Formation of amidine ligands in coordination spheres of Co^{II} and Ni^{II} atoms

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Reactions of polynuclear cobalt and nickel pivalates with amines in MeCN afforded compounds containing the amidine ligands (MeC(NHR)=NH). The reactions with 2,6-diaminopyridine yielded the $Ni(Me_3CCOO)_2\{H_2N(C_5H_3N)NHC(Me)=NH\}$, $Co_2(Me_3CCOO)_4\{H_2N(C_5H_3N)NHC(Me)=NH\}$, $Co(Me_3CCOO)_2\{H_2N(C_5H_3N)NHC(Me)=NH\}$ complexes and the solvate of the latter with Me_3CCOH and C_6H_6. The reaction with *S*-(−)-α-methylbenzylamine gave rise to the ionic chiral compound with composition $[PhCH(Me)NHC(Me)NH_2]^+[Co_2(Me_3CCOO)_5]^-$ as a diastereomeric salt. According to the results of X-ray diffraction analysis, the asymmetric carbon atom in the cation and the asymmetric cobalt atom in the binuclear anion of this salt have the *S* absolute configuration.* The compounds were characterized by elemental analysis data and the results of IR and electronic spectroscopy. Their structures were established by X-ray diffraction analysis. The chiroptical properties of the ionic compound in solution were studied by circular dichroism spectroscopy.

Key words: amidines, cobalt trimethylacetate complexes, nickel trimethylacetate complexes, X-ray diffraction analysis, electronic spectra, optical activity.

It is known that the reactions of amines with nitriles RC≡N readily proceed provided that either the substituent R is a strong electron acceptor or the reaction is catalyzed by the Friedel—Crafts catalysts.[2] Acetonitrile is generally not involved in such reactions and is often used as an inert solvent in organic synthesis.[2] However, coordination of nitriles by metal atoms leads to the electron density redistribution in the C≡N fragment, which can increase its reactivity.[3] In coordinated aromatic amines, the amino group exhibits activity in the reactions with aldehydes, ketones, or other oxygen-containing compounds.[4—6] Studies of the reaction products of cobalt and nickel trimethylacetate complexes with amines in acetonitrile demonstrated that these reactions did not produce complexes containing charged ligands or neutral molecules formed due to interactions of amines with MeCN.[7—10] Apparently, inertness of acetonitrile in these processes is associated with fairly mild conditions of the synthesis and isolation of reaction products as well as with the nature of amine. At the same time, it cannot be excluded that the reactions of amines with acetonitrile proceeded but amounts of compounds with new ligands were too low to be detected. In the present study, we report the results of detailed study of the reactions of polynuclear cobalt trimethylacetate complexes with 2,6-diaminopyridine and *S*-(−)-α-methylbenzylamine in the presence of MeCN, which demonstrate possibilities of its direct interaction with coordinated amine molecules. Taking into account that numerous reactions in coordination chemistry are carried out in acetonitrile and these investigations are often concerned with transition metal amino complexes, it is, in our opinion, of considerable importance to find the conditions under which coordinated amines can interact with this solvent.

Results and Discussion

Recently, we have demonstrated that the reaction of the polymeric cobalt trimethylacetate complex $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ [11] (**1**) with 2,6-diaminopyridine in CH_2Cl_2 afforded the binuclear complex

* The notations *S* and *R* for the metal centers in an octahedral environment were given in the monograph by C. I. Hawkins:[1] *S* and *R* correspond to the Δ and Λ configurations, respectively.

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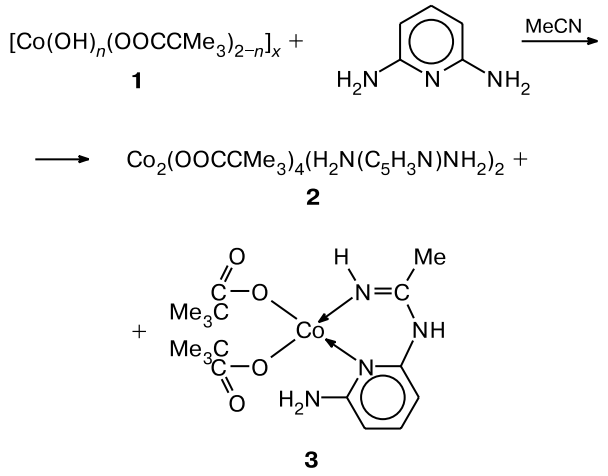
$Co_2(OOCCMe_3)_4(H_2N(C_5H_3N)NH_2)_2$ (**2**) with a Chinese-lantern-like structure as the major product (in 86% yield).[12] It was found that the reaction in acetonitrile afforded compound **2** (in a yield of up to 40%) and the mononuclear complex $Co(OOCCMe_3)_2\{H_2N(C_5H_3N)NHC(Me)=NH\}$ (**3**) (Scheme 1) containing the chelate-coordinated ligand, which is a product of interaction of the amine with acetonitrile. The yield of complex **3** was 10—25% depending on the temperature and the ratio between the starting components.

Scheme 1



In complex **3** (Fig. 1, Table 1), the cobalt atom is bound to two oxygen atoms of the monodentately coordinated pivalate ligands ($Co—O(OOCCMe_3)_{conc}$, 1.939(4) Å and 1.961(4) Å; the Co—O(2) and Co—O(4) distances (3.312 Å and 3.079 Å, respectively) are nonbonded). These oxygen atoms together with two nitrogen atoms of the chelate-coordinated molecule of the amidine derivative (Co—N(4), 1.939(4) Å; Co—N(1), 2.022(5) Å; the $Co...N_{NH_2}(3)$ distance (3.025(5) Å) is nonbonded) form a distorted tetrahedral environment about the metal atom. The chelate-coordinated *N*-(6-amino-2-pyridyl)acetamidine molecule and the cobalt atom are in a single plane to form a six-membered metallocycle. The C—N bonds in the amidine ligand are equalized (C(16)—N(3), 1.297(6) Å; C(16)—N(2), 1.308(6) Å), which is typical of the coordinated amidine molecules.[13] Formally, this is associated with the virtually equal contributions of two tautomeric forms (**A** and **B**) to the real structure of the coordinated amidine derivative:

Table 1. Selected geometric characteristics of complexes **3** and **3a**

Bond	*d*/Å	Angle	ω/deg
		Complex **3**	
Co(1)—O(1)	1.939(4)	O(1)—Co(1)—N(4)	123.80(18)
Co(1)—N(4)	1.939(4)	O(1)—Co(1)—O(3)	91.60(19)
Co(1)—O(3)	1.961(4)	N(4)—Co(1)—O(3)	122.22(17)
Co(1)—N(1)	2.022(5)	O(1)—Co(1)—N(1)	109.99(18)
		N(4)—Co(1)—N(1)	93.22(18)
		O(3)—Co(1)—N(1)	117.64(17)
		Solvate **3a**	
Co(1)—O(1)	1.959(3)	O(1)—Co(1)—N(3)	129.68(13)
Co(1)—N(3)	1.950(3)	O(1)—Co(1)—O(3)	101.88(12)
Co(1)—O(3)	2.001(3)	N(3)—Co(1)—O(3)	114.65(12)
Co(1)—N(1)	2.054(3)	O(1)—Co(1)—N(1)	113.07(13)
		N(3)—Co(1)—N(1)	92.23(13)
		O(3)—Co(1)—N(1)	102.39(12)

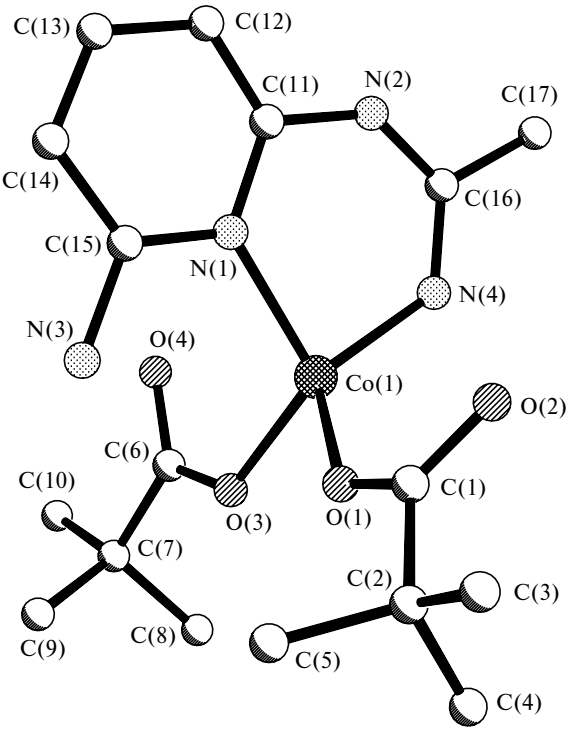
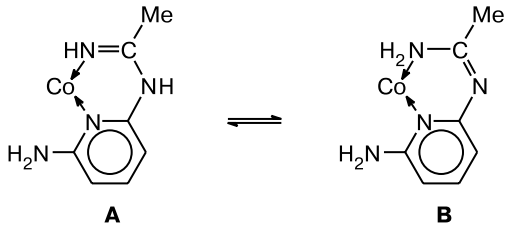


Fig. 1. Structure of complex **3**.



The formation of compound **3** was also observed in the reaction of 2,6-diaminopyridine with another metal-containing agent, *viz.*, the binuclear antiferromagnetic complex $Co_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**4**); the effective magnetic moment varies from 6.902 μ_B (300 K) to 1.110 μ_B (2 K). This complex is formed as the second product (in 20% yield) in the synthesis of the

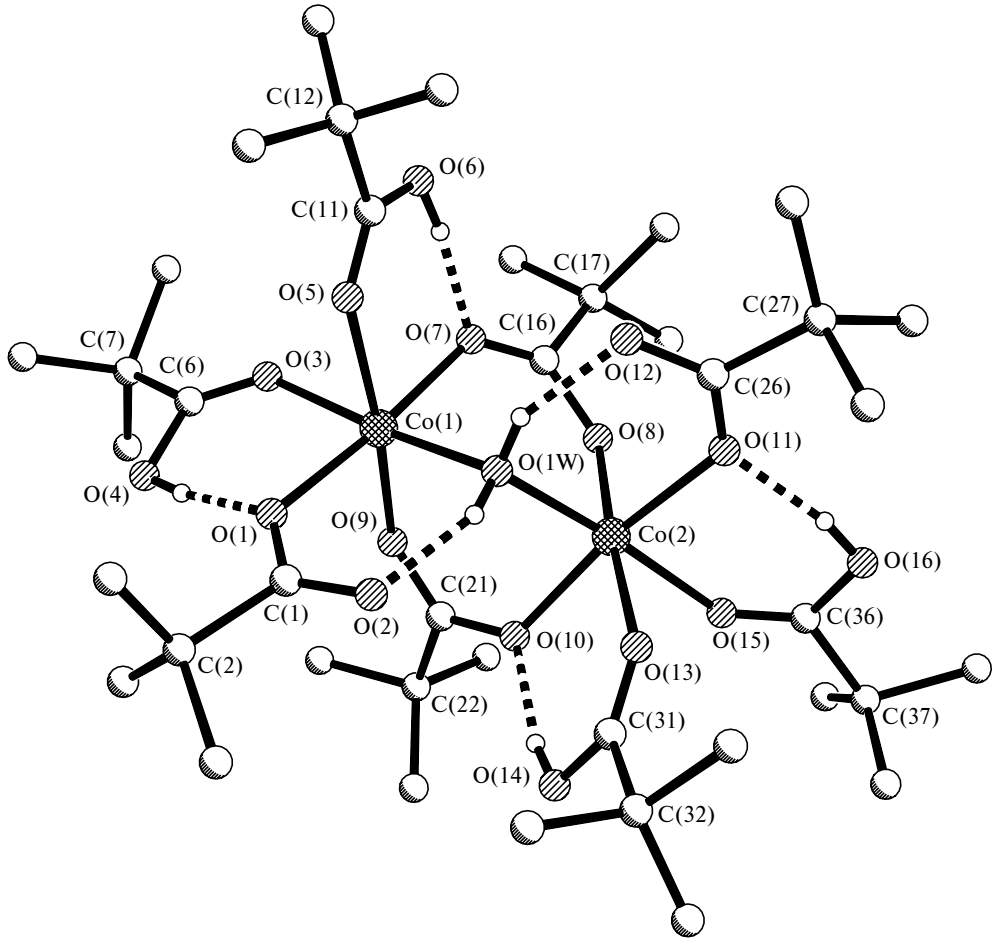


Fig. 2. Structure of complex **4**.

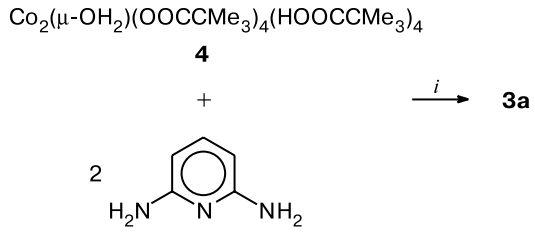
hexamer $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ by thermolysis of the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer in hexane.[11] According to the X-ray diffraction data (Fig. 2, Table 2), binuclear complex **4** contains the $Co_2(\mu\text{-}OOCCMe_3)_2(\mu\text{-}OH_2)$ fragment (Co...Co, 3.405(2) Å), whose geometric characteristics are analo-

Table 2. Selected geometric characteristics of complex **4**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Co(1)...Co(2)	3.405(2)	O(1W)—Co(1)—O(1)	91.2(3)	O(1W)—Co(2)—O(8)	94.7(3)
Co(1)—O(1W)	2.091(5)	O(1W)—Co(1)—O(3)	175.2(3)	O(1W)—Co(2)—O(10)	92.0(3)
Co(1)—O(1)	2.051(8)	O(1W)—Co(1)—O(5)	88.9(3)	O(1W)—Co(2)—O(11)	91.9(3)
Co(1)—O(3)	2.103(8)	O(1W)—Co(1)—O(7)	91.9(3)	O(1W)—Co(2)—O(13)	87.6(3)
Co(1)—O(5)	2.111(8)	O(1W)—Co(1)—O(9)	97.7(3)	O(1W)—Co(2)—O(15)	173.2(3)
Co(1)—O(7)	2.044(7)	O(1)—Co(1)—O(3)	89.6(3)	O(8)—Co(2)—O(10)	95.3(3)
Co(1)—O(9)	2.023(7)	O(1)—Co(1)—O(5)	90.9(3)	O(8)—Co(2)—O(11)	91.1(3)
Co(2)—O(1W)	2.050(6)	O(1)—Co(1)—O(7)	176.0(3)	O(8)—Co(2)—O(13)	176.1(3)
Co(2)—O(8)	2.043(7)	O(1)—Co(1)—O(9)	87.8(3)	O(8)—Co(2)—O(15)	92.1(3)
Co(2)—O(10)	2.032(8)	O(3)—Co(1)—O(5)	86.4(3)	O(10)—Co(2)—O(11)	172.2(3)
Co(2)—O(11)	2.049(7)	O(3)—Co(1)—O(7)	87.2(3)	O(10)—Co(2)—O(13)	87.8(3)
Co(2)—O(13)	2.114(8)	O(3)—Co(1)—O(9)	87.0(3)	O(10)—Co(2)—O(15)	86.5(3)
Co(2)—O(15)	2.068(8)	O(5)—Co(1)—O(7)	86.4(3)	O(11)—Co(2)—O(13)	85.7(3)
		O(5)—Co(1)—O(9)	173.3(3)	O(11)—Co(2)—O(15)	88.8(3)
		O(7)—Co(1)—O(9)	94.4(3)	O(13)—Co(2)—O(15)	85.7(3)

gous to the corresponding characteristics of the $Py_2Co_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)(OOCR)_2$ complex (R = CMe_3) described earlier.[14]

The presence of coordinated Me_3CCOOH molecules in the starting reagent **4** influences the composition of the reaction product. Thus, the reaction afforded the solvate $Co(OOCCMe_3)_2\{H_2N(C_5H_3N)N(H)C(Me)=NH\}\cdot Me_3CCOOH\cdot 1/2C_6H_6$ (**3a**) (see Table 1) with the molecules of trimethylacetic acid and benzene.



i. Hexane—benzene, recrystallization from a benzene—MeCN mixture.

It should be noted that the reaction was carried out in a nonpolar (hexane—benzene) medium, whereas acetonitrile was used only in the step of growth of single crystals suitable for X-ray diffraction study.

In the crystal, molecules **3** interact with each other through the O(2)...H—N(2) and N(2)—H...O(2) hydrogen bonds to form centrosymmetric binuclear fragments, which, in turn, are linked to the adjacent dimers through the N(3)—H...O(4) (O(4)...H—N(3)) hydrogen bonds. Presumably, the presence of such associates in the crystal of complex **3** is responsible for the unusual magnetic behavior of this compound (Fig. 3). In spite of the fact that compound **3** is formally a monomer, it exhibits the ferromagnetic type of spin-spin exhcange interactions at helium temperatures due to intermolecular interactions. At 2 K, the hysteresis loop is observed with a coercive force of 2 kOe (Fig. 4).

Although binuclear complex **2**, which is formed in all solvents as the major product,[12] can serve as the starting compound in the synthesis of **3**, it appeared that refluxing

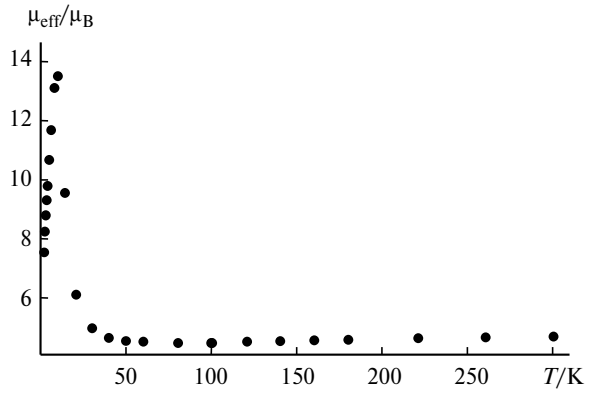


Fig. 3. Temperature dependence of μ_{eff} for complex **3**.

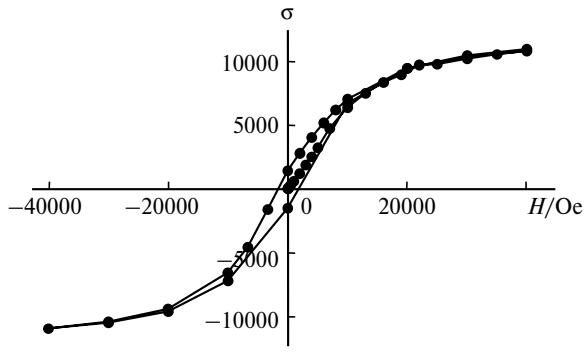
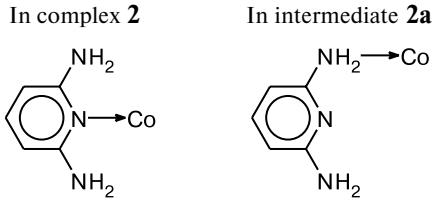


Fig. 4. Plot for magnetization of complex **3** *vs*. magnetic field strength at 2 K.

of **2** in acetonitrile for several hours did not lead to the formation of **3**. Presumably, unstable intermediate **2a** produced in the initial step of the reaction serves as an active intermediate in the process giving rise to **3**. In intermediate **2a**, the diaminopyridine ligand is coordinated to the metal atom through the amino group NH_2 rather than through the nitrogen atom of the pyridine ring, as was observed for "inert" isomer **2**.[12] In this case, the amino group in intermediate **2a** is activated and ready to the reaction with the nitrile fragment.

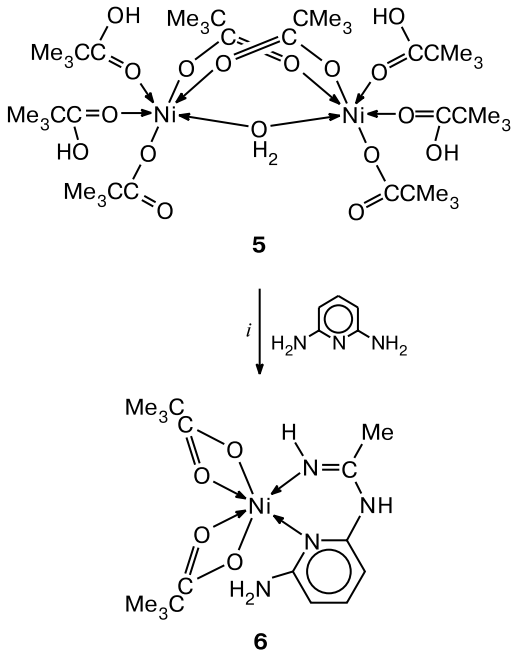


Although attempts to isolate and characterize intermediate **2a** failed, this mode of coordination of diamine ligands (through the amino group) in a binuclear system with a lantern structure has been observed in our recent study of the nickel complex $(NPhHC_6H_4NH_2)_2Ni_2(OOCCMe_3)_4$.[15]

The interaction of 2,6-diaminopyridine with acetonitrile was observed also in the presence of the nickel analog of complex **4**, *viz*., the binuclear ferromagnetic complex $Ni_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**5**) (Scheme 2).[16]

In this reaction, the mononuclear nickel(II) complex $Ni(OOCCMe_3)_2\{H_2N(C_5H_3N)NHC(Me)=NH\}\cdot MeCN$ (**6**) (Fig. 5, Table 3) was isolated in low yield (7%). In this complex, like in complex **3**, the molecule of *N*-(6-amino-2-pyridyl)acetamidine that formed is coordinated to the metal atom in a chelate fashion (Ni—N, 1.967(4) Å and 2.097(3) Å; the Ni...N_{NH_2} distance (3.119(3) Å) is nonbonded). Two trimethylacetate anions are coordinated in a chelate fashion (Ni—O, 2.060(3)—2.154(3) Å). Therefore, the nickel atom is an octahedral environment formed by two nitrogen and four oxygen atoms.

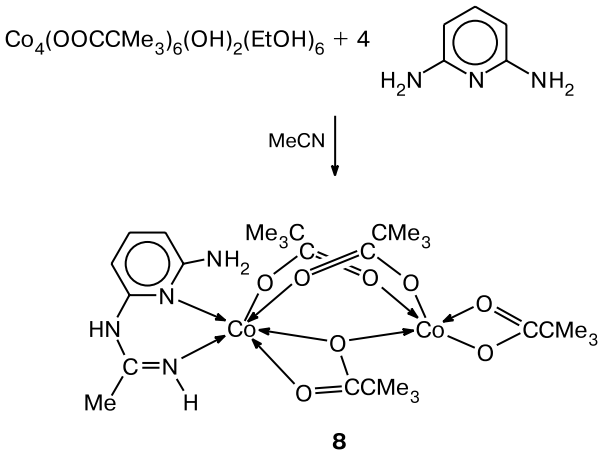
Scheme 2



i. Ni : L = 1 : 1, benzene, air, recrystallization from MeCN.

The structures and compositions of the reaction products of the cobalt trimethylacetate complexes with 2,6-diaminopyridine depend substantially on the nature of the starting polynuclear trimethylacetate compound and reaction conditions. For example, the reaction with the use of the tetranuclear complex $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(EtOH)_6$ as the starting reagent at the ratio Co : L = 2 : 1 and 40 °C afforded the tetranuclear complex $Co_4(\mu_4\text{-}O)(\mu\text{-}H_2N(C_5H_3N)NH_2)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2$ (**7**) as the major product (in 61% yield).[12] However, the reaction performed at 80 °C gave rise not only to complex **7** but also to amidine monomer **3** in a substantial amount. By contrast, an increase in the amount of the starting 2,6-diaminopyridine (Co : L = 1 : 1) led to the formation of a new reaction product, *viz.*, the asymmetric binuclear complex $Co_2(OOCCMe_3)_4\{H_2N(C_5H_3N)NHC(Me)=NH\}$ (**8**, in 9% yield) in which the metal atoms are in a different ligand environment (Scheme 3).

Scheme 3



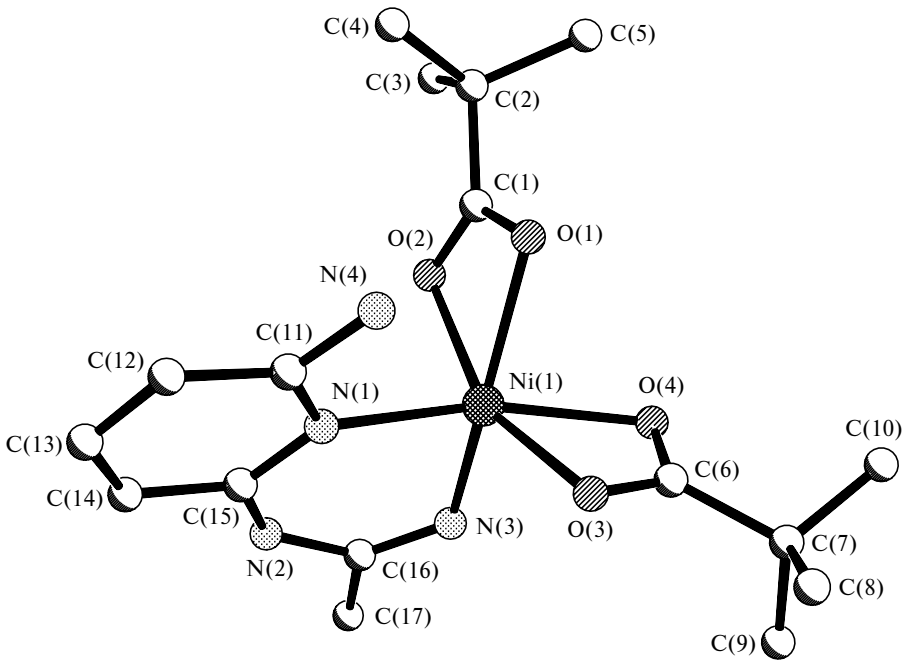


Fig. 5. Structure of complex **6**.

Table 3. Selected geometric characteristics of complex **6**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ni(1)—N(3)	1.967(4)	N(3)—Ni(1)—O(3)	98.59(15)	O(2)—Ni(1)—O(1)	61.60(11)
Ni(1)—O(3)	2.060(3)	N(3)—Ni(1)—N(1)	89.46(14)	N(3)—Ni(1)—O(4)	88.30(14)
Ni(1)—N(1)	2.097(3)	O(3)—Ni(1)—N(1)	101.76(13)	O(3)—Ni(1)—O(4)	62.51(12)
Ni(1)—O(2)	2.127(3)	N(3)—Ni(1)—O(2)	99.73(14)	N(1)—Ni(1)—O(4)	163.52(13)
Ni(1)—O(1)	2.138(3)	O(3)—Ni(1)—O(2)	156.85(12)	O(2)—Ni(1)—O(4)	104.02(12)
Ni(1)—O(4)	2.154(3)	N(1)—Ni(1)—O(2)	92.46(13)	O(1)—Ni(1)—O(4)	85.66(12)
		N(3)—Ni(1)—O(1)	158.06(15)	N(3)—Ni(1)—C(6)	92.88(15)
		O(3)—Ni(1)—O(1)	97.25(12)	O(3)—Ni(1)—C(6)	31.27(14)
		N(1)—Ni(1)—O(1)	102.05(13)		

In compound **8** (Fig. 6, Table 4), one of the cobalt atoms bound to the chelate-coordinated amidine molecule (N(3)—C(26), 1.317(18) Å; C(26)—N(4), 1.321(18) Å) is in an octahedral environment formed by four oxygen atoms of three pivalate ligands (two bidentate-bridging (Co(2)—O(μ-$OOCCMe_3$), 2.040(8) and 2.109(9) Å) and one chelate-bridging (Co(2)—O(4), 2.217(9) Å; Co(2)—μO(μ,η^2-$OOCCMe_3$), 2.010(8) Å)) and two nitrogen atoms of the amidine molecule (Co(2)—N(4), 2.009(10) Å; Co(2)—N(1), 2.162(11) Å; the Co(2)...N_{NH_2} distance (3.248(7) Å) is nonbonded). The second cobalt atom is in a trigonal-bipyramidal donor environment consisting only of the oxygen atoms of the pivalate ligands, *viz.*, one chelate ligand (Co(1)—O(η^2-$OOCCMe_3$), 2.044(8)—2.296(7) Å), two bidentate-bridging ligands (Co(1)—O(μ-$OOCCMe_3$), 1.977(8) and 1.978(8) Å), and one chelate-bridging ligand (Co(1)—μO(μ,η^2-$OOCCMe_3$), 2.010(8) Å). In complex **8**, the cobalt atoms are located at a nonbonded distance (3.360(8) Å). It should be noted that neutral complex **8** crystallizes in the chiral space group $P2_12_12_1$. We studied a single crystal in which the octahedrally coordinated cobalt atom has the *R* configuration.

The observed spontaneous separation of chiral isomers upon crystallization of complex **8** is indicative of a high degree of asymmetry of the metal core in such complexes. With the aim of enhancing asymmetric induction, we used optically active amine, *viz.*,

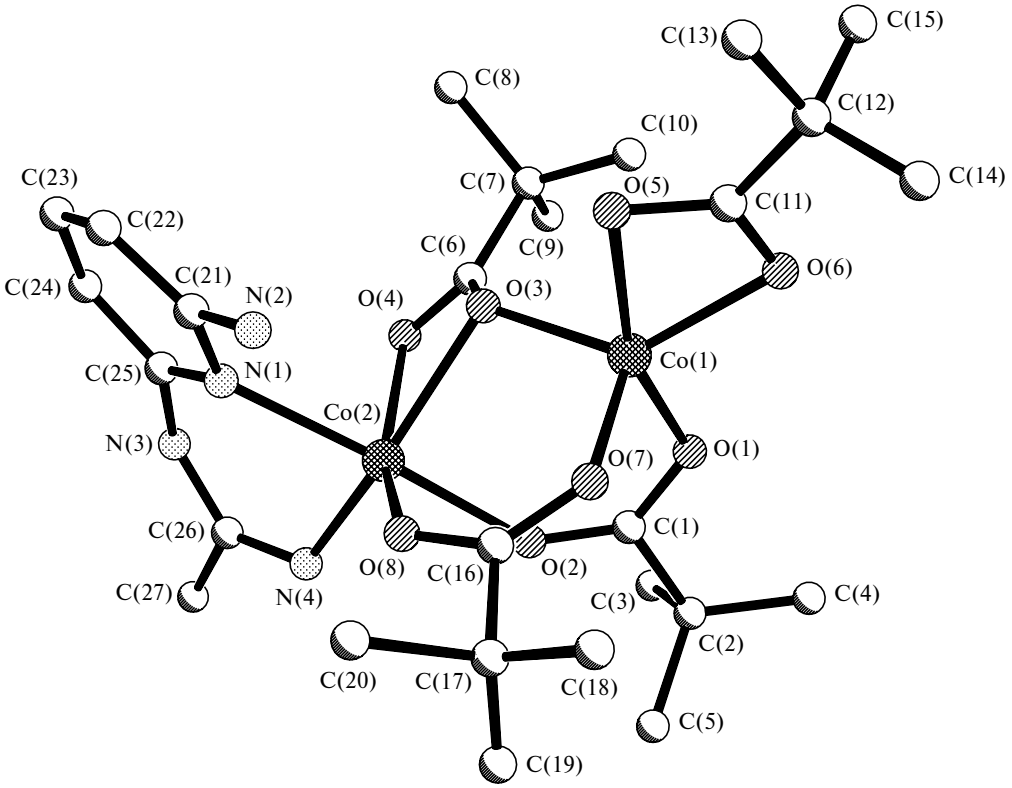


Fig. 6. Structure of complex **8**.

Table 4. Selected geometric characteristics of complex **8**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)...Co(2)	3.360(8)	O(1)—Co(1)—O(7)	100.0(3)	N(4)—Co(2)—N(1)	86.7(4)
Co(1)—O(1)	1.978(8)	O(1)—Co(1)—O(3)	99.4(3)	O(8)—Co(2)—N(1)	97.3(3)
Co(1)—O(7)	1.977(9)	O(7)—Co(1)—O(3)	108.0(4)	O(2)—Co(2)—N(1)	171.5(3)
Co(1)—O(3)	2.010(8)	O(1)—Co(1)—O(6)	102.0(3)	N(4)—Co(2)—O(3)	151.0(4)
Co(1)—O(6)	2.044(8)	O(7)—Co(1)—O(6)	106.4(3)	O(8)—Co(2)—O(3)	96.6(3)
Co(1)—O(5)	2.296(7)	O(3)—Co(1)—O(6)	135.1(3)	O(2)—Co(2)—O(3)	89.0(3)
Co(2)—N(4)	2.009(10)	O(1)—Co(1)—O(5)	162.9(3)	N(1)—Co(2)—O(3)	95.3(3)
Co(2)—O(8)	2.040(8)	O(7)—Co(1)—O(5)	87.6(3)	N(4)—Co(2)—O(4)	93.1(4)
Co(2)—O(2)	2.109(9)	O(3)—Co(1)—O(5)	92.7(3)	O(8)—Co(2)—O(4)	155.0(3)
Co(2)—N(1)	2.162(11)	O(6)—Co(1)—O(5)	61.0(3)	O(2)—Co(2)—O(4)	91.3(3)
Co(2)—O(3)	2.212(9)	N(4)—Co(2)—O(8)	111.9(4)	N(1)—Co(2)—O(4)	84.8(3)
Co(2)—O(4)	2.217(9)	N(4)—Co(2)—O(2)	86.0(4)	O(3)—Co(2)—O(4)	58.5(3)
		O(8)—Co(2)—O(2)	89.4(3)		

S-(−)-α-methylbenzylamine, in the reaction with the binuclear trimethylacetate complex $Co_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**4**). Initially, a colorless crystalline precipitate of the adduct of trimethylacetic acid with *S*-(−)-α-methylbenzylamine (**9**) was isolated from a solution in benzene. This adduct was characterized by X-ray diffraction analysis (Fig. 7). Subsequent crystallization of the metal-containing reaction products from a solution in acetonitrile afforded the ionic complex $[PhC^*H(Me)(NH_2)C(Me)NH]^+[Co_2(Me_3CCOO)_5]^-$ (**10**) in 51% yield (Scheme 4, Fig. 8).

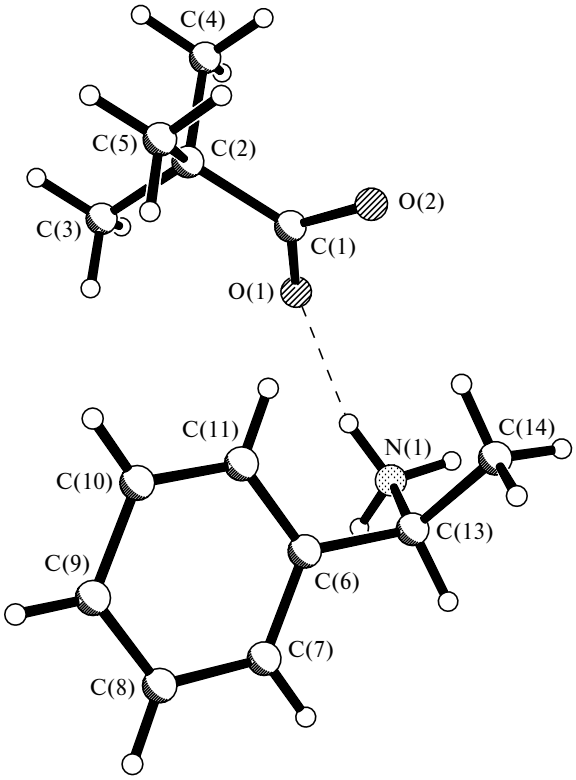
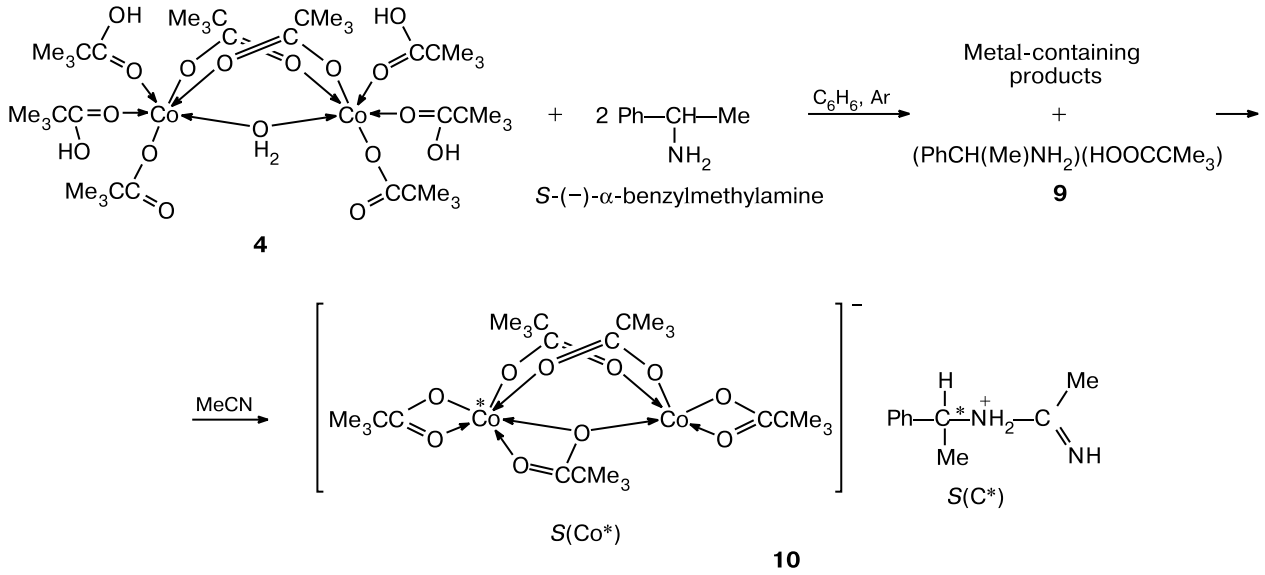


Fig. 7. Structure of the adduct of trimethylacetic acid and *S*-(−)-α-methylbenzylamine (**9**).

Formally, the structure of the binuclear anion $Co_2(\mu\text{-}OOCCMe_3)_2(\mu,\eta^2\text{-}OOCCMe_3)(\eta\text{-}OOCCMe_3)_2$ in ionic complex **10** is analogous to that of neutral complex **8**. However, the anion contains the trimethylacetate anion bound in a chelate fashion instead of the chelate amidine ligand. The cobalt atoms in complex **10** (Table 5) are also linked to each other by two bidentate-bridging carboxylate groups (Co(1)—O(μ-$OOCCMe_3$), 1.959(6) and 1.961(6) Å; Co(2)—O(μ-$OOCCMe_3$), 1.996(7) and 2.027(6) Å) and one chelate-bridging carboxylate group (Co(1)—μO(μ,η^2-$OOCCMe_3$), 2.014(7) Å; (Co(2)—μO(μ,η^2-$OOCCMe_3$), 2.170(7) Å; Co(2)—O(2), 2.113(7) Å). The environment about the Co(2) atom is completed to an octahedron by two oxygen atoms of the chelate-coordinated pivalate ligand (Co(2)—O(η^2-$OOCCMe_3$), 2.062(7) and 2.235(6) Å), whereas the coordination sphere of the Co(1) atom is completed to a trigonal bipyramid by two oxygen atoms of the chelate-coordinated pivalate ligand (Co(1)—O($OOCCMe_3$), 1.925(7) and 2.585(7) Å). A substantial elongation of the Co(1)—O(8) bond (2.585(7) Å) in the binuclear anion of complex **10** is probably attributed to the charge redistribution on the metal atoms in the charged fragment as well as to the involvement of the O(8) atom in a hydrogen bond with the amidine cation. On the whole, the geometry of the binuclear anion in **10** is similar to that observed earlier in the complex $[Co\{(NPhC_6H_4)(NH)\}_2MeCN]^+[Co_2(OOCCMe_3)_5]^-\cdot 2MeCN$.[17]

Complex **10** contains the protonated amidine derivative, *viz.*, *N*-[*S*-(−)-α-methylbenzyl]acetamidine, as the cation. The latter is the product of the reaction of *S*-(−)-α-methylbenzylamine with acetonitrile. The absolute configuration (*S*) of the asymmetric C(26) atom, which was established based on X-ray diffraction data for complex **10**, corresponds to the configuration of

Scheme 4



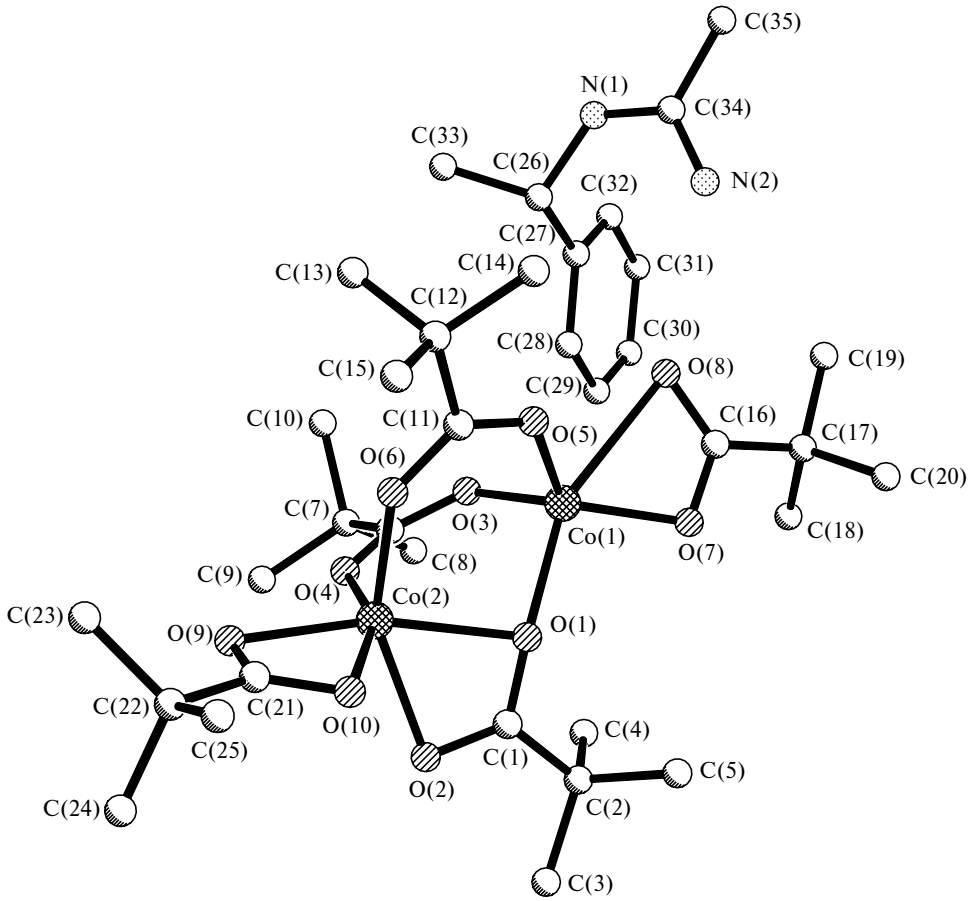
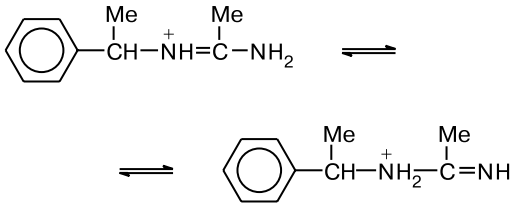


Fig. 8. Structure of complex **10**.

Table 5. Selected geometric characteristics of complex **10**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)...Co(2)	3.277(7)	O(1)—Co(1)—O(3)	98.2(3)	O(1)—Co(2)—O(9)	165.4(3)
Co(1)—O(1)	2.014(7)	O(1)—Co(1)—O(5)	101.3(3)	O(1)—Co(2)—O(10)	108.8(2)
Co(1)—O(3)	1.961(6)	O(1)—Co(1)—O(7)	102.3(3)	O(2)—Co(2)—O(4)	94.4(3)
Co(1)—O(5)	1.959(6)	O(1)—Co(1)—O(8)	157.7(2)	O(2)—Co(2)—O(6)	151.5(3)
Co(1)—O(7)	1.925(7)	O(3)—Co(1)—O(5)	112.2(3)	O(2)—Co(2)—O(9)	107.7(3)
Co(1)—O(8)	2.585(7)	O(3)—Co(1)—O(7)	114.7(3)	O(2)—Co(2)—O(10)	88.6(3)
Co(2)—O(1)	2.170(7)	O(3)—Co(1)—O(8)	93.0(3)	O(4)—Co(2)—O(6)	102.3(3)
Co(2)—O(2)	2.113(7)	O(5)—Co(1)—O(7)	122.9(3)	O(4)—Co(2)—O(9)	99.5(3)
Co(2)—O(4)	2.027(6)	O(5)—Co(1)—O(8)	92.1(3)	O(4)—Co(2)—O(10)	159.5(3)
Co(2)—O(6)	1.996(7)	O(7)—Co(1)—O(8)	55.4(3)	O(6)—Co(2)—O(9)	92.3(3)
Co(2)—O(9)	2.062(7)	O(1)—Co(2)—O(2)	60.3(3)	O(6)—Co(2)—O(10)	83.8(3)
Co(2)—O(10)	2.235(6)	O(1)—Co(2)—O(4)	90.1(3)	O(9)—Co(2)—O(10)	60.4(2)
		O(1)—Co(2)—O(6)	96.4(3)	Co(1)—O(1)—Co(2)	103.0(3)

S-(−)-α-methylbenzylamine used in the reaction. In this amidine, the C—N bonds are equalized to an even larger extent (N(1)—C(34), 1.308(11) Å; C(34)—N(2), 1.315(11) Å) compared to the above-considered complexes, which is typical of protonated amidines.[18] The structure presented in the scheme only formally reflects the nature of the cation because both tautomeric forms make approximately equal contributions to its structure:



Complex **10**, like compound **8**, is separated into chiral isomers upon crystallization. A single crystal of chiral isomer **10** in which the octahedrally coordinated Co(2) atom in the binuclear anion has the *S* configuration (according to the Cahn—Ingold—Prelog stereochemical nomenclature) was studied by X-ray diffraction analysis.[1,19]

Since complex **10** is chiral, we measured its circular dichroism (CD) spectrum in a MeCN solution (Fig. 9). The presence of the asymmetric C(26) atom in the cationic portion of the complex induces the Cotton effects (CE) in all electron transitions of complex **10**, the positions of CD bands correlating well with the energies of the main bands in its absorption spectrum (see Fig. 9).

The intensity of the Cotton effect in the d—d-transition region (30000—10000 cm^{-1}) of the binuclear anion comparable with that for configurationally asymmetric transition metal complexes[1] provides evidence that the chirality of this anion is retained in solution. To elucidate this question in more detail, we plan to prepare a salt of this anion with an optically inactive cation and study its chiroptical properties.

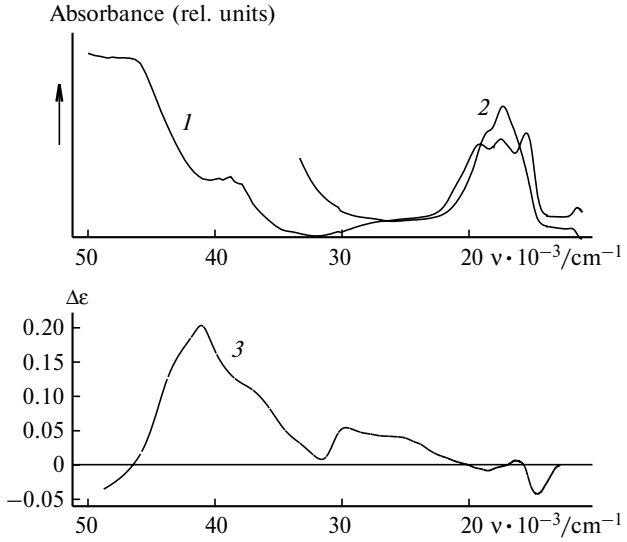


Fig. 9. The DRS (*1*), EAS (*2*), and CD (*3*) spectra of complex **10**; MeCN as the solvent; EAS: $c = 1.50 \cdot 10^{-3}$ mol L^{-1}, $l = 1.0$ cm.

In conclusion, it should be noted that when performing syntheses of complexes in acetonitrile, not only the role of metal as a mediator of the interaction of acetonitrile with amines but also the stability of the newly formed organic species as well as their ability to be bound to metal centers should be taken into account.

Experimental

All operations associated with the synthesis were carried out in an inert atmosphere or in air using anhydrous solvents. The starting Co^{II} trimethylacetate complexes were synthesized according to known procedures.[11] The new compounds were synthesized using 2,6-diaminopyridine and *S*-(−)-α-methylbenzylamine purchased from Fluka. The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets.

The electronic absorption spectra (EAS) of solutions of complexes **3** and **10** in acetonitrile and diffuse reflectance spectra (DRS) of polycrystalline samples were measured on a Specord M-400 spectrophotometer. The CD spectra were recorded on a Mark-III dichrograph (Jobin-Yvon) in the region of $(50.0—12.5)\cdot10^{-3}$ cm^{-1}. The concentration of the starting solutions was ~10^{-3} mol L^{-1}; 1.0—0.1-cm path length quartz cells were used.

The static magnetic susceptibility was measured in the temperature range of 2—300 K on a SQUID MPMS-59 Quantum Desing magnetometer in the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences.

Bis(η-pivalato)[η^2-*N*-(6-amino-2-pyridyl)acetamidine]cobalt(II), Co(OOCCMe$_3$)$_2${H$_2$N(C$_5$H$_3$N)NHC(Me)=NH} (3). 2,6-Diaminopyridine (0.20 g, 1.8 mmol) was added to a suspension of the polymeric cobalt complex $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (0.55 g, 2.1 mmol with respect to the $[Co(OH)_{0.1}(OOCCMe_3)_{1.9}]$ monomeric fragment) in acetonitrile (15 mL). The reaction mixture was heated at 80—85 °C until the starting reagents were dissolved. The resulting solution was concentrated to 10 mL and cooled to ~20 °C to obtain a crystalline precipitate containing a mixture of complexes **2** and **3**. The solution was filtered off and the resulting precipitate was dissolved in benzene to separate benzene-soluble complex **2** from benzene-insoluble compound **3**. The yields of compounds **2** and **3** were 0.32 g (40%) and 0.22 g (25%), respectively. Found (%): C, 49.29; H, 7.14; N, 13.46. $C_{17}H_{28}CoN_4O_4$. Calculated (%): C, 49.50; H, 7.09; N, 13.59. IR (KBr), ν/cm^{-1}: 3291 m, 3218 m, 2956 s, 2869 m, 1664 s, 1636 s, 1616 s, 1564 s, 1552 s, 1564 s, 1531 s, 1464 s, 1408 s, 1356 m, 1301 m, 1256 m, 1220 s, 1172 m, 1048 w, 997 w, 958 w, 896 w, 845 w, 792 m, 608 m, 407 w. DRS, $\nu\cdot10^{-3}$/cm^{-1}: 39.68, 30.39, 29.24 sh, 25.91 sh, 20.41, 17.12, 11.93 sh, 11.31. EAS (MeCN), $\nu\cdot10^{-3}$/cm^{-1} (ε/L mol^{-1} cm^{-1}): 39.68 (3029), 31.85 (1875), 30.49 sh (1743), 27.40 sh (741), 20.16 sh (16), 18.38 (36), 16.13 sh (24), 14.49 sh, 11.88.

The identity of the data from EAS and DRS indicates that the tetrahedral structure of complex **3** is retained in an acetonitrile solution. The energy positions, intensities, and the character of the appearance of the main bands in the ligand-field transition region are consistent with those expected for the $[Co^{II}O_2N_2]$ chromophore.[20,21]

Crystals of complex **3** suitable for X-ray diffraction analysis were prepared by recrystallization of complex **3** from acetonitrile.

Solvate of bis(η-pivalato)[η^2-*N*-(6-amino-2-pyridyl)-acetamidine]cobalt(II) with pivalic acid and benzene, Co(OOCCMe$_3$)$_2${H$_2$N(C$_5$H$_3$N)NHC(Me)=NH}·Me$_3$CCOOH·$\cdot$1/2C$_6$H$_6$ (3a). 2,6-Diaminopyridine (0.15 g, 1.38 mmol) was added with stirring to a solution of the binuclear complex $Co_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ (0.65 g, 0.69 mmol) in hexane (15 mL). The resulting violet solution was concentrated almost to dryness and the dry residue was dissolved in benzene (15 mL) with slight heating and then cooled to ~20 °C to obtain a colorless crystalline precipitate. The solution was filtered off and concentrated to one-half of the initial volume. Then acetonitrile (3—5 mL) was added to the solution and the mixture was kept at ~20 °C. The dark-pink crystals that formed were separated from the solution by decantation, washed with hexane, and dried *in vacuo* (0.1 Torr). The yield of compound **3a** was 0.1 g (12%). Found (%): C, 53.82; H, 7.56; N, 11.09. $C_{25}H_{41}CoN_4O_6$. Calculated (%): C, 54.36; H, 7.43; N, 10.15. IR (KBr), ν/cm^{-1}: 3420 m, 3284 w, 3117 w, 2964 m, 2932 m, 2872 m, 1700 m, 1636 s, 1592 m, 1560 s, 1484 s, 1456 s, 1416 m, 1360 m, 1290 sh, w, 1260 m, 1224 m, 1184 w, 1096 w, 1048 w, 900 w, 864 w, 808 m, 684 w, 616 m, 548 w, 448 w, 440 w. Single crystals suitable for X-ray diffraction analysis were prepared by adding a small amount of hexane to a solution of the complex in a benzene—acetonitrile mixture.

(μ-Aqua)bis(μ-pivalato)bis(η-pivalato)tetrakis(η-pivalic acid)cobalt(II), Co$_2$(μ-OH$_2$)(OOCCMe$_3$)$_4$(HOOCCMe$_3$)$_4$ (4). Potassium pivalate (2.75 g, 19.6 mmol) was triturated with $CoCl_2\cdot6H_2O$ (2.34 g, 9.8 mmol) in the presence of a small amount of water in a porcelain mortar to prepare the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer, which was extracted with hexane (50 mL). The extract was filtered and concentrated to 1/5 of the initial volume. The resulting concentrate was cooled to −5 °C. The red-violet crystals of the $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ complex that precipitated during 1 h were separated from the solution by decantation. The mother liquor was concentrated to one-half of the initial volume in air at ~20 °C for one day. The red-pink crystals that precipitated were separated from the solution by decantation and dried *in vacuo*. The yield of complex **4** was 1.02 g (20% with respect to the amount of the starting cobalt). Found (%): C, 50.45; H, 8.09. $C_{40}H_{78}Co_2O_{17}$. Calculated (%): C, 50.64; H, 8.23. IR (KBr), ν/cm^{-1}: 3415 w, 2972 s, 2932 m, 2872 m, 2701 w, 2588 w, 1676 v.s, 1608 v.s, 1548 w, 1480 v.s, 1456 m, 1404 v.s, 1360 v.s, 1324 w, 1208 v.s, 1099 w, 1032 m, 940 w, 896 w, 876 s, 796 s, 768 w, 608 s, 540 s, 420 m. The crystals prepared by the synthesis were suitable for X-ray diffraction analysis.

Monosolvate of bis(η-pivalato)[η^2-*N*-(6-amino-2-pyridyl)acetamidine]nickel(II) with acetonitrile, Ni(OOCCMe$_3$)$_2${H$_2$N(C$_5$H$_3$N)NHC(Me)=NH}·MeCN (6). Benzene was added to a mixture of binuclear complex **5** (0.58 g, 0.61 mmol) and 2,6-diaminopyridine (0.13 g, 1.19 mmol). The reaction mixture was slightly heated until the precipitate was completely dissolved to form a bright-green solution. Upon cooling, a pale crystalline precipitate formed. The solution was filtered off. The mother liquor was concentrated to dryness and the dry residue was dissolved in acetonitrile (5 mL). The resulting solution was concentrated to one-half of the initial volume and kept at 5 °C for one day. The bright-green crystals that formed were separated from the solution by decantation. The yield of complex **6** was 0.04 g (7.3%) Found (%): C, 49.07; H, 6.54; N, 16.05. $C_{19}H_{31}NiN_5O_4$. Calculated (%): C, 50.42; H, 6.86; N, 15.48. IR (KBr), ν/cm^{-1}: 3372 m, 3236 m, 3124 w, 2960 m, 2924 m, 2868 m, 1640 s, 1560 s, 1524 s, 1484 s, 1416 m, 1452 s, 1432 s, 1360 m, 1256 m, 1228 m, 1204 w, 1164 w, 1084 w, 1044 w, 904 m, 808 m, 796 m, 732 w, 668 w, 608 m, 532 w, 484 w, 416 w. Crystals suitable for X-ray diffraction analysis were prepared by recrystallization of a dry residue (formed upon concentration of the benzene solution) from acetonitrile.

Bis(μ-pivalato)(η^2-*O*,*O*′,μ-*O*,*O*-pivalato)(η^2-pivalato)[η^2-*N*-(6-amino-2-pyridyl)acetamidine]cobalt(II), Co$_2$(OOCCMe$_3$)$_4${H$_2$N(C$_5$H$_3$N)NHC(Me)=NH} (8). A mixture of the tetranuclear cobalt hydroxotrimethylacetate complex $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(EtOH)_6$ (0.79 g, 0.69 mmol) and 2,6-diaminopyridine (0.3 g, 2.75 mmol) was dissolved in acetonitrile (15 mL) with slight heating. The resulting violet solution was concentrated to 7—10 mL and cooled to ~20 °C. A poorly

soluble pink amorphous precipitate formed upon storage of the solution for one day, and dark-pink crystals of complex **8** formed on the surface of the precipitate. The single crystals that precipitated were separated from the solution and the precipitate, washed with hexane, and dried *in vacuo*. The yield of complex **8** was 0.04 g (9.11%). Found (%): C, 48.03; H, 6.68; N, 8.47. $C_{27}H_{47}Co_2N_4O_8$. Calculated (%): C, 48.10; H, 6.98; N, 8.31. IR (KBr), ν/cm^{-1}: 3409 m, 2960 m, 2925 m, 2856 m, 1624 w, 1584 m, 1552 s, 1478 w, 1416 m, 1360 m, 1264 m, 1224 m, 1104 m, 1032 m, 900 w, 865 w, 800 m, 667 w, 624 m, 448 w. The crystals prepared in the synthesis were suitable for X-ray diffraction analysis.

***N*-[*S*-(−)-α-Methylbenzyl]acetamidinium bis(μ-pivalato)(η^2-*O*,*O*′,μ-*O*,*O*-pivalato)bis(η^2-pivalato)cobaltate(II), $[PhCH(Me)NHC(Me)NH_2]^+[Co_2(OOCCMe_3)_5]^-$ (10).** *S*-(−)-α-Methylbenzylamine (0.11 g, 0.12 mL, 0.9 mmol) was added with stirring to a solution of the binuclear complex $Co_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ (0.48 g, 0.5 mmol) in benzene. The reaction mixture was cooled to −5 °C to give a colorless crystalline precipitate of the salt of trimethylacetic acid and amine (**9**). The solution was filtered off and concentrated to dryness. The resulting dry residue was dissolved in acetonitrile (10 mL). The solution was concentrated to 5 mL and cooled to −5 °C. The crystals that precipitated were separated from the solution by decantation and dried *in vacuo* (0.1 Torr). The yield of **10** was 0.20 g (51%). Found (%): C, 53.54; H, 7.47; N, 3.13. $C_{35}H_{60}Co_2N_2O_{10}$. Calculated (%): C, 53.45; H, 7.64; N, 3.56. IR (KBr), ν/cm^{-1}: 3420 v.s, 3246 sh, m, 3089 m, 2960 s, 2926 m, 2870 m, 1664 s, 1596 s, 1556 s, 1524 m, 1484 s, 1420 s, 1376 m, 1356 m, 1260 w, 1228 m, 1028 w, 900 w, 760 w, 700 w, 612 w, 400 w. DRS, ν·10^{-3}/cm^{-1}: 47.62, 38.76, 34.56 sh, 26.32 sh, 19.16, 17.48, 15.83, 11.47. EAS (MeCN), ν·10^{-3}/cm^{-1} (ε/L mol^{-1} cm^{-1}): >47.62 (>2400), 29.76 sh (20), 22.22 sh (11), 20.00 pg, (110), 18.73 sh (303), 17.54 (393), 16.39 sh (309).

The identity of the data from EAS and DRS indicates that the structure of complex **10** is retained in an acetonitrile solution.

CD spectrum (MeCN), ν·10^{-3}/cm^{-1} (Δε/L mol^{-1} cm^{-1}): >46.51 (−CE), 40.82 (+0.216), 37.04 sh (+0.113), 34.48 sh (+0.047), 30.30 (+0.056), 27.03 sh (+0.042), 22.22 sh (+0.013), 18.52 (−0.009), 16.39 (+0.007), 14.71 (−0.043).

The crystals prepared in the synthesis were suitable for X-ray diffraction analysis.

Adduct of trimethylacetic acid and *S*-(−)-α-methylbenzylamine, $(PhCH(Me)NH_2)(HOOCCMe_3)$ (9). The yield of **9** was 0.10 g (91%). Found (%): C, 70.45; H, 10.86; N, 7.54. $C_{13}H_{21}NO_2$. Calculated (%): C, 69.86; H, 9.40; N, 6.27. IR (KBr), ν/cm^{-1}: 3420 m, br, 2960 s, 2552 m, 1608 m, 1568 m,

Table 6. Crystallographic parameters of the complexes

Parameter	**3**	**3a**	**4**	**6**·MeCN	**8**	**9**	**10**
Molecular formula	$C_{17}H_{28}CoO_4N_4$	$C_{25}H_{42}CoO_6N_4$	$C_{40}H_{78}Co_2O_{17}$	$C_{19}H_{31}NiO_4N_5$	$C_{27}H_{47}Co_2O_8N_4$	$C_{13}H_{21}O_2N$	$C_{35}H_{60}Co_2O_{10}N_2$
Molecular weight	411.36	552.55	948.85	452.20	673.55	223.31	786.69
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a/Å	15.108(13)	13.005(2)	12.191(17)	12.221(3)	13.469(11)	6.044(6)	11.107(7)
b/Å	13.458(10)	19.847(3)	20.08(3)	12.150(4)	15.107(9)	12.366(16)	17.010(15)
c/Å	10.310(8)	12.523(2)	23.17(3)	16.367(5)	16.166(12)	17.349(17)	11.909(9)
α/deg	90	90	90	90	90	90	90
β/deg	103.630(19)	113.513(3)	102.35(4)	111.017(6)	90	90	110.44(2)
γ/deg	90	90	90	90	90	90	90
V/Å^3	2037(3)	2964.0(8)	5542(13)	2268.7(12)	3289(4)	1297(2)	2108(3)
Z	4	4	4	4	4	4	2
ρ_{calc}/g cm^{-3}	1.341	1.238	1.132	1.324	1.360	1.144	1.235
μ/cm^{-3}	0.870	0.620	0.655	0.888	1.058	0.076	0.837
Radiation	Mo-Kα (λ = 0.71073 Å)						
Scan range, θ_{min}—θ_{max} /deg	2.05—30.03	1.99—27.51	1.80—30.24	1.80—28.09	1.84—30.04	2.02—24.91	1.96—30.34
Number of measured reflections	10130	12582	16328	10367	7285	1372	7792
Number of reflections with $I > 2\sigma(I)$	4526	6262	7213	4489	4551	1317	6788
Flack's parameter	—	—	—	—	0.00(5)	—	0.00(3)]
R_1	0.0860	0.0659	0.0872	0.0695	0.0989	0.0549	0.0877
wR_2	0.1876	0.1341	0.2004	0.1562	0.2354	0.0894	0.2066

1524 s, 1476 m, 1404 s, 1360 m, 1260 m, 1220 m, 1092 m, 1028 m, 884 m, 796 m, 772 m, 752 m, 700 m, 596 m, 532 m. The crystals prepared in the synthesis were suitable for X-ray diffraction analysis.

X-ray diffraction study. X-ray diffraction data sets for complexes **3**, **3a**, **4**, **6**, **8**, **9**, and **10** were collected on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 110 K (**3**, **8**, **9**), 113 K (**3a**), 293 K (**4**), 120 K (**6**, **10**), ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[22] For all complexes, the semiempirical absorption corrections were applied.[23] The crystallographic parameters and details of structure refinement for all complexes are given in Table 6.

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands and amino groups were generated geometrically and refined using the riding model. All calculations were carried out using the SHELX97 program package.[24] The selected geometric parameters are given in Tables 1—5.

X-ray diffraction studies were carried out in the Center of X-ray Diffraction Studies of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

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