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Application of Bader's *Atoms in Molecules* Theory to the Description of Coordination Bonds in the Complex Compounds of Ca^{2+} and Mg^{2+} with Methylidene Rhodanine and Its Anion

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Abstract—In the framework of Bader's *atoms in molecules* theory a complete analysis of the distribution function of electron density in molecules of complexes of Ca^{2+} and Mg^{2+} with methylidene rhodanine and its anion was carried out. The role of mutual polarization of the metal cation and the ligand in the formation of coordination bonds was demonstrated. The accumulation of electron density in the interatomic space of coordination bonds is assumed to be a consequence of the deformation of the ligand electron shell under the influence of the cation electric field. Based on the magnitude and sign of the Laplacian and the electron energy density at the critical points of coordination bonds the interactions were classified the in terms of the *atoms in molecules* theory. The energy of the coordination bonds was evaluated using the Espinoza's formula. The stability of metal-containing rings was considered basing on the values of the bond ellipticity.

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Methylidene rhodanine (5-methyl-2-thioxothiazolidin-4-one) is among the simplest derivatives of rhodanine (Fig. 1a) known as a building block of a family of the aldose reductase inhibitors [1]. In addition, the rodanine ring exhibits high binding and selecting properties toward the heavy metal ions (Pd^{2+}, Pt^{2+} [2], Ag^{+}, Au^{+} [3], Cu^{+} [4], Ni^{2+}, Co^{2+} [5], Cu^{2+}, Hg_2^{2+}, Au^{3+}, Ru^{3+} [6]), which have been used in develop-ing the spectrophotometric methods for the determination of ions of these metals [6]. In [7, 8] it has been assumed that the ylidene rhodanines, in particular, methylidene rhodanines (mRd), can bind the stable complexes of Ca^{2+} ions and isomorphic to those Mg^{2+} ions, which directly affects the calcium and magnesium exchange in the body. Thus, Ca^{2+} ions are the components of calmodulin, a universal calcium sensor of protein nature, and other calcium-dependent enzymatic systems. It has also been reported in [7] on a possibility of blocking the calcium-dependent enzymes, namely calcium-aspartyl proteases, by methylidene rhodanine. The Mg^{2+} ions are found in the human body in similar sensory systems. They are components of some cofactors and enzyme activators in the replication of nucleic acids, protein biosynthesis, Mg^{2+} dependent ATPase, acetylcholinesterase and others. The sources of rhodanine in the human body can be anti-diabetic drugs (e.g., Epalrestat [1]) and rhodanine-containing drugs, acting as the inhibitors of the enzymes such as cyclooxygenase, 5-lipoxygenase, aldose reductase, β-lactamase, and others [9].

It has been shown in [7, 10] that methylidene rhodanine (**Ib**) dissociates in aqueous solutions ($K_D = 10^{-8}$) at the N–H bond to form methylidene rhodanine anion **Ic**. In a recent paper [8] we described on the basis of quantum-chemical calculations the most probable model of the Ca^{2+} and Mg^{2+} binding by methylidene rhodanine and its anion, and predicted the relative stability of the complexes.

In this paper we consider the mechanism of binding Ca^{2+} and Mg^{2+} ions by methylidene rhodanine and its anion basing on the complete analysis of the distribution function of electron density by the method of Bader [11] for the model complexes, describe the features of coordination of Ca^{2+} and Mg^{2+} ions with mRd, and calculate the energy of the coordination bonds.

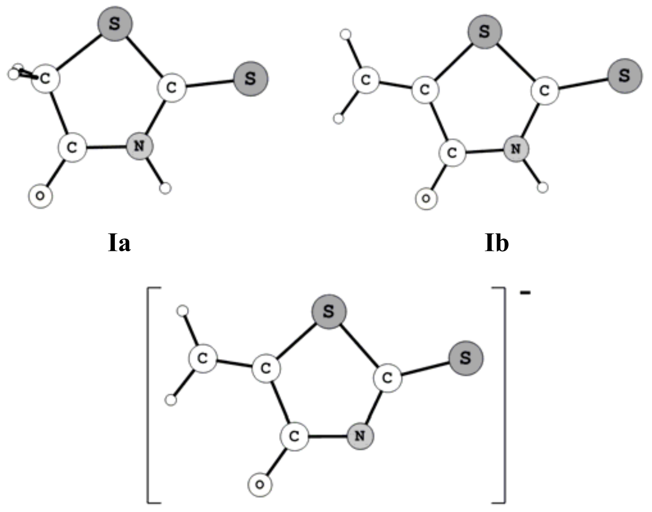
Calculation method. The geometry optimization of the possible spatial forms of the complexes $[Ca(mRd)]^{2+}$, $[Mg(mRd)]^{2+}$, $[Ca(mRd)]^{+}$, $[Mg(mRd)]^{+}$ was performed within the framework of density functional theory (DFT) in a vacuum approximation using the hybrid exchange-correlation functional B3LYP [12, 13] in the 6-31+G(d) valence double-split basis [14]. In the calculated IR spectra of the considered structures all vibrational modes are real indicating the presence of the local energy minima of these molecules.

We performed complete analysis of the electron density distribution function $\rho(r)$ for the equilibrium geometry of the complexes in the framework of the R. Bader *atoms in molecules* (AIM) theory [11, 15, 16].

All calculations were performed by the DFT method within the software package GAUSSIAN 03 [17] on a PDC supercomputer of the Royal High Technical School (Stockholm). The topological analysis of the distribution function of the electron density $\rho(r)$ was carried out using the AIMQB program in the framework of AIMAll software [18].

The AIM theory: fundamentals and applications. The Bader's *atoms in molecules* theory is a powerful tool of modern quantum chemistry for prediction of the properties and reactivity of molecular structures. The distribution function of the electron density $\rho(r)$ is a key concept in the AIM theory. The $\rho(r)$ function can be obtained from both the results of quantum chemical calculations and the precision X-ray diffraction studies [19].

Bader has shown [11] that the function $\rho(r)$ for a given polyatomic system, as well as many critical points of electron density [the $\rho(r)$ gradient in the critical point is zero] determine completely and uniquely the molecular structure of a system. The type and properties of a critical point are defined by the number and sign of the nonzero eigenvalues λ_i of the Hessian in a critical point, also referred to as the $\rho(r)$ curvature in the critical point. In general, the type of critical point has the form (ω, σ), where ω is the Hessian matrix rank, σ is the signature, that is, the sum of signs of the λ [11]. Bader has shown that for an equilibrium and energetically stable molecular systems the Hessian rank ω at a critical point is equal to 3 ($\lambda_1, \lambda_2, \lambda_3 \neq 0$). Under the condition of $\omega = 3$ the signature can have four different values: –3, –1, +1, +3. Consequently, Bader has stated four types of the critical points, which fully and clearly describe any molecular system:



Ia **Ib**

Ic

Fig. 1. Molecular structure of rhodanine (**Ia**), methylidene rhodanine (**Ib**), and methylidene rhodanine anion (**Ic**).

(1) critical point (3, –3) corresponds to the position of the atomic nucleus in the space ($\lambda_1, \lambda_2, \lambda_3 < 0$);

(2) critical point (3, 1) corresponds to the formation of a ring ($\lambda_1 < 0, \lambda_2, \lambda_3 > 0$);

(3) critical point (3, +3) corresponds to the formation of polyhedral (cellular) structure ($\lambda_1, \lambda_2, \lambda_3 > 0$);

(4) critical point (3, –1) is an indicator (a necessary and sufficient condition) for the bonding interactions ($\lambda_1, \lambda_2 < 0, \lambda_3 > 0$).

The critical point (3, –1) plays a key role in describing the molecular structure, as it makes it possible to establish the existence of binding between the atoms through valence bonds and non-valence interactions.

The number and type of critical points that may exist in the final molecular structure are subjected to the Poincare–Hopf relation [11]:

$$n - b + r - c = 1,$$

where n is the number of nuclei [critical point (3, –3)], b is the number of bonding routes [critical point (3, –1)], r is the number of rings [critical point (3, +1)], and c is the number of cells [critical point (3, +3)].

The λ_1/λ_3 ratio describes qualitatively the type of the corresponding chemical bond [11, 20]. When

$|\lambda_1/\lambda_3| > 1$ the electron density is concentrated in the interatomic space, which corresponds to a covalent type of interaction. When $|\lambda_1/\lambda_3| < 1$, the electron density is largely concentrated in the atomic space, which corresponds to the interaction of closed shells (hydrogen, van der Waals, and ionic bonds).

Bader and colleagues have suggested the value of $\varepsilon = \lambda_1/\lambda_2 - 1$, which was called the ellipticity [21], a quantitative description of the deviation of electron density distribution in the critical point (3, –1) from the cylindrical symmetry. In fact, the magnitude of ε is a measure of the π-component of the bond. In addition, ε characterizes the susceptibility of a bond in a ring to cleavage, that is, the ring strain.

An important characteristic of bonding interaction is the magnitude and sign of the electron density Laplacian $\nabla^2\rho(r)$ in the binding critical point. The magnitude of $\nabla^2\rho(r)$ in the critical point is a measure of the concentration of electron density in the interatomic space and it can be calculated as a sum of the curvature ρ(*r*) components in the critical point, $\nabla^2\rho(r) = \lambda_1 + \lambda_2 + \lambda_3$.

The classification of interatomic interactions according to the criterion of $|\lambda_1/\lambda_3|$ magnitude and the Laplacian sign [20] does not explain the existence of an intermediate type of interactions where the electron density is largely concentrated in the interatomic space as in the case of covalent bond, but $\nabla^2\rho(r) > 0$, which is typical for the interaction of closed shells. These interactions comprise, in particular, strong polar covalent bonds, coordination bonds, strong hydrogen bonds, and other interactions. To include these interactions in a system of classification of interatomic contacts, Kremer and Kraka [22] proposed a qualitative criterion for describing the interatomic interactions on the basis of the sign of Laplacian and the sign of the electron energy density $h_e(r)$:

$$h_e(r) = g(r) + v(r),$$

where $g(r)$ is the kinetic energy density in critical point (3, –1), $v(r)$ is the density of potential energy in the critical point (3, –1). The value of $v(r)$ is always negative by definition, whereas $g(r)$ is always positive. For nonpolar and weakly polar covalent bonds $\nabla^2\rho(r) < 0$ and $|v(r)| > g(r)$, and therefore, $h_e(r) < 0$. For the intermediate type of interactions $\nabla^2\rho(r) > 0$, but $|v(r)| > g(r)$, and therefore $h_e(r) < 0$. For the interaction of the closed shells $\nabla^2\rho(r) > 0$, and $|v(r)| < g(r)$, that is, $h_e(r) > 0$.

An important characteristic of a bond in terms of the AIM theory is the index of delocalization of electron density (DI) between the interacting atoms, which indicates the number of electrons in the interatomic space [11]. Index of delocalization of electron density within the AIM theory is obtained by integrating the density of the Fermi hole. The value of DI can be directly interpreted as the bond order [23].

By analogy with the index of the electron density delocalization, in the AIM theory also the index of the electron density localization is used. Its magnitude indicates the number of electrons (taking into account also the core electrons) localized in the atomic space [11]. At 100% electron localization in atomic space the Fermi hole of this electron is completely included in the same space.

An important advantage of the AIM theory is the ability to estimate the energy of intra- and intermolecular interactions on the basis of Espinosa correlation [24]:

$$E_{[\mathrm{au}]} = 1/2v(r) \sim E_{[\mathrm{kcal/mol}]} = 313.754v(r),$$

where *E* is the energy of interatomic interaction (au or kcal mol^{-1}). This relationship links the energy of interaction with the potential energy density in the corresponding critical point. It was originally used for finding the hydrogen bonding energy. However, in a series of recent papers, Antipin, Lyssenko and colleagues expanded the application of the Espinosa formula for determining the energy of coordination [25, 26] and homopolar bonds [27] corresponding to an intermediate type of interaction.

In conclusion, it should be noted that the theoretical and, more so, the applied aspects of the AIM theory in recent years were described in a series of review articles, among which [28–30] should be emphasized.

Now, let us consider the results we obtained with respect to the calcium and magnesium complexes.

Figures 2 and 3 show the optimized structures of complexes of Ca^{2+} and Mg^{2+}, respectively. Numbering of atoms in the rhodanine ring corresponds to the systematic one. Coordination bonds are shown by the dashed lines. The Poincare–Hopf relation is fulfilled for each complex.

According to the Gauss' law for the electrostatic interaction, the binding in model ionic systems $[Ca^{2+}][mRd^-]$ and $[Mg^{2+}][mRd^-]$ is achieved due to the polarization of the ions in the direction opposite to the

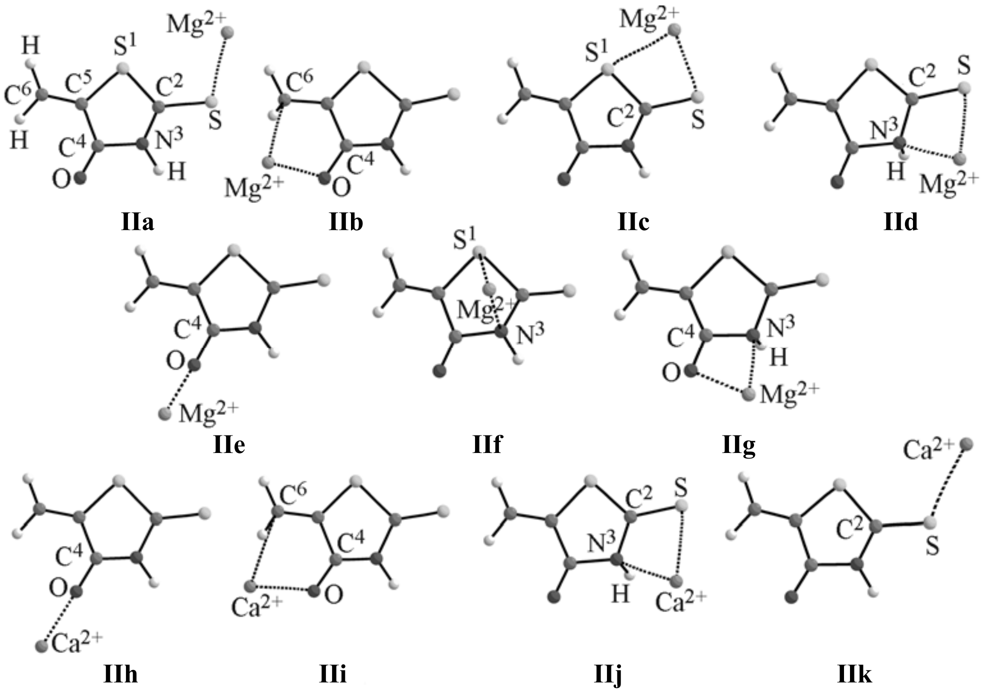


Fig. 2. Optimized structures of the complexes $[Ca(mRd)]^{2+}$ and $[Mg(mRd)]^{2+}$

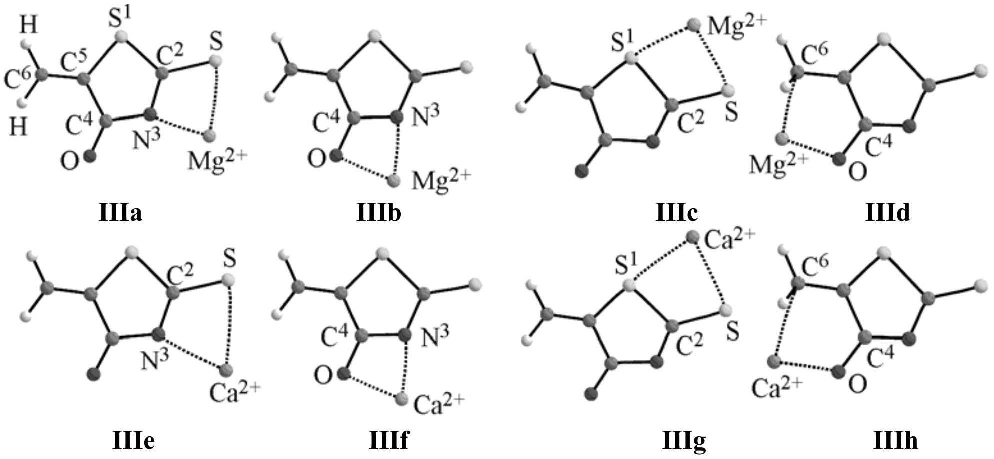


Fig. 3. Optimized structures of the complexes $[Ca(mRd)]^{+}$ and $[Mg(mRd)]^{+}$.

charge transfer. This law can also be applied to the systems of $[Mg^{2+}][mRd]$ and $[Ca^{2+}][mRd]$, considering that the methylidene rhodanine molecule includes the centers of local concentration of the electron charge. It has been shown in [8] that in the methylidene rhodanine molecule in its ground state a significant excess of electron density is concentrated on the oxygen and sulfur atoms of the ketone and thioketone groups, respectively: the Mulliken charges on the O and S atoms are –0.43 *e* and –0.59 *e*, respectively.

Thus, it is the mutual polarization that causes incomplete charge separation in the ionic compounds and determines the degree of the bond covalence. It is well known that multiply charged cations exhibit a strong polarizing power and weak polarizability, while the polarizing ability of anions is weak and polarizability is strong. The Mg^{2+} cation has a greater polarizing power than Ca^{2+} since its ionic radius is smaller.

The application of the AIM theory in the context of the analysis of electron density localization and delocalization indices allowed us the estimation of the degree of covalence of the coordination bonds in the complexes $[Ca(mRd)]^{2+}$, $[Mg(mRd)]^{2+}$, $[Ca(mRd)]^{+}$, and [Mg (mRd)]$^+$, as well as determining the local sites of susceptibility to the polarization of the methylidene rhodanine and the related anion. Analysis of the energy densities and the sign of the Laplacian in the critical point (3, –1) made it possible to classify the coordination bonds as the "interaction of the closed shells" and "intermediate type interaction," and the use of the Espinosa's correlation allowed the estimation of the energy of the coordination bonds in the complexes.

Topological analysis of the electron density of the free spherically symmetric cations Ca^{2+} and Mg^{2+} shows that the indices of the electron density localization for them are respectively 18.000 and 10.000, which is typical for unpolarized cations. As shows Table 1, the localization indices (LI) for the cations in the complexes are not integer values, indicating a deformation of the cation electron shell, which leads to a shift of the center of cation charge relative to the nucleus. The cation polarization occurs in the direction opposite to the charge transfer. For the complexes **IIa**, **IIc**, **IId** and **IIIc**, LI > 10.000, indicating that the Mg^{2+} cation is polarized in the direction of the methylidene rhodanine molecule (ion), that is, in the direction of the bond formation. This is seen, in turn, from the high values of the delocalization indices of the formed coordination bonds (Table 1). This finding suggests that the mutual polarization of ions causes accumulation of the electron density in the space between the nuclei and, consequently, increases the degree of covalence of the bonds between them, as can be seen in Table 1. For the remaining complexes (all except **IIa**, **IIc**, **IId**, and **IIIc**), LI(Mg^{2+}) < 10.000, LI(Ca^{2+}) < 18.000, indicating the cations polarization in the direction opposite to the coordination bonding. It is logical that for all Ca^{2+} complexes with methylidene rhodanine LI(Ca^{2+}) < 18.000, which due to the lower polarizing power and higher polarizability of the Ca^{2+} cation compared with the Mg^{2+}.

Table 1 also shows the values of the charges (*q*) on the atoms calculated in the framework of Bader's theory. It is seen that for all the complexes the calculated charges on the metal atoms are much less than the classical value +2, indicating a deformation of the electron shell of the ligand and the electron density transfer from it to the interatomic space of the coordinating interactions. It must be remembered that the calculated value of the charge is defined largely by the electron density concentrated in the interatomic space near the metal cation. Therefore, analysis of the atomic charges allows us a conclusion on the polarization of the cation in the direction opposite to that of the formed coordination bonds, which is not correct for complexes **IIa**, **IIc**, **IId** and **IIIc**. Table 1 clearly shows that for similar pairs of complexes (**IIa/IIk, IIb/IIi, IId/IIj, IIe/IIh; IIIa/IIIe, IIIb/IIIf, IIIc/IIIg,** and **IIId/IIIh**) the charge on the Mg atom is much lower than on the Ca, which again confirms the stronger polarizing ability of cations Mg^{2+} compared to Ca^{2+} on the qualitative and quantitative levels.

Interactions of S···Mg^{2+} and S···Ca^{2+}, S^1···Mg^{2+} and S^1···Ca^{2+}. Figures 2 and 3 show that the interaction of the type S···Mg^{2+}, S···Ca^{2+}, S^1···Mg^{2+} and S^1···Ca^{2+} occurs in the complexes **IIa, IIc, IId, IIf, IIj, IIk, IIIa, IIIc, IIIe,** and **IIIg**. All contacts of S···Mg^{2+} and S···Ca^{2+} types are characterized by high electron density delocalization indices DI. The index magnitude points to the bond order and generally equals to 0.279–0.581 (Table 1). These DI values indicate a significant accumulation and localization of the electron density between the interacting atoms, that is, show the degree of covalence of these bonds.

In general, the electron density delocalization index of the complexes of the same structure (**IIa** and **IIk, IIIa** and **IIIe, IIIb** and **IIIg**) is larger for the Mg^{2+} complexes compared with complexes of Ca^{2+}. The effect is most clearly seen for a pair of complexes **IIa/IIk**, where the methylidene rhodanine is a monodentate ligand. The value of DI for the complexes **IIa** and **IIk** is 0.581 and 0.387, respectively. Given that the Mg^{2+} ion has a higher polarizing power than the Ca^{2+} ion, it stronger deforms the electron shell of methylidene rhodanine and polarizes it in the direction of critical point (3, –1). Electron density is accumulated in the interatomic space, and also there is a slight reverse charge transfer (0.036 e) onto the Mg^{2+} ion. The value of the reverse electron transfer is the difference between the calculated electron density localization index LI for Mg^{2+} ion in the complex (10.036 *e*, Table 1) and the number of electrons in a free Mg^{2+} ion (10 e). No reverse charge transfer on the Ca^{2+} is observed in the complex **IIk**.

Classifying by the criterion of $|\lambda_1/\lambda_3|$ the S···Mg^{2+} and S···Ca^{2+} interactions, we found that they correspond to the interactions of the closed shells. However, based on the Laplacian signs and the Kramer-Crack electron energy density in the appropriate critical point (3, –1), the S···Mg^{2+} and S···Ca^{2+} contacts should be assigned to an intermediate type of interaction, as in all cases with $\nabla^2\rho(r) > 0$ and $h_e(r) < 0$ (Table 2).

Table 1. Values and ratios of the elements of curvature of the function $\rho(r)$ in the critical point (3, –1) of the coordination bonds, as well as localization parameters of the electron density in the atomic and interatomic space

Comp. no.	Bond	λ_1, $e\cdot a_0^{-5}$ [a]	λ_2, $e\cdot a_0^{-5}$	λ_3, $e\cdot a_0^{-5}$	ε	$\lvert\lambda_1/\lambda_3\rvert$	DI	LI[b]	*q*
IIa	$\mathrm{S\cdots Mg^{2+}}$	–0.0453	–0.0408	0.2589	0.11	0.173	0.581	10.036	1.628
IIb	$\mathrm{O\cdots Mg^{2+}}$	–0.0741	–0.0707	0.5108	0.05	0.145	0.196	9.990	1.706
	$\mathrm{C^6\cdots Mg^{2+}}$	–0.0383	–0.0350	0.2206	0.10	0.174	0.260		
IIc	$\mathrm{S\cdots Mg^{2+}}$	–0.0427	–0.0392	0.2486	0.09	0.172	0.407	10.015	1.656
	$\mathrm{S^1\cdots Mg^{2+}}$	–0.0161	–0.0116	0.0861	0.39	0.187	0.156		
IId	$\mathrm{S\cdots Mg^{2+}}$	–0.0410	–0.0377	0.2400	0.09	0.171	0.357	9.997	1.701
	$\mathrm{N^3\cdots Mg^{2+}}$	–0.0412	–0.0384	0.2650	0.07	0.156	0.172		
IIe	$\mathrm{O\cdots Mg^{2+}}$	–0.0992	–0.0957	0.7660	0.04	0.130	0.265	10.002	1.664
IIf	$\mathrm{N^3\cdots Mg^{2+}}$	–0.0449	–0.0423	0.2857	0.06	0.157	0.184	9.997	1.711
	$\mathrm{S^1\cdots Mg^{2+}}$	–0.0333	–0.0309	0.1873	0.08	0.178	0.282		
IIg	$\mathrm{O\cdots Mg^{2+}}$	–0.0707	–0.0682	0.4862	0.04	0.145	0.202	9.979	1.778
	$\mathrm{N^3\cdots Mg^{2+}}$	–0.0444	–0.0408	0.2835	0.09	0.157	0.193		
IIh	$\mathrm{O^1\cdots Ca^{2+}}$	–0.0626	–0.0598	0.4696	0.04	0.133	0.270	17.944	1.906
IIi	$\mathrm{O\cdots Ca^{2+}}$	–0.0555	–0.0517	0.3562	0.07	0.156	0.216	17.945	1.837
	$\mathrm{C^6\cdots Ca^{2+}}$	–0.0120	–0.0092	0.0706	0.31	0.171	0.106		
IIj	$\mathrm{N^3\cdots Ca^{2+}}$	–0.0206	–0.0193	0.1264	0.07	0.163	0.122	17.961	1.806
	$\mathrm{S\cdots Ca^{2+}}$	–0.0262	–0.0233	0.1405	0.12	0.187	0.279		
IIk	$\mathrm{S\cdots Ca^{2+}}$	–0.0288	–0.0257	0.1600	0.12	0.180	0.387	17.982	1.799
IIIa	$\mathrm{N^3\cdots Mg^{2+}}$	–0.0738	–0.0703	0.5042	0.05	0.146	0.249	9.997	1.647
	$\mathrm{S\cdots Mg^{2+}}$	–0.0412	–0.0386	0.2503	0.07	0.165	0.385		
IIIb	$\mathrm{N^3\cdots Mg^{2+}}$	–0.0727	–0.0699	0.5070	0.04	0.143	0.270	9.997	1.722
	$\mathrm{O\cdots Mg^{2+}}$	–0.0747	–0.0732	0.5231	0.02	0.143	0.237		
IIIc	$\mathrm{S^1\cdots Mg^{2+}}$	–0.0300	–0.0277	0.1803	0.08	0.166	0.257	10.023	1.564
	$\mathrm{S\cdots Mg^{2+}}$	–0.0462	–0.0413	0.2791	0.12	0.166	0.442		
IIId	$\mathrm{O\cdots Mg^{2+}}$	–0.0930	–0.0868	0.6471	0.07	0.144	0.242	9.998	1.629
	$\mathrm{C^6\cdots Mg^{2+}}$	–0.0465	–0.0436	0.2779	0.07	0.167	0.336		
IIIe	$\mathrm{S\cdots Ca^{2+}}$	–0.0291	–0.0260	0.1598	0.12	0.182	0.326	17.945	1.737
	$\mathrm{N^3\cdots Ca^{2+}}$	–0.0524	–0.0475	0.3200	0.10	0.164	0.239		
IIIf	$\mathrm{O\cdots Ca^{2+}}$	–0.0534	–0.0500	0.3311	0.07	0.161	0.225	17.926	1.807
	$\mathrm{N^3\cdots Ca^{2+}}$	–0.0523	–0.0474	0.3242	0.10	0.161	0.241		
IIIg	$\mathrm{S\cdots Ca^{2+}}$	–0.0330	–0.0284	0.1792	0.16	0.184	0.387	17.966	1.684
	$\mathrm{S^1\cdots Ca^{2+}}$	–0.0204	–0.0197	0.1223	0.04	0.167	0.206		
IIIh	$\mathrm{O^1\cdots Ca^{2+}}$	–0.0686	–0.0622	0.4350	0.10	0.157	0.265	17.936	1.751
	$\mathrm{C^3\cdots Ca^{2+}}$	–0.0236	–0.0203	0.1322	0.16	0.179	0.198		

[a] a_0 is Bohr radius, 0.529 Å; [b] LI is the index of the electron density localization indicating the number of electrons in the atomic basin of the metal ion.

Thus, all the $\mathrm{S\cdots Mg^{2+}}$ and $\mathrm{S\cdots Ca^{2+}}$ interaction can be described as closed shell interactions with a significant degree of covalence, induced by the polarization of methylidene rhodanine and its anion under the action of the $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$ ions. Ellipticity values for the $\mathrm{S\cdots Mg^{2+}}$ and $\mathrm{S\cdots Ca^{2+}}$ bonds vary in the range of 0.07–0.16 indicating a rather large deviation of electron density distribution in the critical point (3, –1) from the cylindrical symmetry. The value of ε for the complexes **IIc, IId, IIj, IIIa, IIIc, IIIe,** and **IIIg**, whose $\mathrm{S\cdots Mg^{2+}}$ and $\mathrm{S\cdots Ca^{2+}}$ bonds are involved in the rings, shows little susceptibility of these interactions to rupture and, accordingly, to the ring opening. Binding energy of $\mathrm{S\cdots Mg^{2+}}$ and $\mathrm{S\cdots Ca^{2+}}$ calculated with the Espinosa formula ranges from –7.72 to –15.15 kcal $\mathrm{mol^{-1}}$ (Table 2), contributing considerably to the stabilization of the complexes.

The $\mathrm{S^1\cdots Mg^{2+}}$ and $\mathrm{S^1\cdots Ca^{2+}}$ interactions we found in the complexes **IIc, IIf, IIIc** and **IIIg** (Figs. 1, 2). The DI values for these contacts (0.156–0.282) indicate a slight concentration of electron density in the interatomic space. However, based on the the Laplacian signs and the electron energy density in the corresponding critical point (3, –1), all the $\mathrm{S^1\cdots Mg^{2+}}$ and $\mathrm{S^1\cdots Ca^{2+}}$ bonds should be assigned to an intermediate type of interaction ($\nabla^2\rho(r) > 0$, $h_e(r) < 0$, Table 2). It should be noted that the $\mathrm{S^1\cdots Mg^{2+}}$ bond in the complex **IIc** is characterized by a high ellipticity (0.39), which suggests instability of the $\mathrm{Mg^{2+}}$-

Table 2. Coordination bond lengths (*d*), energies (*E*), and the topological characteristics of the electron density distribution in the critical point (3, –1)

Comp. no.	Bond	*d*, Å	ρ(r), $e\cdot a_0^{-3}$	ν(r), au	*g*(r), au	h_e(r), au	∇^2ρ(r), $e\cdot a_0^{-5}$	*E*, kcal mol^{-1}
IIa	S···Mg^{2+}	2.351	0.0445	–0.0483	0.0456	–0.0027	0.172	–15.15
IIb	O···Mg^{2+}	1.976	0.0486	–0.0667	0.0791	0.0124	0.366	–20.93
	C^6···Mg^{2+}	2.248	0.0367	–0.0374	0.0371	–0.0003	0.147	–11.73
IIc	S···Mg^{2+}	2.382	0.0422	–0.0457	0.0437	–0.0020	0.167	–14.34
	S^1···Mg^{2+}	2.686	0.0207	–0.0171	0.0158	–0.0013	0.058	–5.37
IId	S···Mg^{2+}	2.396	0.0403	–0.0437	0.0420	–0.0017	0.161	–13.71
	N^3···Mg^{2+}	2.192	0.0344	–0.0377	0.0420	0.0043	0.185	–11.83
IIe	O···Mg^{2+}	1.840	0.0594	–0.0988	0.1209	0.0221	0.572	–31.00
IIf	N^3···Mg^{2+}	2.176	0.0373	–0.0418	0.0457	0.0039	0.198	–13.11
	S^2···Mg^{2+}	2.493	0.0346	–0.0345	–0.0326	–0.0019	0.123	–10.82
IIg	O···Mg^{2+}	1.993	0.0476	–0.0648	0.0758	0.0110	0.347	–20.33
	N^3···Mg^{2+}	2.171	0.0361	–0.0402	0.0449	0.0047	0.198	–12.61
IIh	O···Ca^{2+}	2.156	0.0502	–0.0679	0.0773	0.0094	0.346	–21.30
IIi	O···Ca^{2+}	2.266	0.0439	–0.0516	0.0569	0.0053	0.249	–16.19
	C^6···Ca^{2+}	2.898	0.0159	–0.0103	0.0113	0.0010	0.049	–3.23
IIj	N^3···Ca^{2+}	2.663	0.0218	–0.0182	0.0199	0.0017	0.086	–5.71
	S···Ca^{2+}	2.801	0.0292	–0.0246	0.0237	–0.0009	0.092	–7.72
IIk	S···Ca^{2+}	2.740	0.0321	–0.0286	0.0276	–0.0010	0.106	–8.97
IIIa	N^3···Mg^{2+}	1.993	0.0515	–0.0703	0.0802	0.0099	0.360	–22.06
	S···Mg^{2+}	2.369	0.0412	–0.0455	0.0441	–0.0014	0.170	–14.28
IIIb	N^3···Mg^{2+}	1.983	0.0517	–0.0712	0.0811	0.0099	0.364	–22.34
	O···Mg^{2+}	1.971	0.0510	–0.0711	0.0825	0.0114	0.376	–22.31
IIIc	S^1···Mg^{2+}	2.473	0.0318	–0.0319	0.0312	–0.0007	0.123	–10.01
	S···Mg^{2+}	2.330	0.0451	–0.0517	0.0498	–0.0019	0.191	–16.22
IIId	O···Mg^{2+}	1.913	0.0576	–0.0869	0.1019	0.0150	0.467	–27.27
	C^6···Mg^{2+}	2.171	0.0427	–0.0472	0.0471	–0.0001	0.188	–14.81
IIIe	S···Ca^{2+}	2.744	0.0320	–0.0286	0.0274	–0.0012	0.105	–8.97
	N^3···Ca^{2+}	2.326	0.0437	–0.0488	0.0519	0.0031	0.220	–15.31
IIIf	O···Ca^{2+}	2.299	0.0432	–0.0494	0.0532	0.0038	0.228	–15.50
	N^3···Ca^{2+}	2.313	0.0438	–0.0496	0.0529	0.0033	0.225	–15.56
IIIg	S···Ca^{2+}	2.692	0.0360	–0.0340	0.0317	–0.0023	0.118	–10.67
	S^1···Ca^{2+}	2.845	0.0242	–0.0196	0.0201	0.0005	0.082	–6.15
IIIh	O···Ca^{2+}	2.203	0.0521	–0.0663	0.0712	0.0049	0.304	–20.80
	C^6···Ca^{2+}	2.642	0.0264	–0.0216	0.0218	0.0002	0.088	–6.78

containing four-membered ring. It is logical that a similar complex with a Ca^{2+} ion is transformed at the optimization into a structure of **IIk** type [8]. The calculated binding energy S^1···Mg^{2+} and S^1···Ca^{2+} is in the range of –5.37 to –10.67 kcal mol^{-1}.

Interactions O···Mg^{2+}, O···Ca^{2+}, N···Mg^{2+}, and N···Ca^{2+}. The O···Mg^{2+} and O···Ca^{2+} contacts occur in complexes **IIb, IIe, IIg, IIh, IIi, IIIb, IIId, IIIf,** and **IIIh**. Table 1 shows that in the critical points (3, –1) of these interaction the absolute values of the λ_3 term of the electron density curvature is high (Table 2) indicating a strong rarefaction of the electron density along the bonding path from the critical point in the direction of the atomic basins. The electron density rarefaction is also reflected in the positive values of

$h_e(r)$: $|\nu(r)| < g(r)$. Consequently, the O···Mg^{2+} and O···Ca^{2+} bonds should be classified as an interaction of the closed shells with low covalency (DI values are in the range of 0.196–0.270, Table 1), which is defined by the electron shell polarization of mRd and its anion in the direction of the cation.

Table 2 shows that the $\rho(r)$ function and potential energy density at the critical points of the O···Mg^{2+} and O···Ca^{2+} bonds are large enough, and the calculated energy of these interactions range from –15.5 to –31 kcal mol^{-1}. Certainly, a strong electrostatic attraction between the metal cation and the partially negatively charged oxygen atom of the keto group contribute mainly to the energy of these contacts.

The N···Mg^{2+} and N···Ca^{2+} interactions, which appear in complexes **IId, IIg, IIj, IIIa, IIIb, IIIe,** and **IIIf,** are very similar by their nature to the O···Mg^{2+} and O···Ca^{2+} interactions. They should also be classified as a closed shell interaction on the basis of the positive values of $h_e(r)$ and $\nabla^2\rho(r)$. The energy of these bonds, according to the calculations, varies over a wide range from –5.71 to –22.34 kcal mol^{-1} (Table 2).

The C···Mg^{2+} and C···Ca^{2+} interactions. We detected the interaction of this type in four complexes: **IIb, IIi, IIId,** and **IIIh**. As can be seen from Table 2, these contacts are characterized by extremely low electron energy density in the critical points (of the magnitude from –0.0003 to –0.001 a.u.). This fact does not allow the classification of these interactions in the framework of AIM theory. The bonds with $h_e(r) < 0$ should be attributed to the interactions of the intermediate type (the C···Mg^{2+} contacts), and those with $h_e(r) > 0$, to the interaction of closed shells (the C···Ca^{2+} contacts). The C···Ca^{2+} bonds in the complexes **IIi** and **IIIh** are of significant ellipticity (0.31 and 0.16, respectively), and the energy of these bonds is rather low (3.23 and 6.78 kcal mol^{-1}, respectively). Thus, we can conclude on the strain and the potential instability of the Ca^{2+}-containing five-membered rings. The DI of the C···Ca^{2+} contacts are low (0.106 and 0.198 in the complexes **IIa** and **IIIh**, respectively), which proves that the polarizing power of the Ca^{2+} ion is weaker compared with the Mg^{2+}. The latter polarizes methylene center of methylidene rhodanine and its anion rather strongly, resulting in relatively high values of the electron density delocalization indices (0.206 and 0.336 for the complexes **IIb** and **IIId**, respectively, Table 1).

Thus, based on the analysis of the distribution function of electron density in the model Ca^{2+} and Mg^{2+}complexes with methylidene rhodanine and its anion in the framework of theory of *atoms in molecules* we reached the following conclusions. In the molecule of methylidene rhodanine five coordination centers involved in the complexation can be distinguished. Their polarization at the interaction with the cations Ca^{2+} and Mg^{2+} leads to a deformation of the electron shell of methylidene rhodanine and its anion that leads to an accumulation of electron density in the interatomic space of the coordination bonds. For all coordination bonds the Laplacian $\nabla^2\rho(r) > 0$, and the Kramer-Crack density of electron energy can be both positive and negative. Thus, in the terms of the AIM theory all the coordination bonds can be classified as the interaction of closed shells (O···Mg^{2+}, O···Ca^{2+}, N···Mg^{2+}, N···Ca^{2+}, C···Ca^{2+}) and the interaction of the intermediate type (S···Mg^{2+}, S···Ca^{2+}, S^1···Mg^{2+}, S^1···Ca^{2+}, C···Mg^{2+}). The indices of the electron density delocalization between the metal cation and the coordination centers of methylidene rhodanine and its anion show the interaction order, and the degree of concentration of the electron density in the interatomic space allows to judging on the degree of covalency of these bonds. In general, the DI values fall to the range of 0.106–0.581. The ellipticity of the coordination bonds forming the metal-containing rings is a measure of susceptibility of the ring structure to opening that makes it possible to determine the potential stability (instability) of the respective rings.

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