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Crystallochemical Role of Benzoate and Phenylacetate Ions in Structures of Coordination 3*d*-Metal Compounds

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Abstract—A crystal chemical analysis of the 3*d*-metal benzoate- and phenylacetate-containing compounds is carried out in terms of the stereoatomic crystal structure model using characteristics of the Voronoi–Dirichlet polyhedra. Coordination types of benzoate and phenylacetate anions toward the transition metals from Ti to Zn are considered. The influence of the coordination type on the characteristics of M–O bonds in the crystal structures is revealed. The electron-donating ability of benzoate and phenylacetate anions toward 3*d* metals is quantitatively estimated using the 18-electron rule.

Keywords: Voronoi–Dirichlet polyhedra, crystal chemical analysis, crystallochemical formula, coordination types, benzoates, phenylacetates, 18-electron rule, electron-donating ability

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INTRODUCTION

In recent decades, metal carboxylate complexes attract attention of researchers as promising precursors in the design of crystals and, in particular, for the preparation of metal-organic frameworks [1]. The main attention is given to polyfunctional compounds, for example, the metal-organic frameworks based on the benzoic acid derivatives capable of sorbing carbon dioxide and ions of radioactive elements were described [2, 3]. The Cambridge Structural Database (CSD) [4] contains data on more than 2500 structures bearing simultaneously benzoate ions and 3*d* metals and about 100 structures bearing 3*d*-metal ions and phenylacetate ions.

Since benzoic and phenylacetic acids should be considered as progenitors of the series of aromatic carboxylic acids, it was of interest to establish specific features of the main coordination types that are manifested by anions of these acids toward ions of period 4 transition metals and to determine their electron-donating ability.

CRYSTAL CHEMICAL ANALYSIS AND OBJECTS OF THE STUDY

The data on the structures of the 3*d*-metal benzoate- and phenylacetate-containing complexes were taken from the CSD [4] using the TOPOS software [5]. Structural data were considered only if they satisfied the following requirements: the structure was solved with the nonzero reliability factor $R < 0.1$ and no statistical disordering of 3*d*-metal atoms and benzoate or phenylacetate ions was observed. These requirements were valid for 778 structures containing 1840 crystallographically nonequivalent benzoate anions and 60 structures containing 130 crystallographically different phenylacetate anions. The full list of all compounds studied are available from the authors at maxkarasev@inbox.ru.

Crystal chemical analysis was carried out in terms of the stereoatomic crystal structure model using characteristics of the Voronoi–Dirichlet polyhedra (VDP) [6–8].

The intersecting sphere method was used to determine coordination numbers of 3*d*-metal atoms [9].

COORDINATION TYPES FOR BENZOATE AND PHENYLACETATE IONS

According to the data in Table 1, benzoate anions can manifest eight various coordination types toward 3*d* metals, and both the oxygen atoms of the carboxy group bearing lone electron pairs and the benzene ring (due to the π-electron density in it) can be involved in binding. The coordination types are designated in Table 1 according to a published procedure [10]. The coordination of metal atoms via the carboxy group makes the benzoate ion either bidentate (when one O atom participates in metal binding), or bidentate (when both O atoms are involved in metal binding). Owing to two lone electron pairs on each oxygen atom

Table 1. Coordination types for benzoate and phenylacetate ions by 3*d*-metal atoms in the crystal structures*

Coordination type	Benzoate ions		Phenylacetate ions	
	N	*n*, %	*N*	*n*, %
M^1	358	19.5	27	20.8
M^2			2	1.5
B^2	1168	63.5	77	59.2
B^3	18	1.0	2	1.5
B^4	2	0.1		
B^{01}	184	10.0	15	11.5
B^{11}	39	2.1	6	4.6
B^{21}	10	0.5		
H^{000001}	61	3.3	1	0.8
Totally	1840	100	130	100

* *N* is the number of crystallographic sorts of ions, and *n* is the content in the sampling.

of the carboxy group, the $PhCOO^-$ ions can form from one to four M–O chemical bonds.

As can be seen from the data in Table 1, the benzoate anion can act as a monodentate ligand exhibiting the coordination type M^1 in 19.5% cases (358 benzoate ions of 1840). In this case, the $PhCOO^-$ ion forms one chemical bond with the metal atom as shown in Fig. 1a. A similar coordination type of $PhCOO^-$ ions is met for all 3*d* metals, except for scandium (Table 2). It should be mentioned that the database [4] contains no information about complexes of scandium, whose atoms coordinate benzoate ions.

The coordination type B^2 for benzoate ions is the most abundant one: 1168 complexes of 1840, which amounts to ~63.5% (Table 1). In this case, the $PhCOO^-$ ions are coordinated in such a way that each O atom coordinates one metal atom (Fig. 1b) due to which polynuclear complexes can be formed. For instance, the structure of cobalt(II) benzoate trihydrate $Co(PhCOO)_2 \cdot 3H_2O$ {WIJCAW} [11] contains the benzoate anion manifesting the coordination type B^2 and binding two cobalt atoms each. As a result, the crystal structure contains infinite chains, whose repeated unit has the $[Co_2(PhCOO)_2(H_2O_4)]$ composition (Fig. 2). Hereinafter, the literal code is indicated in braces after the formula of the compound. This code was used in the CSD [4] to register structural and bibliographic data for the substance. As in the case of the coordination type M^1, the coordination type B^2 for $PhCOO^-$ ions is met for all 3*d* metals from Ti to Zn (Table 2).

The coordination type of benzoate anions for which $PhCOO^-$ binds three or four metal atoms is observed rather rarely. For example, type B^3 is met only for 18 benzoate anions of 1840, which is about 1% of the whole sampling (Table 1). In this case, one of the oxygen atoms of the $PhCOO^-$ carboxy group forms one M–O chemical bond, whereas another O atom uses both lone electron pairs for binding with the metal atom, due to which this atom is involved in the formation of simultaneously two M–O chemical bonds as shown in Fig. 1c. According to the data in Table 2, this coordination type is observed for binding M^{2+} (M = Mn, Ni, and Zn) and M^{3+} (M = Mn and Fe) ions. The formation of four M–O bonds in the case of the coordination type B^4 (Fig. 1d) is observed only for one structure of $Zn_4(Hfac)_2L_2(PhCOO)_2$ {LEKMEV} [12] (Hfac is hexafluoroacetylacetonate anion, L is 2,2'-(ethane-1,2-diylbis((methylimino)methylene))bis(4,6-dimethylphenolate)) in which the benzoate ions bind zinc atoms to form an island tetranuclear complex.

The bidentate cyclic coordination mode (type B^{01}) when both oxygen atoms of the carboxy group form bonds with the same metal atom (Fig. 1e) is the third type according to the frequency of coordination of benzoate anions. This coordination type is met for 184 $PhCOO^-$ ions and occurs for all metals from Ti to Zn.

Benzoate ions involved in coordination of types B^{11} (39 $PhCOO^-$ ions) and B^{21} (10 $PhCOO^-$ ions) simultaneously bind two or three metal atoms (Figs. 1f and 1g, respectively) and thus act as bidentate cyclic and bidentate bridging ligands. For instance, in the structure of $Zn(C_9H_{17}N_2O)(PhCOO) \cdot 2CH_2Cl_2$ {BAQLEN} [13], the benzoate anion exhibits the coordination type B^{11} binding two zinc atoms with the formation of an island binuclear complex (Fig. 3), whereas the manifestation of the coordination type B^{21} by the benzoate anion results in the formation of infinite chains as it is observed in the structure of $Co(PhCOO)_2$ {FOXHIJ10} [14] based on the alternation of benzoate ions with the coordination types B^2 and B^{21}. Benzoate ions exhibit the coordination type B^{11} toward two-charge ions M^{2+}, where M = Mn–Zn, whereas the coordination type B^{21} is met only in the Mn(II) and Co(II) complexes.

The valence possibilities of benzoate anions are not exhausted by the formation of M–O chemical bonds. The studied sampling contains 37 structures characterized by the fact that the metal binding in them occurs due to the π-electron density of the benzene fragment rather than to the oxygen atoms of the carboxy group of the $PhCOO^-$ ions. A common feature of this binding is the use of all the six carbon atoms of the benzene ring due to which the discussed ions can be characterized as η^6 ligands. As a result, the complexes are formed in which the benzoate anions exhibit the coordination type H^{000001} (Fig. 1h). Note that six structures in which the benzoic acid residue exists as methyl ester rather than anions and four structures containing nonionized benzoic acid molecules were

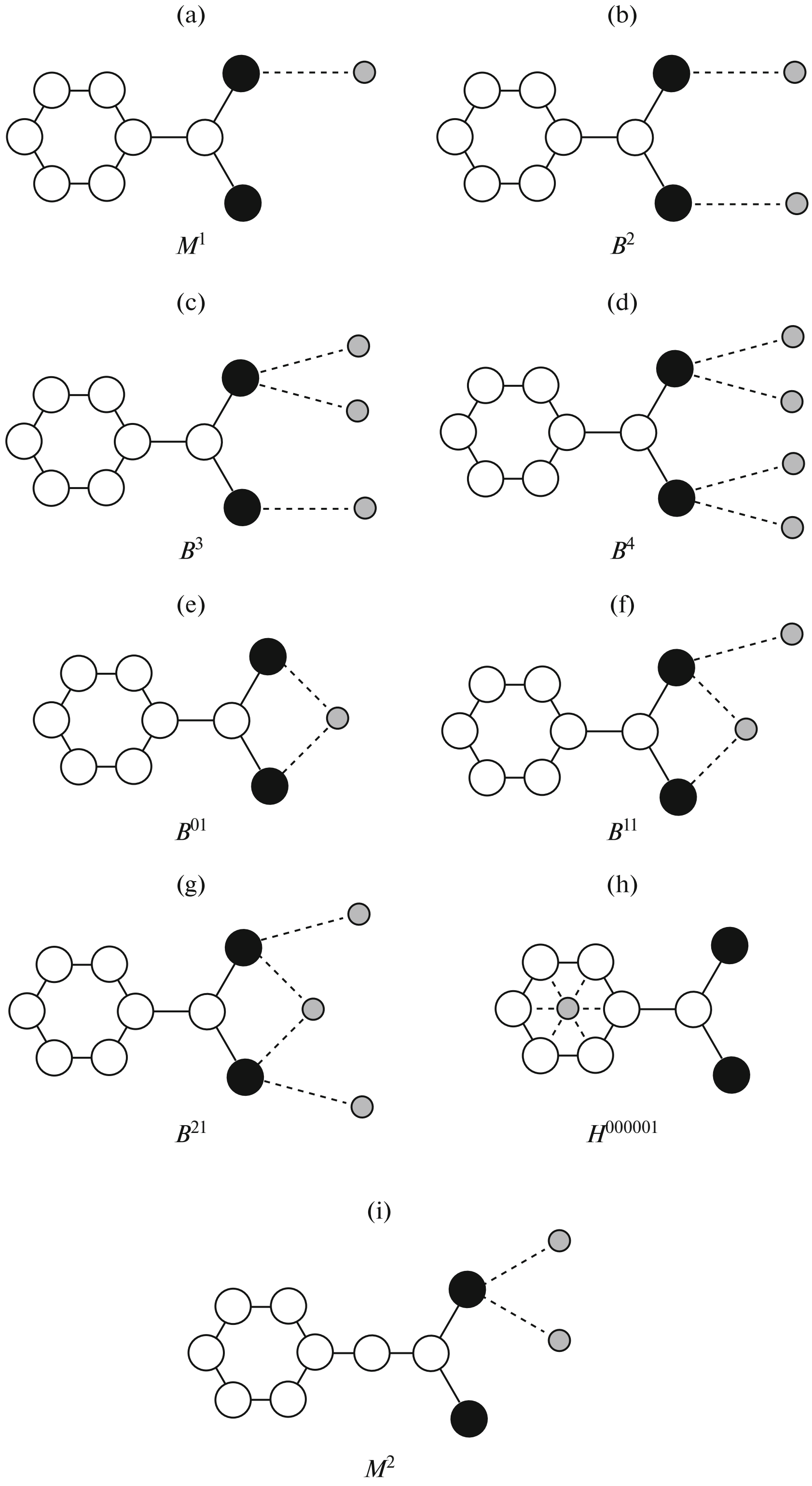

Fig. 1. Coordination types for (a–h) benzoate and (a–i) phenylacetate ions. White circles are C atoms, black circles are O atoms, and gray circles are coordinated metal ions. For simplicity, hydrogen atoms are not shown.

added to the consideration as exceptions. Thus, the coordination type H^{000001} is characteristic of six PhCOOMe molecules ({CACVIL} [15], {COSCOC} [16], {CRMEBZ01} [17], {FLPHCR} [18], {MBZCRP} [19], {MBZCRC} [20]), seven PhCOOH molecules ({FABQEF} [21], {FABQOP} [21],

Table 2. Electron-donating ability of benzoate and phenylacetate ions toward 3*d*-metal atoms in the crystal structures*

Benzoate anion

Metal	*k*	μ	M–O, Å		E_i, $\bar{e}$	E_L, $\bar{e}$
			range	average		
Coordination type M^1						
Ti^{4+}	6	6	1.91–2.02	1.96(5)	3.1(2)	3.1(2)
V^{4+}	2	2	1.98–1.99	1.99(1)	2.91(9)	2.91(9)
Cr^{2+}	1	1	1.97	1.97	2.57	2.57
Cr^{3+}	6	6	1.93–2.30	2.02(14)	2.6(3)	2.6(3)
Cr^{5+}	1	1	1.86	1.86	3.62	3.62
Cr^{6+}	2	2	1.92–1.93	1.93(1)	3.6(3)	3.6(3)
Mn^{+}	3	3	2.05–2.10	2.08(2)	1.92(2)	1.92(2)
Mn^{2+}	42	42	1.90–2.20	2.11(6)	2.4(2)	2.4(2)
Mn^{3+}	8	8	1.90–2.23	2.12(11)	2.1(2)	2.1(2)
Fe^{2+}	6	6	1.95–2.15	2.05(8)	2.1(2)	2.1(2)
Fe^{3+}	17	17	1.95–2.17	2.00(5)	2.2(2)	2.2(2)
Co^{+}	1	1	1.96	1.96	2.21	2.21
Co^{2+}	53	53	1.92–2.16	2.05(6)	1.9(3)	1.9(3)
Ni^{2+}	49	49	1.91–2.20	2.06(5)	1.6(1)	1.6(1)
Cu^{+}	5	5	1.93–2.09	2.00(7)	1.54(8)	1.54(8)
Cu^{2+}	98	98	1.89–2.68	2.01(15)	1.6(2)	1.6(2)
Zn^{2+}	58	58	1.91–2.22	1.97(5)	1.6(1)	1.6(1)
Coordination type B^2						
Ti^{4+}	24	48	1.93–2.19	2.05(6)	2.7(3)	5.5(4)
V^{3+}	12	24	1.99–2.06	2.01(2)	2.66(5)	5.31(7)
V^{4+}	8	16	1.96–2.04	2.00(2)	2.79(5)	5.6(1)
Cr^{3+}	14	28	1.94–2.04	1.98(2)	2.53(9)	5.1(2)
Mn^{2+}	64	128	1.94–2.23	2.12(4)	2.3(1)	4.6(2)
Mn^{3+}	91	182	1.91–2.60	2.07(12)	2.3(3)	4.6(4)
Mn^{4+}	6	12	2.00–2.17	2.10(6)	2.4(1)	4.9(2)
Fe^{2+}	34	68	1.96–2.34	2.07(6)	2.2(2)	4.4(4)
Fe^{3+}	274	548	1.89–2.72	2.03(5)	2.2(1)	4.3(2)
Co^{2+}	55	110	1.92–2.21	2.03(5)	2.0(2)	4.0(2)
Co^{3+}	7	14	1.90–1.95	1.92(1)	1.97(4)	3.94(8)
Ni^{2+}	44	88	1.92–2.16	2.03(4)	1.7(1)	3.4(2)
Cu^{+}	39	78	1.81–2.25	1.90(7)	1.8(1)	3.7(3)
Cu^{2+}	342	684	1.78–2.81	1.99(11)	1.6(1)	3.3(2)
Zn^{2+}	154	308	1.92–2.21	2.01(5)	1.5(2)	3.1(3)
Coordination type B^3						
Mn^{2+}	3	9	2.13–2.35	2.23(7)	2.6(2)	7.8(4)
Mn^{3+}	9	27	1.98–2.60	2.24(13)	1.9(3)	5.8(1)

Table 2. (Contd.)

Benzoate anion

Metal	k	μ	M–O, Å		E_i, $\bar{e}$	E_L, $\bar{e}$
			range	average		
Fe^{3+}	1	3	2.02–2.36	2.19(17)	1.8(3)	5.3
Ni^{2+}	3	9	2.04–2.18	2.10(5)	1.64(9)	4.93(3)
Zn^{2+}	2	4	1.98–2.10	2.05(6)	1.6(1)	4.71(1)
Coordination type B^4						
Zn^{2+}	2	4	2.19–2.25	2.20(3)	1.16(4)	4.65(8)
Coordination type B^{01}						
Ti^{3+}	2	4	2.14–2.16	2.5(1)	2.42(3)	4.85(5)
Ti^{4+}	3	6	2.10–2.21	2.15(4)	2.2(2)	4.30(7)
V^{4+}	1	2	2.15–2.39	2.27(2)	1.9(5)	3.73
Cr^{3+}	1	2	2.05–2.06	2.06(1)	2.36(1)	4.71
Mn^{+}	1	2	2.01–2.10	2.09(2)	1.67(1)	3.34
Mn^{2+}	13	26	2.16–2.41	2.27(6)	1.8(2)	3.6(2)
Mn^{3+}	5	10	1.95–2.51	2.23(24)	1.8(4)	3.5(2)
Fe^{2+}	7	14	2.04–2.36	2.19(9)	1.7(2)	3.3(1)
Fe^{3+}	4	8	2.06–2.20	2.13(6)	1.8(2)	3.62(8)
Co^{2+}	29	58	1.97–2.77	2.19(17)	1.6(3)	3.2(2)
Ni^{2+}	8	16	1.93–2.12	2.09(8)	1.5(2)	3.0(2)
Cu^{+}	1	2	2.16–2.25	2.21(7)	1.27(9)	2.55
Cu^{2+}	55	110	1.93–2.83	2.30(34)	1.2(4)	2.4(2)
Zn^{2+}	54	108	1.92–2.88	2.27(30)	1.1(4)	2.3(1)
Coordination type B^{11}						
Mn^{2+}	9	27	2.12–2.54	2.27(7)	1.9(2)	5.6(1)
Fe^{2+}	3	9	2.18–2.28	2.22(3)	1.8(1)	5.25(3)
Co^{2+}	5	15	2.01–2.56	2.20(19)	1.6(4)	4.9(3)
Ni^{2+}	3	9	2.03–2.20	2.13(6)	1.5(1)	4.4(4)
Cu^{2+}	9	27	1.94–2.87	2.31(31)	1.3(4)	3.75(8)
Zn^{2+}	10	30	2.00–2.78	2.21(19)	1.2(3)	3.6(2)
Coordination type B^{21}						
Mn^{2+}	7	28	2.12–2.56	2.26(9)	1.9(3)	7.6(6)
Co^{2+}	3	12	1.97–2.73	2.26(26)	1.6(6)	6.2(2)
Metal	k	μ	M–C, Å		E_i, $\bar{e}$	E_L, $\bar{e}$
			range	average		
Coordination type H^{000001}						
Cr^{0}	57	342	2.08–2.31	2.21(3)	0.88(6)	5.3(2)
Cr^{+}	4	24	2.10–2.16	2.13(2)	1.08(1)	6.50(1)

Table 2. (Contd.)

Phenylacetate anion

Metal	k	μ	M–O, Å		E_i, $\bar{e}$	E_L, $\bar{e}$
			range	average		
Coordination type M^1						
Mn^{2+}	4	4	2.10–2.19	2.16(3)	2.3(2)	2.3(2)
Mn^{3+}	2	2	2.13–2.14	2.14(1)	2.19(6)	2.19(6)
Co^{2+}	4	4	1.98–2.13	2.08(7)	1.9(2)	1.9(2)
Ni^{2+}	5	5	2.01–2.05	2.02(2)	1.75(3)	1.75(3)
Cu^{2+}	5	5	1.95–1.98	1.96(1)	1.63(2)	1.63(2)
Zn^{2+}	7	7	1.91–2.20	2.00(11)	1.6(2)	1.6(2)
Coordination type M^2						
Cu^{2+}	2	4	1.98–2.55	2.22(28)	1.4(3)	2.7(2)
Coordination type B^2						
Ti^{3+}	3	6	2.06–2.08	2.07(1)	2.51(4)	5.02(6)
Mn^{3+}	1	2	2.11–2.13	2.12(1)	2.31(2)	4.62
Fe^{3+}	5	10	1.99–2.06	2.03(2)	2.14(6)	4.27(7)
Co^{2+}	14	28	1.97–2.11	2.04(4)	2.0(1)	4.0(2)
Ni^{2+}	9	18	2.02–2.10	2.06(3)	1.71(4)	3.41(6)
Cu^{2+}	37	74	1.93–2.32	1.97(5)	1.63(6)	3.26(8)
Zn^{2+}	8	16	1.94–2.93	2.11(26)	1.4(3)	2.9(3)
Coordination type B^3						
Cu^{2+}	2	6	1.95–2.21	2.06(12)	1.5(1)	4.62(1)
Coordination type B^{01}						
Ti^{4+}	2	4	2.12–2.16	2.14(2)	2.41(3)	4.83(2)
Fe^{2+}	1	2	2.16–2.33	2.24(12)	1.7(3)	3.37
Co^{2+}	4	8	1.98–2.36	2.12(13)	1.8(3)	3.5(3)
Ni^{2+}	1	2	2.10–2.13	2.11(2)	1.47(2)	2.94
Cu^{2+}	4	8	1.96–2.82	2.34(39)	1.1(5)	2.3(1)
Zn^{2+}	3	6	1.94–2.72	2.24(31)	1.2(5)	2.35(8)
Coordination type B^{11}						
Co^{2+}	1	3	2.10–2.21	2.15(6)	1.7(1)	4.98
Cu^{2+}	2	3	1.95–2.73	2.27(35)	1.3(4)	3.9(3)
Zn^{2+}	3	6	2.16–2.24	2.20(3)	1.18(8)	2.4(2)
Metal	k	μ	M–C, Å		E_i, $\bar{e}$	E_L, $\bar{e}$
			range	average		
Coordination type H^{000001}						
Cr^0	1	6	2.21–2.23	2.22(1)	0.86(4)	5.17

* k is the number of benzoate or phenylacetate anions, μ is the number of M–O or M–C chemical bonds; E_i is the electron-donating ability of the benzoate or phenylacetate anion per donor atom, and E_L is the electron-donating ability of one benzoate or phenylacetate anion.

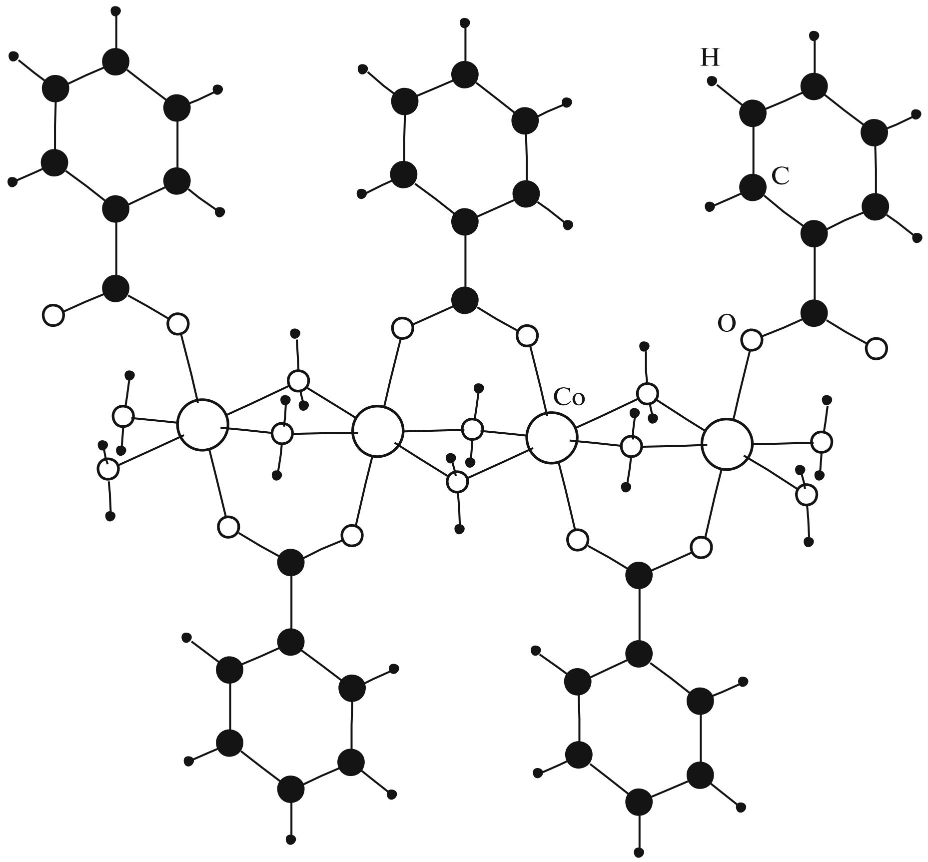

Fig. 2. Fragment of $Co(PhCOO)_2{\cdot}3H_2O$ {WIJCAW} [11].

{FABQOP01} [21], {GOYHIL} [22]), and 48 $PhCOO^-$ ions. An exclusive feature of the coordination type H^{000001} is that this type is manifested only toward low-valence chromium atoms: 34 structures contain Cr(0) atoms and three structures contain Cr(I) atoms.

As can be seen from Table 2, the content of $Ph–CH_2–COO^-$ ions coordinating 3*d*-metal atoms is an order of magnitude lower (60 structures, 130 phenylacetate ions) than the content of benzoate-containing complexes.

The monodentate binding is met for 29 $Ph–CH_2–COO^-$ ions (Table 1) and, as in the case of $PhCOO^-$, occupies the second position in abundance among other coordination types. The coordination type M^1 is observed for 27 $Ph–CH_2–COO^-$ ions. According to the data in Table 2, the coordination type M^1 is manifested by phenylacetate ions toward Mn^{3+} and two-charge cations M^{2+} (M = Mn, Co–Zn). The remained two phenylacetate ions bind simultaneously two metal atoms via one O atom to exhibit the coordination type that is not met for benzoate anions: monodentate bridging mode M^2. The coordination type discussed was found in two related structures $Cu(Bpy)_2(Ph–CH_2–COO)_2{\cdot}2H_2O$ {AZINED} [23] and $Cu(Im)_4(Ph–CH_2–COO)_2{\cdot}2H_2O$ {CEKZAV} [24] in which the $Ph–CH_2–COO^-$ ions bind two copper atoms each to form island binuclear complexes (Fig. 1i).

As in the case of benzoate ions, B^2 is the most characteristic coordination type for phenylacetate groups. Of 130 $Ph–CH_2–COO^-$ ions, the coordination type B^2 is inherent in 77 ions (59.2%). Phenylacetate ions manifest the discussed coordination type toward two-charge M^{2+} (M = Co–Zn) and three-charge M^{3+} (M = Ti, Mn, Fe) cations.

The coordination type B^3 occurs in two structures of copper(II) phenylacetate: {AFEHOK} [25] and {AFEHOK01} [26].

The coordination type B^{01} for phenylacetate groups occupies the third position in abundance: 15 $Ph–CH_2–COO^-$ ions of 130. Both two-charge M^{2+} (M = Fe–Zn) and four-charge Ti^{4+} ions act as cations (Table 2).

The coordination type B^{11} is observed for six $Ph–CH_2–COO^-$ ions in the Co(II), Cu(II), and Zn(II) complexes (Table 2).

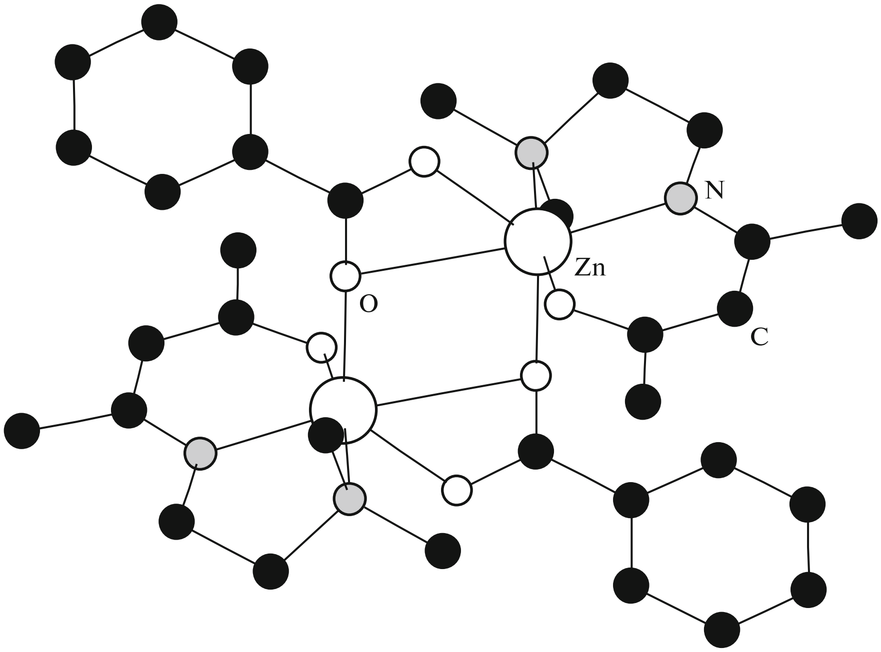

Fig. 3. Fragment of $Zn(C_9H_{17}N_2O)(PhCOO)\cdot 2CH_2Cl_2$ {BAQLEN} [13]. Hydrogen atoms are omitted for simplicity.

A single example in which phenylacetate anions exhibit the coordination type H^{000001} using the π-electron density of the benzene ring is the structure of (η^6-phenylacetic acid)tricarbonylchromium $Cr(CO)_3(PhCH_2COOH)$ {ISANUM} [27] containing the Cr atom (coordination number 9) due to the coordination of the CO molecules by the C atoms and six C atoms of the benzene ring. Note that the coordination type H^{000001} for benzoate ions was observed only in the case of the chromium compounds.

According to the data in Table 1, phenylacetate anions do not exhibit coordination types in which they would simultaneously form four M–O bonds via the oxygen atoms of the carboxy group, unlike benzoate ions for which the coordination types B^4 and B^{21} (two and 10 $PhCOO^-$ ions, respectively) are observed. In our opinion, this is related to the absence of conjugation of π-electron clouds of the benzene core and carboxy group (because they are linked by the methylene unit) in the phenylacetate anion. As a consequence, the electron density on the oxygen atoms of the carboxy group decreases owing to which the formation of four M–O chemical bonds becomes impossible for phenylacetate ions, unlike benzoate ions.

The choice of this or another coordination type by benzoate and phenylacetate ions is caused by both the nature of the metal with which the discussed anions form chemical bonds and the nature of additional ligands coordinated to the metal atom, as well as by the presence of any outer-sphere molecules capable of forming weak interactions with benzoate and phenylacetate anions. The data listed in Table 2 show that the coordination types M^1, B^2, and B^{01}, being most abundant in the case of benzoate groups (totally 1710 benzoate ions of 1840 fall onto the fraction of these types, which corresponds to 93% of the whole sampling), occur for all 3*d* metals, except for scandium. At the same time, more complicated coordination types, such as B^3, B^4, B^{11}, or B^{21}, are observed more rarely and only for heavier 3*d* metals beginning from manganese. For instance, benzoate anions manifest the coordination types M^1, B^2, B^3, B^{01}, B^{11}, and B^{21} toward Mn^{2+} ions (Table 2). Types B^2 (64 ions) and M^1 (42 ions) are the most characteristic coordination types.

ELECTRON-DONATING ABILITY OF BENZOATE AND PHENYLACETATE IONS

According to the data in Table 2, for the benzoate ions exhibiting the coordination types M^1, B^2, B^3, and B^4, the M–O bond length varies in a sufficiently broad range from 1.78 to 2.81 Å. On going to the coordination types B^{01}, B^{11}, and B^{21} characterized by metallocycle formation, the M–O bond length for benzoate ions ranges from 1.92 to 2.88 Å (Table 2). For example, for the Ti(IV) benzoate complexes, a change in the coordination type of the benzoate ion in the series M^1, B^2, and B^{01} is accompanied by a change in the Ti–O bond length, which takes values of 1.965(5), 2.05(6), and 2.15(4) Å, respectively. Similar regularities are also observed for phenylacetate anions.

Similar changes in the bond lengths in the structures of the carboxylates discussed show a change in the donor-acceptor interaction formed between the oxygen atoms of the carboxy groups of the benzoate and phenylacetate ions and 3*d*-metal atoms. These changes can quantitatively be characterized in terms of the stereoatomic crystal structure model [6–8] using characteristics of the Voronoi–Dirichlet polyhedra [28]. It is shown [29] that the electron-donating ability of one donor atom of any ligand can be characterized as the number of electrons (E_i), which are donated to the complexing atom from the donor atom of the ligand. The number of these electrons can be estimated using Eq. (1)

$$E_i = (18 - n)\Omega_i/100, \tag{1}$$

where n is the number of electrons localized on the valence level of the complexing ion, and Ω_i is the solid angle of the VDP face expressed in % of the total solid angle equal to 4π steradian corresponding to the M–X bond (X is the donor atom of the ligand). For instance, in the case of Mn^+, Mn^{2+}, and Mn^{3+} ions, in Eq. (1) $n = 6$, 5, and 4, respectively.

The VDP of all 3*d*-metal atoms in the studied sampling were calculated using the TOPOS topological software [5], and E_i of the oxygen atoms of the carboxy groups of the benzoate and phenylacetate ions and of the carbon atoms of the benzene fragments in these anions were determined by Eq. (1) depending on the coordination type of the latter. According to the data obtained (Table 2), the oxygen atoms of the carboxy groups in $PhCH_2COO^-$ and $PhCOO^-$ ions act most frequently toward 3*d*-metal ions as donors of approximately two electrons. As can be seen from the values presented in Table 2, the coordination type toward 3*d*-metal ions and the chemical nature of the bound 3*d* metal and its oxidation state affect the electron-donating ability of benzoate and phenylacetate anions. The electron-donating ability of the considered acid residues decreases regularly, on the whole, within the same coordination type on going from Ti to Zn, which is related to the occupation of the 3*d* orbitals on moving along the period from left to right. For example, the electron-donating ability of benzoate anions with the coordination type B^2 toward two-charge ions decreases regularly in the series Mn^{2+}–Fe^{2+}–Co^{2+}–Ni^{2+}–Cu^{2+}–Zn^{2+} and takes values of 2.3(1), 2.2(2), 2.0(2), 1.7(1), 1.6(1), and 1.5(2) ē, respectively. If benzoate and phenylacetate ions form no metallocycle (coordination types M^1, M^2, B^2, and B^3), their electron-donating ability toward the same 3*d*-metal ion remains unchanged within an inaccuracy. For instance, in the case of the benzoate anion with the coordination types M^1, B^2, and B^3, its electron-donating ability toward Mn^{2+} ions takes values of 2.4(2), 2.3(1), and 2.6(2) ē, respectively. The transition to the coordination types B^{01}, B^{11}, and B^{21} results in the situation where the Mn^{2+} ion becomes a component of the four-membered metallocycle and the electron-donating ability of the benzoate ion somewhat decreases taking the values 1.8(2), 1.9(2), and 1.9(3) ē, respectively. A decrease in E_i of benzoate ions toward Zn^{2+} on going from B^3 to B^4 is related, most likely, to the steric factor causing the arrangement of simultaneously four Zn^{2+} ions relatively to one carboxy group.

A change in the oxidation state of the complexing metal affects a change in the electron-donating ability of the considered carboxylate anions. For example, $PhCOO^-$ can bind chromium ions via the monodentate mode, and the oxidation state of these ion changes from +2 to +6, except for +4. As can be seen from the data in Table 2, an increase in the oxidation state of chromium ions is accompanied by a regular increase in the electron-donating ability from 2.57 for Cr^{2+} to 3.6(3) ē for Cr^{6+}. It should be mentioned that only benzoate ions exhibit an electron-donating ability of 3 ē and higher toward some metals in the high oxidation state (Ti^{4+}, V^{4+}, Cr^{5+}, and Cr^{6+}), which can be explained by an enhanced electron density on the oxygen atoms due to the conjugation between the benzene core and carboxy group. In the case of phenylacetic acid, this conjugation is impossible because of the presence of the hybrid sp^3-carbon atom between the phenyl radical and carbon atoms of the carboxy group.

The electron-donating ability (E_L) of benzoate and phenylacetate ions considered as united polydentate ligands (Table 2) can be determined using Eq. (1). Thus, E_L represents the total electron-donor contribution of all coordinated oxygen/carbon atoms of one benzoate or phenylacetate ion. For example, the structure of $Mn_2(Bipy)_2(PhCOO)_3NO_3 \cdot MeOH$ [30] {ZARZIB} contains benzoate ions manifesting the coordination type B^{11} and forming three Mn–O bonds due to donating 2.60, 2.64, and 1.64 ē by the oxygen atoms. Each O atom donates 2.3(6) ē, on the average, to the Mn–O bond, and the electron-donating ability of the whole ligand is determined by the sum E_L = 2.60 + 2.64 + 1.64 = 6.89 ē. The data in Table 2 show that the benzoate anion can act as a donor of 1.6(1)–7.8(4) ē by the oxygen atoms of the carboxy groups, whereas the phenylacetate anion exhibits the total electron-donating ability E_L ranging from 1.6(2) to 5.02(6) ē. The value of E_L for $PhCOO^-$ is higher than that for $PhCH_2COO^-$ due to the conjugation of the carboxy group and benzene core in the benzoate anion.

The carbon atoms forming the six-membered aromatic system serve as donor atoms in the case where benzoate and phenylacetate ions exhibit the coordination type H^{000001}. These ligands act as donors of approximately five electrons toward Cr(0) atoms (Table 2). When binding Cr^+ ions, the benzoate anion increases its electron-donating ability E_L to 6.50(1) ē.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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