THEORETICAL STUDIES OF THERMAL DECOMPOSITION OF ANHYDROUS CADMIUM AND SILVER OXALATES
Part II. Correlations between the electronic structure and the ways of thermal decomposition

*A. Koleżyński and A. Małecki**

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Al. Mickiewicza 30, 30-059 Cracow, Poland
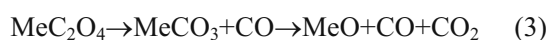
Detailed analysis of the results of full potential linearized augmented plane wave (FP LAPW) *ab initio* calculations for anhydrous silver and cadmium oxalates, reported in first part of this paper [1] has been presented. Additional calculations of Bader's AIM (Atoms in Molecules) topological properties of the electron density, bond orders (Pauling, Bader, Cioslowski and Mixon) and bond valences according to bond valence model have been done. The obtained results show the similarities in electronic structure of both compounds and support the conclusion, that during the thermal decomposition process, these compounds should most probably decompose to metal and carbon dioxide, in agreement with the experiment.

Keywords: bond order, bond valence, electron density topology, FP LAPW ab initio calculations, thermal decomposition

Introduction

In our previous paper [1], we have presented the results of *ab initio* calculations of the electronic structure for silver and cadmium anhydrous oxalates. The aim of present work is detailed analysis of these results and the results of bond orders and bond valences calculations, in the light of thermal decomposition process.

Anhydrous cadmium and silver oxalates belong to the isostructural family of anhydrous oxalates β-MC_2O_4 with monoclinic unit cell (Jeanneau *et al.* [2], Kondrashev *et al.* [3], Naumov *et al.* [4]). The thermal decomposition reaction, despite the similarities within this isostructural family, leads to different reaction products [5, 6], which can be described figuratively by following reactions (Malecki, Labus [7], Malecka *et al.* [8]):

$$MeC_2O_4 \rightarrow Me + 2CO_2 \tag{1}$$

$$MeC_2O_4 \rightarrow MeO + CO + CO_2 \tag{2}$$

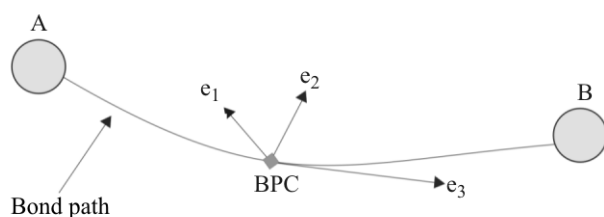$$MeC_2O_4 \rightarrow MeCO_3 + CO \rightarrow MeO + CO + CO_2 \tag{3}$$

There is still lack of consistent description and explanation of the origin and thermal decomposition reaction path in given oxalate. It is our intention in current work, to try to explain the thermal decomposition reaction path in case of silver and cadmium oxalates on the basis of *ab initio* calculations. Since these both compounds, decompose according to Eq. (1) reaction type, we have decided to analyze them simultaneously.

In following paragraphs, the detailed analysis of density of states, electronic structure, bond orders and bond valences is presented.

Band structure and density of states

The band structure and density of state are two most important descriptors of the electronic structure in the crystal, defined in momentum space. While the band structure provides the essential information about the number of bands, their width, type and the width of band gap and the shapes of bands for chosen high symmetry directions in reciprocal space, the density of states is defined for a crystal as a whole as a number of allowed energy levels per unit volume and allows to analyze the overall properties of energy states in crystal. When the partial densities of states are taken into account, additional information can be obtained, e.g. the relative contribution to the total DOS from different atoms in crystal or mixing of energy states associated with s, p, d or f electrons. For our current task, detailed analysis of electronic structure from the point of view of thermal decomposition process, the most important data in reciprocal space are contained in band characters and total and partial DOS-es. The band characters for highest symmetry Γ-point and total DOS calculated for both compounds, have been presented at Figs 3, 4 and 6 in [1]. The results of total DOS show, that in valence region,

* Author for correspondence: malecki@uci.agh.edu.pl

Fig. 1 Bond critical point: A, B – atoms, e_1, e_2, e_3 – electron density Hessian eigenvectors.

there is three sharp peaks where only carbon and oxygen electrons are mixed (about -1.3 Ry, -1.1 Ry, -0.5 Ry). Close to Fermi level, there are two broader regions – first one broader containing metal electrons mixed with carbon and oxygen ones, and little narrower shared mainly by carbon and oxygen electrons with small amount metal electrons. The partial densities of states presented in Fig. 1 below show, that in case of silver and cadmium, in principle only d-electrons contribute to total DOS and their energy states are mainly located in energy region close to Fermi level (however in case of cadmium the majority of d-states lies lower in energy and next to Fermi level there is much smaller number of states while in silver it is reversed), shared with energy states of p-electrons from oxygen (silver oxalate) or p-electrons from oxygen and carbon (cadmium oxalate). The oxygen s-electrons are mixed with carbon s- and p-electrons. The bands characters acknowledge this picture – there are few bands dominated by metal d-electrons, with small participation

of oxygen and carbon electrons, and the rest, where the carbon and oxygen electron are mixed. Thus in both structures, metal–oxygen bonds are created by metal d-electrons and oxygen p-electrons, the C–O bonds are built from carbon s- and p-electrons and oxygen s-electrons and the latter bonds should be stronger than former ones. This conclusion is strongly supported in direct lattice by electron density distribution and its topological properties.

Electron density topology

As the basis for the topological Bader QTAiM [9] analysis (Quantum Theory of Atoms in Molecules), we used electron density distribution obtained from *ab initio* calculations, performed with WIEN2k package [10] (which use highly precise full potential linearized augmented plane wave (FP LAPW) method within density functional theory (DFT) formalism). The calculated parameters for electron density in bond critical points are presented in Table 1.

According to Bader's formulation, every bond critical point, can be described by its position, electron density in this point, Hessian matrix eigenvalues λ_1, λ_2, λ_3 and Laplacian $\nabla^2\rho(r)$, defined as a trace of Hessian matrix (Fig. 2). The negative values of the Laplacian ($\nabla^2\rho(r)<0$) are characteristic for covalent bonding (charge is concentrated between bonded atoms), while charge depletion in bond region associated with positive value of Laplacian ($\nabla^2\rho(r)>0$), is characteristic for ionic bonding. Bond ellipticity, defined as $\varepsilon=|\lambda_1/\lambda_2-1|$,

Table 1 Topological properties of bond critical points calculated for electron density obtained in FP LAPW *ab initio* calculations for cadmium and silver anhydrous oxalates (bonds and atoms indices as defined in our previous paper [1], experimental bond lengths are calculated from structure data taken from [2–4] for cadmium and silver oxalates, respectively)

$Ag_2C_2O_4$		Bond length/Å	$\lambda_1/Å^{-5}$	$\lambda_2/Å^{-5}$	$\lambda_3/Å^{-5}$	$\nabla^2\rho(r)/Å^{-5}$	$\rho(r)/e\ Å^{-3}$	ε
r_1	$Ag_1-O_1^{ii}$	2.2861	−1.5843	−1.5715	8.7649	5.6100	0.3864	0.0081
r_2	$Ag_1-O_1^{iii}$	2.5512	−0.7639	−0.7345	4.5210	3.0220	0.2130	0.0400
r_3	$Ag_1-O_2^{ii}$	2.2458	−1.7626	−1.6992	9.7530	6.2900	0.4170	0.0373
r_4	$Ag_1-O_2^{iii}$	2.4712	−0.9473	−0.9208	5.5356	3.6680	0.2520	0.0280
r_5	$C_1-O_1^{i}$	1.2304	−26.1718	−24.9669	40.6073	−10.5050	2.7257	0.0483
r_6	$C_1-O_2^{ii}$	1.2409	−24.3403	−24.2439	37.0888	−11.4980	2.6528	0.0040
r_7	C_1-C_3	1.5950	−11.1869	−9.9385	9.7819	−11.3440	1.5217	0.1116

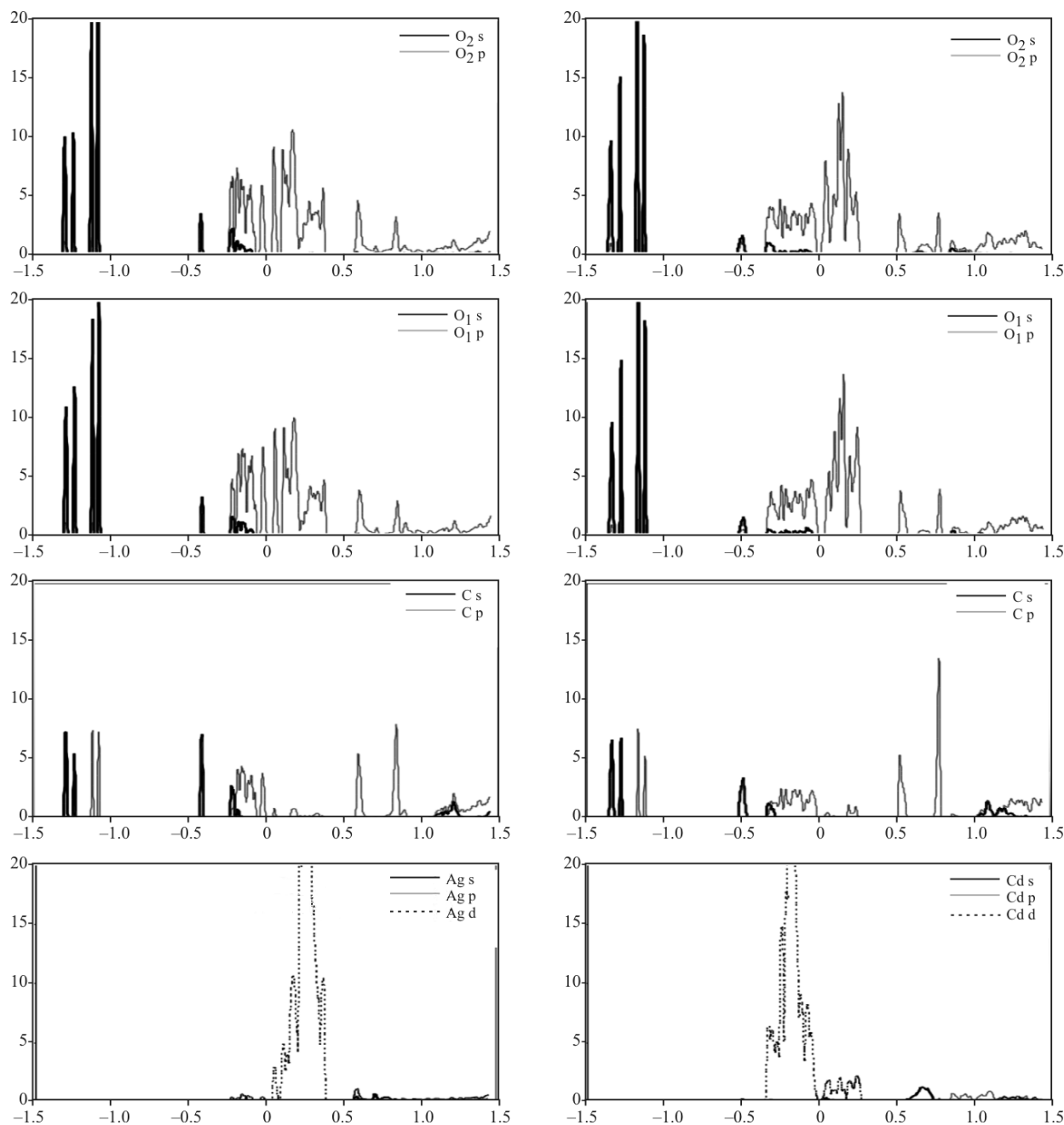| CdC_2O_4		Bond length/Å	$\lambda_1/Å^{-5}$	$\lambda_2/Å^{-5}$	$\lambda_3/Å^{-5}$	$\nabla^2\rho(r)/Å^{-5}$	$\rho(r)/e\ Å^{-3}$	ε
r_1	$Cd-O_1$	2.2421	−1.9034	−1.8809	9.9578	6.1740	0.4324	0.0118
r_2	$Cd-O_2^{i}$	2.3210	−1.5207	−1.5023	8.0275	5.0030	0.3608	0.0121
r_3	$Cd-O_2^{ii}$	2.3469	−1.4211	−1.3763	7.4587	4.6630	0.3344	0.0315
r_4	C_1-O_1	1.2462	−24.9187	−23.3980	34.4861	−13.8280	2.6474	0.0610
r_5	$C_1-O_2^{i}$	1.2642	−23.1546	−21.7689	30.4374	−14.4960	2.5327	0.0637
r_6	C_1-C_2	1.5580	−12.5798	−11.4664	9.9289	−14.1200	1.6635	0.0885

Fig. 2 Partial densities of states calculated for silver and cadmium oxalates (left and right column respectively)

measures how much the bond is elongated in e_1 direction, compared to e_2 – large value of ellipticity indicates, that bond has a significant π-character.

The results presented in Table 1 indicate, that in both structures, the highest electron density concentration is in carbon oxygen bonds; the less concentration is in C–C bonds and much smaller in metal oxygen bonds. The C–O and C–C bonds show covalent, while metal–oxygen bonds the ionic-covalent character. The calculated ellipticities are small, so there is no visible evidence for π-component in bonds. As the consequence, the strongest bonds in these structures should be C–O bonds, followed by

C–C bonds and weakest and most easily breakable are Ag–O and Cd–O bonds, which suggest that during thermal decomposition process, metal atoms and carbon dioxide molecules should be obtained as products.

Bond order

The concept of bond order has provided for generations of chemist very useful tool to analyze and compare the relative strength of chemical bond. There is many different methods for calculating the bond order, both

theoretical and experimental. An excellent review can be found in Jules and Lombardi [11]. The main problem with theoretical bond orders, defined in terms of quantum mechanical properties of molecule or crystal, is in the inability to easily compare the values derived from different types of bonds. One can avoid this, by defining uniquely geometrical (topological) parameters, which are readily identifiable and comparable for any molecule or crystal. One such method is Bader's QTAiM, where entire space is partitioned uniquely and every bond can be described by properties of bond critical points. Bader *et al*. [12] have defined following relationship between the bond order n_B and the electron density in critical point $\rho_{BX\Pi}$:

$$n_B = e^{A(\rho_{BCP} - B)}$$

The constants A and B in above formula have simple physical interpretation: $A = d\ln n_B/d\rho_B$ represents the fractional change in bond order, due to the unit change in electron density and B is the electron density in the critical point for single bond ($n_B=1$). Bader have estimated the values of the parameters to be $A=0.957$ and $B=1.70$, in single determinant SCF calculations for 6-31G* basis sets assuming bond order 1,2,3 for C–C bond in ethane, ethylene and acetylene, respectively. This method was widely used, providing the information about the covalency of bonds. Another widely used, classical definition of bond order is due to Pauling [13] and is based on interatomic distances R only:

$$n_P = e^{\frac{r_0 - R}{a}}$$

where $r_0 = 1.521$ is an idealized single-bond length and $a=0.293$. Both mentioned definition have limitations – Bader's gives reasonable good results for C–C bonds, but much worse for heterovalent bonds, while Pauling's bond order is not sufficiently sensitive to the bond environment and electronic charge distribution. Nevertheless, they are sufficient for qualitative analysis of bond orders.

Cioslowski and Mixon [14] proposed a covalent bond order index, within the Bader's QTAiM method. Based on their formalism, Howard and Lamarche [15] proposed much improved bond order definition, where parameters where fitted to generated set of the covalent bond-order data, using the topological BCP properties:

$$n_{CM(HL)} = a_0 + a_1(\lambda_1 + \lambda_2) + a_2\lambda_3 + a_3\rho_{BCP}$$

where $\lambda_1, \lambda_2, \lambda_3$ – eigenvalues of the electron density Hessian matrix in bond critical point. Since the values ρ_{BCP} and λ_3 measures the σ character of the covalent bond, while the curvatures of the electron density perpendicular to the bond line, λ_1 and λ_2, measure the degree of its π character, this formula is suitable for different types of bonds.

Recently Jules and Lombardi [6] have proposed generalization of Bader's bond order formula, based on observations due to Gugenheimer formula [16], that the bond order should vary inversely with $\sqrt{z_1 z_2}$, where z_1, z_2 are the number of valence electrons for each atom joined by the bond:

$$n_{B(JL)} = \frac{\alpha}{\sqrt{z_1 z_2}} e^{A_{ij}(\rho_{BCP} - B_{ij})}$$

where α – is set to value of $\sqrt{z_1 z_2}$ for some reference bond (for given i and j). Based on experimental bond order obtained from Gugenheimer formula and theoretically calculated ρ_{BCP} for C–C bond, taking $\alpha=4$, they have estimated the values of $A_{ij}=0.666$ and $B_{ij}=1.49$. In Table 2, the results of calculated bond orders for all above definitions are presented. For Bader and Pauling formulas, instead of original, the improved parameters, obtained by Howard and Lamarche [15] were used. Since there are no available parameters for metal–oxide bonds, we used for such bonds the same parameters, as for carbon–oxide bond. Thus, the bond order values presented in Table 2 are quite reasonable for C–C and C–O bonds, but those calculated for metal–oxide bonds should be considered more qualitatively. Despite the differences, all these calculated bond orders show, that carbon–oxygen bonds are similar in value and much stronger, than carbon–carbon ones and metal–oxygen bonds (bearing in mind their approximate values) are the weakest (except for n_{CM} case). This allow us to assume that

Table 2 Bond orders obtained for anhydrous silver and cadmium oxalates from theoretical electron density bond critical points parameters, calculated by FP LAPW method (bonds and atoms indices as defined in [1])

$Ag_2C_2O_4$		n_P	n_B	$n_{CM(HL)}$	$n_{B(JL)}$
r_1	$Ag_1-O_1^{ii}$	0.10	0.46	0.87	0.78
r_2	$Ag_1-O_1^{iii}$	0.05	0.43	0.83	0.70
r_3	$Ag_1-O_2^{ii}$	0.11	0.47	0.88	0.80
r_4	$Ag_1-O_2^{iii}$	0.07	0.44	0.84	0.72
r_5	$C_1-O_1^{i}$	1.35	1.38	1.23	1.86
r_6	$C_1-O_2^{ii}$	1.31	1.33	1.19	1.77
r_7	C_1-C_3	0.78	0.89	0.70	1.02

CdC_2O_4		n_P	n_B	$n_{CM(HL)}$	$n_{B(JL)}$
r_1	$Cd-O_1$	0.11	0.47	0.89	0.57
r_2	$Cd-O_2^{i}$	0.09	0.46	0.86	0.54
r_3	$Cd-O_2^{ii}$	0.09	0.45	0.86	0.53
r_4	C_1-O_1	1.30	1.33	1.16	1.76
r_5	$C_1-O_2^{i}$	1.24	1.26	1.11	1.64
r_6	C_1-C_2	0.88	1.02	0.87	1.12

in process of thermal decomposition, as the first, metal–oxide bonds will break, than C–C bonds, resulting in metal and carbon dioxide as the final products of thermal decomposition.

Bond valence

The use of empirical correlations between the bond length and strength of chemical bonds, have a long history in crystal chemistry, starting from Pauling [17], Byström and Wilhelmi [18], Zachariasen [19] and Smith [20]. In 1970, Donnay and Allmann [21] suggested to use the notion 'bond valence' instead 'valence strength' proposed by Pauling. The bond valence concept that it does not require an a priori distinction between covalent and ionic bonds and terms cation and anion are used in it only for classification of particles according to their electronegativity, thus are equivalent to Lewis acid and bases. Bond valence and bond length are related by the inverse power relationship:

$$s_{ij} = (R_{ij}/R_0)^{-N}$$

where N and R_0 are the empirical constants, with R_0 being the length of a bond of unit valence.

Another expression for the dependence $s(R)$, was suggested by Allmann [22] and Zachariasen [23]:

$$s_{ij} = e^{(R_0 - R_{ij})/b}$$

where R_0 has the sense of unit valence ($s_{ij}=1$), whereas b varies within a range from 0.32 to 0.48 Å. Values for these constants have been determined by many workers, by requiring, that the values of s_{ij} obey the valence sum rule (stated that the valence of given atom is equal to the sum of bond valences around this atom $V_i - \sum_j s_{ij}$) in many different compounds. The present state of the art and perspectives of bond valence model in inorganic crystal chemistry has been reviewed by Urusov and Orlov [24] and recently more extensively by Brown [25].

The 'experimental' s_{ij}^{exp} values can be easily calculated from the experimental bond lengths. The sum of the experimental bond valences will not, in general, be exactly equal to the atomic valence i.e. will not fulfill the valence sum rule. The measure of the difference between the 'experimental' atomic valence $\sum s_{ij}^{exp}$ and the expected value V_i,

$$d_i = V_i - \sum_j s_{ij}^{exp}$$

can be used for calculating the reliability factor of the crystal structure. A convenient measure of the agreement over the whole structure is given by the index, D, which is the root-mean-square average of the d_i values:

$$D = \sqrt{\langle d_i^2 \rangle}$$

Experimental uncertainty in the determination of bond length can lead to the values of D as large as 0.1 v.u. (valence units), depending on the accuracy of the bond length. Larger values of d_i and D indicate the existence of strained bonds, which can lead to instabilities in the crystal and show most strained regions in the structure (which can simultaneously be the sites of the highest reactivity or liability). Another indicator of bond strain can be the difference between the theoretically predicted and experimentally observed bond lengths. In this case, the strain factor δ for a certain group of bonds or the structure as a whole, can be described by following formula:

$$\delta = \sqrt{\frac{\sum_{i=1}^{N}(s_i^{theor} - s_i^{exp})^2}{N}}$$

While d_i indicates the magnitude of unbalanced charge for given atom in the structure, the strain factors δ provide us additional information about the differences in strains acting on single bonds or group of bonds.

Brown and Shannon [26] pointed out, that bond valence not only measures the number of electrons associated with a bond, but also, in practice, the degree of covalency. Thus, bond valence model can serve as additional (complementary to bond order) tool for crystal bond properties analysis. In Tables 3–5, the results of the calculations within BVM for silver and cadmium oxalates are presented: in Table 3 calculated bond valences with residual strain factors d_i and D; in Table 4 theoretical bond valences and bond lengths according to valence sum rule equations and in Table 5 the values of bonds strain factors δ for bond groups and the whole structure.

The obtained results show almost no overall strains in silver and cadmium oxalates (D=0.0667 and 0.1215 v.u., respectively). In both structures, most electrically unbalanced are carbon atoms, while metal atoms are nearly perfectly balanced. In cadmium oxalate, one oxygen is much more unbalanced than the other (still less than carbon), which is due to different environment of these atoms – one of them is shared corner of octahedra, the other belong to only one octahedron. Thus – the highest strains in the structure are associated with carbon atoms.

The bond lengths R_{theor}, calculated from theoretical valences obtained via the electroneutrality sum rule, indicate that all experimental bond lengths only slightly differ from theoretical ones (less than 2%, except C–C bond in silver oxalate and Cd–O_1 and C–O_1 in cadmium oxalate, where the deviation is about 3%). The bond strain factors (Table 5) are small – the highest are for

Table 3 Bond valences with residual strain factors d_i and D, calculated from bond valence model for silver and cadmium oxalates. Experimental bond lengths calculated from structure data taken from [2, 4] for cadmium and silver oxalates, respectively

		Bond length/Å/bond valence				V_{ij}	d_i	D
		O_2^{ii}	O_1^{ii}	O_2^{iii}	O_1^{iiii}			
Ag	R_{exp}	2.2454	2.286	2.4706	2.5509			
	s_{ij}	0.3362	0.301	0.1829	0.1472	0.9674	0.0326	
		C_1	Ag	Ag				
O_1	R_{exp}	1.2300	2.2861	2.5509				0.0667
	s_{ij}	1.5410	0.3011	0.1472		1.9893	0.0107	
		C_1	Ag	Ag				
O_2	R_{exp}	1.2412	2.2454	2.4706				
	s_{ij}	1.4949	0.3362	0.1829		2.0140	−0.0140	
		O_1^{i}	O_2^{ii}	C_3				
C_1	R_{exp}	1.2300	1.2412	1.5950				
	s_{ij}	1.5410	1.4949	0.8619		3.8978	0.1022	
		$2O_1$	$2O_2^{i}$	$2O_2^{ii}$				
Cd	R_{exp}	2.241	2.321	2.346				
	s_{ij}	0.402	0.324	0.303		2.0573	−0.0573	
		C	Cd					
O_1	R_{exp}	1.2463	2.2414					0.1215
	s_{ij}	1.4747	0.4018			1.8765	0.1235	
		C	Cd	Cd				
O_2	R_{exp}	1.2640	2.3207	2.3462				
	s_{ij}	1.4056	0.3242	0.3027		2.0324	−0.0324	
		O_1	O_2	C				
C	R_{exp}	1.2463	1.2640	1.5570				
	s_{ijC}	1.4747	1.4056	0.9551		3.8354	0.1646	

Table 4 Theoretical bond valences and bond lengths calculated from bond valence model for silver and cadmium oxalates. Experimental bond lengths calculated from structure data taken from [2, 4] for cadmium and silver oxalates, respectively

$Ag_2C_2O_4$		s_{ij}^{theor}	R_{theor}/Å	R_{exp}/Å	$\Delta R/R$/%	Valence sum rule
r_1	$Ag_1–O_1^{ii}$	1/3	2.2485	2.2861	1.64	
r_2	$Ag_1–O_1^{iii}$	1/6	2.5050	2.5509	1.80	$Ag=r_1+r_2+r_3+r_4=1/3+1/3+1/6+1/6=1$
r_3	$Ag_1–O_2^{ii}$	1/3	2.2485	2.2454	0.14	$O_1=r_1+r_2+r_5=1/3+1/6+1\ 1/2=2$
r_4	$Ag_1–O_2^{iii}$	1/6	2.5050	2.4706	1.37	$O_2=r_3+r_4+r_6=1/3+1/6+1\ 1/2=2$
r_5	$C_1–O_1^{i}$	1 1/2	1.2400	1.2300	0.80	
r_6	$C_1–O_2^{ii}$	1 1/2	1.2400	1.2412	0.10	$C=r_5+r_6+r_7=1\ 1/2+1\ 1/2+1=4$
r_7	$C_1–C_3$	1	1.5400	1.5950	3.45	
CdC_2O_4		s_{ij}^{theor}	R_{theor}/Å	R_{exp}/Å	$\Delta R/R$/%	Valence sum rule
r_1	$Cd–O_1$	1/3	2.3105	2.2414	2.99	
r_2	$Cd–O_2^{i}$	1/3	2.3105	2.3207	0.44	$Cd=2\ r_1+2\ r_2+2\ r_3=2\ 1/3+2\ 1/3+2\ 1/3=2$
r_3	$Cd–O_2^{ii}$	1/3	2.3105	2.3406	1.29	$O_1=r_1+r_4=1/3+1\ 2/3=2$
r_4	$C_1–O_1$	1 2/3	1.2010	1.2463	3.63	$O_2=r_2+r_3+r_5=1/3+1/3+1\ 1/3=2$
r_5	$C_1–O_2^{i}$	1 1/3	1.2836	1.2640	1.52	$C=r_4+r_5+r_6=1\ 2/3+1\ 1/3+1=4$
r_6	$C_1–C_2$	1	1.5400	1.5570	1.09	

Table 5 Bonds strain factors δ calculated for silver and cadmium oxalates

$Ag_2C_2O_4$	δ_{Ag-O}	δ_{C-O}	δ_{C-C}	δ_{struct}
	0.0205	0.0292	0.1381	0.0567
CdC_2O_4	δ_{Cd-O}	δ_{C-O}	δ_{C-C}	δ_{struct}
	0.0436	0.1450	0.0449	0.0911
	δ_{C-O_1}	δ_{C-O_2}		
	0.1920	0.0722		

C–C bond and C–O bonds in silver and cadmium oxalates, respectively. These BVM results, bearing in mind the respective bond orders, allow us to state, that since metal cations environment are almost not disturbed, the main area where decomposition processes will take place should be located in oxalate anions regions. While it seems that in silver oxalate as the first the Ag–O bonds, than C–C bond will be broken, than in cadmium oxalate the picture is less clear – as the first one probably Cd–O_1 bond should be broken, then due to structure relaxation this can be the Cd–O_2 or simultaneously both Cd–O_2 and C–C. Nevertheless – in both structures, the decomposition process will lead most probable to metal and carbon dioxide as final products.

Conclusions

The main purpose of the undertaken studies presented in [1] and in this paper, was the attempt to analyze and explain the thermal decomposition process in silver and cadmium anhydrous oxalates on a basis of their electronic structure. The results of the *ab initio* calculations of band structure, density of states and electron density topology, in conjunction with calculated bond orders and bond valences, have shown many similarities between these two structures. The strongest interactions and thus bonds are between carbon and oxide atoms and weakest between silver and cadmium and oxygen. This conclusion is confirmed in coherent way by the properties in both reciprocal (band structure and densities of states) and direct (the magnitude of electron densities in bond critical points and bond orders) spaces. In our opinion, presented results support the supposition that the most probable products of thermal decomposition reaction in case of these two compounds should be metal and carbon dioxide, which is in agreement with the experiment. We have undertaken similar extensive studies for anhydrous zinc oxalate [27], decomposing according to Eq. (2) type of reaction and the obtained results confirmed experimentally checked way of decomposition as most probable in this structure. Thus it allows us to consider such type of theoretical studies as promising additional tool for analysis of the properties of metalorganic materials and their thermal decomposition reactions.

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