Experimental and theoretical studies of anions of transition-metal chelate complexes in alkylation reactions at a metal atom

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Electrochemical reduction of a number of chelate complexes of transition metals $(Chel)_2M$ or $(Chel)_2MXY$ (M = Co, Rh, Ir, or Ni; Chel are anions of dmgH (dmg is dimethylglyoxime), (3,5-di-*tert*-butyl-4-hydroxyphenyl)mgH (mg is methylglyoxime), *N*-aryl-3-methoxysalicylaldoxime, *N*-aryl-3-methyl-2-thiocarboxamidopyridine, or 2-acetylindan-1,3-dione; X = Y = py, Ph_3P, or H_2O or X = Cl and Y = Ph_3P) in MeCN or DMF was studied using the cyclic voltammetry and rotating disk electrode techniques. Under the action of Bu^nBr, some electrochemically generated anions $[(Chel)_2M]^-$ enter into the rather fast alkylation reactions (apparently, at the metal atom) to form $(Chel)_2M$—Alk. The geometries of four model neutral and anionic cobalt complexes were calculated using the semiempirical ZINDO/1 method. According to calculations, the transformation of the neutral complex $(Chel)_2M$ into the anion $[(Chel)_2M]^-$ leads to a change in the configuration from square-planar to square-pyramidal or from tetrahedral to disphenoid. The effects of steric hindrances, the HOMO energies, and the charge of the metal atom in the anionic complexes on the alkylation reactions at the metal atom are discussed.

Key words: cobalt, nickel, rhodium, iridium, chelate complexes, electrochemical reduction; metallocomplex anions, alkylation; quantum-chemical calculations, ZINDO/1 method.

One-electron reversible electrochemical reduction of complexes of transition metals (M) often affords rather stable metallate monoanions. These anions can rapidly react with alkyl halides to form compounds alkylated at the M atom. The reactivity of metallate anions is substantially higher than that of very strong nucleophiles such as iodide and cyanide ions. For this reason, it was suggested to call metallocomplex anions "supernucleophiles."[1–3] The reactions of metallocomplex anions with alkylating agents can result in alkylation either of a ligand in the coordination sphere of the metal atom or of the metal as such to form the M—C σ-bond. The latter process is sometimes accompanied by replacement of the monodentate ligand.[4]

Studies of alkylation reactions that afford derivatives containing the M—C σ-bond are of particular interest in connection with the role that these derivatives play in the formation of alkyl compounds of heavy metals, for example, of mercury, in the environment. The latter are formed as a result of transfer of the alkyl group from transition-metal atoms to inorganic ions of heavy metals according to mechanisms of chemical or biological alkylation.[5,6]

Metallate anions, which enter into alkylation reactions, are commonly generated by chemical reduction of neutral complexes (with alkali metals or alkyllithium compounds) or by electrochemical reduction at a cathode. The possibility of alkylation and the mechanism of the reaction depend on the nature of the ligands in the metallocomplex anion as well as on the nature of the central M atom. The metal complexes that form rather stable alkyl compounds containing the M—C σ-bond are promising objects of studies. For example, in the case of porphyrin complexes, among these metals are Fe, Ru, Co, Rh, Ir, Ti,[7] and Ni.[3] The carbonylmetallate anions $CpFe(CO)_2^-$, $CpNi(CO)^-$, $Re(CO)_5^-$, $CpW(CO)_3^-$, $Mn(CO)_5^-$, $CpCr(CO)^-$, and $Co(CO)_4^-$[4] as well as other metallocomplex anions containing Co,[8] Fe,[9] Cr,[10,11] W,[10,12,13] Mn, Re,[10,14,15] or Mo[10] are readily alkylated at the metal atom. Not only monoanions but also di- or trianions can be involved in the alkylation reactions.[15,16] The trianions of Mn and Re tetracarbonyls undergo double alkylation to form monoanions of dialkyl derivatives of these metals.[15]

In this work, using the reactions of electrochemically generated anions of chelate metal complexes with *n*-butyl bromide as an example, we attempted to reveal certain general regularities of alkylation associated with the effect of the nature both of the chelating ligands and of the central M atom on the reactivity of the anions under consideration.

Experimental

The reactive anions were generated elecrochemically from metal complexes **1a—e**, **2**, **3a**, **3b**, **4a—d**, and **5**, whose

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structures are given below. Complexes **1a,b,d,e**,[17] **1c**,[18] and **2—4** [19—21] were prepared according to procedures reported previously.

Bis(2-acetylindan-1,3-dionato)cobalt(II) (5). A mixture of 2-acetylindan-1,3-dione (2.5 mmol) and cobalt acetate (2.5 mmol) was refluxed in methanol for 1 h. The finely crystalline yellow-brown precipitate that formed upon cooling was filtered off, washed with water until the reaction of the wash water to the Co^{2+} ion (reaction with α-nitroso-β-naphthol) became negative, and dried. The yield was 30%, m.p. 275—280 °C (sublimated). Found (%): C, 59.53; H, 2.88. $C_{22}H_{14}O_6Co \cdot CH_3OH$. Calculated (%): C, 59.36; H, 3.25.

Chemically pure dimethylformamide was purified by successive boiling and distillation *in vacuo* over anhydrous $CuSO_4$ and P_2O_5. Acetonitrile was purified by successive treatment with CaH_2, a mixture of H_2SO_4 and KNO_3, and P_2O_5.

Electrochemical studies of the complexes were carried out in DMF or MeCN in the presence of Bu_4NBF_4 (0.05 mol L^{-1}) on mercury-film and platinum electrodes. The potentials were measured relative to a silver-chloride electrode. Cyclic voltammetry and the rotating disk electrode techniques were used. The mercury-film electrode was prepared by electrolysis of a 0.05 *M* $Hg(OCOMe)_2$ solution in aqueous acetonitrile at a platinum cathode at −0.7 V during 10 min.[22] Electrochemical studies were performed using a PI-50-1.1 potentiostat. All measurements were carried out under an atmosphere of argon.

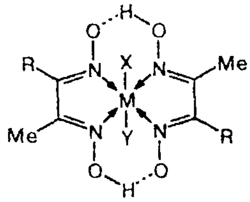
Semiempirical calculations were carried out by the ZINDO/1 method[23] using the HyperChem program (Release 5.01).

Results and Discussion

We studied chelate complexes **1—4**.

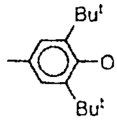
Electrochemical studies of complexes **1a—e**, **2**, **3a**, **3b**, and **5** were carried out in MeCN. Electrochemical studies of poorly soluble complexes **4a—d** were performed in DMF. The results are given in Table 1. All the complexes of divalent metals under study are reduced in two one-electron steps (in the voltammograms of complexes **1b** and **1c**, these steps are preceded by the peak of one-electron reduction M^{III}/M^{II} at the potential of −0.46 and −0.13 V for **1b** and **1c**, respectively). In all cases, except for complex **5**, which undergoes irreversible reduction, transfer of the first electron results in the formation of rather stable monoanions (the ratio of the heights of the anodic and cathodic peaks $i_p{}^a/i_p{}^c$ = 0.5—0.9) and corresponds to the M^{II}/M^{I} transition. In a solution, the dimethylglyoximate complex of Rh^{II} exists as a dimer.[24] Consequently, oxidation of the monoanionic Rh^{I} complex proceeds according to the *EC* mechanism, namely, transfer of the electron from the anion to the electrode is followed by dimerization of the paramagnetic neutral complex. Apparently, this is explained by the fact that the difference between the values of $E_p{}^{ox}$ and $E_p{}^{red}$ (Fig. 1, peaks *A* and *B*) observed in this case is 1700 mV. The products of two-electron reduction (dianions) are substantially less stable as indicated by the irreversibility of the second stage of reduction of most of the complexes under study. The exceptions are only complexes **1e** and **3b** for which the formation of reverse anodic peaks ($i_p{}^a/i_p{}^c$ = 0.5 and 0.36 for **1e** and **3c**, respectively) is observed at the second step, which indicates that this step of reduction of these compounds is partially reversible.

For all the complexes under study, the cyclic voltammograms were measured in the absence and in the presence of *n*-butyl bromide ($5 \cdot 10^{-3}$ mol L^{-1}) (see Fig. 1). In the absence of Bu^nBr, a reversible or quasireversible pair (peaks *A* and *B*) is observed in the cathodic region. This pair corresponds to the transformation of the neutral complex into the monoanion (Eq. (1), reaction *1*). In the presence of Bu^nBr, the character of the voltammetric dependence changes, namely, a new reduction peak (peak *C*) appears, the height of reverse anodic peak *B* decreases sharply, and an oxidation peak of Br^- anions (according to our data, $E_p{}^{ox}$ = 1.02 V for the bromide ion) appears in the region of anodic potentials. These changes (which were observed for complexes **1a**, **1b**, **1d**, **2**, **4a**, and **4b**) indicate that the electrochemically activated alkylation reaction proceeds in a solution (for more details, see Ref. 22).

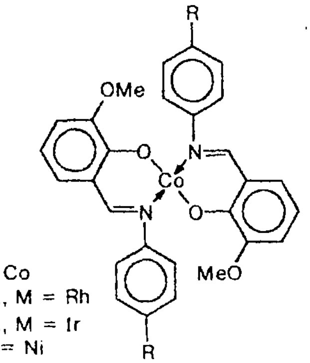


1a—e, 2

1a: R = Me, X = Y = py, M = Co
1b: R = Me, X = Ph_3P, Y = Cl, M = Rh
1c: R = Me, X = Ph_3P, Y = Cl, M = Ir
1d: R = Me, X = Y = H_2O, M = Ni
1e: R = Me, X = Y = H_2O, M = Co

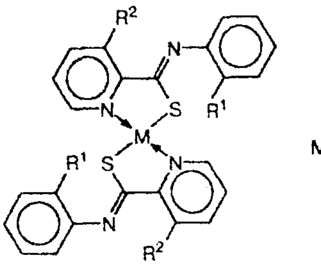
2: R =


, X = Y = py, M = Co



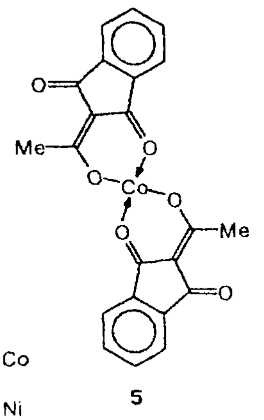
3a—c

3a: R = Me
3b: R = OMe
3c: R = H



4a—e

4a: R^1 = R^2 = Me, M = Co
4b: R^1 = OMe, R^2 = Me, M = Co
4c: R^1 = R^2 = Me, M = Ni
4d: R^1 = OMe, R^2 = Me, M = Ni
4e: R^1 = Me, R^2 = H, M = Co



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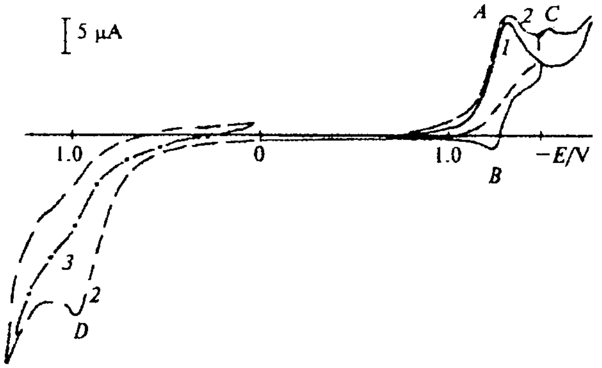


Fig. 1. Cyclic voltammograms of complex **4b** on a mercury-film electrode in DMF ($1 \cdot 10^{-3}$ mol L^{-1}; Bu_4NBF_4 (0.05 mol L^{-1})): *1*, in the absence of Bu^nBr; *2*, in the presence of Bu^nBr ($5 \cdot 10^{-3}$ mol L^{-1}); *3*, the anodic branch after the potential was scanned between E = 0 and 1.2 V (relative to Ag/AgCl/KCl(sat.)) five times.

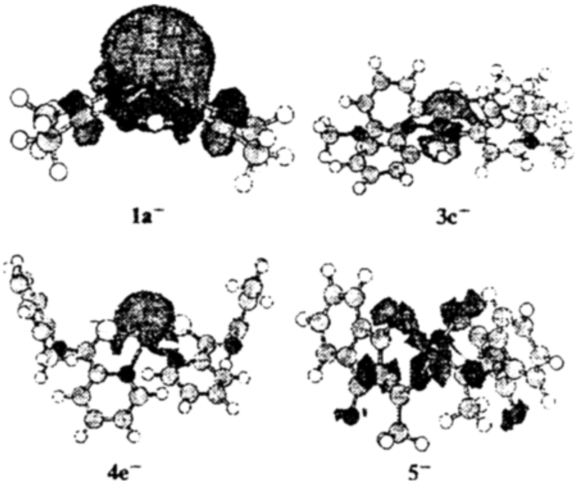


Fig. 2. The geometries and shapes of HOMOs of the model anionic chelate complexes calculated by the ZINDO/1 method.

$$(Chel)_2M^{II} \underset{1}{\overset{\bar{e}}{\rightleftarrows}} [(Chel)_2M^{I}]^- \xrightarrow[2]{AlkX} (Chel)_2M^{III}Alk + X^- \quad (1)$$

In the case of compounds **1c**, **1e**, **3a**, **3b**, **4c**, **4d**, and **5**, no changes in the voltammetric dependences were observed when Bu^nBr was added, *i.e.*, apparently, alkylation (see Eq. (1), reaction *2*) did not occur or proceeded slowly.

As can be seen from Table 1, alkylation was observed for the dimethylglyoximate complexes of Co, Rh, and Ni and did not occur in the case of the Ir and Pd complexes (note that, unlike the Co and Rh complexes, attempts to alkylate the dimethylglyoximate complex of Ir by chemical methods in the presence of a reducing agent also failed[24]). However, the ability of anions to undergo alkylation depends on the nature not only of the metal atom but also of the ligand. Thus, the salicylideneimine (**3a,b**) and indandione (**5**) complexes of Co do not undergo alkylation. The iminopyridinethiocarboxylate Co-containing complexes, unlike the Ni-containing complexes, undergo alkylation. Therefore, there is no simple relationship between the nature

Table 1. Parameters of electrochemical reduction of complexes **1**—**5** in MeCN (Bu_4NBF_4 (0.05 mol L^{-1}), mercury-film electrode, Ag/AgCl/KCl(sat.))

Complex	$-E_{p_1}/V^a$	$E_{p_1}{}^a - E_{p_1}{}^c$ /mV^b	$-E_{p_2}/V^a$	$E_{p_2}{}^a - E_{p_2}{}^c$ /mV^b	$-E_p{}^{red}/V$ (of the product of the reaction with Bu^nBr)
1a	1.17	90	2.19	Irreversibly	1.71
1b	1.20	1700	2.15	The same	1.78
1c	1.02	290	1.57	»	^{c}
1d	1.22	110	1.83	»	1.77
1e	1.28^d	60	2.06	60	^{c}
2	0.98	120	1.96	Irreversibly	1.55
3a	1.55^d	70	1.98	The same	^{c}
3b	1.67^d	60	2.06	110	^{c}
4a^e	1.41	150	1.78	Irreversibly	1.56
4b^e	1.27	330	1.93	The same	1.52
4c^e	1.54	80	1.80	»	^{c}
4d^e	1.32	110	1.97	»	^{c}
5	1.68	Irreversibly	2.20	»	^{c}

[a] E_{p_1} and E_{p_2} are the potentials of the first and second reduction peaks, respectively.

[b] The difference between the potentials of the anodic and cathodic peaks.

[c] The reduction peak of the product was not observed.

[d] The standard potential of the $Chel_2M/Chel_2M^-$ pair.

[e] In DMF.

of the central metal ion or the structure of the chelating ligands and the ability of the metallocomplex anions to enter into the alkylation reactions.

We believed that in addition to the electronic factors, the steric factors, namely, the accessibility of the lone electron pair localized on the M atom in the metallocomplex anion, are of primary importance for the S_N2 reactions with Bu^nBr. We assumed that in all the cases under study alkylation occurs at the metal atom. This assumption is confirmed by the fact that the potential of reduction peak *C* (see Fig. 1), which appears in the course of alkylation, coincides with the potentials of reduction peaks of a number of authentic complexes containing the M—Alk σ-bond.[22]

The complexes under study and all the more so their anions have not been investigated by X-ray diffraction analysis. Therefore, we calculated the geometries of the neutral initial compounds and their monoanions by the semiempirical ZINDO/1 method.[23] The geometric and energy parameters were also calculated for the Co complexes, which are structurally similar to compounds **1a**, **3c**, **4e**, and **5**. In complex **1a**, the axial ligands (py) were removed. The calculated structures of **3c** and **4e** differ from those studied experimentally in that some substituents in the above formulas were replaced by H. The geometric parameters of the complexes and of the corresponding anions in the low-spin (singlet) state are given in Table 2.

Neutral complex **1a** is characterized by the planar configuration about the Co atom. Compounds **3c** and **5** have a slightly distorted tetrahedral configuration. Complex **4e** has a strongly distorted tetrahedral configuration. In going to the anionic form, the geometries of all the complexes under study change substantially. In anion **1a**$^-$, the Co atom deviates by 0.71 Å from the plane formed by four N atoms as a result of which the anion adopts the tetragonal-pyramidal configuration. When anion **3c**$^-$ is formed, the configuration changes to the nearly disphenoid one. Complex **4e** is converted to anion **4e**$^-$ with a very strongly distorted tetrahedral configuration, which is very similar to the square-planar configuration with the Co atom deviating by 0.37 Å from the line between the S atoms and by 0.15 Å from the line passing through the N atoms. Only in the case of complex **5** does the configuration remain virtually unchanged (is very close to the tetrahedral one) when anion **5**$^-$ is formed.

The ball-and-stick models of the anions of the Co complexes under study, which were calculated by the ZINDO/1 method, are shown in Fig. 2. In addition to the spatial arrangement of the atoms, Fig. 2 also displays the three-dimensional representation of the highest occupied molecular orbitals (HOMOs) of the corresponding anions. The following conclusions can be drawn: (1) in all cases, HOMOs of the anions are primarily localized on the metal atoms (*i.e.*, alkylation should proceed at the metal atom); (2) in anions **1a**$^-$ and **4e**$^-$, HOMO is sterically most accessible for overlapping with the unoccupied orbital of an electrophilic agent. For anions **3c**$^-$ and **5**$^-$, the approach of an alkylating agent

Table 2. The bond lengths and bond angles in complexes **1a**, **3c**, **4e**, and **5** and in the corresponding monoanions calculated by the ZINDO/1 method

Parameter	**1a** (without py)	**1a**$^-$ (without py)[a]	**3c** [b]	**3c**$^-$ [c]	**4e**	**4e**$^-$ [d]	**5** [b]	**5**$^-$ [b]
Bond lengths/Å								
Co—N	1.916	1.849	1.838	1.887	1.915	2.040		
Co—O			1.747	1.798			1.945 (O$^-$), 1.974 (O=)	2.162 (O$^-$), 2.333 (O=)
Co—S					2.270	2.350		
Bond angles/deg								
N—Co—N	90[e]	82	114	169	171	93		
N—Co—O			111	92				
O—Co—O			108	167			103,[f] 102,[g] 122,[h] 104[i]	157,[f] 78,[g] 80,[h] 119[i]
N—Co—S					82	89		
S—Co—S					161	157		

[a] Four N atoms, four O atoms, and two H atoms are in a single plane, while the Co atom deviates from this plane by 0.71 Å.

[b] The configuration about the Co atom is a distorted tetrahedron.

[c] The configuration about the Co atom is a disphenoid one.

[d] The configuration about the Co atom is a strongly distorted tetrahedron; it is very close to the square-planar configuration in which the Co atom deviates by 0.37 Å from the line passing through the S atoms and by 0.15 Å from the line passing through the N atoms.

[e] The average value of the angle; the N—Co—N angle opposite to the C—C bond is 85°; the N—Co—N angle opposite to the hydrogen bond is 95°.

[f] The $^-$O—Co—O$^-$ angle.

[g] The =O—Co—O= angle.

[h] The $^-$O—Co=O angle in the OCoOCCC ring.

[i] The exocyclic $^-$O—Co=O angle.

is sterically somewhat hindered and there is no pronounced outward directionality of HOMO on the Co atom, as is the case in anions **1a**$^-$ and **4e**$^-$.

The results of calculations demonstrate that in going from the neutral chelate complexes to the anions, the geometry reorganizes from square-planar or tetrahedral to pyramidal or disphenoid, respectively. It is believed that if electronic changes that occur upon reduction are localized on the central metal atom, the lone electron pair that appears on this atom plays the role of the fifth ligand to form a five-coordinate compound, which is typified by the trigonal-bipyramidal or tetragonal-pyramidal geometry. The trigonal-bipyramidal complex L_5M is an analog of the disphenoid anion L_4M^-. The square-pyramidal complex L_5M is analogous to the square-pyramidal anion L_4M^-, in which one vertex is occupied by the lone electron pair. Unlike the simple complexes L_4M, the nature of Chel and steric interactions between the substituents in the chelating ligands of the chelate compounds $(Chel)_2M$ can exert a strong effect both on the geometry of the complex and on its tendency to change in going to the anion. Therefore, the configurations of these particles may be substantially different.

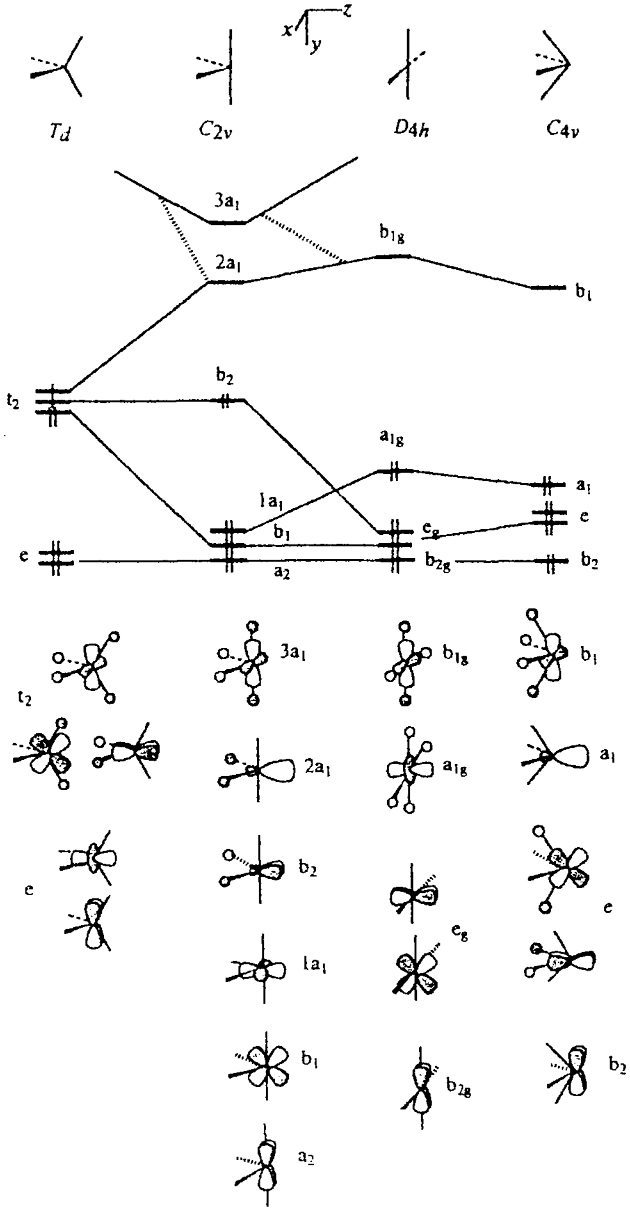
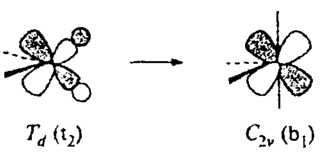


Fig. 3. The Walsh diagram for the transformations between the tetrahedral (T_d), disphenoid (C_{2v}), square-planar (D_{4h}), and pyramidal (C_{4v}) configurations of the 16-electron model complex L_4M.

Let us consider the changes in the energy of the highest occupied and lowest unoccupied MOs of the anions of the four-coordinate complexes that occur under changes of their geometries. For simplicity, let us use the noncharged complex ML_4 containing four identical monodentate ligands (L) and a d^8 metal atom as the model. The total number of electrons in the valence shell of the metal atom in this complex is equal to 16 and this complex can serve as an adequate model of the anions $(Chel)_2Co^-$ under study. Four basic geometrical configurations, namely, the tetrahedral (T_d), disphenoid (C_{2v}), square-planar (D_{4h}), and tetragonal-bipyramidal (C_{4v}) configurations (Fig. 3), can be considered for the complex ML_4 and, consequently, for the anions $(Chel)_2Co^-$. The true structures of the anions $(Chel)_2Co^-$ depend substantially on the nature of the chelating ligands Chel (see Fig. 2). In principle, these structures can be described by a linear combination of certain of the above-mentioned basis configurations. In the case of the model compound ML_4, the symmetry of the four basic structures can change, for example, from C_{2v} to C_{4v} or to the tetrahedral one.

The tetrahedral complex d^8-ML_4 has doubly degenerate fully occupied e levels and triply degenerate t_2 levels occupied by four electrons. For this complex, the high-spin (triplet) state is highly probable. When the configuration is distorted from tetrahedral toward disphenoid (C_{2v}), one of three t_2 orbitals is stabilized and becomes the b_1 orbital (see Fig. 3). Stabilization occurs due to the disappearance of antibonding interactions between the metal atom and two of four ligands:



The second t_2 orbital transforms into the b_2 orbital without noticeable changes in the energy because an increase in the L—M—L angle (from 109.5° to 180°), which results from the $T_d \rightarrow C_{2v}$ transformation, occurs in the nodal plane of the orbital. The third t_2 orbital is destabilized and is turned to the $2a_1$ orbital (their shapes are shown at the bottom of Fig. 3). The $2a_1$ and $3a_1$

orbitals are formed by the s and p_z orbitals (the system of coordinates is shown at the top of Fig. 3) of the metal atom,[25] whose levels are higher than the t_2 level (indicated by dashed lines in Fig. 3). As a result, the $2a_1$ orbital acquires a somewhat higher energy compared to that of the above t_2 orbital. At the same time, the energy of the $2a_1$ orbital is rather close to that of the b_2 orbital (see Fig. 3). This means that the probability of the existence of the disphenoid complex (C_{2v}) in the triplet state (the b_2 and $2a_1$ orbitals are occupied by one electron each) is high.

Previously,[25] it was noted that the complexes ML_4 (C_{2v}) are similar to carbene CH_2. This similarity lies in the fact that both structures are characterized by small differences in the energies of the b_2 and a_1 levels and, therefore, can exist both in the singlet and triplet states. Based on the results of qualitative analysis, it can be stated that the triplet anion (Chel)$_2$Co$^-$ tends to exist in the disphenoid (C_{2v}) rather than in the tetrahedral form because a decrease in the energy of two electrons ($t_2 \to b_1$) in the case of the $T_d \to C_{2v}$ transformation is unlikely to be compensated by an increase in the energy of one electron ($t_2 \to 2a_1$).[25] This is all the more true for the singlet anion in which the $2a_1$ orbital is unoccupied. In the tetrahedral complex ML_4, bonding equivalents of the t_2 orbitals (omitted in Fig. 3), which are destabilized in going to the symmetry C_{2v}, exist along with the antibonding t_2 orbitals. This partially compensates for the decrease in the energy when one t_2 orbital is transformed into the b_1 orbital. Consequently, the true structure is intermediate between the tetrahedral and disphenoid ones, which was demonstrated by the calculation of anion **3c**$^-$ (see Fig. 2).

When the number of electrons in the valence shell of the metal atom decreases to 15, which corresponds to the neutral Co^{II} complexes, a change from the tetrahedral configuration to the disphenoid one for a high-spin complex (quadruplet) becomes less favorable than that in the case of the 16-electron anions because in the former case the energy of the one-electron level rather than that of the two-electron level decreases ($t_2 \to b_1$). However, the transformation of the high-spin complex with the symmetry C_{2v} into the low-spin (doublet) complex, as a result of which the $2a_1$ orbital becomes unoccupied, should be favorable for the formation of the disphenoid configuration. For the chelate complexes, which we calculated, the final results depend substantially on the structure of the ligands. Thus, complex **3c** has an approximately tetrahedral configuration and its anion has a nearly disphenoid configuration. At the same time, the configurations of neutral complex **5** as well as of its anion **5**$^-$ are close to the tetrahedral one. In the 18-electron complexes (for example, in Pd(PPh$_3$)$_4$ and Na$_2$Fe(CO)$_4$), the b_2 and $2a_1$ orbitals are fully occupied and their structures should be very close to the tetrahedral one.[25]

As can be seen from Fig. 3, the transformation of the disphenoid configuration of the singlet complex ML_4 into the square-planar configuration (D_{4h}) should exert a stabilizing effect. As a result of a decrease in the antibonding interactions between the d orbitals of the metal atom and the n orbitals of the ligands, the b_2 level is substantially stabilized and the orbital hybridization is lost (see Fig. 3). As a consequence of a rather complex mixing of three orbitals with the a_1 symmetry, the $1a_1$ orbital is transformed into a_{1g} (into d_{z^2} when the system of coordinates shown in Fig. 3 is used), the $2a_1$ orbitals are transformed into a_{2u} (p_z), and the $3a_1$ orbitals are transformed into b_{1g} ($x^2 - y^2$).[25] The b_2 and b_1 orbitals are transformed into the e_g orbitals and the a_2 orbitals are transformed into the b_{2g} orbitals.

The pyramidalization of the complex (a change from the symmetry D_{4h} to C_{4v}) is accompanied by a lowering of the a_{1g} level (two electrons) and by an elevation of the e_g levels (four electrons). The efficiency of these processes are affected by the degree of pyramidality. In the case of a small degree of pyramidality, the curve of a decrease in the energy of the a_{1g} orbital shows a steeper decline than the curve of an increase in the energy of the e orbitals.[25] Consequently, in the case of a small degree of pyramidality, the effect of stabilization may prevail due to which the pyramidal form is favored over the planar-square configuration. According to our calculations, anion **1a**$^-$, (dmgH)$_2$Co$^-$, has the pyramidal configuration (see Fig. 2). However, neutral complex **1a** is planar. This is attributable to the fact that in the latter case the a_{1g} orbital is occupied by only one electron and, therefore, the energy of stabilization associated with a decrease in the a_{1g} level is half as large as that in the former case.

Of special note is the fact that in our calculations we ignored solvation of anions. However, the solvent molecule can be coordinated with the lone electron pair on the M atom, *i.e.*, can occupy the fifth position in the coordination sphere. As a result, the symmetry of the complex ML_4 should be necessarily decreased, for example, from T_d to C_{2v} or from D_{4h} to C_{4v}.

The theoretical analysis allows a qualitatively adequate explanation of the specificity of the calculated geometry of the chelate complexes and of their anions if the number of electrons in the valence shell of the metal atom, the changes in the energy of the antibonding levels, and the steric factors, which can play a decisive role, are taken into account (see Fig. 2).

Therefore, for geometrical reasons, anions **1a**$^-$ and **4e**$^-$ can react with an alkylating agent according to the S_N2 mechanism,* while for anions **3c**$^-$ and **5**$^-$ this reaction is sterically hindered. This conclusion agrees

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* Studies of the reactions of the electrochemically generated anion [(TPP)Co^I]$^-$ (TPP is the dianion of tetraphenylporphyrin) and various AlkX in THF by cyclic voltammetry and the analysis of kinetic data suggested[26] that these reactions in the case of X = Br, Cl, or F proceed according to the S_N2 mechanism. However, when X = I the outer-sphere mechanism of electron transfer is possible.

Table 3. Energies of HOMOs ($\varepsilon_{\text{HOMO}}$) of the anions of complexes **1a**, **3c**, **4e**, and **5** and the charges (q) on the Co atom and on the heteroatoms of the ligands calculated by the ZINDO/1 method

Anion	$\varepsilon_{\text{HOMO}}$ /eV	q/e			
		Co	O	N	S
1a$^-$	0.54	−1.089	−0.448	0.217	
3c$^-$	0.11	−0.258	−0.349	−0.195	
4e$^-$	−0.64	−0.502		−0.078	−0.368
5$^-$	−1.31	−0.354	−0.405 (O$^-$) −0.363 (=O)		

with the results of electrochemical studies according to which anions **1a**$^-$ and **4e**$^-$ are alkylated with n-butyl bromide, while anions **3c**$^-$ and **5**$^-$ do not undergo alkylation (see Table 1).

The energy factors should be considered along with the steric factors. The energies of HOMOs of the anions of the complexes under consideration, which were calculated by the ZINDO/1 method, and the charges on the cobalt atom and on the heteroatoms of the ligand are given in Table 3. The largest negative charges are located on the Co atoms in anions **1a**$^-$ and **4e**$^-$, *i.e.*, from the viewpoint of charge control, these compounds are most prone to enter into the reaction with n-butyl bromide, which agrees well with the data of electrochemical studies.

If the orbital control is important for alkylation, which is true for S_N2 reactions, the reactivity depends on the energy of HOMO of the anion, namely, the higher the energy, the higher the reactivity of the anion. According to the results of calculations (see Table 3), the energy of HOMOs of the anions decreases in the order **1a**$^-$ > **3c**$^-$ > **4c**$^-$ > **5**$^-$. This means that the donating ability of HOMO of the anion with respect to LUMO of the alkylating agent should decrease in the above order. However, the negative charge on the Co atom decreases in magnitude in the order **1a**$^-$ > **4e**$^-$ > **5**$^-$ > **3c**$^-$. As a result of competition between the charge and orbital control over the reaction rate, the true order of the reactivities of the anions with respect to n-butyl bromide may differ from the series, which were predicted based only on the charges or on the energies of HOMOs.

The coefficient with which the orbital of the Co atom is involved in HOMO of the anion is also of importance. As can be seen from Fig. 2, this coefficient is large in the case of anion **1a**$^-$, which should enhance its reactivity due to the efficient overlap of the orbital of the Co atom and HOMO of the alkylating agent. In the case of anion **1c**$^-$, steric hindrances are virtually absent compared to other anions under study. Therefore, the combination of a sufficiently high energy of HOMO, the substantial negative charge on the Co atom, the large orbital coefficient of the Co atom in HOMO, and the absence of steric hindrances suggests that the anion of the dimethylglyoximate complex of cobalt should most readily undergo alkylation.

It is of interest to compare the calculated energies of HOMOs of the anions with the electrochemical data on reduction of the neutral complexes. According to the crude approach based on the Koopmans theorem, the electron affinity (EA) of the neutral compound (*i.e.*, E° of the first reduction stage) was taken equal to the energy (ε) of HOMO of the corresponding anion, which was taken with the opposite sign:[27]

$$EA \approx -\varepsilon_{\text{HOMO}} \approx aE^\circ,$$

where E° is the standard potential of the $(\text{Chel})_2\text{M}/(\text{Chel})_2\text{M}^-$ pair and a is the coefficient, which depends on the conditions of the electrochemical experiment. A comparison of the results given in Tables 1 and 3 demonstrates that the energy of HOMOs of the anions (**1a**$^-$ > **3c**$^-$ > **4e**$^-$ > **5**$^-$) and ease of electrochemical reduction of the neutral complexes (**1a—e** > **4a—d** ≥ **3a—b** > **5**) change similarly, *i.e.*, there is the satisfactory agreement between the electrochemical and calculated data.

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