

Reviews

Design of molecular switches based on transition metal bis(dicarbollide) complexes*

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The paper presents a review of the state of the art and prospects for the development of rotary molecular switches based on transition metal bis(dicarbollide) complexes.

Key words: metallocarboranes, bis(dicarbollide) complexes, rotational conformations, molecular switches.

The design of molecular machines — molecules or molecular complexes capable of producing quasi-mechanical movements to perform useful work — is a highly interesting and rapidly growing field of modern chemistry.^{1–4} The importance and relevance of this area of research was recognized by the award of the Nobel Prize in Chemistry in 2016 to Jean-Pierre Sauvage, Bernard Feringa, and Fraser Stoddart “for the design and synthesis of molecular machines”.⁵ All molecular machines can be divided into two main groups according to the type of motion — those producing linear or rotational motion. In turn, molecular machines producing rotational motion can be divided into the following two types: molecular motors (rotors) and molecular switches. Molecular motors are molecular machines that are able

to produce 360° rotation in response to external stimuli. Molecular switches are molecules or supramolecular assemblies capable of existing in two or more stable states, which differ in the mutual orientation of components and which can be converted from one state to another by various external stimuli *via* rotation of these components with respect to each other.^{6,7} Molecular switches are main structural elements of any molecular electronic device, in particular, of molecular logic gates, which are capable of performing all simplest logic operations and arithmetic operations, such as summation and subtraction, encoder and decoder functions, and so on. Therefore, molecular switches provide the basis for the development of nanoscale computing devices.^{8–10} Most research has focused on photochromic molecular switches based on azobenzenes, stilbenes, dithienylethenes, spiropyranes, and spirooxazines, as well as switches based on host–guest interactions and switches based on mechanically interlocked molecular systems, rotax-

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anes and catenanes, in which bistable states differ in the mutual orientation of components of the supramolecular assembly.⁶

Despite a considerable progress in the synthesis and characterization of such molecules, there are a number of problems associated primarily with relatively low stability of many organic materials against atmospheric oxygen and moisture. Therefore, it is necessary to look for new types of compounds, which could be used as structure-forming components in the design of efficient molecular switches. Recent years have seen a growing interest in the development of molecular switches and other molecular electronic devices based on transition metal complexes.^{11–13} However, like organic molecular machines, devices based on transition metal complexes are often characterized by low stability. Therefore, the choice of a stable organometallic module unit is of great importance for the design of molecular electronic devices. An example is the ferrocene molecule, derivatives of which can form stable rotational conformers (rotamers) capable of undergoing electrochemically, photochemically, or chemically induced interconversions.^{14,15} Apart from extremely high stability, the major advantages of ferrocene are availability and low cost along with well-elaborated methods for its functionalization. Besides, aromatic substituents in the ferrocene molecule lie in the plane of cyclopentadienyl rings, resulting in stabilization of *cis* conformers through intramolecular π – π aromatic interactions. However, the stabilization of *trans*-rotamers is based mainly on repulsive interactions between like-charged substituents, which makes it impossible to precisely set the ligand rotation angle when the repulsion is weakened with increasing distance between the charges. The binding of cyclopentadienyl ligands *via* an additional bridge capable of changing its geometry in response to external stimuli allows the rotation angle of the ligands to be rigidly fixed, but leads to a considerable decrease in this angle. Besides, the introduction of an additional substituent gives rise to mixtures of *rac* and *meso* diastereomers of 1,1',3,3'-tetrasubstituted ferrocenes, which substantially differ in the efficiency as molecular switches.¹⁶

Other promising module units for the design of molecular machines are transition metal bis(dicarbollide) complexes serving as isoelectronic analogs of metallocenes.^{17–19} Unlike cyclopentadienyl ligands, dicarbollide ligands contain two carbon atoms and three boron atoms in the open pentagonal face, resulting in that different rotational conformers (rotamers) of bis(dicarbollide) complexes are energetically nonequivalent (Fig. 1). The favorability of a particular conformation is determined by both the nature of the metal and its oxidation state.

Typical examples are nickel complexes, which can exist in two stable states — paramagnetic nickel(III) bis(dicarbollide) $[3,3'-\text{Ni}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ and diamag-

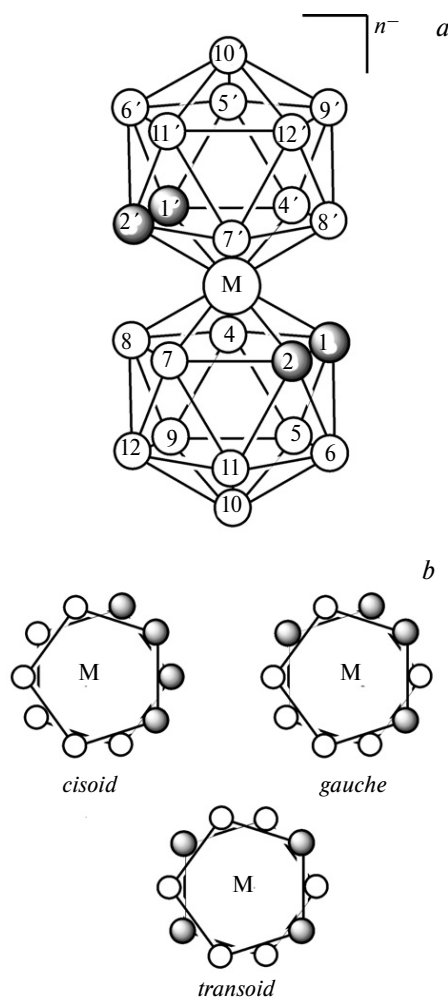
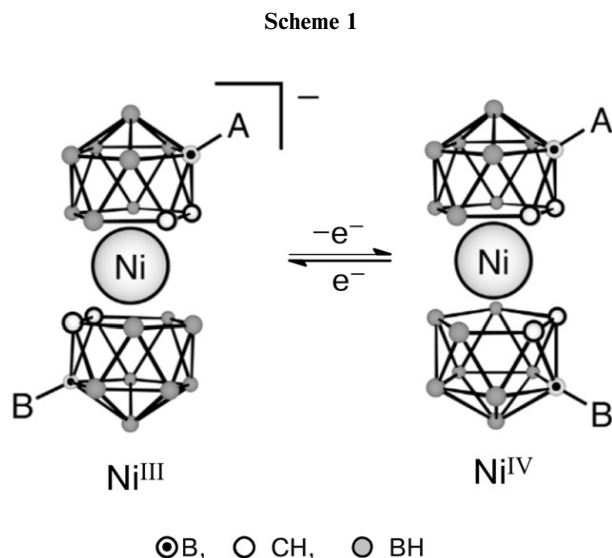


Fig. 1. Atom numbering (a) and the mutual orientation of the ligands (b) in transition metal bis(dicarbollide) complexes $[3,3'-\text{M}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^{n-}$.

netic nickel(IV) bis(dicarbollide) $[3,3'-\text{Ni}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]$.¹⁸ These states easily undergo interconversion when treated electrochemically ($E_{\text{Ni(IV)/Ni(III)}} - 0.17 \text{ V vs Fc}^+/\text{Fc}$)²⁰ or chemically.²¹ The *transoid* conformation is most favorable for nickel(III) bis(dicarbollide), whereas the *cisoid* conformation is energetically most favorable for nickel(IV) bis(dicarbollide).^{22,23} The results of quantum chemical calculations are in good agreement with the X-ray diffraction data for nickel(IV) bis(dicarbollide)²⁴ and a series of simple salts of nickel(III) bis(dicarbollide)^{25–28} and are consistent with a high dipole moment of nickel(IV) bis(dicarbollide) in solution.²⁹ High stability of the *cisoid* conformation of nickel(IV) bis(dicarbollide) complexes is illustrated by the fact that the rearrangement of C,C'-disubstituted dicarbollide ligands involves the isomerization of ligands accompanied by the migration of one substituted carbon atom away from the upper (adjacent to

the metal atom) to the lower (remote from the metal atom) rim⁹ instead of the rotation of one ligand to form sterically less hindered *transoid* or *gauche* rotamers.

Relying on this reversible isomerization from the *transoid* to *cisoid* conformation, Hawthorne *et al.*^{22,30} proposed nickel bis(dicarbollide) as a module unit for the construction of rotary molecular switches (Scheme 1) and formulated general principles of the design of such devices. As opposed to ferrocene derivatives, substituents in the upper (adjacent to the metal atom) rims of ligands in transition metal bis(dicarbollide) complexes are not in the plane of the open pentagonal face but point away from the center of the icosahedron. On the one hand, this may lead to an interaction between substituents in different ligands and, in particular, this excludes the possibility of stabilization of the *cisoid* conformation due to π - π interactions between aryl substituents. On the other hand, the structure of the dicarbollide ligand allows the synthesis of 6,6',8,8'-tetrasubstituted symmetric derivatives, which, makes it possible, as opposed to 1,1',3,3'-tetrasubstituted ferrocene derivatives, to avoid the formation of diastereomeric mixtures.



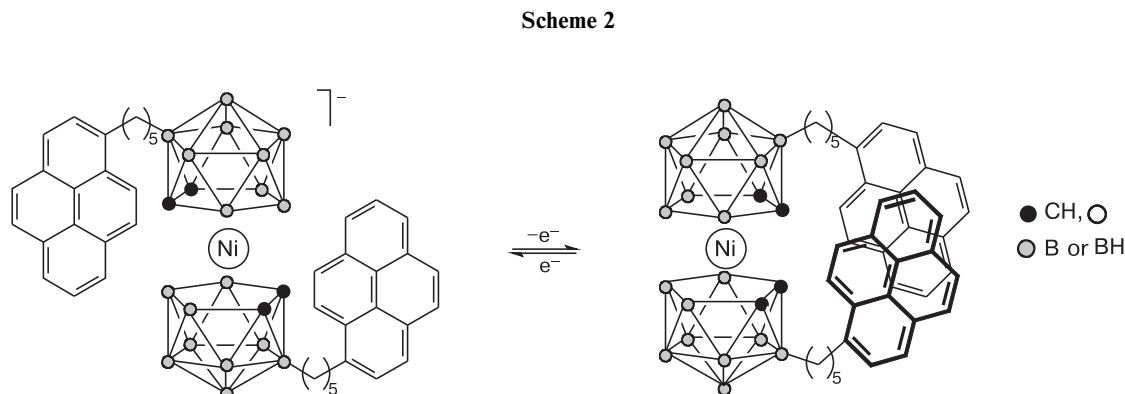
This approach was implemented *via* the attachment of pyrene-containing substituents as fluorescent probes (Scheme 2).³¹

As expected, the nickel(III) complex displayed only monomeric fluorescence emission, whereas the related nickel(IV) complex showed mainly intramolecular excimer fluorescence with a small contribution of residual monomeric fluorescence, which can be attributed to the flexibility of the spacer between the bis(dicarbollide) complex and pyrene moieties. For instance, the nickel(IV) bis(dicarbollide) adopts a *cisoid* conformation in the crystal; however, the pyrene moieties point away from each other due to intermolecular π - π stacking and $C_{\text{carb}}-\text{H}\dots\pi$ interactions.³¹

The synthesis of a nickel bis(dicarbollide) complex with two different fluorophore molecules, tryptophan and 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) capable of producing fluorescence resonance energy transfer (FRET), was reported more recently. The fluorophore molecules are linked to the bis(dicarbollide) complex by rigid spacers containing two pairs of alternating ethynyl and *para*-phenylene groups, thereby creating a certain distance (l) between the fluorophore molecules depending on the conformation of nickel bis(dicarbollide) (Fig. 2).³²

Since the energy transfer between fluorophores depends on the distance between these moieties, this effect ($l < 39$ Å) or its absence ($l > 39$ Å) provides information about the conformation of bis(dicarbollide) complexes in solution. The fluorescence spectra of the complexes show that the energy transfer between two fluorophores occurs not only in the Ni^{IV} complex (*cisoid* conformation) but also partially in the Ni^{III} complex, which is apparently attributed to the fact that nickel(III) bis(dicarbollide) partially exists in solution in the *gauche* conformation with $l < 39$ Å.³² This is in good agreement with an insignificant energy difference (about 0.5 kcal mol⁻¹) between the *transoid* and *gauche* conformations of the parent nickel(III) bis(dicarbollide) with a barrier to transformation between them of about 2 kcal mol⁻¹ (see Ref. 22).

The above examples show that transition metal bis(dicarbollide) complexes provide a promising platform



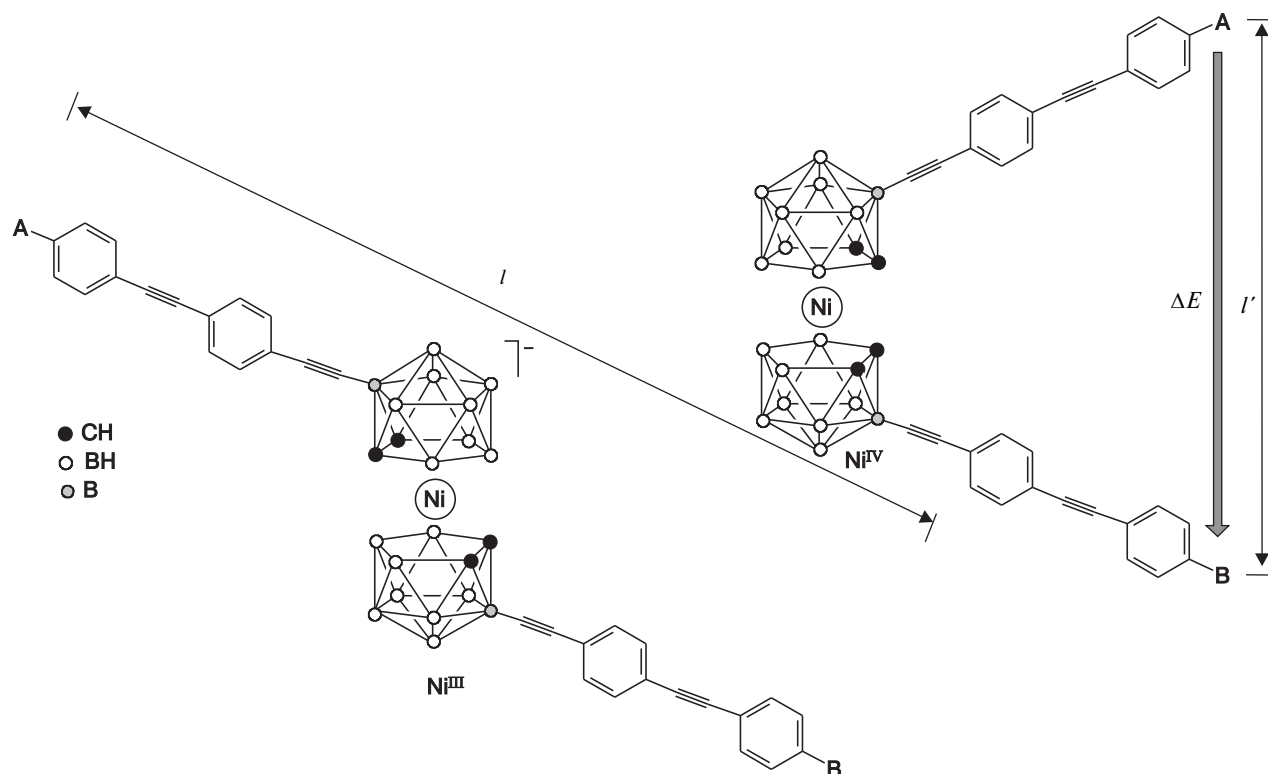


Fig. 2. A FRET-type molecular switch based on nickel bis(dicarbollide) (A is tryptophan, $\lambda_{\text{abs}} = 280$ nm, $\lambda_{\text{em}} = 326$ nm; B is BODIPY, $\lambda_{\text{abs}} = 354, 505$ nm, $\lambda_{\text{em}} = 531$ nm): $l = 45$ Å, $l' = 22$ Å, ΔE is the transfer energy.

for the design of rotary molecular switches; however, a small energy difference between rotational conformers (rotamers) generates a need for additional stabilization of individual rotamers.^{22,23,33} This stabilization can be achieved by introducing additional substituents into dicarbollide ligands, the interactions between which can stabilize particular rotamers. Examples of modification of dicarbollide ligands and their influence on stabilization of certain rotamers are considered below.

The simplest example of such a modification is the introduction of halogen atoms at the upper rim of the dicarbollide ligand to form 8,8'-dihalogenated derivatives $[8,8'-X_2-3,3'-M(1,2-C_2B_9H_{10})_2]^-$ ($X = F, Cl, Br, I$).³⁴ This gives rise to intramolecular CH...X hydrogen bonds between weakly acidic CH groups of the metallocarborane in one ligand and the halogen atoms in another ligand, which are responsible for stabilization of the *transoid* conformation in salts and complexes of different 8,8'-dihalogenated transition metal bis(dicarbollides) $[8,8'-X_2-3,3'-M(1,2-C_2B_9H_{10})_2]^-$ ($M = Co, X = Cl,^{35-37} Br,^{38} I,^{39-41} M = Fe, X = Cl,^{35,42} Br,^{43} I^{43}$) (Fig. 3). According to Pauling, the hydrogen bond strength should increase with increasing electronegativity of the acceptor atom,⁴⁴ however, the van der Waals radius of the halogen atom in bis(dicarbollide) complexes plays a greater role than its

electronegativity. Thus, although the fluorine atom has the highest electronegativity, its size is insufficient for the formation of intramolecular CH...F hydrogen bonds in the 8,8'-difluorinated cobalt bis(dicarbollide) $[8,8'-F_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$, resulting in the *cisoid* conformation of the latter.⁴⁵ Moreover, in some cases intramolecular CH...Cl hydrogen bonds are also insufficiently strong for stabilization of the *transoid* conformation in the 8,8'-dichlorinated derivative $[8,8'-Cl_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$.⁴⁶

The results of the recent study of the translocation of dihalogenated derivatives of cobalt bis(dicarbollide) across a lipid bilayer membrane suggest that the *transoid* conformation of the $[8,8'-X_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ anions ($X = Cl, Br, I$) is retained in solution.⁴⁷

According to the quantum chemical calculations for the $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ anion, the energy of the *transoid* conformation stabilized by two pairs of intramolecular CH...I hydrogen bonds is 4.7 kcal mol⁻¹ lower than the energy of the *gauche* conformation stabilized by two individual CH...I bonds and is 15.7 kcal mol⁻¹ lower than the energy of the *cisoid* conformation, in which these interactions are absent.⁴⁸

In some cases, for example, in the 8-iodinated cobalt bis(dicarbollide) $[8-I-3,3'-Co(1,2-C_2B_9H_{10})-$

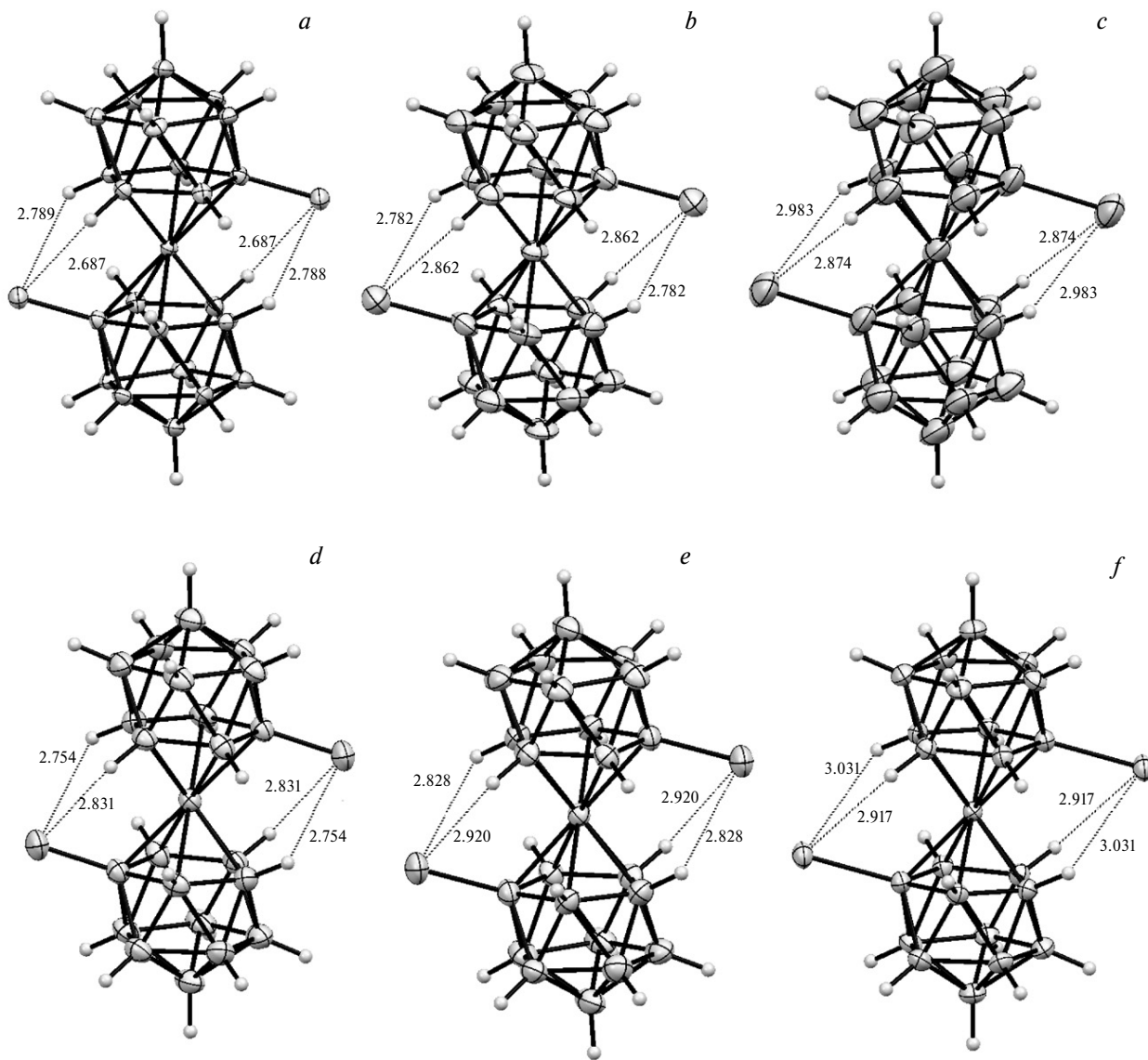


Fig. 3. Stabilization of the *transoid* conformation in 8,8'-dihalogenated derivatives $[8,8'-\text{Cl}_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 36) (a), $[8,8'-\text{Br}_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 37) (b), $[8,8'-\text{I}_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 39) (c), $[8,8'-\text{Cl}_2-3,3'-\text{Fe}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 42) (d), $[8,8'-\text{Br}_2-3,3'-\text{Fe}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 43) (e), and $[8,8'-\text{I}_2-3,3'-\text{Fe}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 43) (f).

$(1',2'-\text{C}_2\text{B}_9\text{H}_{11})^-$, the *transoid* conformation can be efficiently stabilized even by one pair of intramolecular $\text{CH}\cdots\text{I}$ hydrogen bonds.^{49,50} However, this stabilization is rather weak and is impaired if one substituent can be involved in the formation of stronger coordination bonds with the counterion as, for example, in $\text{Cs}[8-\text{HO}-8'-\text{I}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2] \cdot 2\text{H}_2\text{O} \cdot \text{acetone}$, in which the hydroxy group is coordinated to the cesium ion, resulting in the $\text{CH}\cdots\text{I}$ bond cleavage.⁵¹ Noteworthy is that, due to a small size of the oxygen atom, the hydroxy group, like the fluorine atom, cannot form intramolecular hydrogen bonds with the CH groups of the opposite dicarbollide

ligand to stabilize particular rotamers of bis(dicarbollide) complexes.⁵²

Another type of stabilization was observed in the crystal structures of 8-aryl derivatives of cobalt bis(dicarbollide) $[8-\text{Ar}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})(1',2'-\text{C}_2\text{B}_9\text{H}_{11})]^-$ (Ar = Ph, 4-Bu-C₆H₄), in which the *transoid* conformation is stabilized by intramolecular $\text{CH}\cdots\pi$ bonds between acidic CH groups of one dicarbollide ligand and the phenyl substituent in another ligand (Fig. 4).^{53,54} The derivatives $[8-\text{Ar}-8'-\text{I}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ characterized by combined stabilization of the *transoid* conformation by intramolecular $\text{CH}\cdots\text{I}$ and $\text{CH}\cdots\pi$ bonds between dicarbollide

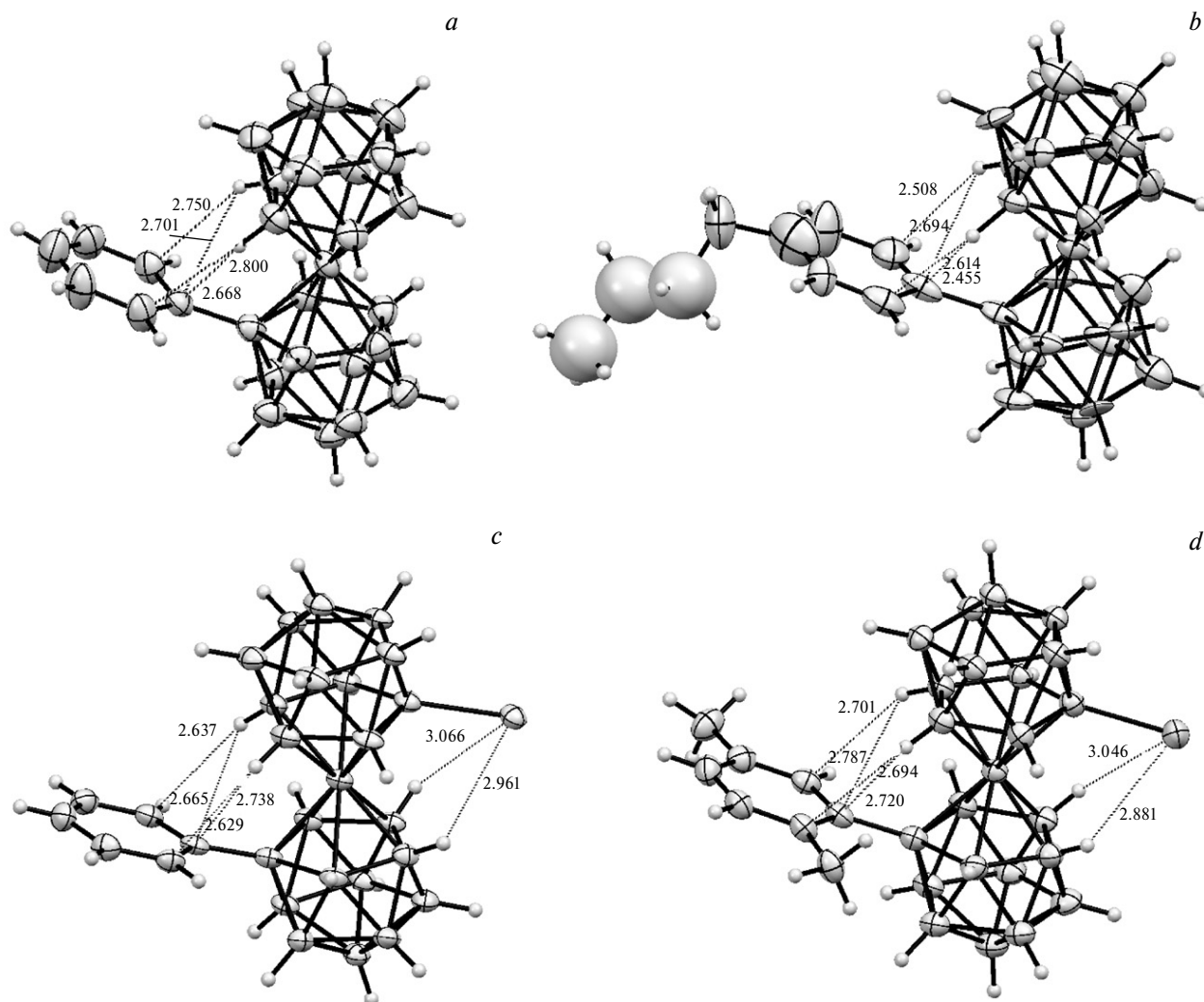


Fig. 4. Stabilization of the *transoid* conformation in derivatives [8-Ph-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (see Ref. 53) (a), [8-(4-BuC₆H₄)-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (see Ref. 54) (b), [8-Ph-8'-I-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ (see Ref. 55) (c), and [8-(2,5-Me₂C₆H₃)-8'-I-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ (see Ref. 56) (d).

lide ligands (see Fig. 4) were also described.^{55,56} The ¹H—¹H NOESY NMR study showed that intramolecular CH... π interactions occur not only in the solid state but also in solution.⁵⁶

Several examples of stabilization of the *cisoid* conformation of transition metal bis(dicarbollide) complexes involving substituents were also reported. One example is the formation of intramolecular CH...N hydrogen bonds between the CH group of one dicarbollide ligand and the nitrogen atom of the pyrrolidine or piperidine substituent of another ligand in the complexes [1-(CH₂)₄N-1'-(CH₂)₄NH-3,3'-Co(1,2-C₂B₉H₁₀)₂] and [1-(CH₂)₅N-1'-(CH₂)₅NH-3,3'-Co(1,2-C₂B₉H₁₀)₂] (Fig. 5).⁵⁷

Another example of stabilization of the *cisoid* conformation is the coordination of alkali metal cations by the open dioxane ring in the complexes [8-R(OCH₂CH₂)₂O-

3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (see Refs 58–61). In this case, the deficiency of oxygen atoms in the metal coordination sphere is compensated by coordination of BH groups of the unsubstituted dicarbollide ligand, resulting in stabilization of the *cisoid* conformation (Figs 6 and 7). According to ¹H NMR spectroscopic data, the coordination of BH groups to the metal atoms is retained in solution.⁵⁸ It should be noted that, in the absence of alkali metal cations, the bis(dicarbollide) moiety adopts predominantly the *transoid* conformation.⁶²

The above examples show that intramolecular interactions between dicarbollide ligands can serve as an efficient tool for stabilization of particular rotamers of transition metal bis(dicarbollide) complexes.

Cobalt and iron bis(dicarbollides), which, unlike nickel bis(dicarbollide), have only one stable degree of substitu-

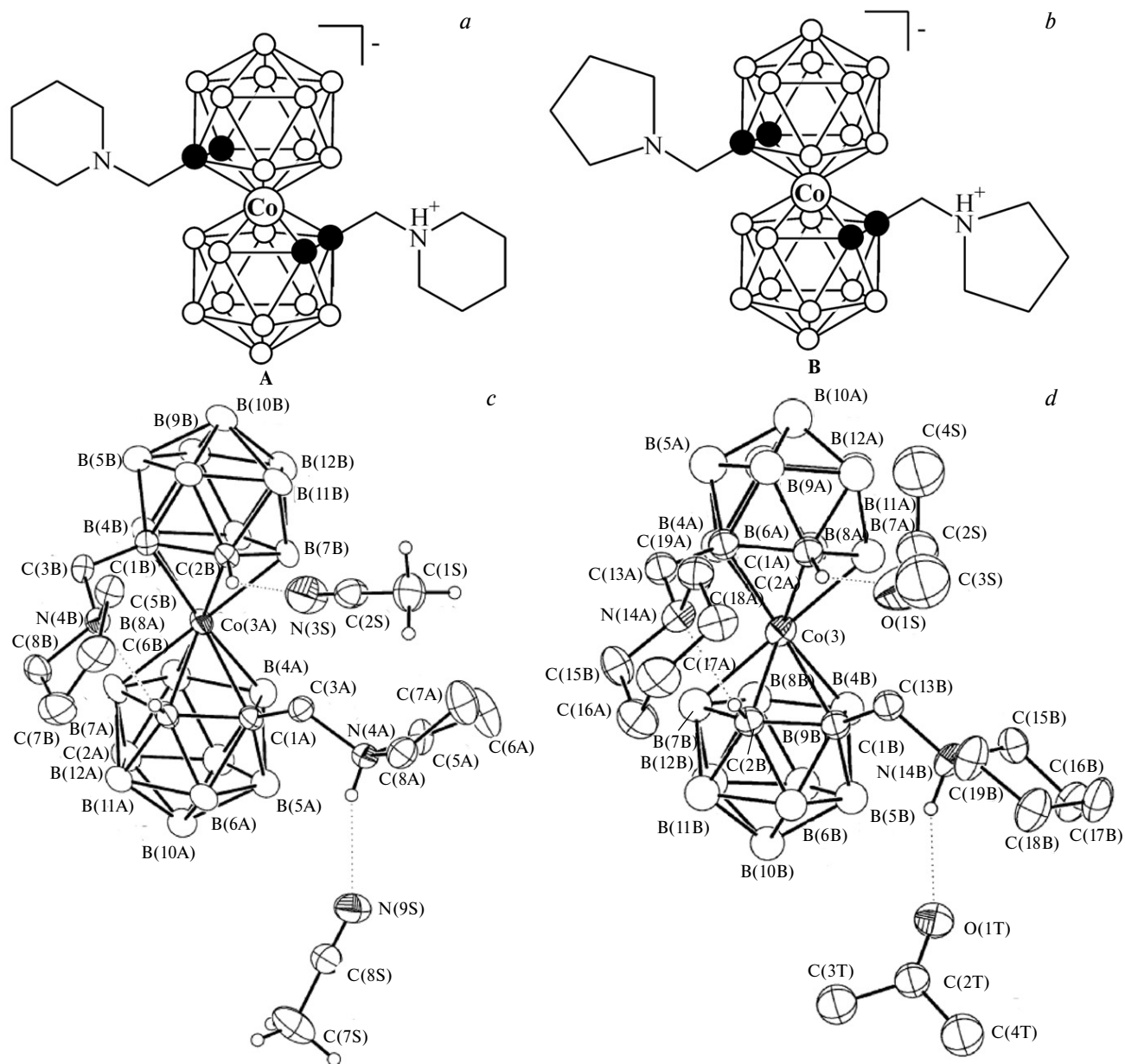


Fig. 5. Structures of bis(dicarbollide) complexes $[1-(\text{CH}_2)_5\text{N}-1'-(\text{CH}_2)_5\text{NH}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]$ (**A**) (a) and $[1-(\text{CH}_2)_4\text{N}-1'-(\text{CH}_2)_4\text{NH}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]$ (**B**) (b) and intra- and intermolecular bonds in the structures of **A**·2 MeCN (c) and **B**·2 Me₂CO (d).

tion, can be made bistable by introducing substituents capable of forming weak intramolecular hydrogen bonds between dicarbollide ligands and stronger dative bonds with external transition metals. In this case, the complexation with external metals will lead to stabilization of the *cisoid* conformation, while the *transoid* conformation will be stabilized by intramolecular hydrogen bonds between the ligands. These complexes can serve as a platform for the design of molecular switches, in which the conversion of one conformation to another one will be initiated by external complex-forming metal cations (Scheme 3).

Several examples of complexation of external metals with cobalt bis(dicarbollide) derivatives are known. These are silver and gold complexes with the bis(diphenylphosphine) derivative of cobalt bis(dicarbollide) $[1,1'-(\text{Ph}_2\text{P})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 63) and sodium complexes with thiacycrown ethers bearing the incorporated bis(dicarbollide) moiety, $[1,1'-\mu\{-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 58) and $[8,8'-\mu\{-\text{C}_6\text{H}_4-1,2-(\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O})-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (see Ref. 64). However, the complexation of the

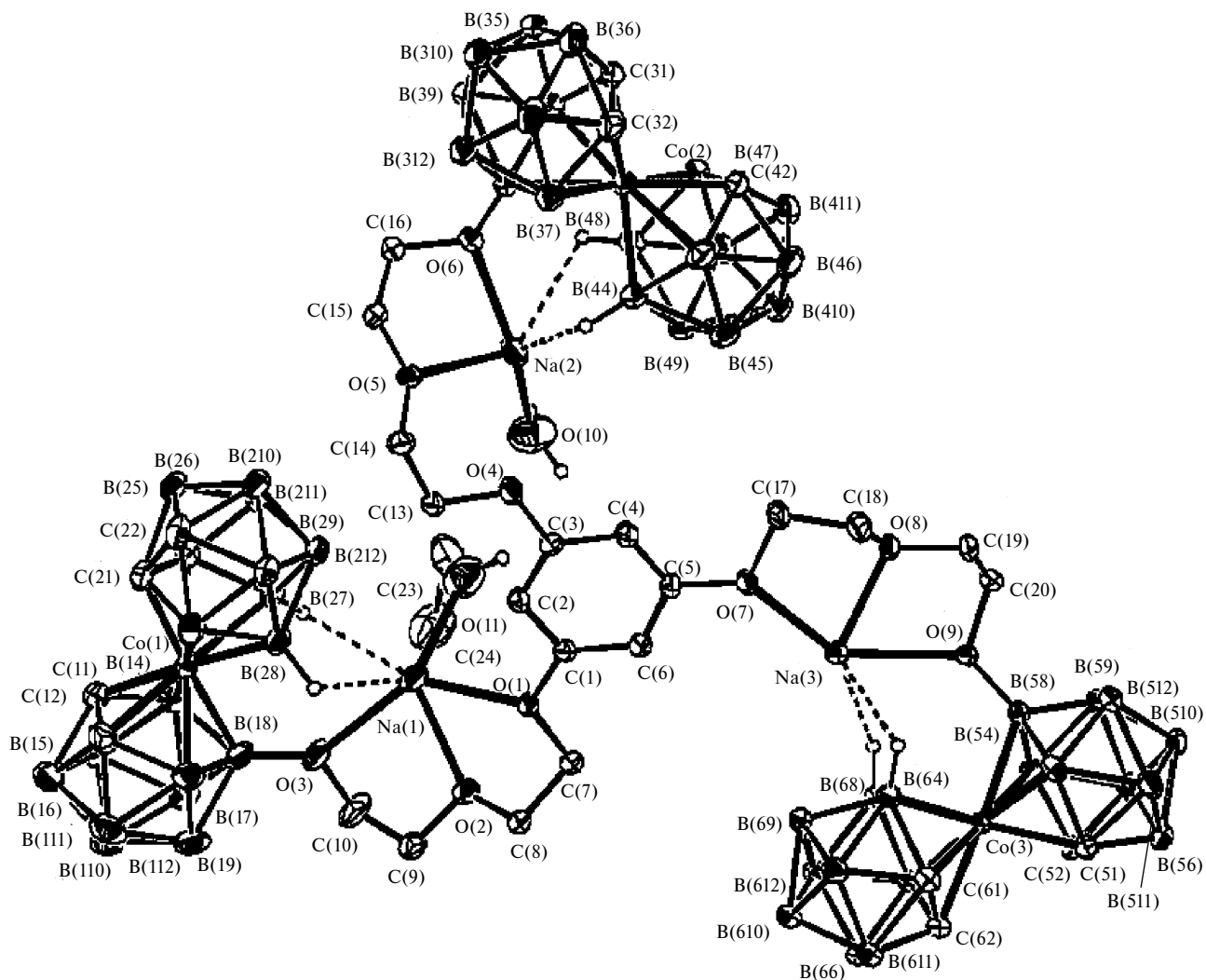


Fig. 7. Crystal structure of $\text{Na}_3[\mu\text{-}1,3,5\text{-C}_6\text{H}_3\text{O}_3(8\text{-(CH}_2\text{CH}_2\text{O)}_2\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11}))_3] \cdot \text{EtOH}$.⁶¹

Recently, our research team has synthesized, starting from *B*-methylsulfanyl derivatives of *nido*-carborane $[10\text{-MeS-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]^-$ (see Ref. 65) and $[9\text{-MeS-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]^-$ (see Ref. 66), a series of methylsulfanyl derivatives of cobalt bis(dicarbollide) $[\text{X,Y}'\text{-(MeS)}_{2-3,3'}\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ containing MeS groups capable of coordination in different positions of the upper rim of dicarbollide ligands.⁶⁷ The X-ray diffraction study of tetrabutylammonium salts of the resulting *B*-methylsulfanyl derivatives demonstrated that the *transoid* conformation of the symmetric 8,8'-isomer is stabilized by two pairs of intramolecular CH...S hydrogen bonds (2.683–2.712 Å), whereas the *gauche* conformation of the 4,4'-isomer (*rac*) is stabilized in a similar way. For the 4,7'-isomer (*meso*), the *gauche* conformation is stabilized by only one pair of intramolecular CH...S hydrogen bonds (Figs 9 and 10). The ¹H NMR spectroscopic data suggest that the *transoid*

conformation of the 8,8'-isomer, which is stabilized by intramolecular CH...S hydrogen bonds, is retained in solution. These results are in good agreement with quantum chemical calculations.⁶⁷

A similar series of *B*-substituted methylsulfanyl derivatives of iron(III) bis(dicarbollide) $[\text{X,Y}'\text{-(MeS)}_{2-3,3'}\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ were synthesized by demethylation of known dimethylsulfonium derivatives of iron(II) bis(dicarbollide) $[8,8'\text{-(Me}_2\text{S)}_{2-3,3'}\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{10})_2]$,⁶⁸ $[4,4'\text{-(Me}_2\text{S)}_{2-3,3'}\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{10})_2]$,⁶⁹ and $[4,7'\text{-(Me}_2\text{S)}_{2-3,3'}\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{10})_2]$ ⁷⁰ followed by the oxidation of the resulting methylsulfanyl derivatives of iron(II) bis(dicarbollide) $[\text{X,Y}'\text{-(MeS)}_{2-3,3'}\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{10})_2]^{2-}$ (see Ref. 71). As in the case of methylsulfanyl derivatives of cobalt bis(dicarbollide), *transoid* and *gauche* conformations of the symmetric 8,8'-isomer and the 4,4'-isomer (*rac*), respectively, are stabilized by two

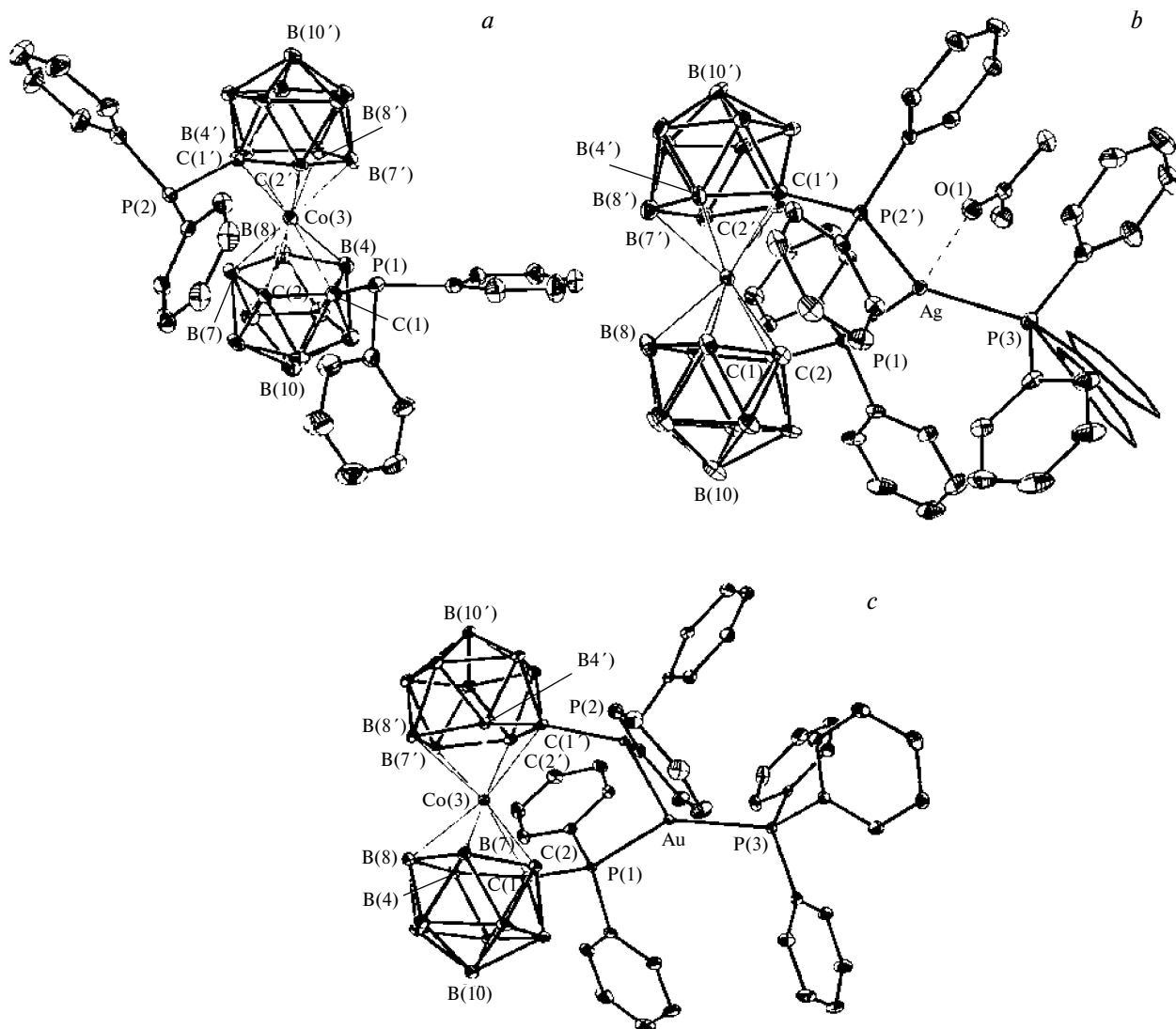


Fig. 8. Crystal structures of the bis(diphenylphosphine) derivative of cobalt bis(dicarbollide) $[1,1'-(\text{Ph}_2\text{P})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (a) and its complexes with silver (b) and gold (c).

pairs of intramolecular CH...S hydrogen bonds, while the *gauche* conformation of the 4,7'-isomer (*meso*) is stabilized by only one pair of intramolecular CH...S hydrogen bonds (Figs 11 and 12, a). These results are in line with the results of quantum chemical calculations.⁷¹

As opposed to the 8,8'-bis(methylsulfanyl) derivative of cobalt bis(dicarbollide) $[8,8'-(\text{MeS})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$, the *transoid* conformation of the related 8,8'-bis(methoxy) derivative $[8,8'-(\text{MeO})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ is stabilized only by two intramolecular CH...O hydrogen bonds between dicarbollide ligands (Fig. 12, b). The X-ray diffraction data are in line with the results of quantum chemical calculations.⁷²

In the related nickel(IV) complex $[8,8'-(\text{MeO})_2-3,3'-\text{Ni}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]$, two intramolecular CH...O hydrogen bonds between dicarbollide ligands stabilize the *gauche* conformation.⁷³ This is the only known example of the non-*cisoid* conformation for nickel(IV) bis(dicarbollide) derivatives.

The preliminary study of the complexation of 8,8'-bis(methylsulfanyl)bis(dicarbollide)cobalt- $[8,8'-(\text{MeS})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ with $(\text{MeCN})_3\text{W}(\text{CO})_3$ demonstrated that, due to the electron-donating effect of the boron core, methylsulfanyl groups act as rather strong Lewis bases capable of forming complexes with transition metals, which suggests that this derivative is a promising module unit for the design

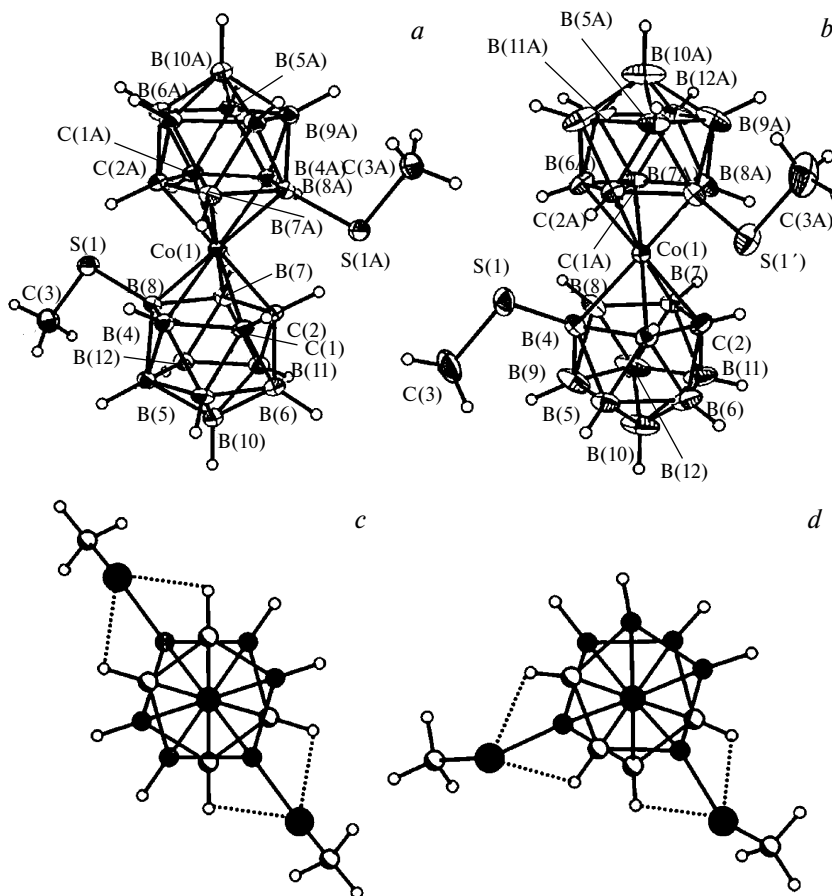


Fig. 9. Crystal structures (*a*, *b*) and the mutual orientation of dicarbollide ligands (*c*, *d*) in methylsulfanyl derivatives of cobalt bis(dicarbollide) $[8,8'-(\text{MeS})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (*a*, *c*) and $[4,4'-(\text{MeS})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (*b*, *d*).

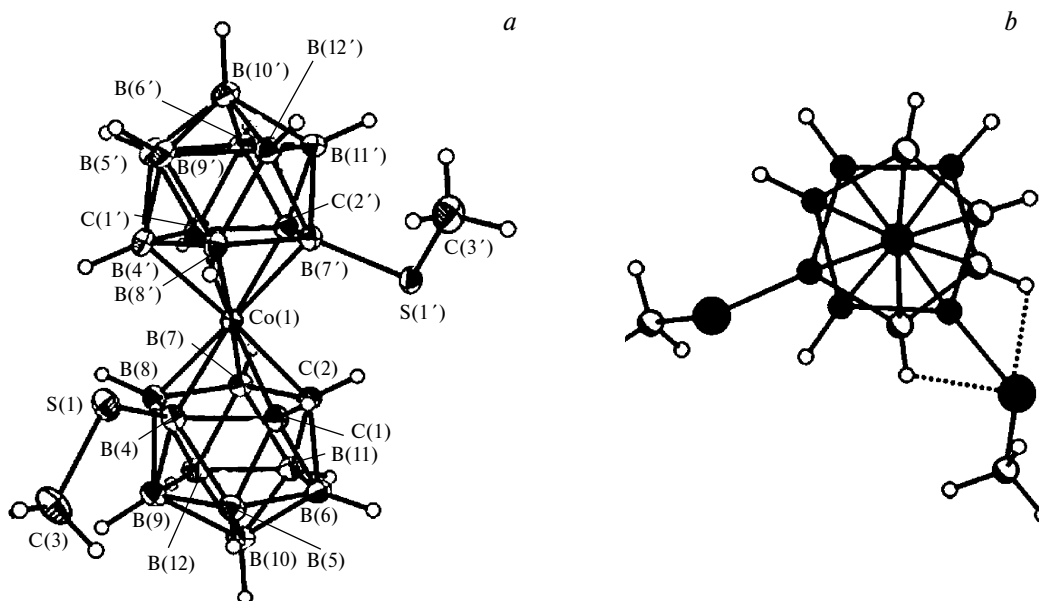


Fig. 10. Crystal structure (*a*) and the mutual orientation of dicarbollide ligands (*b*) in the methylsulfanyl derivative of cobalt bis(dicarbollide) $[4,7'-(\text{MeS})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$.

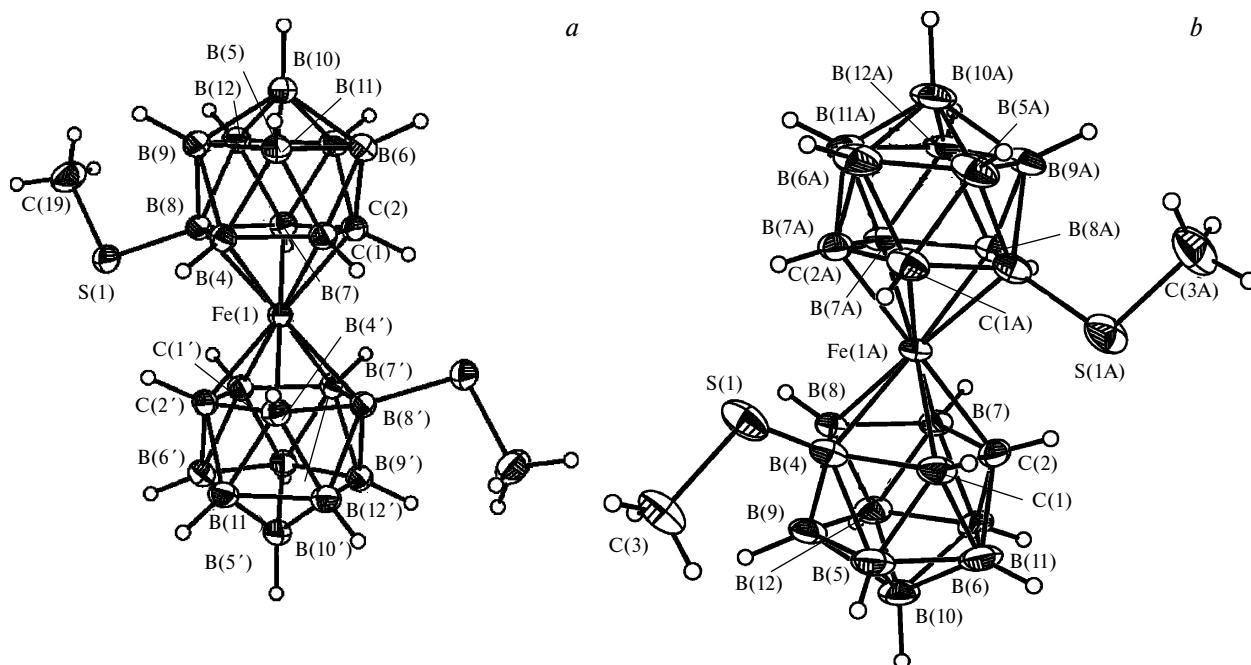


Fig. 11. Crystal structures of methylsulfanyl derivatives of iron bis(dicarbollide) $[8,8'-(\text{MeS})_2-3,3'-\text{Fe}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^{2-}$ (a) and $[4,4'-(\text{MeS})_2-3,3'-\text{Fe}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (b).

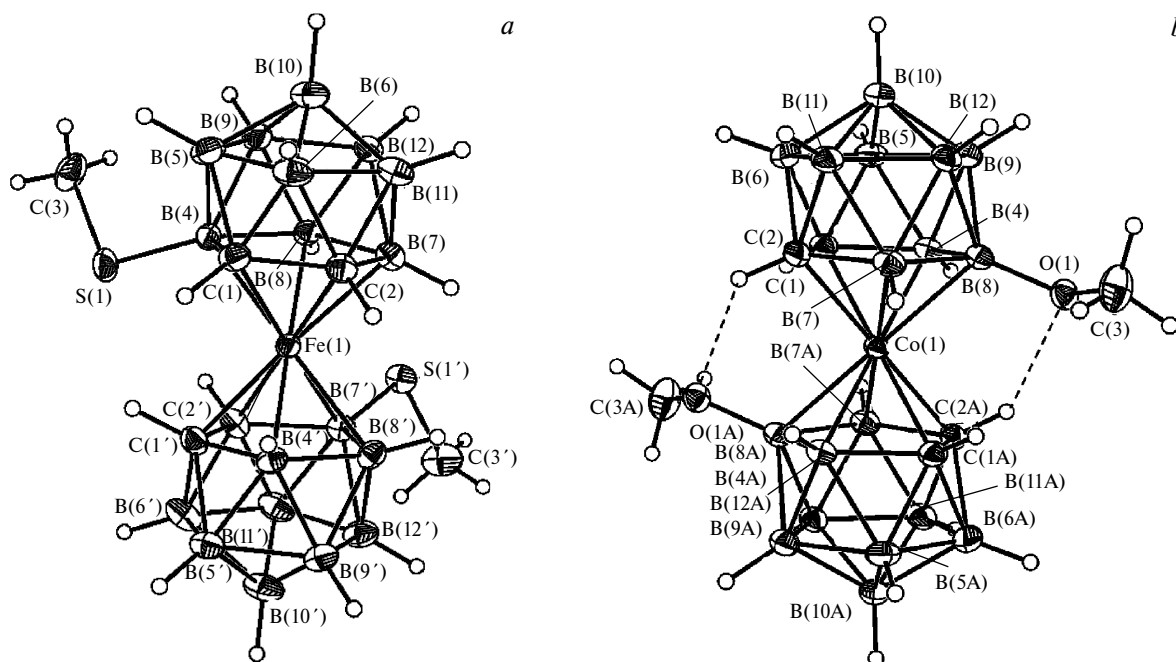


Fig. 12. Crystal structures of the methylsulfanyl derivative of iron bis(dicarbollide) $[4,7'-(\text{MeS})_2-3,3'-\text{Fe}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (a) and the 8,8'-bis(alkoxy) derivative of cobalt bis(dicarbollide) $[8,8'-(\text{MeO})_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-$ (b).

of molecular switches.⁷⁴ Investigations of complexation of the 8,8'-bis(methylsulfanyl) derivative of cobalt bis(dicarbollide) with other transition metals are currently underway.

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References

1. B. L. Feringa, *Acc. Chem. Res.*, 2001, **34**, 504.
2. J.-P. Sauvage, *Molecular Machines and Motors* (Structure and Bonding, Vol. 99), Springer, Berlin, 2001, 302 pp.
3. A. Credi, S. Silvi, M. Venturi, *Molecular Machines and Motors: Recent Advances and Perspectives (Topics in Current Chemistry, Vol. 354)*, Springer, Heidelberg, 2014, 342 pp.

4. S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan, A. L. Nussbaumer, *Chem. Rev.*, 2015, **115**, 10081.
5. *The Nobel Prize in Chemistry 2016*, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2016/.
6. *Molecular Switches*, 2nd ed., Eds B. L. Feringa, W. R. Browne, Wiley-VCH, Weinheim, 2011, 792 pp.
7. S. Durot, V. Heitz, A. Sour, J.-P. Sauvage, in *Molecular Machines and Motors: Recent Advances and Perspectives (Topics in Current Chemistry, Vol. 354)*, Eds A. Credi, S. Silvi, M. Venturi, Springer, Heidelberg, 2014, p. 35.
8. B. L. Feringa, W. R. Browne, A. P. de Silva, T. P. Vance, B. Wannalser, M. E. S. West, in *Molecular Switches*, 2nd ed., Eds B. L. Feringa, W. R. Browne, Wiley-VCH, Weinheim, 2011, p. 669.
9. G. Copley, T. A. Moore, A. L. Moore, D. Gust, *Adv. Mater.*, 2013, **25**, 456.
10. M. F. Budyka, *Russ. Chem. Rev.*, 2017, **86**, 181.
11. B. L. Feringa, W. R. Browne, C. Tock, J. Frey, J. P. Sauvage, in *Molecular Switches*, 2nd ed., Eds B. L. Feringa, W. R. Browne, Wiley-VCH, Weinheim, 2011, p. 97.
12. J. W. Canary, S. Mortezaei, J. Liang, *Coord. Chem. Rev.*, 2010, **254**, 2249.
13. A. Bianchi, E. Delgado-Pinar, E. García-España, C. Giorgi, F. Pina, *Coord. Chem. Rev.*, 2014, **260**, 156.
14. S. Ø. Scottwell, J. D. Crowley, *Chem. Commun.*, 2016, **52**, 2451.
15. I. B. Sivaev, *Molecules*, 2017, **22**, 2201.
16. K. Kinbara, T. Muraoka, T. Aida, *Org. Biomol. Chem.*, 2008, **6**, 1871.
17. I. B. Sivaev, V. I. Bregadze, *Collect. Czech. Chem. Commun.*, 1999, **64**, 783.
18. I. B. Sivaev, V. I. Bregadze, *J. Organomet. Chem.*, 2000, **614–615**, 27.
19. B. P. Dash, R. Satapathy, B. R. Swain, C. S. Mahanta, B. B. Jena, N. S. Hosmane, *J. Organomet. Chem.*, 2017, **849–850**, 170.
20. R. Nuñez, M. Tarres, A. Ferrer-Ugalde, F. Fabrizi de Biani, F. Teixidor, *Chem. Rev.*, 2016, **116**, 14307.
21. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.
22. M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. B. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, *Science*, 2004, **303**, 1849.
23. M. Bühl, J. Holub, D. Hnyk, J. Macháček, *Organometallics*, 2006, **25**, 2173.
24. D. St. Clair, A. Zalkin, D. H. Templeton, *J. Am. Chem. Soc.*, 1970, **92**, 1173.
25. F. V. Hansen, R. G. Hazell, C. Hyatt, G. D. Stucky, *Acta Chem. Scand.*, 1973, **27**, 1210.
26. T. M. Polyanskaya, V. A. Nadolnnyi, V. V. Volkov, E. A. Il'inchik, M. K. Drozdova, *Russ. J. Struct. Chem.*, 2006, **47**, 894.
27. T. M. Polyanskaya, M. K. Drozdova, V. V. Volkov, *Russ. J. Struct. Chem.*, 2008, **49**, 560.
28. T. M. Polyanskaya, M. K. Drozdova, V. V. Volkov, *Russ. J. Struct. Chem.*, 2013, **54**, 547.
29. L. F. Warren, M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 1157.
30. M. F. Hawthorne, B. M. Ramachandran, R. D. Kennedy, C. B. Knobler, *Pure Appl. Chem.*, 2006, **78**, 1299.
31. A. V. Safronov, N. I. Shlyakhtina, T. A. Everett, M. R. VanGordon, Yu. V. Sevryugina, S. S. Jalisatgi, M. F. Hawthorne, *Inorg. Chem.*, 2014, **53**, 10045.
32. N. I. Shlyakhtina, A. V. Safronov, Yu. V. Sevryugina, S. S. Jalisatgi, M. F. Hawthorne, *J. Organomet. Chem.*, 2015, **798**, 234.
33. M. Bühl, D. Hnyk, J. Macháček, *Chem. Eur. J.*, 2005, **11**, 4109.
34. V. I. Bregadze, S. V. Timofeev, I. B. Sivaev, I. A. Lobanova, *Russ. Chem. Rev.*, 2004, **73**, 433.
35. N. I. Kirillova, A. S. Zhdanov, A. I. Gusev, V. N. Kirin, S. P. Knyazev, T. V. Sokolova, *Organomet. Chem. USSR*, 1989, **2**, 448.
36. P. K. Hurlburt, R. L. Miller, K. D. Abney, T. M. Foreman, R. J. Butcher, S. A. Kinkhead, *Inorg. Chem.*, 1995, **34**, 5215.
37. O. N. Kazheva, A. V. Kravchenko, G. G. Aleksandrov, I. B. Sivaev, V. I. Bregadze, I. D. Kosenko, I. A. Lobanova, L. I. Buravov, V. A. Starodub, O. A. Dyachenko, *Russ. Chem. Bull.*, 2014, **63**, 1322.
38. O. Kazheva, G. Alexandrov, A. Kravchenko, V. Starodub, I. Lobanova, I. Sivaev, V. Bregadze, L. Buravov, O. Dyachenko, *Solid State Sci.*, 2008, **10**, 1734.
39. P. Sivy, A. Preisinger, O. Baumgartner, F. Valach, B. Koreň, L. Matel, *Acta Cryst. C*, 1986, **42**, 28.
40. O. N. Kazheva, G. G. Alexandrov, A. V. Kravchenko, V. A. Starodub, I. A. Lobanova, I. B. Sivaev, V. I. Bregadze, L. V. Titov, L. I. Buravov, O. A. Dyachenko, *J. Organomet. Chem.*, 2009, **694**, 2336.
41. A. A. Zaulet, PhD Thesis, Barcelona, 2015 (<https://ddd.uab.cat/record/148880>).
42. O. N. Kazheva, A. V. Kravchenko, G. G. Aleksandrov, I. D. Kosenko, I. A. Lobanova, V. I. Bregadze, D. M. Chudak, L. I. Buravov, S. G. Protasova, V. A. Starodub, O. A. Dyachenko, *Russ. Chem. Bull.*, 2016, **65**, 2195.
43. O. N. Kazheva, A. V. Kravchenko, I. D. Kosenko, G. G. Alexandrov, D. M. Chudak, V. A. Starodub, I. A. Lobanova, V. I. Bregadze, L. I. Buravov, S. G. Protasova, O. A. Dyachenko, *J. Organomet. Chem.*, 2017, **849–850**, 261.
44. L. Pauling, *The Nature of the Chemical Bond*. 3rd ed., Cornell University Press, Ithaca, 1960, 644 pp.
45. A. N. Gashti, J. C. Huffman, A. Edwards, G. Szekeley, A. R. Siedle, J. A. Karty, J. P. Reilly, L. J. Todd, *J. Organomet. Chem.*, 2000, **614–615**, 120.
46. O. N. Kazheva, G. G. Alexandrov, A. V. Kravchenko, I. B. Sivaev, V. A. Starodub, I. D. Kosenko, I. A. Lobanova, V. I. Bregadze, L. V. Buravov, O. A. Dyachenko, *J. Chem. Eng. Chem. Res.*, 2015, **2**, 497.
47. T. I. Rokitskaya, I. D. Kosenko, I. B. Sivaev, Yu. N. Antonenko, V. I. Bregadze, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25122.
48. A. Zaulet, F. Teixidor, P. Bauduin, O. Diat, P. Hirva, A. Ofori, C. Viñas, *J. Organomet. Chem.*, 2018, **865**, 214.
49. P. Sivy, A. Preisinger, O. Baumgartner, F. Valach, B. Koreň, L. Matel, *Acta Cryst. C*, 1986, **42**, 30.
50. O. N. Kazheva, G. G. Alexandrov, A. V. Kravchenko, V. A. Starodub, I. B. Sivaev, I. A. Lobanova, V. I. Bregadze, L. I. Buravov, O. A. Dyachenko, *J. Organomet. Chem.*, 2007, **692**, 5033.
51. I. D. Kosenko, I. A. Lobanova, I. A. Ananyev, I. A. Godovikov, L. A. Chekulaeva, Z. A. Starikova, S. Qi, V. I. Bregadze, *J. Organomet. Chem.*, 2014, **769**, 72.
52. O. N. Kazheva, G. G. Alexandrov, A. V. Kravchenko, I. D. Kosenko, I. A. Lobanova, I. B. Sivaev, O. A. Filippov, E. S. Shubina, V. I. Bregadze, V. A. Starodub, L. V. Titov, L. I. Buravov, O. A. Dyachenko, *Inorg. Chem.*, 2011, **50**, 444.

53. J. Plešek, S. Heřmánek, A. Franken, I. Císařová, C. Nachtigal, *Collect. Czech. Chem. Commun.*, 1997, **62**, 47.
54. I. Rojo, F. Teixidor, C. Viñas, R. Kivekäs, R. Sillanpää, *Chem. Eur. J.*, 2003, **9**, 4311.
55. V. I. Bregadze, I. D. Kosenko, I. A. Lobanova, Z. A. Starikova, I. A. Godovikov, I. B. Sivaev, *Organometallics*, 2010, **29**, 5366.
56. I. D. Kosenko, I. A. Lobanova, I. A. Godovikov, Z. A. Starikova, I. B. Sivaev, V. I. Bregadze, *J. Organomet. Chem.*, 2012, **721–722**, 70.
57. M. F. Hawthorne, C. L. Beno, D. E. Harwell, S. S. Jalisatgi, C. B. Knobler, *J. Mol. Struct.*, 2003, **656**, 239.
58. F. Teixidor, J. Pedrajas, I. Rojo, C. Viñas, R. Kivekäs, R. Sillanpää, I. Sivaev, V. Bregadze, S. Sjöberg, *Organometallics*, 2003, **22**, 3414.
59. J. Plešek, B. Grüner, S. Heřmánek, J. Bača, V. Mareček, J. Jänchenova, A. Lhotsky, K. Holub, P. Selucky, J. Rais, I. Císařová, J. Časlavsky, *Polyhedron*, 2002, **21**, 975.
60. M. Tarrés, C. Viñas, P. González-Cardoso, M. M. Hänninen, R. Sillanpää, V. Dordovič, M. Uchman, F. Teixidor, P. Matějček, *Chem. Eur. J.*, 2014, **20**, 6786.
61. P. Farrás, F. Teixidor, R. Kivekäs, R. Sillanpää, C. Viñas, B. Grüner, I. Císařová, *Inorg. Chem.*, 2008, **47**, 9497.
62. I. B. Sivaev, Z. A. Starikova, S. Sjöberg, V. I. Bregadze, *J. Organomet. Chem.*, 2002, **649**, 1.
63. I. Rojo, F. Teixidor, C. Viñas, R. Kivekäs, R. Sillanpää, *Chem. Eur. J.*, 2004, **10**, 5376.
64. G. S. Kazakov, M. Yu. Stogniy, I. B. Sivaev, K. Yu. Suponitsky, I. A. Godovikov, A. D. Kirilin, V. I. Bregadze, *J. Organomet. Chem.*, 2015, **798**, 196.
65. S. A. Anufriev, I. B. Sivaev, K. Yu. Suponitsky, I. A. Godovikov, V. I. Bregadze, *Eur. J. Inorg. Chem.*, 2017, 4436.
66. S. A. Anufriev, I. B. Sivaev, K. Yu. Suponitsky, V. I. Bregadze, *J. Organomet. Chem.*, 2017, **849–850**, 315.
67. S. A. Anufriev, S. A. Erokhina, K. Yu. Suponitsky, I. A. Godovikov, O. A. Filippov, F. Fabrizi de Biani, M. Corsini, A. O. Chizhov, I. B. Sivaev, *Eur. J. Inorg. Chem.*, 2017, 4444.
68. J. Plešek, B. Štíbr, P. A. Cooke, J. D. Kennedy, T. D. McGrath, M. Thornton-Pett, *Acta Cryst. C*, 1998, **36**, 36.
69. Y.-K. Yan, D. M. P. Mingos, T. E. Müller, D. J. Williams, M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1994, 1735.
70. Y.-K. Yan, D. M. P. Mingos, D. J. Williams, *J. Organomet. Chem.*, 1995, **498**, 267.
71. S. A. Anufriev, S. A. Erokhina, K. Yu. Suponitsky, A. A. Anisimov, J. N. Laskova, I. A. Godovikov, F. Fabrizi de Biani, M. Corsini, I. B. Sivaev, V. I. Bregadze, *J. Organomet. Chem.*, 2018, **865**, 239.
72. M. Yu. Stogniy, K. Yu. Suponitsky, A. O. Chizhov, I. B. Sivaev, V. I. Bregadze, *J. Organomet. Chem.*, 2018, **865**, 138.
73. V. Petříček, K. Maly, A. Petřina, K. Baše, A. Linek, *Z. Kristallogr.*, 1984, **166**, 1.
74. S. V. Timofeev, S. A. Anufriev, I. B. Sivaev, V. I. Bregadze, *Russ. Chem. Bull.*, 2018, **67**, 570.

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