

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2024; 6(2): 181-187
www.chemistryjournals.net
 Received: 11-10-2024
 Accepted: 15-11-2024

Uday Sankar Agarwalla
 Department of Chemistry,
 P.D. Women's College,
 Jalpaiguri, West Bengal, India

TD-DFT study of palladium (II) complexes with 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene ligand

Uday Sankar Agarwalla

DOI: <https://doi.org/10.33545/26646781.2024.v6.i2c.242>

Abstract

The electronic structures of the palladium (II) complexes with 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene ligand have been calculated using a TD-DFT (time-dependent density functional theory) model and the simulated spectra of the palladium (II) complexes are in close agreement with the experimental spectra.

Keywords: Palladium-diazeno, O,N,O donors, density functional calculations, TD-DFT

Introduction

We have already reported the synthesis and characterization of palladium (II) complexes with 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene (H_2L) ligand, $[Pd(L)(D)]$, 1a and 1b, in presence of neutral Lewis base, D ($D = 4$ -picoline and PPh_3 respectively) ^[1]. The crystal structure of the cyclopalladates has revealed that diazene ligand H_2L bind to the metal ion as dianionic tridentate O,N,O donors and the fourth coordination position is occupied by N of donor 4-picoline (1a) or P of triphenylphosphine (1b) ^[2]. The tetra co-ordination around Pd (II) is almost planar. In continuation of our previous work, herein we wish to report the TD-DFT calculation for better understanding of the electronic structure of palladium (II) complexes and the nature of spectral transitions.

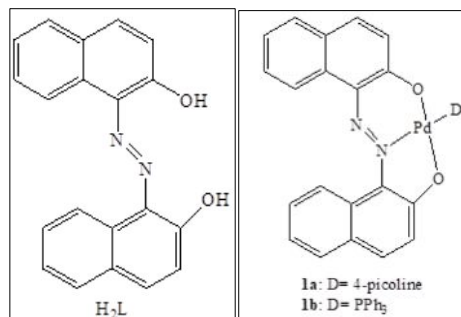
Method and computational details

The calculations have been performed within the TD-DFT formalism as implemented in ADF2007 ^[3-8]. Two approximations are generally made: one for the XC potential, and one for the XC kernel, which is the functional derivative of the time-dependent XC potential with respect to density. We used LDA (local density approximation) including the VWN parametrization ^[9] in the SCF step and Becke ^[10] and Perdew-Wang ^[11] gradient corrections to the exchange and correlation respectively and Adiabatic Local Density Approximation (ALDA) for the XC kernel, in the post-SCF step. TD-DFT calculations have been performed with the uncontracted triple-STO basis set with a polarization function for all atoms. In the calculation of the optical spectra, 70 lowest spin-allowed singlet-singlet transitions have been taken into account. Transition energies and oscillator strengths have been interpolated by a Gaussian convolution with a σ of 0.2 eV. Solvent effects were modelled by the "Conductor-Like Screening Model" (COSMO) ^[12-13] of solvation as implemented in ADF.

Results and Discussion

The palladium (II) complexes 1a and 1b (Scheme 1) are soluble in common organic solvents and produce pink solution in dichloromethane. The spectral data of the palladium cyclometallates are given in Table 1 ^[1].

Corresponding Author:
 Uday Sankar Agarwalla
 Department of Chemistry,
 P.D. Women's College,
 Jalpaiguri, West Bengal, India



Scheme 1: 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene ligand (H_2L) and palladium (II) complexes of H_2L

Table 1: Electronic spectral data of the cyclopalladates in dichloromethane

Compound	λ_{max}/nm ($\epsilon / M^{-1} cm^{-1}$)
1a	296 (11,200), 520 (4,550), 554 (7,050)
1b	232 (57,450), 263 (24,860), 523 (7,630), 558 (10,720)

The cyclopalladates (1a and 1b) show several absorptions in the ultraviolet and visible region. The bands appearing in the

ultraviolet region with high molar extinction coefficient are generally thought to be arisen from intraligand charge transfer transition whereas absorptions in the visible region are attributed to the metal-to-ligand charge transfer transition [14]. In order to gain further insight into the nature of the absorptions, TD-DFT calculations of both the cyclopalladates have been done. The coordinates of these cyclopalladates are directly imported from their crystal data. The frontier molecular orbital compositions, excitation energies and oscillator strengths for the various absorption bands have been presented in Table 2-5, together with the composition of the solution vectors in terms of most relevant transitions.

Orbital analysis: Both the palladium (II) complexes have been found to have similar molecular orbitals. A detailed analysis of the highest occupied and lowest unoccupied molecular orbitals of 1a and 1b are presented in Table 2 and 3 respectively, where orbital energies and composition in terms of atomic contributions are reported.

Table 2: Energies and percentage composition of the lowest unoccupied and highest occupied Kohn-Sham Orbitals of 1a in terms of Pd and the ligand fragment^a

MO	Occ	E(eV)	Pd	Ligand
86	0	-1.781		85.07
85	0	-1.889		97.99
84	0	-2.151		89.74
83	0	-2.281		94.92
82	0	-2.619	16.99(d_{yz}), 13.79(d_{xz}), 7.17($d_{x^2-y^2}$), 6.23(d_{z^2}), 1.13(d_{xy})	39.61
81	0	-3.308	2.85($d_{x^2-y^2}$)	83.16
80	2	-5.114		83.26
79	2	-5.523	10.51(d_{xz}), 5.78($d_{x^2-y^2}$), 4.65(d_{z^2}), 3.59(d_{xy})	52.97
78	2	-5.984	35.22(d_{xy}), 15.40(s), 7.29(d_{xz}), 4.44($d_{x^2-y^2}$), 3.90(d_{yz}), 2.31(d_{z^2})	20.77
77	2	-6.100	4.01($d_{x^2-y^2}$)	75.96
76	2	-6.152	4.14($d_{x^2-y^2}$), 1.53(d_{z^2})	68.59
75	2	-6.359	20.18(d_{z^2}), 8.82(d_{yz}), 5.57(d_{xz})	45.67

^aBold characters are used for the HOMO and the LUMO

The highest occupied molecular orbitals (HOMOs) of 1a (80a) and 1b (108a) are mostly based on the naphtholato fragment of the ligand, resulting from the combination of the carbon and nitrogen *p* orbitals. In HOMO-1, substantial amount of Pd-d character (25% for 1a and 21% for 1b) contribution has been noted for both the complexes. For the

complex 1a, HOMO-2 (78a) is localized mostly on palladium (69%) whereas in 1b, HOMO-3 (105a) is mostly palladium based (71% d character). The next three lowest highest occupied molecular orbitals of 1a (77a, 76a and 75a) have 4%, 6% and 35% metal character respectively.

Table 3: Energies and percentage composition of the lowest unoccupied and highest occupied Kohn-Sham Orbitals of 1b in terms of Pd and the ligand fragment^a

MO	Occ	E(eV)	Pd	Ligand
114	0	-1.860		88.23
113	0	-1.963		89.29
112	0	-2.007		85.02
111	0	-2.138		87.04
110	0	-2.864	17.01(d_{yz}), 14.06(d_{xy}), 3.47(d_{z^2})	46.12
109	0	-3.180	1.89(d_{xy})	86.15
108	2	-5.151		84.12
107	2	-5.444	8.44($d_{x^2-y^2}$), 5.50(d_{z^2}), 5.31(d_{yz}), 1.73(d_{xy})	63.84
106	2	-5.862	2.52($d_{x^2-y^2}$), 2.27(d_{z^2}), 1.29(d_{xz})	75.7
105	2	-6.012	25.38(d_{xz}), 16.86(s), 12.84($d_{x^2-y^2}$), 11.30(d_{xy}), 4.32(d_{yz})	13.36
104	2	-6.059		77.56
103	2	-6.116		80.71

^aBold characters are used for the HOMO and the LUMO

The calculations show that the lowest unoccupied molecular orbital of both the cyclopalladates 1a and 1b (81a and 109a respectively) are mostly concentrated on the naphthaloto fragment of the ligand, with very little contribution from the d(Pd) orbitals. The LUMO+1 of the cyclopalladates has substantial metal *d* character (45% for 1a and 35% for 1b). LUMO+2 (83a) and LUMO+4 (85a) of 1a molecular orbitals are mostly concentrated on the Lewis base, 4-

picoline resulting from the combination of the p-orbitals of carbon and nitrogen which mix in an antibonding fashion whereas LUMO+2 (111a) and LUMO+3 (112a) of 1b are largely based on the donor molecule, triphenylphosphine. The other LUMO's have predominant ligand character (Table 2 and 3). The HOMO-LUMO gaps in 1a and 1b have been computed to be 1.806 and 1.971 eV respectively.

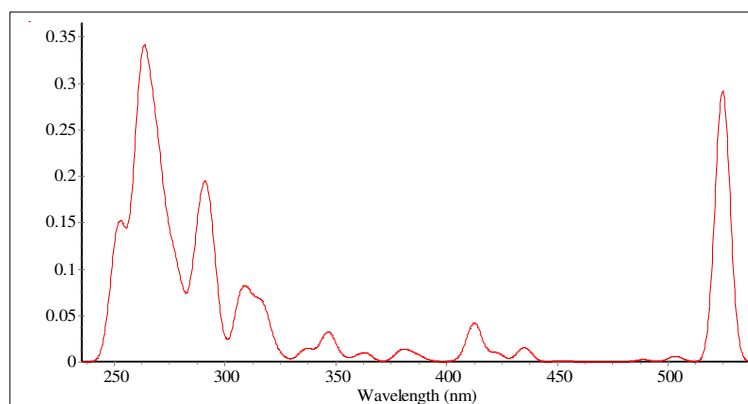


Fig 1: Spectrum of 1a computed in dichloromethane

Table 4: Selected TD-DFT calculations of excitation energies, wavelength (λ), oscillator strengths (*f*) and compositions of the low-lying singlet states in dichloromethane solution for 1a

State	Energy (eV)	λ_{cal} (nm)	λ_{exp} (nm)	<i>f</i>	Composition	Character
S ₁	2.3645	524	554	0.292	HOMO→LUMO (93.4%)	MLCT + ILCT
S ₇	3.0064	412		0.042	HOMO-4→LUMO (68.7%) HOMO-3→LUMO (10.4%)	MLCT + ILCT
S ₃₀	4.0388	307		0.058	HOMO→LUMO+7 (63.7%)	ILCT + LLCT
S ₃₇	4.2296	293		0.068	HOMO-2→LUMO+5 (49%) HOMO-5→LUMO+1 (15.9%)	MLCT + ILCT + LLCT
S ₃₉	4.2824	290		0.082	HOMO-6→LUMO+1 (39.9%) HOMO-5→LUMO+1 (18.6%) HOMO-1→LUMO+6 (14.7%) HOMO-4→LUMO+4 (13.1%)	MLCT + LLCT
S ₄₃	4.4556	278		0.055	HOMO-6→LUMO+2 (51.2%) HOMO-7→LUMO+2 (24.5%)	MLCT + LLCT
S ₅₂	4.6267	268		0.097	HOMO-7→LUMO+2 (15.2%) HOMO-6→LUMO+2 (14.4%) HOMO-8→LUMO+1 (12.4%) HOMO-5→LUMO+5 (11.0%) HOMO-12→LUMO (10.9%)	MLCT + LLCT
S ₆₁	4.7764	260		0.056	HOMO→LUMO+8 (19.6%) HOMO-13→LUMO (17.7%)	MLCT + LLCT
S ₆₆	4.9055	253	296	0.101	HOMO-15→LUMO (20.0%) HOMO-6→LUMO+5 (13.7%) HOMO-4→LUMO+7 (11.8%)	MLCT + LLCT

Table 5: Selected TD-DFT calculations of excitation energies, wavelength (λ), oscillator strengths (*f*) and compositions of the low-lying singlet states in dichloromethane solution for 1b

State	Energy (eV)	λ_{cal} (nm)	λ_{exp} (nm)	<i>f</i>	Composition	Character
S ₂	2.4396	508	558	0.213	HOMO→LUMO (82.9%)	ILCT + MLCT
S ₈	3.1390	395		0.069	HOMO-5→LUMO (71.6%) HOMO→LUMO+2 (17%)	ILCT + MLCT
S ₁₂	3.2469	382		0.0536	HOMO→LUMO+2 (46.9%) HOMO→LUMO+3 (10.4%)	ILCT + LLCT
S ₁₇	3.4494	359		0.064	HOMO-7→LUMO (66.7%) HOMO-3→LUMO+1 (12.4%)	ILCT + MLCT + LLCT
S ₁₉	3.4731	357		0.156	HOMO-7→LUMO (30.9%) HOMO-3→LUMO+1 (28.3%) HOMO-2→LUMO+1 (18.7%)	ILCT + MLCT + LLCT
S ₂₂	3.5688	347		0.047	HOMO-3→LUMO+1 (35.5%) HOMO-2→LUMO+1 (20.8%)	ILCT + MLCT + LLCT
S ₅₀	4.0921	303	263	0.072	HOMO→LUMO+11 (15.7%) HOMO-3→LUMO+4 (13.8%) HOMO-4→LUMO+4 (11%)	MLCT + LLCT
S ₇₀	4.4500	279	232	0.045	HOMO-14→LUMO+1 (23.7%) HOMO-1→LUMO+11 (10%)	MLCT + LLCT

The absorption spectra of cyclopalladates obtained using TD-DFT procedure showed a number of transitions within the visible and ultraviolet region and good correlation with the experimentally observed spectra of 1a and 1b in dichloromethane are observed (Table 4-5 and Fig. 1-2). As shown in Table 4, the first absorption band at ca. 524 nm involves excitation from the highest occupied to the lowest unoccupied molecular orbital and has mixed character of ILCT and MLCT transition. The most intense transition

observed in 1a in ultraviolet region (ca. 253 nm) involves multi excitations from 65a (HOMO-15), 74a (HOMO-6) and 76a (HOMO-4) to 81a (LUMO), 86a (LUMO+5) and 88a (LUMO+7) respectively. These transitions have a mixed character of MLCT and LLCT. The assignment of the characters of all other excited states is presented in Table 4. The simulated electronic spectrum and isodensity surface plot of the relevant MO's of 1a is presented in Fig. 1 and 3 respectively.

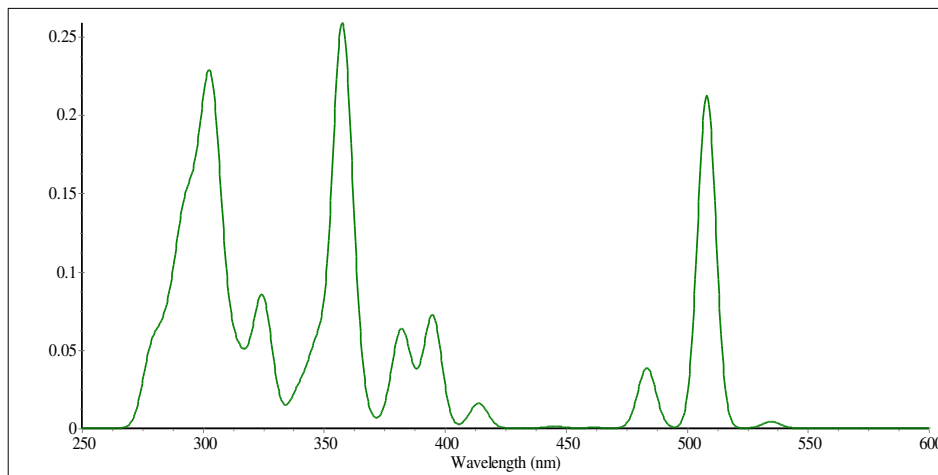


Fig 2: Spectrum of **1b** computed in dichloromethane

On the other hand, the low-lying absorption band at 508 nm for 1b corresponds to the electronic transition from HOMO to LUMO and has dominant ILCT character (Table 5). The calculated most intense transition observed in 1b at 303 nm involves multiexcitation from HOMO (108a) to LUMO+11 (120a), HOMO-3 (105a) to LUMO+4 (113a) and HOMO-4 (104a) to LUMO+4 (113a) with MLCT and LLCT character. The simulated electronic spectrum and isodensity surface plot of the relevant MO's of 1b is shown in Fig. 2 and 4 respectively.

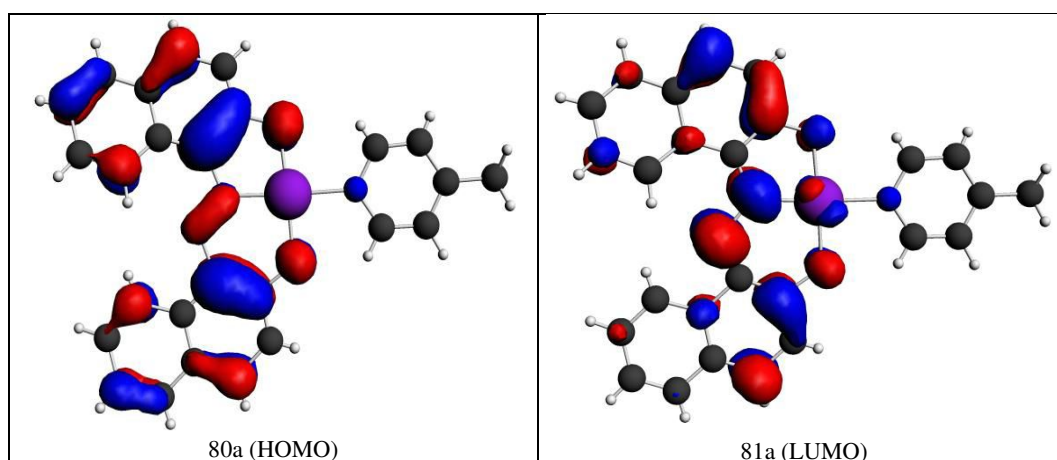
Conclusion

A time dependent (TD)-DFT study of the palladium (II) complexes has been performed. Optical absorption spectra of the cyclopalladate compounds in dichloromethane have

been simulated using the TD-DFT method, and the experimental spectra are in very good agreement. The low energy absorptions are attributed to intraligand charge transfer transitions (ILCT) having admixtures of metal-to-ligand charge-transfer transitions (MLCT) whereas the high energy absorptions are due to MLCT and LLCT transitions.

Acknowledgements

The financial support from Department of Science & Technology, and CSIR, New Delhi are gratefully acknowledged. The author expresses his sincere gratitude to Dr. P. Bandyapadhyay for his guidance. Instrumentation facilities obtained from the Department of Chemistry; University of North Bengal are gratefully acknowledged.



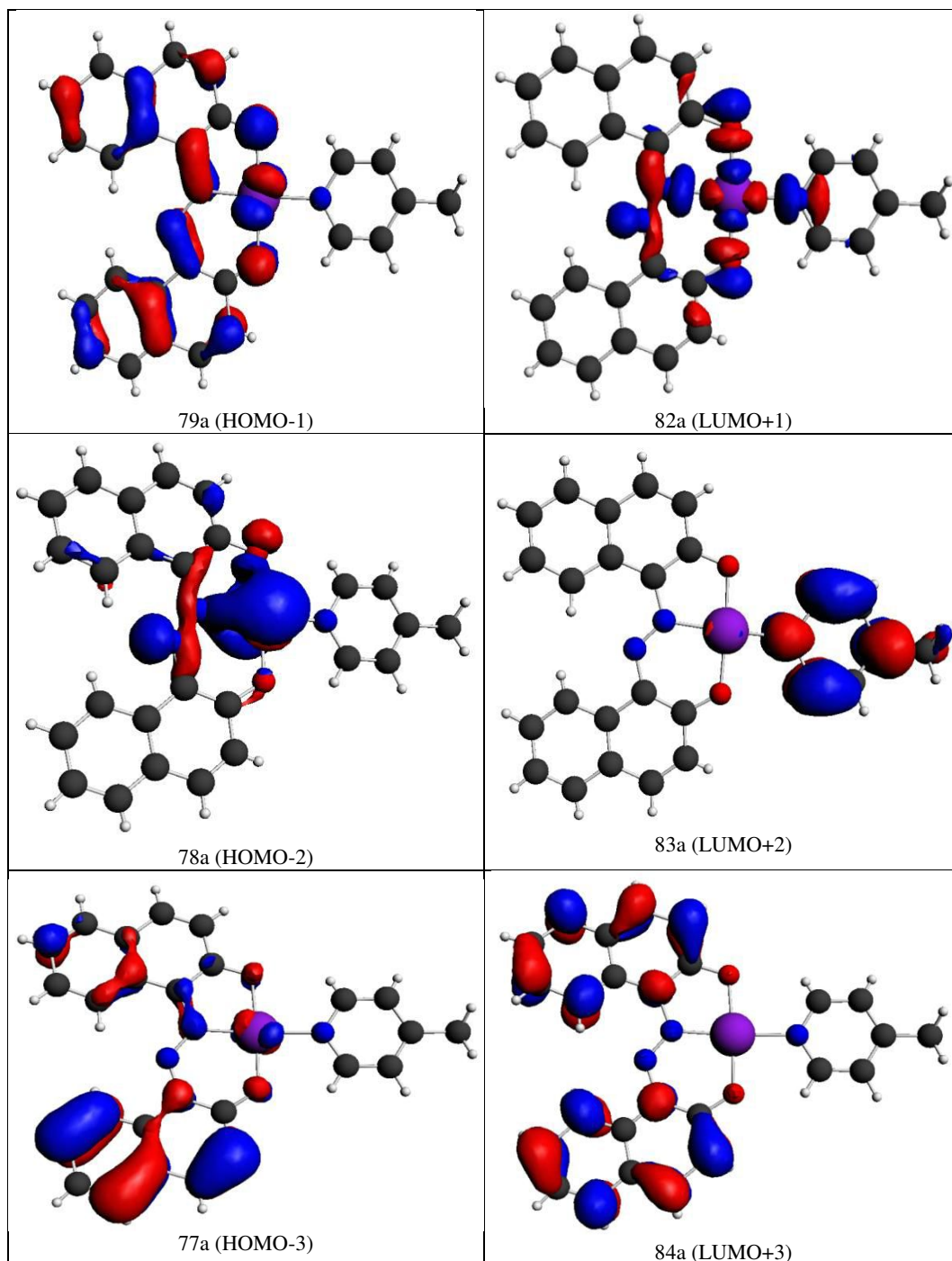
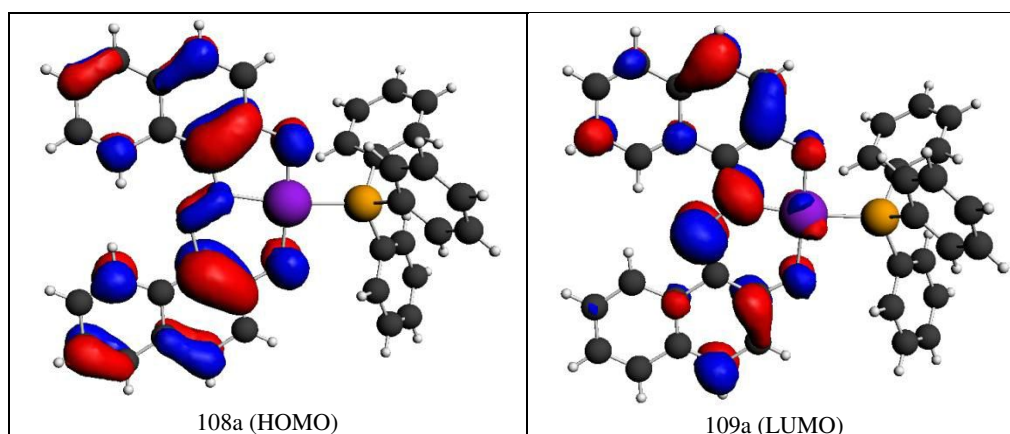


Fig 3: Molecular orbital plots for the FMO's of the cyclopalladate 1a



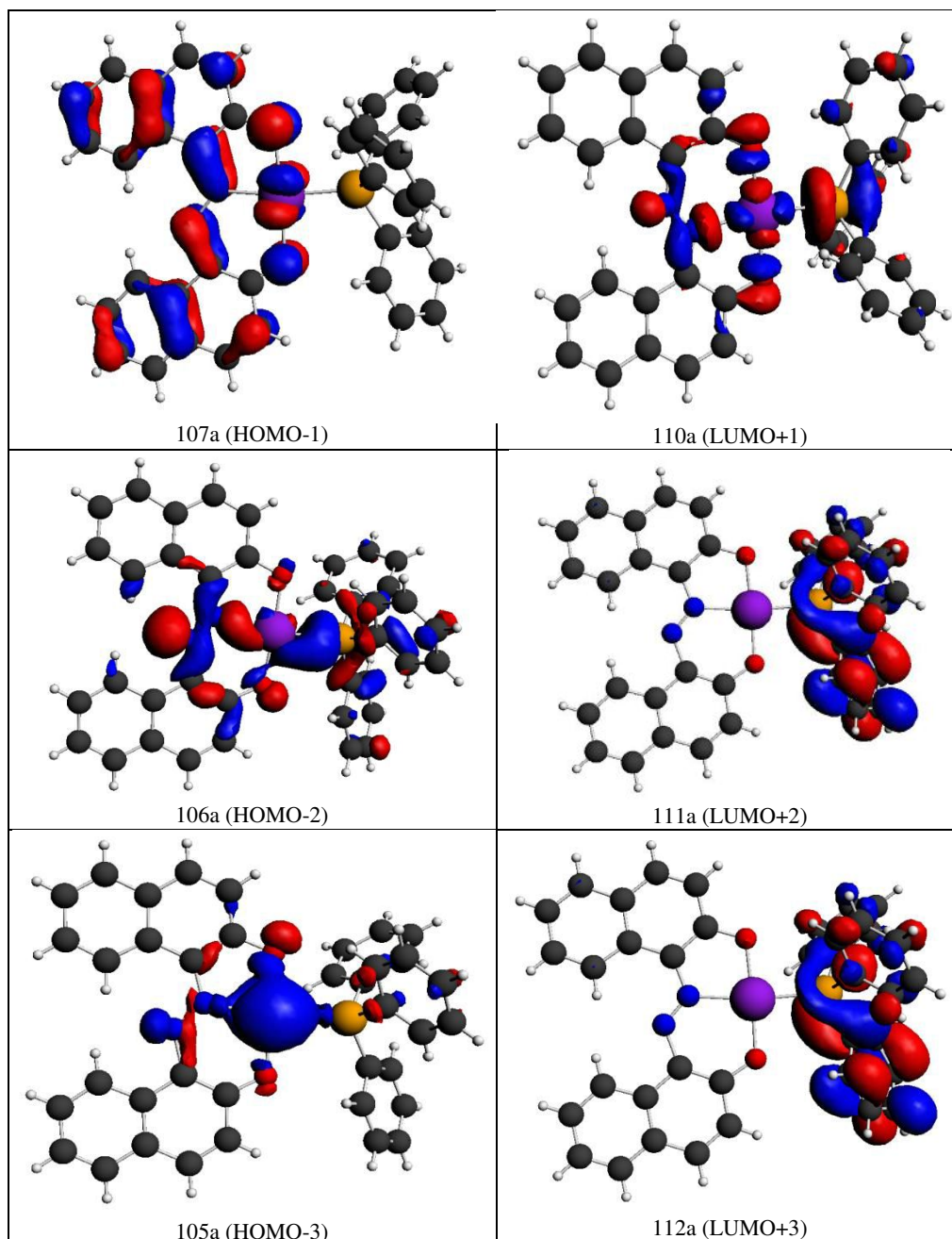


Fig 4: Molecular orbital plots for the FMO's of the cyclopalladate 1b

References

1. Agarwalla US. Cyclopalladates of 1-(2'-hydroxynaphthylazo) naphthalene complexes: Oxygen insertion into the palladium-carbon(naphthyl) bond. *International Journal of Chemical Research and Development*. 2023;5(2):4-10.
2. Agarwalla US. Crystal structure of palladium(II) complexes with tridentate diazene ligand having O, N, O donor set. *International Journal of Science and Research*. 2024;13(6):1827-1833.
3. The ADF program system was obtained from Scientific Computing and Modeling, Amsterdam (<http://www.scm.com/>). For a description of the methods used in ADF, see: Velde GT, Bickelhaupt FM, Baerends EJ, Guerra CF, Van Gisbergen SJA, Snijders JG, Ziegler T. *Journal of Computational Chemistry*. 2001;22(9):931-967.
4. Baerends EJ, Ellis DE, Ros P. Self-consistent molecular Hartree-Fock-Slater calculations I. The computational procedure. *Chemical Physics*. 1973;2(1):41-51.
5. Velde te G, Baerends EJ. Numerical integration for polyatomic systems. *Journal of Computational Physics*. 1992;99(1):84-98.
6. Fonseca Guerra C, Visser O, Snijders J, Velde te G, Baerends EJ. Parallelisation of the Amsterdam Density Functional Program. In *Methods and Techniques for Computational Chemistry*; Clementi E, Corongiu G. Eds. STEF: Cagliari, 1995;305.
7. van Gisbergen SJA, Snijders JG, Baerends EJ. A density functional theory study of frequency-dependent polarizabilities and Van der Waals dispersion coefficients for polyatomic molecules. *Journal of Chemical Physics*. 1995;103(21):9347-9354.
8. van Gisbergen SJA, Snijders JG, Baerends EJ. Implementation of time-dependent density functional

- response equations. *Journal of Computer Physics Communications*. 1999;118(2-3):119-138.
9. Vosco SH, Wilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Canadian Journal of Physics*. 1980;58(8):1200-1211.
 10. Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*. 1988;38(6):3098-3100.
 11. Perdew JP, Wang Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Physical Review B*. 1992;45(23):13244-13249.
 12. Klamt A, Schüürmann GJ, COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *Journal of the Chemical Society, Perkin Transactions 2*. 1993;799-805.
 13. Klamt A, Jonas V. Treatment of the outlying charge in continuum solvation models. *Journal of Chemical Physics*. 1996;105(22):9972-9981.
 14. Dutta S, Peng S, Bhattacharya S. Synthesis, structure and redox properties of some 2-(aryazo)phenolate complexes of rhodium(III). *Journal of the Chemical Society, Dalton Transactions*. 2000;4623-4627.