllen, *J. Chem. Phys.* **109** (1998) 392 (<https://doi.org/10.1063/1.476576>)
45. D. A. Pantazis, F. Neese, *J. Chem. Theory Comput.* **5** (2009) 2229 (<https://doi.org/10.1021/ct900090f>)
46. F. Weigend, *Phys. Chem. Chem. Phys.* **8** (2006) 1057 (<https://doi.org/10.1039/b515623h>)
47. F. Neese, *J. Chem. Phys.* **115** (2001) 11080 (<https://doi.org/10.1063/1.1419058>)
48. F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **356** (2009) 98 (<https://doi.org/10.1016/j.chemphys.2008.10.036>)
49. A. Hellweg, C. Hättig, S. Höfener, W. Klopper, *Theor. Chem. Acc.* **117** (2007) 587 (<https://doi.org/10.1007/s00214-007-0250-5>)
50. A. D. Becke, *Phys. Rev., A* **38** (1988) 3098 (<https://doi.org/10.1103/PhysRevA.38.3098>)
51. J. P. Perdew, *Phys. Rev., B* **33** (1986) 8822 (<https://doi.org/10.1103/PhysRevB.33.8822>)
52. J. P. Perdew, *Phys. Rev., B* **34** (1986) 7406 (<https://doi.org/10.1103/PhysRevB.34.7406>)
53. C. Lee, W. Yang, R. G. Parr, *Phys. Rev., B* **37** (1988) 785 (<https://doi.org/10.1103/PhysRevB.37.785>)
54. B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* **98** (1993) 5612 (<https://doi.org/10.1063/1.464906>)
55. T. V. Russo, R. L. Martin, P. J. Hay, *J. Chem. Phys.* **101** (1994) 7729 (<https://doi.org/10.1063/1.468265>)
56. N. C. Handy, A. J. Cohen, *Mol. Phys.* **99** (2001) 403 (<https://doi.org/10.1080/00268970010018431>)

57. M. Swart, A. W. Ehlers, K. Lammertsma, *Mol. Phys.* **102** (2004) 2467 (<https://doi.org/10.1080/0026897042000275017>)
58. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **120** (2008) 215 (<https://doi.org/10.1007/s00214-007-0310-x>)
59. Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* **125** (2006) 194101 (<https://doi.org/10.1063/1.2370993>)
60. V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, *J. Chem. Phys.* **119** (2003) 12129 (<https://doi.org/10.1063/1.1626543>)
61. J. Tao, J. Perdew, V. Staroverov, G. Scuseria, *Phys. Rev. Lett.* **91** (2003) 146401 (<https://doi.org/10.1103/PhysRevLett.91.146401>)
62. A. D. Becke, *J. Chem. Phys.* **98** (1993) 5648 (<https://doi.org/10.1063/1.464913>)
63. M. Reiher, O. Salomon, B. Artur Hess, *Theor. Chem. Accounts Theory, Comput. Model. (Theor. Chim. Acta)* **107** (2001) 48 (<https://doi.org/10.1007/s00214-001-0300-3>)
64. L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **7** (2010) 291 (<https://doi.org/10.1021/ct100466k>)
65. H. Iikura, T. Tsuneda, T. Yanai, K. Hirao, *J. Chem. Phys.* **115** (2001) 3540 (<https://doi.org/10.1063/1.1383587>)
66. Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, *J. Chem. Phys.* **120** (2004) 8425 (<https://doi.org/10.1063/1.1688752>)
67. T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **393** (2004) 51 (<https://doi.org/10.1016/j.cplett.2004.06.011>)
68. J. Da Chai, M. Head-Gordon, *J. Chem. Phys.* **128** (2008) 084106 (<https://doi.org/10.1063/1.2834918>)
69. A. E. Shvelashvili, M. A. Porai-Koshits, A. S. Antsyshkina, *J. Struct. Chem.* **10** (1969) 552 (<https://doi.org/10.1007/BF00743627>)
70. H. D. Bian, W. Gu, Q. Yu, S. P. Yan, D. Z. Liao, Z. H. Jiang, P. Cheng, *Polyhedron* **24** (2005) 2002 (<https://doi.org/10.1016/j.poly.2005.06.011>)
71. T. Kumar Maji, G. Mostafa, J. M. Clemente-Juan, J. Ribas, F. Lloret, K. Okamoto, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* **2003** (2003) 1005 (<https://doi.org/10.1002/ejic.200390123>)
72. M. Monfort, J. Ribas, X. Solans, *Inorg. Chem.* **33** (1994) 4271 (<https://doi.org/10.1021/ic00097a013>)
73. F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente, S. S. Massoud, *Polyhedron* **85** (2015) 20 (<https://doi.org/10.1016/j.poly.2014.08.031>)
74. A. Escuer, R. Vicente, M. S. El Fallah, X. Solans, M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* (1996) 1013 (<https://doi.org/10.1039/DT9960001013>)
75. Z. Mahendrasinh, S. Ankita, S. B. Kumar, A. Escuer, E. Suresh, *Inorg. Chim. Acta* **375** (2011) 333 (<https://doi.org/10.1016/j.ica.2011.05.027>)
76. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **132** (2010) 154104 (<https://doi.org/10.1063/1.3382344>)
77. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **32** (2011) 1456 (<https://doi.org/10.1002/jcc.21759>)
78. T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, K. Yamaguchi, *Chem. Phys. Lett.* **319** (2000) 223 ([https://doi.org/10.1016/S0009-2614\(00\)00166-4](https://doi.org/10.1016/S0009-2614(00)00166-4))
79. A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* **11** (1972) 2884 (<https://doi.org/10.1021/ic50118a006>)

80. C. Adhikary, S. Koner, *Coord. Chem. Rev.* **254** (2010) 2933 (<https://doi.org/10.1016/j.ccr.2010.06.001>)
81. M. Swart, M. Gruden, *Acc. Chem. Res.* **49** (2016) 2690 (<https://doi.org/10.1021/acs.accounts.6b00271>)
82. Y. Zhang, W. Yang, *J. Chem. Phys.* **109** (1998) 2604 (<https://doi.org/10.1063/1.476859>)
83. M. Parthey, M. Kaupp, *Chem. Soc. Rev.* **43** (2014) 5067 (<https://doi.org/10.1039/C3CS60481K>).