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Dedicated to Academician V.T. Kalinnikov of Blessed Memory (1935–2015)

The Role of Inner- and Outer-Sphere Ligands in Pivalate and Cymantrenecarboxylate Complexes of Transition Metals

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Abstract—The formation of transition metal complexes with pivalate and cymantrenecarboxylate ligands in the presence of axial cyclopentadienyl and α-substituted pyridine ligands is discussed. The latter present steric hindrances due to repulsion from the O atoms of the carboxylate bridges. Particular emphasis is placed on the role of outer-sphere ammonium cations: their hydrogen bonding to fluoride bridges limits the growth of cyclic chromium(III) complexes with the pivalate and fluoride ligands that possess the properties of molecular magnets.

Keywords: transition metal carboxylates, structure, steric effects of ligands, magnetic properties

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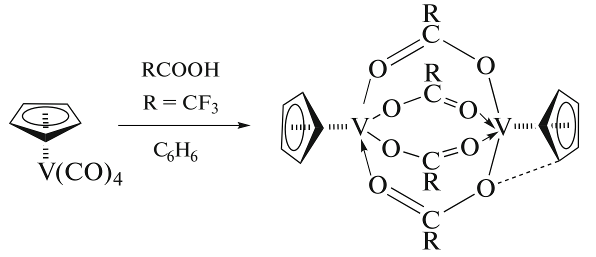
Interest in transition metal complexes with carboxylate bridges arose in the mid-1950s after the cupric carboxylates LCu(μ-OOCR)$_4$CuL with a structure like a “Chinese lantern” or, more precisely, a paddle-wheel had been found to exhibit antiferromagnetism [1]. Either Cu atom in those complexes lies in the equatorial plane made up of four O atoms, with the axial positions occupying the electron-donating atom of ligand L and the other Cu atom. The short Cu···Cu distance (~2.64 Å for Cu(OAc)$_2$ · H$_2$O) [1, 2] formally corresponds to the Cu–Cu bond (2.56 Å in metallic copper). However, quantum chemical calculations show that the unpaired electron on either Cu atom is on the d^2_{x-y} orbital in the equatorial plane and that antiferromagnetic exchange must involve the carboxylate bridges only [3]. It should be noted that the Cu···Cu distance and the exchange parameter $-2J$ (~350 cm^{-1}) depend on the electron-donating properties of substituents R in carboxylate bridges but are only slightly sensitive to the electronic characteristics of the axial ligand L, which is mainly coordinated to the d^2_z-orbital not involved in exchange interactions.

The situation changes abruptly when the coordination of L is sterically hindered. This is especially pronounced after four carboxylate bridges have been replaced by isoelectronic diphenyltriazenide ones to give the dinuclear complex Cu(μ-PhN-N=NPh)$_4$Cu, in which the phenyl groups preclude the attachment of axial ligands. As a result, the Cu atoms can shift into the lantern cavity to form a Cu–Cu bond shortened to 2.44 Å and making the molecule diamagnetic [4]. On the other hand, if substituted anilines are used as a nitrogen-containing ligand, then the resulting dinuclear complexes are only doubly bridged, while another carboxylate group is a terminal one. Its copper-bound O atom, like the N atom of aniline, is in the plane of CuO$_3$N, also acting as an axial ligand to the Cu atom of an adjacent dinuclear molecule to form a chain of doubly bridged complexes. In this case, such a structure is again due to the steric features of coordinated aniline that cause repulsion between the carboxylate O atoms and the C atoms of the phenyl groups that are *ortho* to nitrogen. Moreover, no such structure is formed when these C atoms bear substituents or when arenecarboxylates are replaced by more electron-donating alkanoates [5].

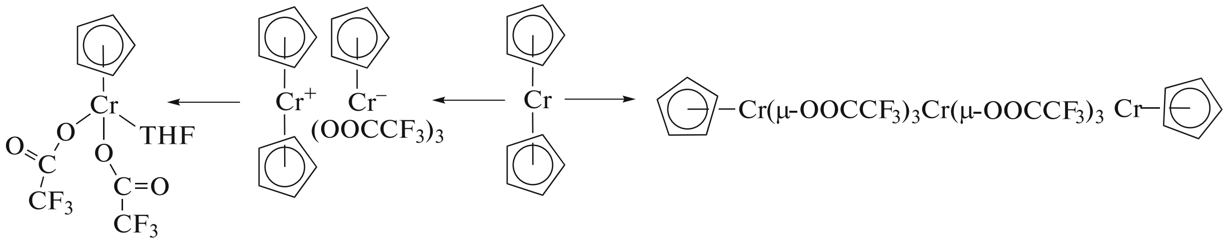
In turn, in the trifluoroacetate complex CpV(μ-OOCCF$_3$)$_4$VCp obtained from CpV(CO)$_4$ in boiling trifluoroacetic acid (Scheme 1), the bulky cyclopentadienyl ligands firmly bound to the vanadium(III) atoms are repulsed from the O atoms (C···O, ~3.0 Å) and draw the vanadium atoms out of the planes of the O atoms of the carboxylate bridges. Because of this, the V···V distance is nonbonding (~3.6 Å). Although either vanadium atom has two unpaired electrons, their antiferromagnetic exchange occurs only via the carboxylate bridges [6].



Scheme 1.

The geometry and magnetic properties of the complexes only slightly depend on the electronic properties of substituents R in the carboxylate bridges: the exchange parameter $-2J$ randomly changes from 220 to 330 cm^{-1} when R is varied from electron-withdrawing groups (CF_3) to weak electron-withdrawing (Ph) and strong electron-donating ones (CMe_3) [7]. These complexes can be obtained from $CpV(CO)_4$ as well as in reactions of carboxylic acids with vanadocene Cp_2V. Here is again the case of steric repulsion between the axial ligands and the carboxylate O atoms surrounding the metal atom since it is impossible to ensure four carboxylate bridges in the complex $Cp_2V(OOCPh)_2$, which initially forms in a reaction of vanadocene with benzoyl peroxide but readily loses one Cp ligand to give the dimerizing moiety $CpV(OOCPh)_2$ [8].

Equally ready elimination of one cyclopentadienyl ligand occurs when chromocene is treated with trifluoroacetic acid (Scheme 2). The first step (in benzene) involves the formation of the ionic complex $[Cp_2Cr]^+[CpCr(OOCCF_3)_3]^-$, whose magnetic moment decreases from the intrinsic spin value (3.70 μ_B) to 3.41 μ_B between 295 and 77 K. Recrystallization from THF results in elimination of the ionic complex $[Cp_2Cr]^+[OOCCF_3]^-$ and formation of dark blue crystals of the monomer $CpCr(OOCCF_3)_2 \cdot THF$ [9]. By slow diffusion of trifluoroacetic acid into a toluene solution of chromocene, Cotton and Rice obtained purple crystals of the trinuclear linear complex [CpCr(μ-$OOCCF_3)_3$Cr(μ-$OOCCF_3)_3$CrCp], in which the Cr atoms are not directly bound to each other (Cr···Cr, 3.717 Å) and two bridges are coordinated through both the O atoms, while the third bridge is coordinated through only one O atom (the magnetic properties of this complex are not cited) [10].



Scheme 2.

A reaction of chromocene with excess pivalic acid in heptane is accompanied by elimination of both cyclopentadienyl rings to give red crystals of, hypothetically, the dinuclear complex [$Me_3CCOOH \cdot$ Cr(μ-$OOCCMe_3)_4$Cr $\cdot$ $HOOCCMe_3$]. The complex extremely readily undergoes oxidation, is soluble even in pentane, is diamagnetic, and shows a quadruple bond between the Cr atoms [11], probably by analogy with dimeric Cr(II) diacetate hydrate.

Using stoichiometric amounts of the same reactants in benzene, Cotton et al. obtained the less soluble dimers [Cr(μ-$OOCCMe_3)_4Cr]_2$ also containing a quadruple Cr–Cr bond (2.388 Å). The dimers are united into chains through the O atoms of the pivalate bridges acting as axial ligands to the Cr atoms in adjacent molecules [12]. Obviously, because the Cr atom is substantially smaller than the V atom (1.39 and 1.53 Å, respectively [13]), the cyclopentadienyl ligand at the Cr atom can coexist with no more than three O atoms. If their electron-donating properties are sufficiently high (as in pivalates), the cyclopentadienyl ring is eliminated to be compensated by the formation of a short quadruple bond between the Cr atoms.

At the same time, titanocene dicarboxylate, $Cp_2Ti(OOCPh)_2$, containing a metal with a large covalent radius (1.60 Å [13]) and terminal benzoate groups is highly stable. For this reason, the formation of similar cyclopentadienyl dicarboxylate paddlewheels [Cp_2Ti_2(μ-$OOCPh)_4$] for Ti(III) is possible only when the monocyclopentadienyl complex $CpTi^{III}(BH_4)_2$ is used as a starting material for reactions with carboxylic acids. An X-ray diffraction study revealed only slight changes in the geometry of the dinuclear complexes compared to the vanadium complexes: the same short C···O contacts (~3.0 Å) and the nonbonding Ti···Ti distance (3.6 Å). However, the exchange parameter $-2J$ is increased sharply (up to 1000 cm^{-1}) [14].

Rakitin et al. [15] explained this phenomenon using an exchange channels model, in which the $-2J$ value is defined as the total antiferromagnetic exchange $-2J_\Sigma$ divided by a quadruplicate product of the spins ($4S_1S_2$) of the metal ions so that the complex will be antiferromagnetic as long as $-2J$ is lower than 1000 cm^{-1} (the condition for antiferromagnetism):

$$-2J = \frac{-2J_\Sigma}{4S_1S_2} = <1000\,\text{cm}^{-1}.$$

It is this relationship that accounts for the different exchange parameters of isostructural vanadium and titanium complexes: when the total interactions through carboxylate bridges are equal, the exchange parameter for vanadium with the spin $S = 1$ must be a quarter of that for titanium, which is observed experimentally.

If one takes into account that an exchange interaction of 300 cm^{-1} roughly corresponds to 1 kcal/mol, it becomes clear why the aforementioned dinuclear tetraphenyltriazene complex of Cu(II), in which the low spin $S = 1/2$ is combined with the presence of the Cu–Cu bond (2.44 Å), is diamagnetic. The same explanation is valid for the diamagnetism of dinuclear organometallic molecules ($Co_2(CO)_8$, $Mn_2(CO)_{10}$, and many others): because the spins of the metal ions are $S = 1/2$, even the quite weak Co–Co (9 kcal/mol) or Mn–Mn bonds (17 kcal/mol), which are prone to cleavage in solutions or during the sublimation of the complexes, do ensure the diamagnetism of the complexes.

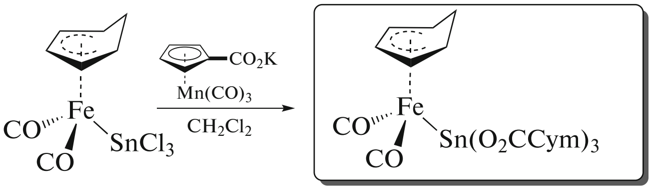
It should be emphasized that such ligand repulsion from all O atoms is not necessary. For instance, English chemists obtained green (tetrabenzoato)(diquinoline)dicobalt(II), $[C_9H_7NCo(\mu\text{-}OOCPh)_4NCoC_9H_7N]$; its short O···C contacts (3.1 Å) involve the phenylene C atom in the α-position relative to the N atom of the pyridine ring in either half of the complex. This makes the Co–O bonds nonequivalent and causes the exit of the Co atoms from the plane of the O atoms. No Co–Co bond is present (Co···Co, 2.83 Å) [16]. Interestingly, a pink polymer-network form of the same composition is unstable because of such an effect of ligand-ligand repulsion. This form seems to have an additional intermolecular coordination of cobalt to the carboxylate O atom of an adjacent molecule (so the coordination polyhedron is extended to an octahedron), is produced by prompt precipitation of the product from the reaction mixture, but turns dark green upon slow crystallization leading to a dinuclear paddle-wheel form with the pentacoordinated Co atom [17].

The green dinuclear form is also obtained with α-picoline (2-methylpyridine) as an axial ligand, while sterically unhindered γ-picoline yields only the pink polymeric form. An especially easy way to the green dinuclear form involves the use of disubstituted α-pyridines (lutidine and quinaldine) and phenazine forming green crystals of chains of dinuclear paddle-wheels, each having the phenazine halves as axial ligands [18].

Additional stabilization of the green dinuclear form is achieved with pivalic (trimethylacetic) acid, which not only makes pivalates well soluble in benzene but also lowers the probability of additional intermolecular coordination required for formation of the pink polymer form with an octahedral environment of the Co atoms [19] (because the pivalate groups are stronger electron donors).

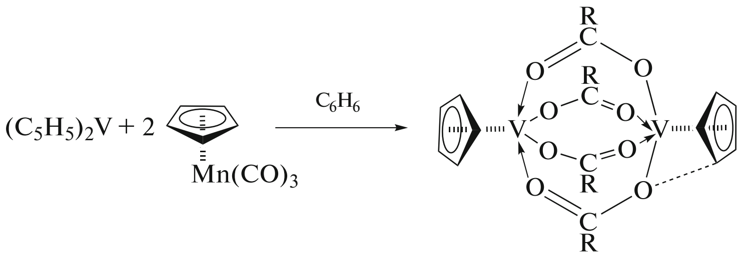
Finally, a combination of axial disubstituted α-pyridine ligands (specifically, quinaldine) and pivalate bridges [20] is of fundamental importance for the preparation of the green paddle-wheel dimers $[LNi^{II}(\mu\text{-}OOCR)_2]_2$, although the Ni^{2+} ion usually tends to produce blue monomers $L_2Ni(OOCR)_2$. The colorless, yellowish, or faintly greenish paddle-wheel dimers $[LMn^{II}(\mu\text{-}OOCR)_2]_2$ and the green complexes $[LFe^{II}(\mu\text{-}OOCCMe_3)_2]_2$ were synthesized in a similar way. All complexes of this type are antiferromagnetic; for the high-spin Mn^{2+} ions ($S = 5/2$), the $-2J$ values are low (25–30 cm^{-1}) since they are 25 times (!) lower than the total antiferromagnetic exchange (600–750 cm^{-1}). Unfortunately, iron complexes are very prone to oxidation, so we failed to obtain reliable magnetic data.

The above steric and electronic trends are appreciably different for cymantrenecarboxylate complexes with R = $C_5H_4Mn(CO)_3$ (Cym) in $RCOO^-$ (Scheme 3). Although the cymantrenyl moiety is bulky, three terminal cymantrenecarboxylate groups are readily arranged around the tetrahedral Sn atom bound to dicarbonyl(cyclohexadienyl)iron. All the three Sn–O bonds are single (2.057(2) Å), and the Fe–Sn bond remains strongly shortened to 2.4787(4) Å because of additional Fe → Sn dative interactions [21].



Scheme 3.

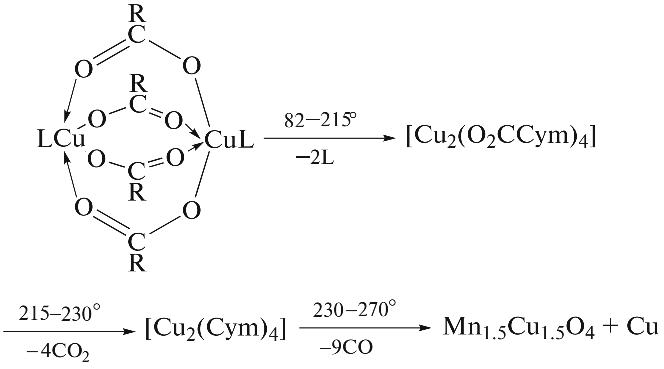
In the dinuclear vanadium cymantrenecarboxylate complex, as in other vanadium carboxylates (trifluoroacetate [6], furancarboxylate [7], and pivalate [20]), the carboxylate O atoms are repulsed from the C atoms of the cyclopentadienyl rings, which prevents the vanadium atoms from coming closer to each other (V···V, 3.650 Å) (Scheme 4) [22]:



$R = C_5H_4Mn(CO)_3$

Scheme 4.

However, dinuclear paddle-wheel complexes of the type $[LM^{II}(\mu\text{-OOCR})_2]$ (M = Cu, Co, or Ni) are formed only when the coordination of the axial ligands L (L = THF, Et_2O, PPh_3, or CymCOOH) is sterically unhindered. According to the TG data, these ligands are eliminated first in the pyrolysis, e.g., for a copper complex (Scheme 5). This is followed by decarboxylation and only then by decarbonylation of the cymantrenyl moieties. The final pyrolysis products are a mixed manganese–copper oxide and metallic copper [23]:



Scheme 5.

When bulky disubstituted α-pyridine ligands like lutidine (L) are used, the complexation gives no paddle-wheel dimers; instead, the reaction products are either the monomer $L_2Cu(OOCCym)_2$ with the *trans*-arranged terminal carboxylate groups or trinuclear complexes: the heteronuclear copper manganese complex $LCu(\mu\text{-OOCCym})_3Mn(\mu\text{-OOCCym})_3CuL$ [22] or the homonuclear cobalt complex $LCo(\mu\text{-OOCCym})_3Co(\mu\text{-OOCCym})_3CoL$ [24], in which the metal atoms are bridged by only three carboxylate groups. Apparently, the formation of four-bridge paddle-wheel dimers is precluded by the steric hindrances due to the bulky cymantrenyl moieties in the carboxylate groups. The arrangement of these moieties differs greatly from that of the bulky *tert*-butyl groups in pivalates as well as from that of the tetrahedron-like groups $CCo_3(CO)_9$. The coordination polyhedra of the central metal atoms, the terminal Co atoms, and the terminal Cu atoms are octahedra, distorted square pyramids, and distorted tetrahedra, respectively. It is worth noting that the Cu and Mn atoms are linked by bidentate bridges, while the Co atoms are linked by two bidentate and a monodentate bridge coordinated through one O atom (the other O atom is weakly bound to the terminal Co atom) [24] (Fig. 1).

The latter type of three-bridge asymmetric coordination is very interesting since this geometry is characteristic of complexes in which the monodentate carboxylate bridge is replaced by a F atom or an alkoxy group and which form a great family of cyclic molecular magnets. Their first examples were obtained by Lippard et al. (USA) for a decanuclear iron(III) complex [25] (Scheme 6) and by Gerbeleu, Timco, et al. (Moldavia) for the octanuclear complex (fluorido)(dipivalato)chromium (Scheme 7) housing two acetone molecules in its macrocycle [26]. It should be emphasized that benzene-soluble pivalates important for the synthesis of paddle-wheel dimers (see above) are also very useful for the synthesis of cyclic molecular magnets (Fig. 2).

$$[Fe_3O(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_3]NO_3 + 3Fe(NO_3)_3MeOH \rightarrow [Fe(\mu\text{-}OMe)_2(\mu\text{-}O_2CCH_2Cl)]_{10}$$

Scheme 6.

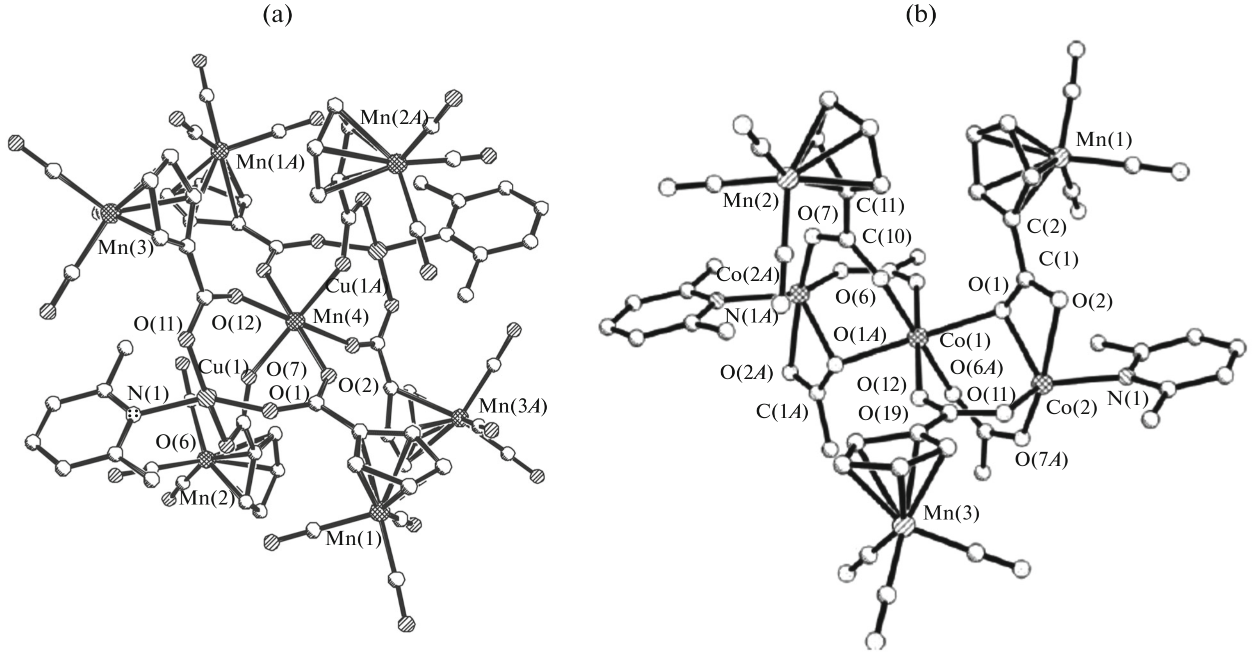


Fig. 1. Complex LCu(μ-OOCCym)$_3$Mn(μ-OOCCym)$_3$CuL (a) and the trinuclear cobalt complex LCo(μ-OOCCym)$_3$Co(μ-OOCCym)$_3$CoL (b); L is lutidine.

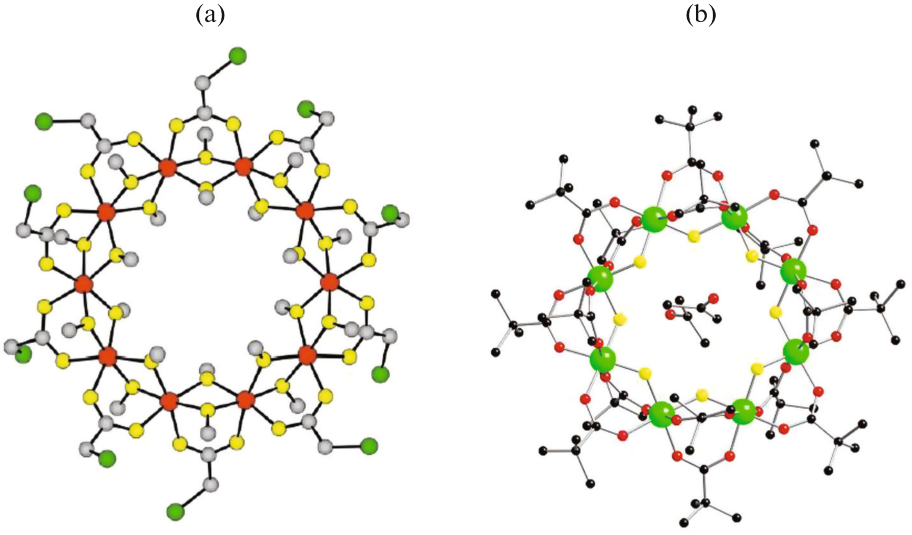
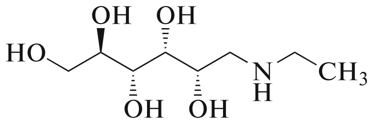


Fig. 2. Decanuclear Fe(III) complex with the methoxy and chloroacetate ligands (a) and the octanuclear Cr(III) complex with the fluoride and pivalate ligands and with two guest acetone molecules (b).

$$\mathrm{CrF_3 \cdot 4H_2O\ + Me_3CCOOH + Me_2NCOH \rightarrow [Cr(\mu\text{-}F)(\mu\text{-}OOCMe_3)_2]_8 \cdot 2(Me_2CO)}$$

Scheme 7.

This raises some questions: how is the macrocycle formed, what are the factors regulating its size, and what is the role of molecules or cations inside the macrocycle? According to Timco, who has transferred from Moldova to England to work in the laboratory headed by R. Winpenny in Manchester, these endocyclic compounds function as templates controlling the formation of macrocycles. However, only *N*-ethyl-D-glucamine (H_5Etglu)



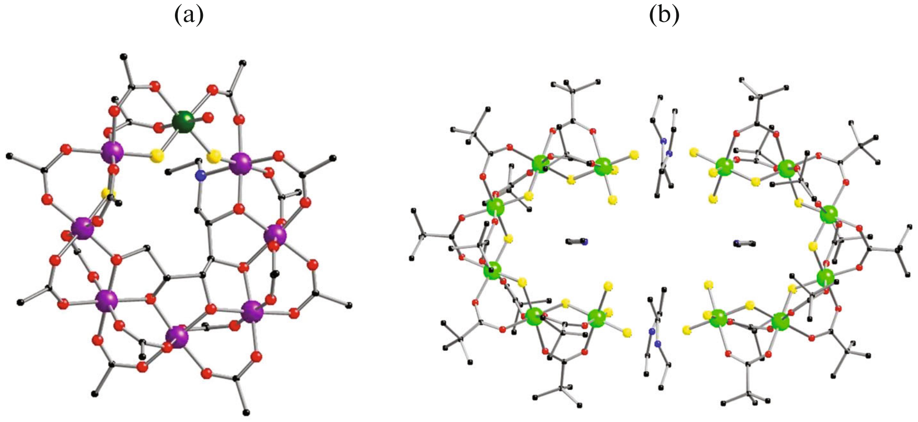


Fig. 3. Octanuclear chromium-nickel macrocycle $[Cr_7Ni(\mu\text{-}F)_3(\mu\text{-}Etglu)(\mu\text{-}O_2CCMe_3)_{15}(H_2O)]$ (a) and the pseudoring made up of two anionic six-membered horseshoes of the Cr atoms bridged by the fluoride and pivalate ligands (the horseshoes are linked by the diethylamine cations) (b).

may be considered the true template used. This compound is housed instead of five F atoms to give purple crystals of the octanuclear chromium-nickel complex $[Cr_7Ni(\mu\text{-}F)_3(\mu\text{-}Etglu)(\mu\text{-}O_2CCMe_3)_{15}(H_2O)]$; the hydrocarbon part of the template is in the macrocyclic cavity [27] (Fig. 3).

The key factor found by English chemists is the intermediate formation of anionic "horseshoes" of different length that are stabilized by substituted ammonium cations hydrogen-bonded to fluoride bridges. This meets the conditions for crystallization of green pseudocyclic ionic complexes [28]:

$$3CrF_3 \cdot 4H_2O + 18{}^tBuCO_2H + 2Et_2NH \rightarrow [Et_2NH_2]_3[Cr_6(\mu\text{-}F)_{11}(\mu\text{-}O_2C{}^tBu)_{10}]\}_2.$$

An alternative way to limit the chain growth for pivalate fluoride complexes of M^{3+} ions (M = Cr, Fe, V, Ga, Al, and In) involves their ring closure via addition of a heterometal atom, specifically an M^{2+} ion (M = Ni, Co, Mn, Fe, Zn, Cd, Mg, Ca, Sr, and Cu), in combination with secondary amines R_2NH, which are transformed into endocyclic ammonium cations [29]:

$$7CrF_3 \cdot 4H_2O + 16{}^tBuCO_2H + R_2NH + M^{2+} \rightarrow [R_2NH_2][Cr_7M(\mu\text{-}F)_8(\mu\text{-}O_2C{}^tBu)_{16}].$$

Ring closure is possible for not only seven-membered but also six-, eight-, and nine-membered horseshoes; moreover, not only one but two metal heteroatoms (including lanthanides and different metal atoms) can be employed for this purpose. It is worth noting that branched secondary amines are required for the enlargement of the macrocycle because they produce the corresponding endocyclic ammonium cations favoring crystallization of ionic complexes. Alternatively, an alkali metal ion should be added as an endocyclic cation: $[(Cy\text{-}C_6H_{11})_2NH_2][Cr_7(VO)_2F_9(OOCMe_3)_{17}]$ [30] and $\{CsCr_7CoF_8(O_2C{}^tBu)_{16}\}$ ([16]-MC-8, fluorometallocrown) [31] (Fig. 4).

Furthermore, four-, five-, six-, and seven-membered horseshoes can be joined together to give macrocycles or "eyeglasses" by including two individual heterometal atoms, e.g., copper(II) atoms coordinated by benzimidazole [32] or gadolinium(III) atoms bridged by pivalate ligands inside the macrocycle [33]:

$$\begin{gathered}(C_7H_6N_2H)_2[Cr_8Cu_2(\mu\text{-}F)_{14}(\mu\text{-}O_2CCMe_3)_{16}(C_7H_6N_2)_2]\\ (Et_2NH_2)_2Gd_2Cr_{12}(\mu\text{-}F)_{18}(\mu\text{-}O_2CCMe_3)_{26} \qquad \text{(Fig. 5).}\end{gathered}$$

Finally, cyclization into a Cr_7Ni complex in the presence of a reduced Schiff base affords the pyridine-containing rotaxane $[NC_5H_4CH_2NH_2CH_2C_6H_4SMe][Cr_7Ni(\mu\text{-}F)_8(\mu\text{-}O_2C{}^tBu)_{16}]$ [34] (Fig. 6).

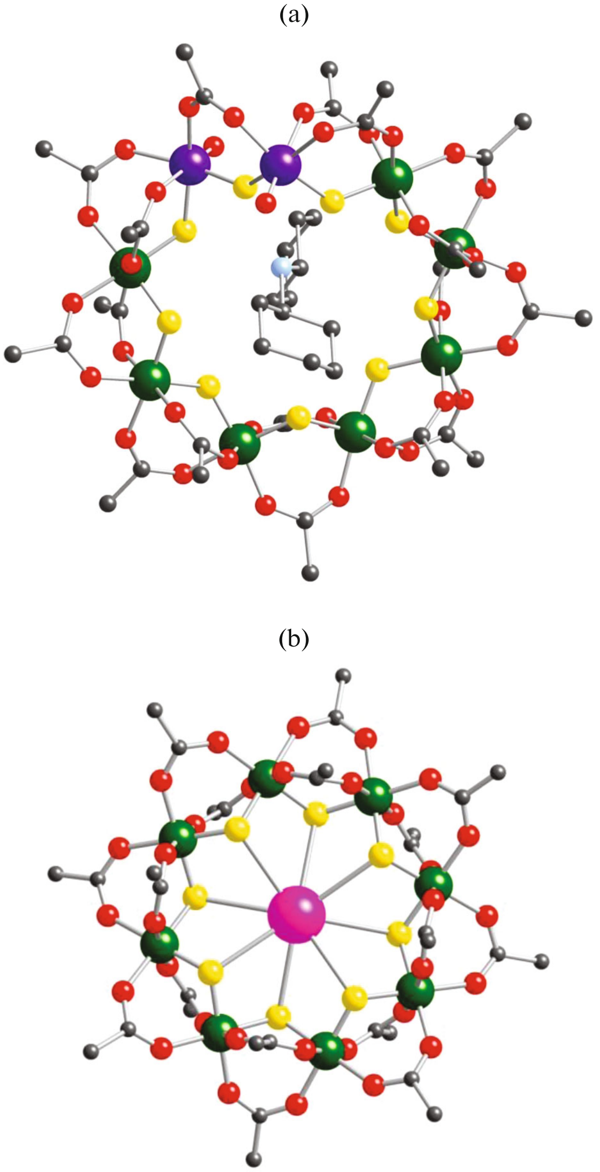


Fig. 4. Nonanuclear macrocycle made up of seven Cr atoms and two VO groups bridged by the fluoride and pivalate ligands, with the endocyclic dicyclohexylammonium cation (a) and the octanuclear anionic macrocycle $\{CsCr_7CoF_8(O_2C^tBu)_{16}\}$ containing the endocyclic Cs^+ cation (b).

Two molecules of this complex can in turn coordinate through the pyridine N atoms with dinuclear copper pivalate to give a new rotaxane complex, $\{[NC_5H_4CH_2NH_2CH_2C_6H_4SMe][Cr_7Ni(\mu\text{-}F)_8(\mu\text{-}O_2C^tBu)_{16}]\}_2[Cu_2(\mu\text{-}O_2C^tBu)_4]$ [34] (Fig. 7).

Such an approach to the formation of heterometallocycles containing pivalate and fluoride ligands has culminated in the synthesis of Cr-Co and Cr-Cu rotaxanes and molecular shuttles [35] (Fig. 8).

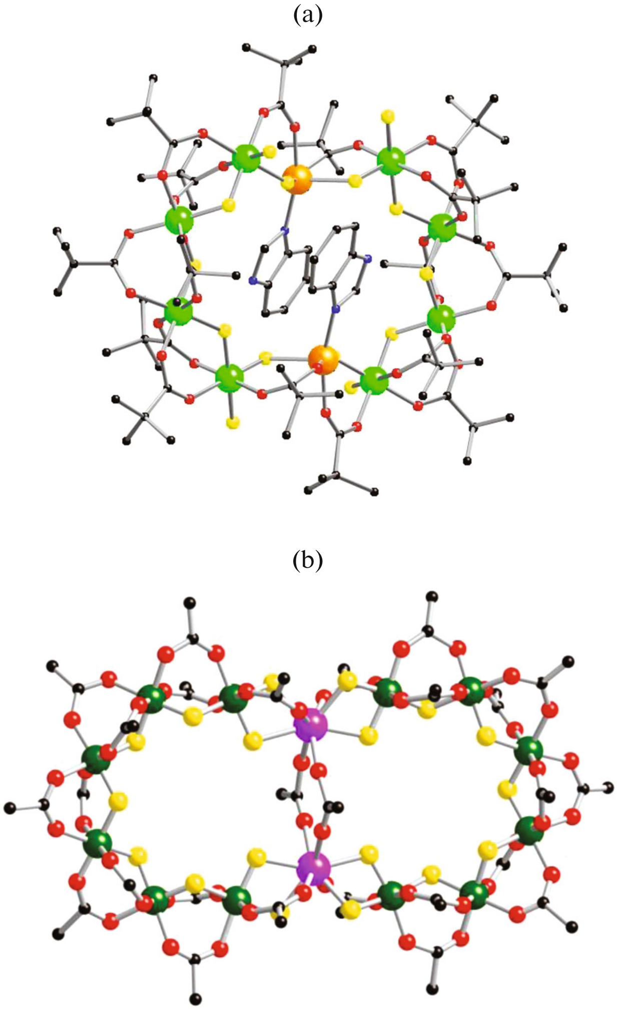


Fig. 5. Decanuclear macrocycle made up of two tetrachromium horseshoes linked by two copper-benzimidazole moieties (a) and the eyeglasses-like 14-nuclear dianion made up of two hexachromium horseshoes linked by the (dipivalato)digadolinium moiety (b).

To sum up, we can note that axial cyclopentadienyl and α-substituted pyridine ligands presenting steric hindrances because of the repulsion from the O atoms of the carboxylate bridges are decisive for the formation of four-bridge paddle-wheel dimers. However, bulky cymantrenyl substituents in cymantrenecarboxylates preclude the formation of four-bridge structures for disubstituted α-pyridines (lutidine) to give the monomers $L_2Cu(OOCCym)_2$ containing terminal carboxylate groups or three-bridge complexes (for manganese and cobalt). In the case of cyclic heterometallic chromium(III) complexes with pivalate and fluoride ligands, which possess the properties of molecular magnets, their growth is limited by hydrogen bonding between the fluoride

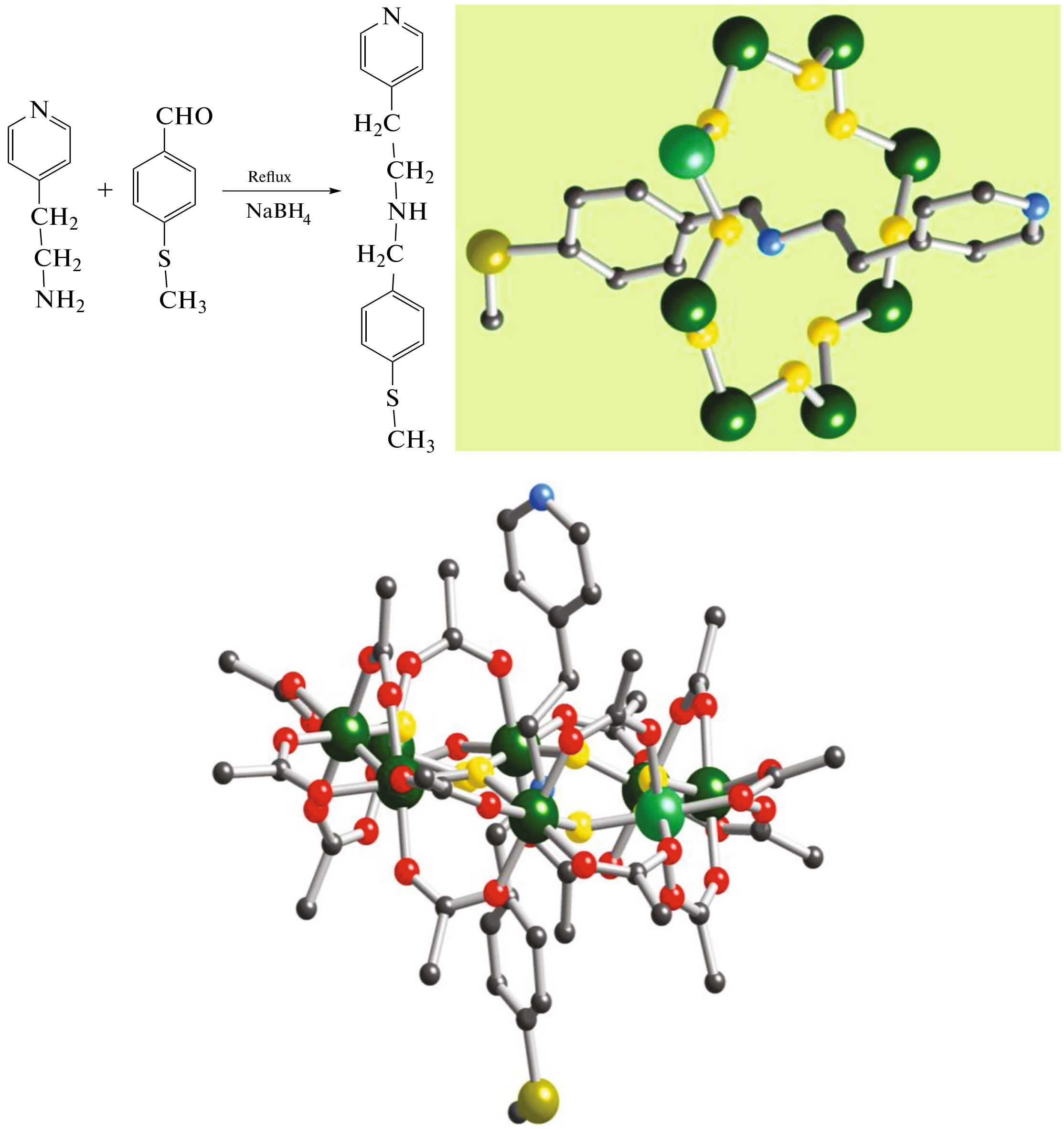


Fig. 6. Synthesis and structure of the octanuclear Cr-Ni macrocycle in the rotaxane $[NC_5H_4CH_2NH_2CH_2C_6H_4SMe][Cr_7Ni(\mu\text{-}F)_8(\mu\text{-}O_2C^tBu)_{16}]$.

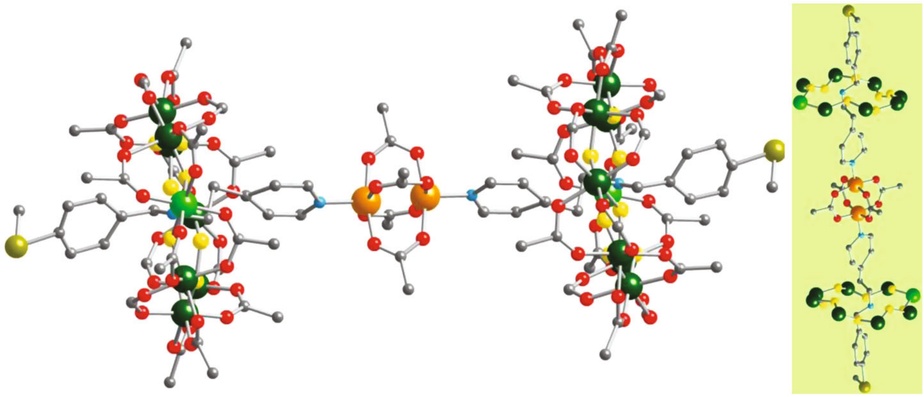


Fig. 7. Rotaxane complex with (tetrapivalato)dicopper as a held molecule, $\{[NC_5H_4CH_2NH_2CH_2C_6H_4SMe][Cr_7Ni(\mu\text{-}F)_8(\mu\text{-}O_2C^tBu)_{16}]\}_2[Cu_2(\mu\text{-}O_2C^tBu)_4]$.

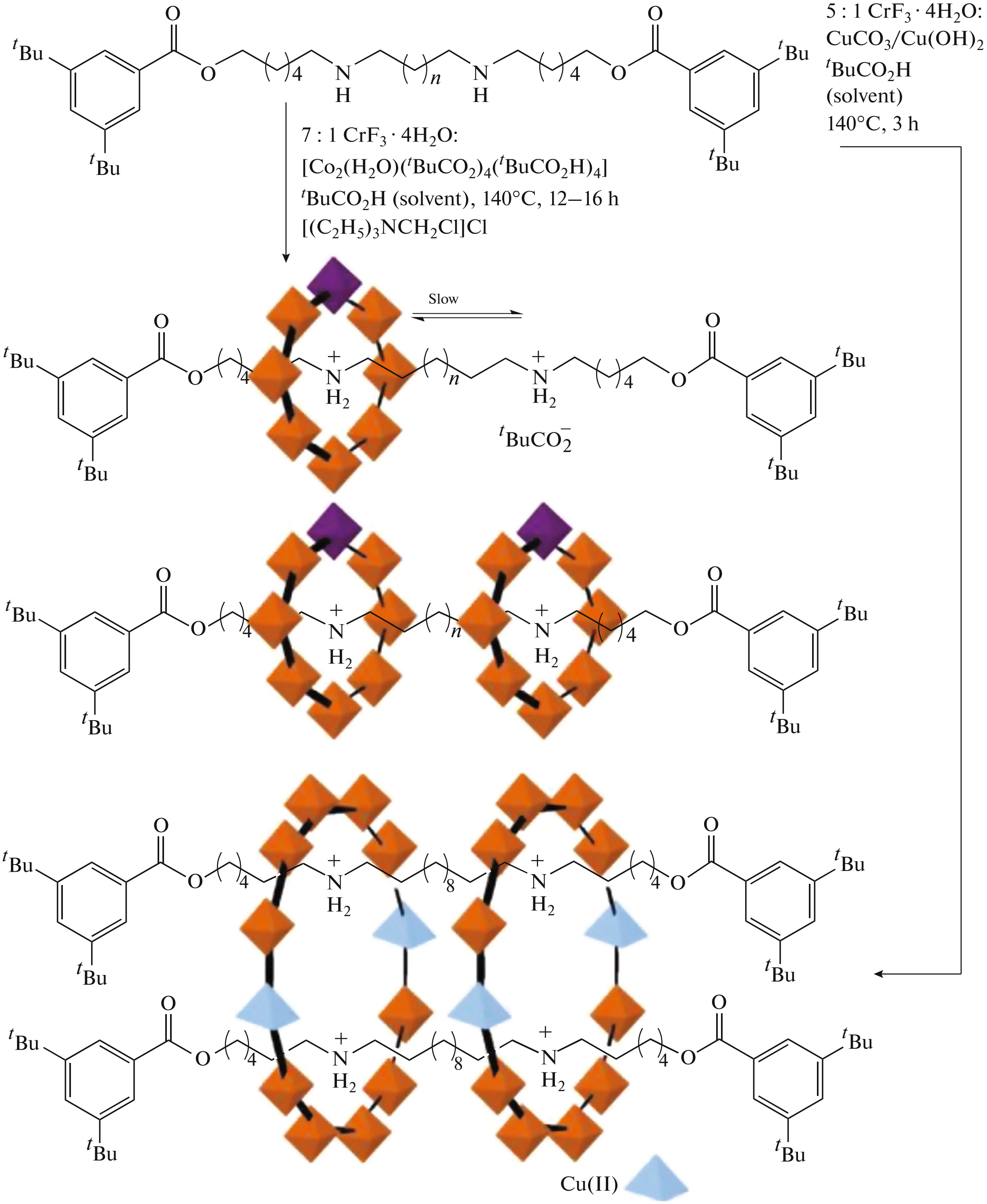


Fig. 8. Synthesis and structure of the Cr-Co rotaxane and the Cr-Cu shuttle.

bridges and the outer-sphere ammonium cations, which are housed in the macrocycles and favor crystallization of certain (including rotaxane and shuttle structures).

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