

Aromaticity in Metal Dithiolene Complexes

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Abstract: We have studied aromatic nature of series of metal dithiolene molecules using structural, energetic and magnetic criteria based on density functional theory. And the influence of charge state in aromatic character have been also explored. The computation shows that all dithiolene molecule can exist in 2D planar geometry and the structural parameters in-line with ligand based redox behaviour rather than metal. However metal oxidation state can tune the ring as aromatic or anti-aromatic or non-aromatic. Irrespective of their aromatic nature, all complexes are stable stationary states which attributes to the metallo cyclic ring and their unique behaviour of metallo-aromaticity. Among many methods applied in this work, NICS found to be appropriate and simple to determine the aromatic nature of the molecules. The NICS values predict that dithiolene complexes with Nickel, Gold, Palladium, Platinum result aromatic ring in all three charge states while Molybdenum, Tungsten, Cobalt and Copper gives anti-aromatic system.

I. Introduction

Aromaticity is the physical concept developed by August Kekule in 1865 to describe the chemical bonding, extra stability and reactivity of benzene.¹ This has taken many twist along the line and made researchers to realize that this concept cannot be defined using a single criteria. As mentioned by Schleyer in quote that “Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalisation also may result in bond length equalization, abnormal chemical shift and magnetic anisotropies as well as physical and chemical properties which reflect energy stabilization.”³ Though, it is tedious to define aromaticity, it has been extensively used to understand the cyclic molecules starting from simple organic molecules to complicated 3D networks. And based on type of molecules, aromaticity has also been defined in many ways resulting many types of⁴ such as metallo-,⁵ mobius-⁶, topological-⁶ aromaticity etc., which will give specific features on an individual system.

This work focuses on metallo-aromaticity⁵ which has more complication because of different ring size, larger vacancy at the metal centre and the orientation of *d*-orbital. Further, metal complexes with cyclic structures has a potential applications in various field starting from natural system to higher end metallo-organic frame work. In natural system, cyclic moieties act as an active site in many enzymes and proteins, such as porphyrin, chlorophyll, haemoglobin, vitamin B₁₂ and so on. The physical and chemical nature of cyclic compounds are hard to understand using advanced experimental techniques. Computational approaches based on quantum mechanics have proven to be valuable to improve the understanding in bonding and reactivity of these cyclic rings.¹⁻⁶

Metal complexes containing dithiolene ligand is one such type of molecules have attracted much attention owing to their versatile redox behaviour intense and characteristic colour, novel geometry and their presence at the active site of Mo and W containing oxido-reductase enzymes.^{7,8,9} The chemistry of dithiolene is notable with two extreme oxidation state and can undergo two electron redox process. This lead researchers to name this ligand as non-innocent for complicating the process of metal centre in their complexes. For example in [Au(S₂C₂H₂)₂] complex, the metal oxidation state can be Au(IV), Au(II), Au(0) based on oxidation state chosen for dithiolene ligands.¹⁰ Already reported studies on dithiolene complexes¹⁶⁻²¹ indicate that dithiolene complex tune its nature with respect to its metal centre and *vice versa*. In other words, nature of dithiolene ligand is vary from system to system.¹¹⁻¹² Hence, this work aim to study the role of dithiolene unit in many metal complexes. Though consideration of an individual system can be informative it is the similarities or dissimilarities between related systems that enhance understanding in dithiolene chemistry. This can be achieved by measuring the electronic nature of metallo-dithiolene using such as aromaticity. Herein, the metallo aromaticity in these complexes have been studied using structural, energetics, and magnetic criteria.^{1-6,13}

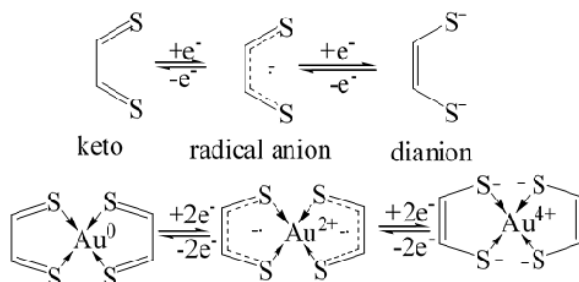


Figure 1. Schematic representation of redox behaviour of dithiolene ligand and metal dithiolene complexes. Note the change in metal oxidation state with respect to the dithiolene oxidation state.

II. Computational details

All the geometry optimization were performed with density functional theory using the three parameter hybrid functional B3LYP (Becke exchange with Lee, Yang and Parr correlation) with LANL2DZ pseudo potential and basis set for all metal atoms includes gold, molybdenum, tungsten, palladium, platinum, nickel, cobalt, copper and 6-31+G** for all other atoms as implemented in the Gaussian 09 package.¹⁴ Computed all real harmonic vibrational normal mode validate the stationary state nature of geometry. The HOMO-LUMO gaps are calculated using the equation and reflects the chemical stability or reactivity of the system, $\Delta = E_{\text{LUMO}} - E_{\text{HOMO}}$. Nucleus Independent Chemical Shift (NICS) values are calculated using the gauge including atomic orbital (GIAO) method at the same level of theory. NICS (0) and NICS (1) proposed by Schleyer *et. al.*,¹³ are the magnetic index of aromaticity and defined as the negative value of the absolute shielding at the centre of ring and 1Å above the ring that one is probing. And the ¹H- and ¹³C- NMR chemical shift values have been calculated using GIAO method as considering tetra methyl silane as a reference. The aromatic molecules will have their impression in the downfield region in both ¹H-NMR(7-12 ppm) and ¹³C-NMR (100-160 ppm). Finally, the stabilization energy is proposed by Frenking as index of aromaticity and calculated using the below equation.¹⁵ Stabilization energy = Energy of delocalized metal dithiolene complex- (Energy of metal + 2 × energy of individual dithiolene ligand).

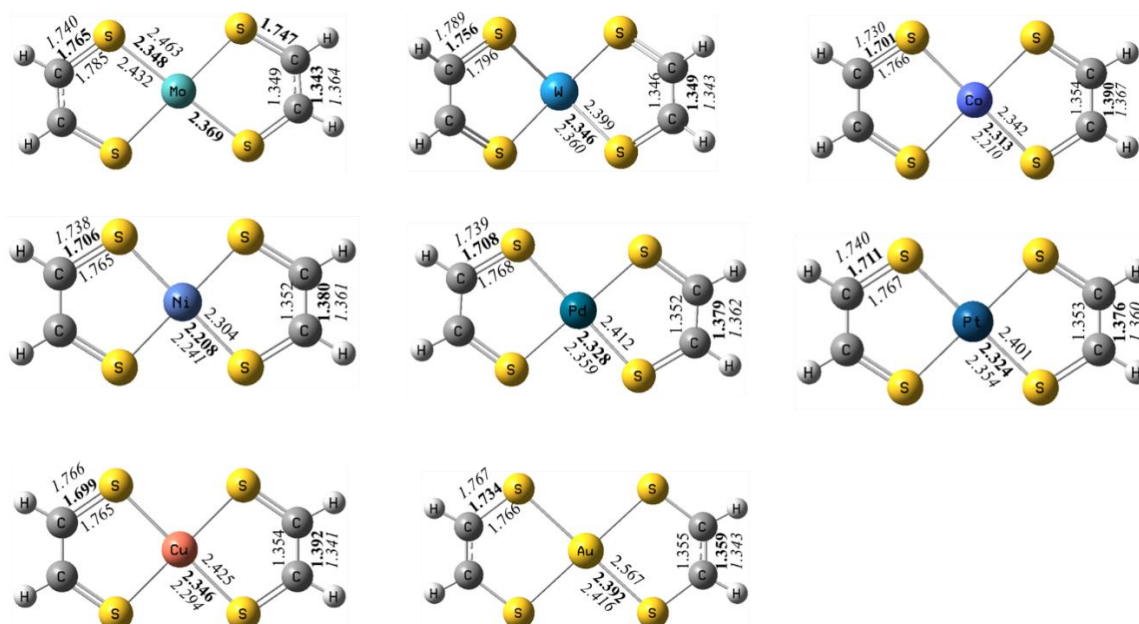


Figure 2. Optimized geometry of $[M(S_2C_2H_2)_2]^n$ complexes with important bond distances are given in Å in different font for three charge states ($n=-2$ normal; $n=-1$ italic and $n=0$ in bold).

III. Result and Discussions

All the structures are optimized and verified as minima based on the normal mode analysis. Irrespective of metal and its oxidation state, all metal dithiolene complexes used in the work assumed to undergo two electron redox process resulting the molecules in three oxidation states, neutral(0), monoanion(-1) and dianion(-2) as in accordance with experimental observation of gold dithiolene complexes. In all charge state molecular structures are relaxed by considering planar geometry as an initial structure. The geometry optimization does not change the planarity in all three charge states. The computed structural parameters of gold and nickel complexes are in good agreement with reported values,^{12,16-21} which validates the method adopted here (see Table 1). Following that the aromaticity criteria has been evaluated one by one.

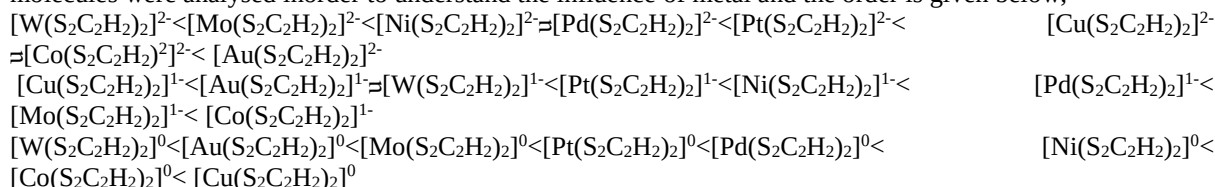
Table 1. Computed bond distances in Å and angles (°) are given for metal dithiolene molecules. The reported values are given in italic.

$[M(S_2C_2H_2)_2]^n$	Distance (Å)			Angle (°)	
	M-S	C-S	C-C	C-S-M	S-M-S
M=Mo					
n=0	2.348	1.747	1.343	108.87	137.52
n=-1	2.463	1.740	1.364	104.98	96.44
n=-2	2.432	1.786	1.349	107.40	123.86

M=W n=0 n=-1 n=-2	2.346 2.360 2.399	1.756 1.789 1.796	1.349 1.342 1.346	106.66 105.95 105.83	86.11 92.13 95.16
M=Co n=0 n=-1 n=-2	2.313 2.210 2.342	1.701 1.730 1.766	1.390 1.367 1.354	101.66 103.99 102.11	90.24 89.57 90.77
M=Ni n=0 n=-1 n=-2	2.208/2.178 2.241 2.304	1.706 1.738 1.765	1.380 1.361 1.352	102.21 102.29 102.15	87.98 88.69 89.83
M=Pd n=0 n=-1 n=-2	2.328/2.310 2.359 2.412	1.708 1.739 1.768	1.379 1.362 1.352	102.33 101.91 101.58	91.28 91.39 92.09
M=Pt n=0 n=-1 n=-2	2.324/2.406 2.354 2.401	1.711 1.740 1.767	1.376 1.360 1.353	102.98 102.34 101.95	91.81 91.66 91.91
M=Cu n=0 n=-1 n=-2	2.346 2.294 2.425	1.699 1.766 1.765	1.392 1.341 1.354	100.16 101.77 101.00	89.68 89.41 91.82
M=Au n=0 n=-1 n=-2	2.392/2.395 2.416 2.567	1.734 1.767 1.766	1.359 1.343 1.355	100.50 100.40 100.21	91.60 91.29 94.55

(i) Structural Criteria

One means of assessing the nature of dithiolene ligand in a complex is to compare the length of dithiolene C-C and C-S bond in a complex to free ligand. Our computations show that sometimes C-S (1.75 Å) and C-C (1.34 Å) bonds are consistent for dithiolene being present as ene-1,2-dithiolate. Similarly some of them are having in between C=S and C=C bond distance. The calculated bond distance are given in the table 1 and reflect the different pattern present in the bond distances. The C-C bond distance vary from 1.35 to 1.40 Å depending upon the oxidation state, which is larger than the C-C bond distance observe for the free ligand. In general irrespective of nature of metal, at neutral charge state C-C bond distance is larger than mono- and di-anion charge states. The change in order in C-C bond distances indicate the dithiolene based redox process as shown in figure 1. The same pattern has been observed in C=S, which are given in table 1. Hence, the similar charge state molecules were analysed in order to understand the influence of metal and the order is given below,



The order shows that except d^8 group metal, d^7 and d^9 has a larger influence on the charge state of dithiolene ligand and the same has been reflected in the M-S bond distance and the angles. According to the bond distance there is some delocalization and has been varied and dominated by the dithiolene ligands.

(ii) Stabilization energy

Aromatic molecules are defined as less reactive molecule and the same can be measured using delta values (HOMO-LUMO gaps) using DFT method (see table 2). All the molecules are chemically inert with > 1 eV energy that increases their possibility to become an aromatic molecule. And the calculation tunes the stabilization energy order depending upon the transition metal atom. And the atom from d^7 and d^9 groups dianion is chemically more stable than neutral and monoanion than from an atom from d^8 group metals. In the metal dithiolene complexes with d^8 group metal, the monoanion is less reactive than the neutral and dianion. Though, the computed energy are indicating their chemical stability there is no concrete proof to indicate aromaticity. Hence, the stabilization energy were calculated as proposed by Frenking *et al.*¹⁵ and have been successfully used for metal-chelate complexes. Irrespective of the charge state, all molecules are stable with larger negative energy of more than 10 eV. And all molecules are having extensive opportunity to make aromatic molecule. And the stabilization energy is directly proportional to the charge state of the system, where dianion has larger stabilization than monoanion and neutral as given in table 2.

Table 2. Calculated stabilization energy and the HOMO-LUMO gaps in eV for all dithiolene molecules in three charge states.

$[M(S_2C_2H_2)_2]^n$	Stabilization Energy	Δ
M=Co n=0 n=-1 n=-2	-26.21 -24.30 -28.91	-3.38 -1.95 -2.52
M=Ni n=0 n=-1 n=-2	-31.92 -29.13 -33.87	-1.72 -2.59 -2.47
M=Pd n=0 n=-1 n=-2	-24.76 -22.86 -26.57	-1.57 -2.69 -2.37
M=Pt n=0 n=-1 n=-2	-34.00 -32.40 -36.78	-1.80 -3.19 -2.60
M=Cu n=0 n=-1 n=-2	-20.41 -18.57 -22.50	-1.26 -1.05 -3.02
M=Au n=0 n=-1 n=-2	-19.47 -17.57 -21.86	-2.01 -1.86 -2.89
M=Mo n=0 n=-1 n=-2	-26.21 -24.89 -28.90	-2.35 -1.56 -2.11
M=W n=0 n=-1 n=-2	-45.70 -43.67 -47.76	-2.03 -2.28 -2.19

(iii) Magnetic Criteria

The presence of diatropic and paratropic ring current induce by external magnetic field in chelate complexes have been used to measure aromaticity. Two magnetic phenomenon has been proposed to monitor the aromaticity, one is by monitoring the chemical shielding at ^1H and ^{13}C nucleus centre and other one is determining the nucleus independent chemical shift as proposed by Schleyer.³

(i) Chemical Shift

Nuclear based chemical shielding always reported as chemical shift with reference to tetra methyl silane. The computed values are given in table 3. The computed ^1H -NMR chemical shift values are all in the range of 4 ppm-10 ppm. The ^1H present above 7 ppm considered to be sign of aromaticity. In the monoanion and neutral charge state of Nickel, Palladium, Copper and Platinum containing dithiolene complexes are aromatic, while the dianion charge state is non-aromatic with up field proton. The same trend has been observed with ^{13}C NMR chemical shift. And Mo and W dithiolene molecules are showing downfield shift at both ^1H and ^{13}C -NMR in all three charge states. However, cobalt dithiolene molecule reflects the aromatic nature only in neutral charge state and they are not aromatic in mono and di-anion charge states. The computed chemicals shift values are dividing the complete series in to three groups unlike the same trend observed in energetic and structural criteria. And, the downfield or upfield shift in both ^1H - and ^{13}C -NMR can occur due to the ring current generated from metal core. Hence, the magnetic criteria was incorporated in form NICS. It is nucleus independent shielding at the ring centre where the electron density believe to be zero and labelled as a ring critical point. Hence, the NICS values have been calculated at the ring centre and above the ring.

(ii) NICS

The computed NICS(0) values show that cobalt, nickel, palladium, platinum and gold complexes havenegativevalue, which indicates their aromatic nature. Inorder to check whether it occurs due to in-plane or out-of plane orbital contribution, the NICS(1) values have been calculated. Increase in negative value above the plane in the above mentioned molecules confirm the out-of-plane orbital contribution at the negative isotropic shielding values and confirms the aromaticity. Nevertheless, in tungsten, molybdenum, and copper molecules the negative value decreases at 1Å above the plane indicates the in-plane orbital contribution more. And, still it's in negative in magnitude

which indicates their aromatic nature. The tungsten, molybdenum and copper dithiolene molecules are having positive magnitude at both points indicate their anti-aromatic nature. However, those system are observe to have reasonable stabilization energy and Δ values indicating their chemical and physical stability. In order to understand it further, all out of plane orbitals are plotted and reported in the figure 3. At dianion charge state, the nickel, platinum, and palladium metal dithiolene complexes are aromatic with 14 electron in out-of plane orbital and other metals are having 12 electron in out-of plane orbital. Moreover, the Ni, Pd and Pt are more aromatic than any other in di-anion charge state and the same has been reflected in NICS values.

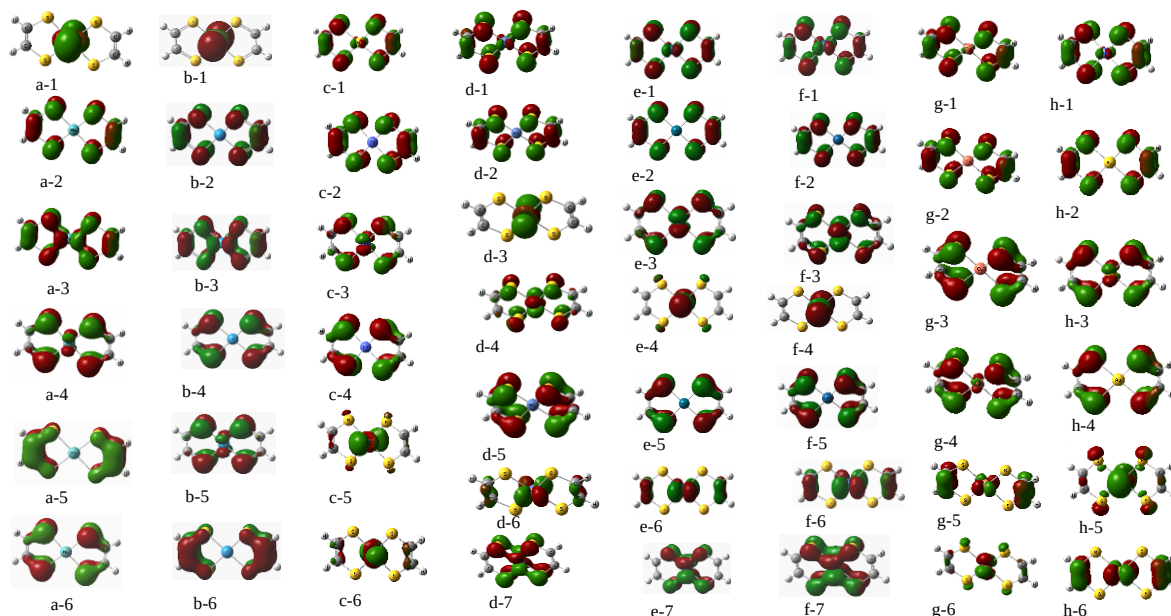


Figure 3. Computed occupied out-of-plane orbitals for $[M(S_2C_2H_2)_2]^{2n}$ molecules, where at (a) $M=Mo$, (b) $M=W$, (c) $M=Co$, (d) $M=Ni$ (e) $M=Pd$, (f) $M=Pt$, (g) $M=Cu$, (h) $M=Au$

Table 3. The total and π - molecular orbital contribution (p_y character more than 10%) to ^1H , ^{13}C and S isotropic NMR chemical shielding (ppm) values of the metal dithiolene complexes with a various oxidation states. The bold value represent the reported value for dithiolene proton chemical shielding

$[M(S_2C_2H_2)_2]^{2n}$	^{13}C	^1H	NICS(0)		NICS(1)	
			A	B	A	B
Co						
n=0	170.02	6.96/ 16.59	-35.25	-35.25	-20.92	-21.94
n=-1	127.15	6.03/ 14.32	-49.62	-49.62	-35.45	-35.07
n=-2	121.32	4.22/ 15.58	-40.19	-40.19	-23.78	-23.34
Ni						
n=0	166.33	9.37/ 25.65	-6.99	-6.99	-7.43	-7.88
n=-1	142.14	7.34/ 25.05	-8.62	-8.62	-6.44	-6.40
n=-2	126.58	5.84/ 24.52	-7.46	-7.46	-2.85	-2.80
Pd						
n=0	167.47	9.15	-3.98	-3.98	-5.61	-5.63
n=-1	143.06	7.33	-6.27	-5.71	-4.86	-4.67
n=-2	125.43	5.84	-6.41	-6.41	-3.15	-3.15
Pt						
n=0	160.56	9.02	-5.85	-5.85	-6.76	-6.76
n=-1	138.32	7.29	-7.40	-7.40	-5.90	-5.87
n=-2	123.51	5.90	-7.29	-7.29	-4.40	-4.34
Cu						
n=0	175.49	11.44/ 28.51	4.68	4.68	0.86	0.81
n=-1	173.65	9.64/ 26.00	4.33	4.33	29.96	29.42
n=-2	124.12	5.82/ 25.35	-6.17	-6.17	-3.13	-3.16
Au						
n=0	144.22	7.53	-5.25	-5.25	-4.56	-4.54
n=-1	119.97	5.65	-6.94	-6.95	-3.95	-3.90
n=-2	124.16	5.47	-6.03	-6.03	-3.14	-3.19

Mo n=0 n=-1 n=-2	144.52,29.44 121.67 152.68	7.83 10.91 15.25	41.05 45.37 96.16	13.63 45.41 96.16	1.96 23.74 49.92	15.95 22.58 49.53
W n=0 n=-1 n=-2	112.64 110.11 119.43	7.37 7.33 9.40	6.32 13.15 32.42	6.33 13.18 32.42	-4.95 9.17 13.77	-5.31 8.73 13.48

III. Conclusions

The computation shows that various metal dithiolene complexes can be easily formed and stabilized with larger negative stabilization energy. Further the larger HOMO-LUMO gaps indicate their chemical stability. Though, metal complexes can have extra stability and stabilization energy, there is no need to aromatic which has been reflected in computed chemical shift and NICS values. ¹H and ¹³C cannot be also used as a criteria for aromaticity since they have huge contribution from metal current. The NICS values can be appropriate, which categorised nickel, palladium, platinum and gold dithiolene molecule as aromatic and other as anti-aromatic. The out-of-plane orbitals are plotted to analyse the reason and found the 14 π electron system are more aromatic other molecules studies in this work.

Acknowledgements

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