

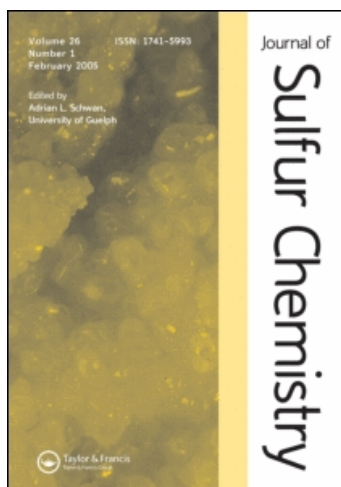
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Theoretical study of interaction of alkaline earth metal with and : structure, electronic properties and aromaticity

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RESEARCH ARTICLE

Theoretical study of interaction of alkaline earth metal with
 $C_4O_4^{2-}$ and $C_4S_4^{2-}$: structure, electronic properties and
aromaticity

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The electronic structure, harmonic vibrational frequencies, thermochemical analysis, nucleus independent chemical shifts (NICS) and HOMO–LUMO gaps of the MC_4X_4 (M = alkaline earth metals, X = O, S) species have been investigated using *ab initio* calculations. Calculations show metalated squarate species have the aromatic character, but metalated tetrathiosquarate species are anti-aromatic. Also, NICS and HOMO–LUMO gaps values predict metalation increases aromaticity MC_4O_4 species and decreases anti-aromaticity of MC_4S_4 species.

Keywords: Squarate; Tetrathiosquarate; Aromaticity; Nucleus independent chemical shifts (NICS)

1. Introduction

The cyclic oxocarbons represent an intriguing class of compounds. The simplicity of the structures and the existence of the electroisomers tempt one to conclude that there might be simple regularities and trends in the properties of these compounds that call for more attention to systematization.

In 1960, West *et al.* [1] reported that cyclic oxocarbons of general formula $C_nO_n^{2-}$ represented a new class of aromatics compounds. The main oxocarbon representatives are rhodizonate ($n = 6$), croconate ($n = 5$), squarate ($n = 4$) and deltate ($n = 3$). Their structures are predicted to be planar with D_{nh} symmetry, as proposed from Raman and infrared (IR) spectroscopic analysis [2–8] and confirmed by the X-ray diffraction studies [9–12]. For over four decades, interest in the series of oxocarbons has focused on their aromaticity and electronic structure [13–15].

The complete or partial replacement of oxygen in the oxocarbons by analogue substituents, viz. sulfur ones leads to a series of compounds that are called ‘pseudooxocarbons’ [16].

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The structure and spectroscopic properties of the squarate [17] ions have been analysed in gas phase and aqueous solution using quantum mechanical *ab initio* methods and Monte Carlo simulation [18]. The main conclusion drawn from these studies was that the solvent and counter-ion effects are important to reproduce the observed electronic spectra of the oxocarbon anions in solution. Experimental and theoretical investigations of squarate salts $[M_2(C_4O_4)]$ ($M = \text{Li, Na, K and Rb}$) were performed by Georgopoulos *et al.* aiming to correlate the structures, vibrational analysis and aromaticity [19]. The squarate anion and its coordination compounds with Li^+ , Na^+ and K^+ are studied in gas phase and aqueous solution using *ab initio* quantum chemical methods and a sequential Monte Carlo/quantum mechanical procedure [17].

In the present study, we investigated the interaction of alkaline earth metals with $\text{C}_4\text{O}_4^{2-}$ and $\text{C}_4\text{S}_4^{2-}$ and its effects on the structures, electronic properties and aromaticity of the dianion.

2. Computational details

Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee *et al.* (B3LYP) [20, 21] method in combination with basis sets, 6-31 + G(d,p) [22–26] for C, O, S, Be, Mg has been employed in searching for the most stable for all structures. Standard LANL2DZ basis set has been used for other elements (Ca, Sr, Ba) [27–30]. Ca, Sr, Ba atoms described by effective core potential of Wadt and Hay pseudopotential with a doublet- ξ valance using the LANL2DZ. In all the cases, the steady-state nature (minimum on the potential energy surface) of the optimized complexes has been confirmed by calculating the corresponding frequencies at the same computational level. Geometry optimization has been performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee *et al.* (B3LYP) [20, 21]. Vibrational, thermochemical stability and population analysis have been carried out for the optimized structures using the same level of theory and basis set. All the calculations have been performed using the GAUSSIAN 98 quantum chemical package [31].

The interaction energies ($\Delta E_{\text{complex}}$) have been determined as:

$$\Delta E_{\text{complex}} = E(\text{MC}_4\text{X}_4) - [E(\text{C}_4\text{X}_4^{2-}) + E(\text{M}^{2+})]$$

$E(\text{MC}_4\text{X}_4)$ is the optimized energy of the metalated systems, $E(\text{M}^{2+})$ is the energy of the metal cation and $E(\text{C}_4\text{X}_4^{2-})$ is the energies of the oxocarbon or thiocarbon.

To evaluate the basis set superposition error (BSSE) [32] produced in the calculations of the interaction energies; the Boys–Bernardi's counterpoise technique has been employed.

The calculations have been performed using the following general scheme.

$$\Delta E_{\text{BSSE}} = \Delta E_{\text{complex}} - [E_{\text{complex (A)}} + E_{\text{complex (B)}}] + (E_A + E_B)$$

Where, ΔE_{BSSE} denotes the interaction energy taking into consideration BSSE. $\Delta E_{\text{complex}}$, the interaction energy value without consideration of BSSE (calculated as the difference between the energy of complex and the sum of energies of the isolated submits A and B). $E_{\text{complex(A)}}$ and $E_{\text{complex(B)}}$ are the energy values of the complexes on the assumption that the orbitals of molecules A and B are the so-called 'ghost' orbitals. E_A and E_B refer to the energy values of A and B monomers, respectively.

The nucleus independent chemical shift (NICS) has been used as a descriptor of aromaticity from the magnetic point of view. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers [33] or another interesting point of the system [34].

The NICS denoted as NICS(1) is calculated 1 \AA above the center and is expected to better reflect the π -electron structure details [35]. Rings with highly negative values of NICS are quantified as aromatic by definition, whereas those with positive values are anti-aromatic. NICS values have been calculated with GIAO method at B3LYP level of theory [36–40].

The electronic spectra in the gas phase were calculated within the CIS, at the HF level of theory.

The magnetic susceptibilities have been calculated at B3LYP level of theory by using the CSGT (continuous set of gauge transformations) method [41–43].

3. Results and discussion

3.1 Energetic

The optimized geometric structures for MC_4X_4 ($M =$ alkaline earth metals, $X = O, S$) species are illustrated in figure 1. We performed *ab initio* calculations on all structures at B3LYP level of theory. Table 1 shows the interaction energies and BSSE and ΔE_{BSSE} of MC_4X_4 species.

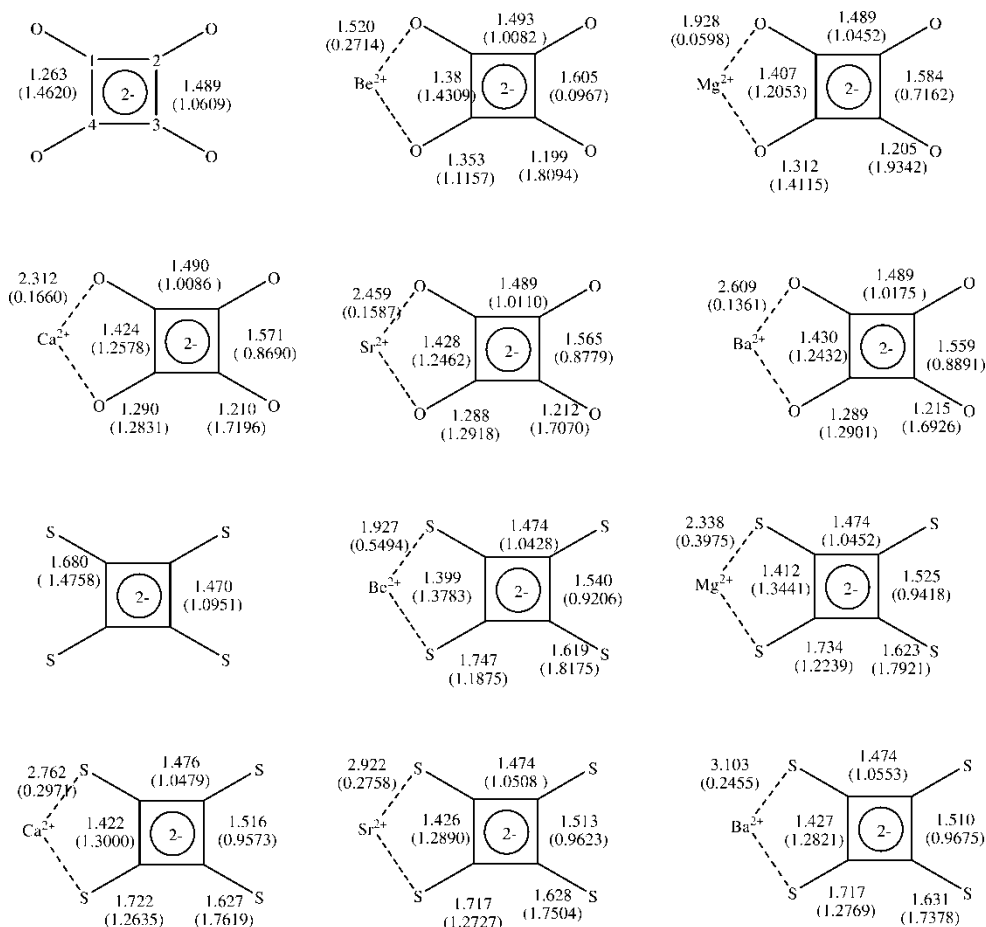


Figure 1. The bond distances and Wiberg bond orders (in parentheses) of the MC_4X_4 ($M =$ earth alkaline metal, $X = O, S$).

Table 1. Relative energies (kcal mol⁻¹), lowest frequency (cm⁻¹), interaction energies ($\Delta E_{\text{complex}}$), basis set superposition error (BSSE), ΔE_{BSSE} (kcal/mol), and charge of metal for MC₄X₄ (X = O, S).

Structure	E (Hartree)	Lowest frequency (cm ⁻¹)	$\Delta E_{\text{complex}}$	BSSE	ΔE_{BSSE}	Q(M ²⁺)	$\angle\text{OMO}$
C ₄ O ₄ ²⁻	-453.2996513	94.7	-	-	-	-	-
BeC ₄ O ₄	-468.0813435	126.1	-720.2	1.4	-718.8	1.64772	123.2
MgC ₄ O ₄	-653.4130442	111.9	-555.7	1.6	-554.2	1.50710	97.2
CaC ₄ O ₄	-489.8916112	86.1	-445.6	1.5	-444.1	1.52776	81.6
SrC ₄ O ₄	-483.7768923	68.4	-417.5	1.1	-416.4	1.54523	76.6
BaC ₄ O ₄	-478.5715251	58.1	-388.9	1.6	-387.3	1.62158	72.0
C ₄ S ₄ ²⁻	-1745.2097545	48.8	-	-	-	-	-
BeC ₄ S ₄	-1759.9346073	66.2	-657.4	0.6	-656.8	1.28231	131.5
MgC ₄ S ₄	-1945.2805778	62.1	-535.4	0.6	-534.8	1.39543	110.
CaC ₄ S ₄	-1781.7343837	30.1	-409.7	0.6	-409.0	1.54788	91.0
SrC ₄ S ₄	-1775.6166358	32.1	-379.7	0.5	-379.2	1.57426	85.3
BaC ₄ S ₄	-1770.4093156	23.5	-349.9	0.8	-349.1	1.63698	79.9

The interaction energies of MC₄O₄ complexes are systematically larger than those of MC₄S₄ complexes (table 1). These values show that the interaction of metal with anion decreases with increasing atomic number of the metal ions. It is compatible with symbiosis effect.

Values of the BSSE are also presented in table 1. Clearly, for the complexes of both types the BSSE is rather small.

3.2 Molecular structures

The bond lengths (in Å) and Wiberg bond orders are shown in figure 1. As can be observed in table 1 and figure 1, the structural values show that a systematic increasing in the M–X (X = O, S) bond length with of the metal size. The C3–O3, C3–S3 bonds are shorter for larger ions and a significant decreasing of the X–M–X bond angle is observed from Be²⁺ to Ba²⁺.

The computed Wiberg bond indices (WBI) of bonds for CC and CO bonds are illustrated in figure 1. The calculated CC WBI 1.069 for squarate and 1.0951 for tetrathiosquarate ions, indicates the C–C bonds to have very little double bond character. The CO and CS WBI, which range from 1.1 to 1.4 indicate delocalization. In other hand, the WBI between the metal atom and O or S atoms show that the very high ionic character in the chemical bonds of these species is obvious. On the basis of natural population analysis (NPA) for all metalated species, positive charges mainly populate on the metal, carbon atoms and all negative charges populate on the oxygen atoms, which suggests that most interactions between the squarate, tetrathiosquarate unit and metals are ionic, with some back transfer from anion to M²⁺. See table 1.

3.3 Frequencies

The harmonic vibrational frequencies of C₄X₄²⁻, MC₄X₄ species (X = O, S, M = earth alkaline metals) have been calculated at the B3LYP level of theory. The vibrational frequency calculations show that they are all local minima without imaginary frequency. See table 1.

Calculations show that squarate ion has four bands in IR spectrum: 244.7 (A_{2u}, $\delta\text{oop}(\text{CO})$), 321.2 (E_u, $\delta(\text{CO})$), 1072.1 (E_u, $\nu(\text{CC})$), 1531.4 (E_u, $\nu(\text{CO})$). The most intense band in 1531.4 cm⁻¹ assigned to a $\nu(\text{CO})$ mode (table 2). This band displays blue shift in metalated

Table 2. The Most intensity band in infrared for MC_4X_4 (X = O, S).

Structure	ν (cm^{-1})	Intensity
$C_4O_4^{2-}$	1532.2805	1871.4581
BeC_4O_4	1860.663	432.5662
MgC_4O_4	1843.395	1893.176
CaC_4O_4	1818.9605	3028.3916
SrC_4O_4	1810.5668	3573.7622
BaC_4O_4	1801.9243	4217.6859
$C_4S_4^{2-}$	1237.3308	1338.3306
BeC_4S_4	1323.286	680.1931
MgC_4S_4	1298.486	781.7154
CaC_4S_4	1278.2006	671.5963
SrC_4S_4	1271.3735	678.2832
BaC_4S_4	1268.4391	762.4284

species. On the other hand, its frequency decreases with the decreasing of atomic number of metals.

For the metalated species, the number of bands in some cases is different from the listed for $C_4O_4^{2-}$ and $C_4S_4^{2-}$ ions, due the breaking of degeneracy of the e_u or e_g species.

The IR active modes of MC_4O_4 species have been shown in figure 2. The A_1 and B_2 modes assigned to $\nu(\text{CO})$. The most intensity band of MC_4O_4 has b_2 symmetry and assigned to ν_{18} (figure 2).

Also, $C_4S_4^{2-}$ has four bands in IR spectrum and its most intense band in 1237.2 cm^{-1} assigned to a $\nu(\text{CS})$ mode. This band displays blue shift in metalated species and its frequency decreases with the decreasing of atomic number of metals.

The IR active modes of MC_4S_4 species have been shown in figure 2. The A_1 and B_2 modes assigned to $\nu(\text{CC})$ and $\nu(\text{CS})$, respectively. The most intensity band of MC_4S_4 has a_1 symmetry and assigned to ν_{20} (figure 2).

3.4 Frontier orbital energies and chemical hardness

Absolute chemical hardness (η) has been used as a measure of kinetic stability or the reactivity of organic compounds. Within Koopman's approximation, hardness (η) is defined as half of the magnitude of the energy difference between the HOMO and LUMO [44–49].

$$\eta = \frac{(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})}{2}$$

The frontier orbital energies and the hardness of all structures are given in the table 3. This table shows that, the $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ values decrease in metalated species. Also, the $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ values increase with the increasing of atomic number of metal. An increase in the HOMO energy level shows better donors and increasing of nucleophilicity. On the other hand, an increase in the LUMO energy level causes decreasing of electron accepting nature of compounds. The decrease in the η values of MC_4X_4 indicates the lowering of kinetic stability of these species [50].

For an aromatic compound, HOMO–LUMO gaps must be large enough to prevent electron localization and fixation rather than the preferable and more stable delocalization bonding agreement [51]. From table 3, the amount of HOMO–LUMO band gap is larger for oxo species.

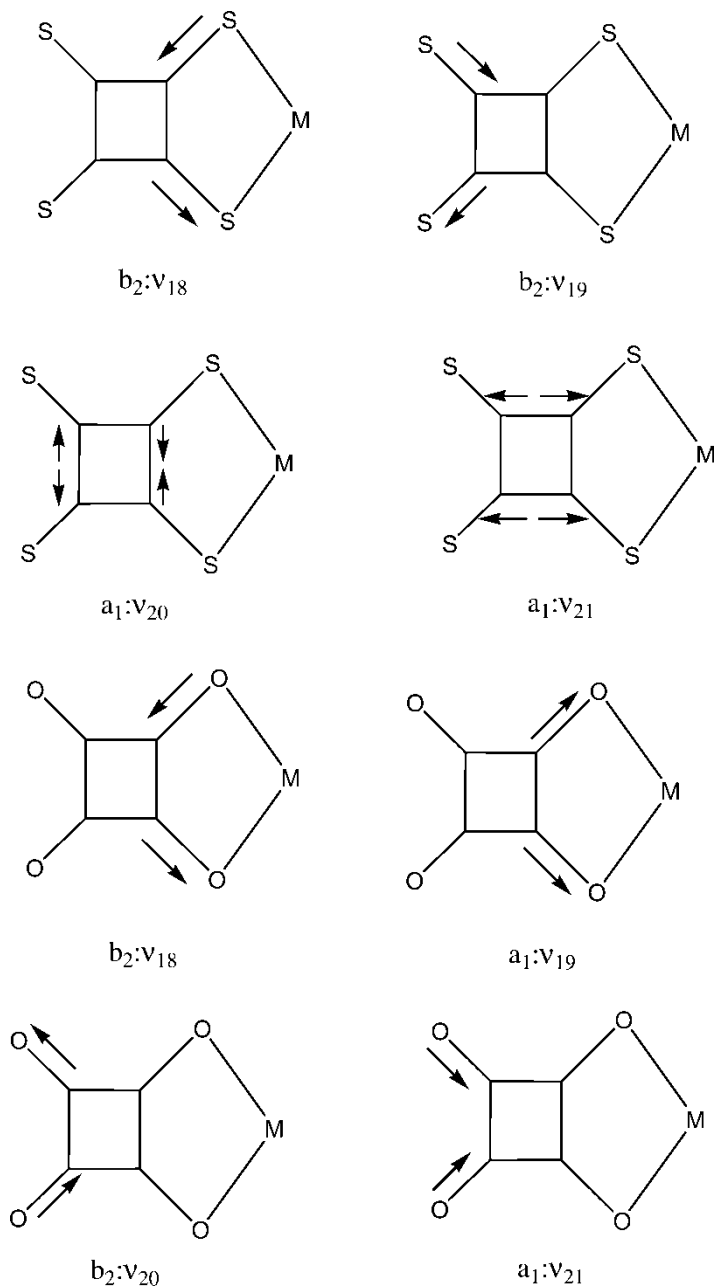


Figure 2. Infrared active modes for MC_4X_4 (M = earth alkaline metal, $X = O, S$).

The computed gas phase electronic transitions for the all species are reported in table 3. These calculations show that the squarate ion have two degenerate transitions centered at 356.10 nm. On the other hand, the $C_4S_4^{2-}$ anion has four degenerate transitions centered at 328.40 nm. By comparing with the values for the free anion, the HOMO \rightarrow LUMO transition undergoes a red shift in metalated species (except BeC_4O_4).

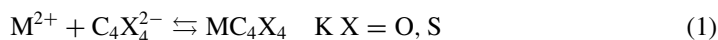
Table 3. Frontier orbital energies (ϵ_{HOMO} and ϵ_{LUMO}), absolute chemical hardness (η), electronic transitions (λ nm) calculated for the free ion ($C_4O_4^{2-}$, $C_4S_4^{2-}$) and the complexes MC_4X_4 in the gas phase.

Structure	ϵ_{HOMO} (Hartree)	ϵ_{LUMO} (Hartree)	ΔE (eV) [†]	$\eta = (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})/2$	HOMO \rightarrow LUMO (nm)
$C_4O_4^{2-}$	0.14	0.27	0.13	1.79	356.10
BeC_4O_4	-0.26	-0.13	0.13	1.72	272.66
MgC_4O_4	-0.23	-0.16	0.07	0.89	606.67
CaC_4O_4	-0.20	-0.15	0.05	0.63	975.92
SrC_4O_4	-0.19	-0.14	0.04	0.60	969.32
BaC_4O_4	-0.17	-0.13	0.04	0.54	820.18
$C_4S_4^{2-}$	-0.16	-0.04	0.12	1.58	328.40
BeC_4S_4	-0.26	-0.13	0.12	1.66	402.09
MgC_4S_4	-0.22	-0.14	0.07	0.99	396.47
CaC_4S_4	-0.20	-0.16	0.04	0.57	687.66
SrC_4S_4	-0.19	-0.15	0.04	0.55	731.03
BaC_4S_4	-0.18	-0.14	0.04	0.53	703.82

[†]Hartree = 27.2116 eV.

3.5 Thermochemistry

Thermochemical analysis has been carried out to investigate thermal stabilities of these compounds. Some calculated thermochemical properties have been tabulated in table 4. Thermochemical quantities reported in this table are defined for the gas phase formation reaction at 298.15 K and 1 atm for 1 mol of MC_4X_4 ($X = O, S$) according to equation (1).



$$\Delta Y = Y(MC_4X_4) - Y(C_4X_4^{2-}) - Y(M^{2+}) \quad Y = E, H, G \text{ and } S \quad (2)$$

It can be seen from ΔG values listed in table 4 that formation of all of these MC_4X_4 ($X = O, S$) is thermodynamically spontaneous at standard conditions of temperature and pressure. B3LYP method predicts that the maximum values of ΔG belong to heavier metals.

The equilibrium constants of the all complexes are given in table 4. This shows that the equilibrium constant decreases with the increasing of metals. Table 4 shows that with increasing metal ion radius the value of ΔG will decrease which shows complex stability decline. It sounds right, because as we have indicated previously, with metal ion radius increment-B bond length will increase. As a result, the bonding strength will decrease.

It is obvious that ΔS should be negative, since in this reaction two particles formed one.

Table 4. Thermochemical properties calculated at B3LYP level of theory for the MC_4X_4 species.

Structure	ΔH (kcal/mol)	ΔS (cal/mol K ⁻¹)	ΔG (kcal/mol ⁻¹)	K
BeC_4O_4	-706.5	-0.031	-697.0	3.2
MgC_4O_4	-555.0	-0.030	-546.2	2.5
CaC_4O_4	-445.1	-0.027	-436.3	2.1
SrC_4O_4	-417.1	-0.028	-408.5	2.0
BaC_4O_4	-388.5	-0.027	-380.2	1.9
BeC_4S_4	-671.7	-0.031	-662.6	3.1
MgC_4S_4	-528.6	-0.030	-519.7	2.4
CaC_4S_4	-403.2	-0.027	-395.1	1.9
SrC_4S_4	-373.3	-0.028	-365.1	1.9
BaC_4S_4	-343.5	-0.027	-335.6	1.8

3.6 Magnetic properties

3.6.1 Relative aromaticities of MC_4X_4 species from NICS. The relative aromaticity of the MC_4X_4 species was derived from the nucleus-independent chemical shifts. The GIAO NICS values for the all species (B3LYP/6-31 + G(d,p) level) are given in table 5. For a point located at the geometrical ring center and at point located above these rings center, equally spaced by 0.5 Å. Hence, NICS(0.5) values are better suited for the interpretation of π contributions perpendicular to the ring plane.

The NICS(0.0) values for $C_4O_4^{2-}$ dianion is -0.6 ppm, suggesting the nonaromatic or weakly aromatic. To further analyse the aromaticity, we also calculate NICS(0.5) values above (by 0.5 Å) the geometric centers of the four-membered ring. These values for the MC_4O_4 ($M = Be, Mg, Ca, Sr, Ba$) are all negative, exhibiting aromatic character. However, NICS values in the molecular planes are influenced by the local contributions of the C–C and C–O σ -bonds and lone pairs [52]. Therefore, NICS(0.5) values are better suited for the interpretation of e -contributions and answer to the question whether the MC_4O_4 and $C_4O_4^{2-}$ structures are reality aromatic. As shown in table 5, the absolute NICS(0.5) values for all MC_4O_4 species are more negative than that of $C_4O_4^{2-}$ dianion. The metalation seems to result in an increase in aromaticity to some extent. The similar effect has been shown for alkaline metals [19].

The positive NICS(0.5) values of the MC_4S_4 suggesting the anti-aromatic. These values indicate that metalation causes to decreasing of anti-aromaticity. Therefore, electron delocalization decreases in thiosquarate species.

3.6.2 Relative aromaticities of MC_4X_4 species from global magnetic indices. Aromaticity of the MC_4X_4 species was also assessed with global magnetic aromaticity indicators, such anisotropy [53]. This is defined [equation (3)] as the difference between the out-of-plane and the average in-plane diamagnetic susceptibilities ($\Delta\chi$) for a ring lying in the (xy) plane.

$$\Delta\chi = \chi_{zz} - \left(\frac{1}{2}\right) [\chi_{xx} + \chi_{yy}] \quad (3)$$

An advantage of this index is the independence from a reference system. The estimates of the magnetic susceptibility and magnetic susceptibility anisotropies at the B3LYP quantum-mechanical levels can be found in table 5.

Table 5. Anisotropic susceptibility magnetic (using CSGT method, ppm), nucleus-independent chemical shifts (NICS, using GIAO method, ppm) properties related to aromaticity for MC_4X_4 .

Structure	χ (aniso)	NICS (0.0)	NICS (0.5)	NICS (1.0)
$C_4O_4^{2-}$	-38.0	-0.6	-5.3534	-5.4
BeC_4O_4	-35.2	-2.4	-6.1715	-5.4
MgC_4O_4	-39.0	-7.5	-9.6966	-6.9
CaC_4O_4	-37.7	-7.5	-9.6961	-6.8
SrC_4O_4	-33.6	-7.3	-9.5930	-6.8
BaC_4O_4	-29.5	-5.9	-8.6125	-6.4
$C_4S_4^{2-}$	-65.7	18.3	5.2300	-2.1
BeC_4S_4	-53.6	14.9	4.5933	-1.3
MgC_4S_4	-53.1	16.0	4.9851	-1.4
CaC_4S_4	-57.5	14.6	3.8805	-1.9
SrC_4S_4	-58.2	14.8	4.0260	-1.8
BaC_4S_4	-56.3	15.5	4.3914	-1.7

The magnetic susceptibility tensor describes the quadratic response of a molecule to an external magnetic field, and as such its isotropic and anisotropic components are relevant quantities to consider for the types of molecules studied here.

The anisotropic values predict that metalation cause to decreasing of aromaticity. This result is not compatible with NICS(0.5) values for MC_2O_4 species.

4. Conclusion

In this paper the interaction between $C_4O_4^{2-}$, $C_4S_4^{2-}$ and alkaline earth metals has been studied. The geometries, energies, harmonic vibrational frequencies and thermochemical analysis have been computed. Calculations show that formation of MC_4O_4 is thermodynamically more spontaneous rather than MC_4S_4 at standard conditions of temperature and pressure.

The aromaticity of all species has been probed with diverse aromaticity indicators. The structural parameters, magnetic and HOMO–LUMO gap effectively provide insight in π electron delocalization tendencies. The results showed that aromaticity differs depending on the criterion used. The NICS(0.5), HOMO–LUMO gap predict that aromaticity increases in metalated squarate species and anti-aromaticity decreases in metalated tetrathiosquarate species.

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