Co(II)-Mediated and microwave assisted coupling between 2,6-diaminopyridine and nitriles. A new synthetic route to *N*-(6-aminopyridin-2-yl)carboximidamides

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The Chinese-lantern-type $Co_2(O_2CBu^t)_4\{2,6\text{-}(NH_2)_2C_5H_3\underline{N}\}_2$ complex reacts with RCN (R = Me or Pr^n) under microwave irradiation (MWI) to give the mononuclear amidine complexes $Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(R)=\underline{N}H\}$ (R = Me (**4a**) or Pr^n (**4c**)). Under microwave irradiation, the addition of 2,6-diaminopyridine to acetonitrile in the presence of the pivalate complexes $Co_2(\mu_2\text{-}OH_2)(O_2CBu^t)_4(HO_2CBu^t)_4$ (**1**) or $[Co(OH)_n(O_2CBu^t)_{2-n}]_x$ (**2**) afforded complex **4a** in higher yield compared to the corresponding reaction performed earlier without MWI. The use of MWI makes it possible to perform analogous reactions with nitriles RCN (R = Et, Pr^n, or Ph) giving rise to complexes **4b—d**, respectively. Compounds **4a—d** were characterized by elemental analysis and IR spectroscopy. The structure of complex **4c** was established by X-ray diffraction. Amidines $H_2N(C_5H_3N)NHC(R)=NH$, which formed in the coordination sphere of cobalt(II), were isolated in the free state from methanolic solutions of complexes **4a—d** under the action of Na_2S and were characterized by electrospray mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The reactions of 2-aminopyridine with both complexes **1** and **2** in acetonitrile under microwave irradiation produced the $Co(O_2CBu^t)_2(H_2NC_5H_4N)_2$ complex.

Key words: microwave synthesis, coordinated nitriles, ligand reactivity, cobalt complexes, aminopyridines, amidines.

In recent years, microwave irradiation (MWI) has found increasing use in various areas of preparative chemistry.[1—12] The main advantages of the use of MWI are a substantial shortening (by an order of magnitude) of the duration of the chemical process, an increase in selectivity of the major reaction, and an increase in the purity of the reaction product.[2,4,6—8,10—12] Most examples of the successful use of microwave activation, where the advantages of the use of MWI are obvious, refer to organic synthesis.[1,6—10,12] Nevertheless, the microwave-promoted synthesis of coordination compounds has been documented in numerous publications.[13—25] In particular, MWI is used for the preparation of nanophases and nanocrystalline compounds starting from metal complexes,[16,19,20] the substitution of ligands,[17,18,21] and the synthesis of phthalocyanines.[13—15,22,23] In two recent publications,[24,25] it has been demonstrated that MWI can be used for a substantial acceleration of reactions of coordinated ligands, such as [2+3] cycloaddition reactions[25] and the nucleophilic addition[24] to inner-sphere nitriles RCN.

It is known[26—29] that coordination to a metal center already leads to electrophilic activation of nitriles, which depends substantially on the nature and oxidation state of the central atom. The aim of the present study was to examine the possibility of combining two methods of activation of the RCN ligand, *viz.*, MWI and coordination, for the preparation of amidine complexes of cobalt starting from heterocyclic amines (aminopyridines) and Co^{II} pivalate complexes in nitrile media. Another purpose was to develop an alternative two-step synthesis of free amidines, including the preparation of inner-sphere *N*-(6-aminopyridin-2-yl)carboximidamides followed by their liberation as a result of the substitution.

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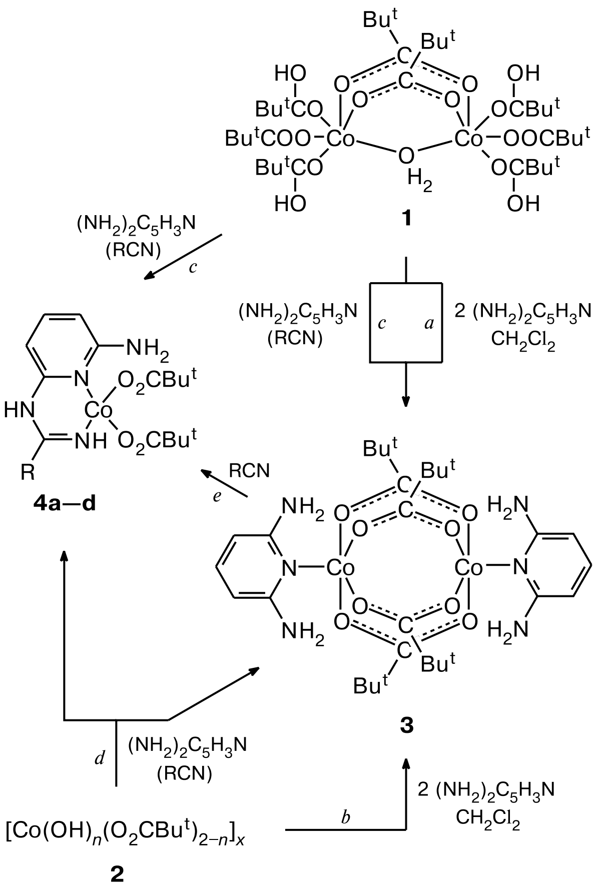
Results and Discussion

The reactions of the cobalt complexes $Co_2(\mu_2\text{-}OH_2)(O_2CBu^t)_4(HO_2CBu^t)_4$ (**1**) and $[Co(OH)_n(O_2CBu^t)_{2-n}]_x$ (**2**) with 2,6-diaminopyridine in a CH_2Cl_2 solution were demonstrated[29—31] to give Chinese-lantern-like dinuclear complex **3** in almost quantitative yield (Scheme 1, reactions *a* and *b*, respectively). It was also found[29] that the reactions of complexes **1** and **2** with 2,6-diaminopyridine in MeCN afforded, along with compound **3**, mononuclear complex **4** in low yield (see Scheme 1, reactions *c* and *d*). In the present study, we demonstrated that the use of MWI makes it possible to activate complex **3**, which is inert under normal conditions, perform the addition of nitriles giving rise to amidine complexes **4a** and **4c**, and increase the yields of complexes **4a—d** in the reactions of compounds **1** and **2** with 2,6-diaminopyridine in the corresponding nitrile media.

Scheme 1



R = Me (**a**), Et (**b**), Pr^n (**c**), Ph (**d**)

Earlier, it has been noted[29] that compound **3** does not react with MeCN even when refluxed for several hours. However, in the present study we demonstrated that microwave irradiation (2 h, 90 °C) of a solution of complex **3** in acetonitrile or butyronitrile gives rise to mononuclear complexes **4a** or **4c** (in 12% yield), respectively. These complexes contain chelate amidine, *N*-(6-aminopyridin-2-yl)carboxamidine, generated as a result of coupling of coordinated nitrile with one of the NH_2 groups of 2,6-diaminopyridine (see Scheme 1, reaction *e*). The yield of product **4** can be increased by increasing the duration of exposure of the reaction mixture to microwave irradiation. In addition, we studied the reactions of complexes **1** and **2** with 2,6-diaminopyridine in various nitriles RCN (R = Me, Et, Pr^n, or Ph) under MWI and compared the results of activation by MWI combined with coordination and the results obtained by activation using merely coordination.

The yield of amidine complex **4** and the reaction rate were demonstrated to depend on the nature of the starting compound (**1** or **2**), the nature of the substituent in RCN, and the reaction conditions (the temperature and the method of heating). Both reactions afforded Chinese-lantern-like complex **3** as the major product (see Scheme 1). However, the use of MWI makes it possible to increase the yield of product **4a** by 10% in the reaction *c* and by 20% in the reaction *d* (see Scheme 1) compared to the reactions, where activation is performed with the use of only coordination, the amounts of the starting compounds being the same. The highest yield of product **4a** (30%) was achieved in the reaction with polynuclear complex **2** performed with heating under MWI (2—3 h, 90 °C). Apparently, the yield of compound **4a** increases due to the involvement of complex **3** (the main product of the reactions *c* and *d*) in the reaction *e* (see Scheme 1). Under microwave irradiation, the latter (see above) in nitriles gives amidine complexes. It should also be noted that further heating of product **4a** in acetonitrile (6 h, 90 °C, 30—40 W) does not lead to the addition of the NH_2 group of the amidine ligand to the triple bond of the nitrile molecule.

Amidine complexes 4a—d. The elemental analysis data for compounds **4a—d** are consistent with the calculated data for the complexes of composition $Co\{amidine\}(O_2CBu^t)_2$. The IR spectra of compounds **4a—d** show bands characteristic of the free NH_2 group of the pyridine fragment and the NH group of the amidine fragment (ν(N—H), 3426—3410, 3346—3352 and 3236—3223 cm^{-1}) and bands corresponding to vibrations ν(C=N) of the imino group (1625—1636 cm^{-1}). The structure of compound **4c** was established by X-ray diffraction (Fig. 1).

Complex **4c** crystallizes from the reaction mixture as a solvate with two molecules of the complex per Pr^{n}CN molecule. The cobalt atom is coordinated by four oxygen atoms of two bidentate trimethylacetate ligands. The oxygen atoms together with two nitrogen atoms of the chelated amidine form a distorted octahedral environment

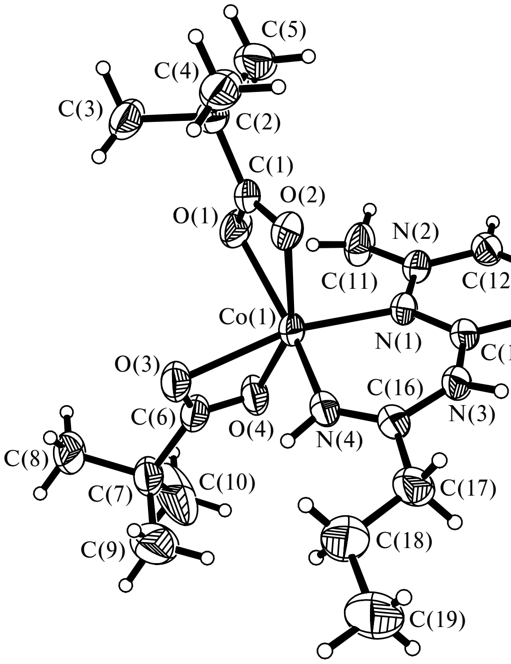


Fig. 1. Molecular structure of complex **4c**.

Bond	N(2)—C(11)	N(3)—C(16)	N(3)—C(15)	N(4)—C(16)
d/Å	1.353(6)	1.361(6)	1.398(6)	1.277(6)

about the central atom. The C—O bond lengths in two carboxylate ligands (in one ligand: C(1)—O(1), 1.270(6) Å; and C(1)—O(2), 1.257(5) Å; in another ligand: C(6)—O(3), 1.254(6) Å; and C(6)—O(4) 1.288(6) Å) are indicative of a high degree of delocalization and are comparable with the bond lengths in the carboxylate CO groups (1.263—1.275 Å) in the nickel complex $Ni(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Me)=\underline{N}H\}$,[29] which also has an octahedral structure. It should be noted that, although the C—O bond lengths in the carboxylate ligand in the tetrahedral cobalt complex $Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Me)=\underline{N}H\}$ (**4a**) described earlier[29] are somewhat smaller (1.237—1.252 Å) than the corresponding bond lengths in complex **4c**, complex **4a** is also characterized by a substantial degree of delocalization.

The cobalt atom in the latter complex lies in the plane of chelated *N*-(6-amino-2-pyridyl)butyroamidine and is involved in a six-membered metallacycle (the maximum deviations from the plane are 0.115(5) Å for C(16) and 0.077(4) Å for N(3)). The C—N bond lengths in the amidine fragment of the ligand (C(16)—N(4), 1.277(6) Å; and C(16)—N(3), 1.361(6) Å) are different and correspond to the average C—N and C=N bond lengths, respectively,[32] which is evidence that delocalization is absent and coordination of the amidine group to cobalt occurs through the imine nitrogen atom.

It should be emphasized that coordination of pyridine to the metal center and the addition of nitrile to one of the NH_2 groups influence the character of the free NH_2 group. For example, the C—N bond length in the free NH_2 group is shorter than the C—N bond length in the NH group involved in the formation of amidine (1.353(6) and 1.398(6) Å, respectively, Table 1), which is in agreement with the more pronounced amide character of the former group. The same situation has been observed for the salt *N*-(6-aminopyridin-2-yl)acetamidinium cyanoborohydride, $[2\text{-}\{NH_2=C(Me)NH\}\text{-}C_5H_3N\text{-}6\text{-}NH_2]CNBH_3$, characterized earlier (see Table 1).[33] The C(11)—N(2) bond length (1.353(6) Å) and the H—N(2)—H...C(11) torsion angle (143.39°) in the free NH_2 group of molecule **4c**, like those in the amidine complexes documented

Table 1. Comparison of the main geometric parameters of the NH_2 groups in 2-aminopyridine, 2,6-diaminopyridine, and its derivative, *N*-(6-aminopyridin-2-yl)carboximidamide, in the free state and in complexes

Compound	Bond length/Å $N—C_{arom}$	Torsion angle/deg $H—N—H...C_{arom}$
2,6-Diaminopyridine		
free[34]	1.378(4), 1.396(5)	129.03, 137.89
protonated[35—37]	1.325—1.350	127.69—174.48
in copper and platinum(II) complexes[38—41]	1.333—1.372	180
N-(6-Aminopyridin-2-yl)ethanimidamidinium cyanoborohydride[33]	1.355(3), 1.410(3)*	153.20
	1.350(3), 1.418(3)*	174.60
N-(6-Aminopyridin-2-yl)butanimidamide in complex **4c**	1.353(6), 1.398(6)*	143.39
N-(6-Aminopyridin-2-yl)ethanimidamide in complexes		
4a (see Ref. 29)	1.417(23), 1.390(19)*	179.92
4a $\cdot Bu^tOOH \cdot 0.5C_6H_6$ (see Ref. 29)	1.356(27), 1.401(18)*	179.97
$Co_2(O_2CBu^t)_4\{H_2N(C_5H_3\underline{N})NHC(Me)=\underline{N}H\}$ (see Ref. 29)	1.372(15), 1.403(14)*	179.86
$[Ni(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Me)=\underline{N}H\}] \cdot MeCN$ (see Ref. 29)	1.349(23), 1.389(19)*	179.94
2-Aminopyridine in cobalt,[42,43] nickel,[42] and zinc[44] complexes	1.328—1.341	180
7	1.345(6), 1.344(7)	163.7, 159.5

* The C—N bond length of the group involved in the amidine fragment.

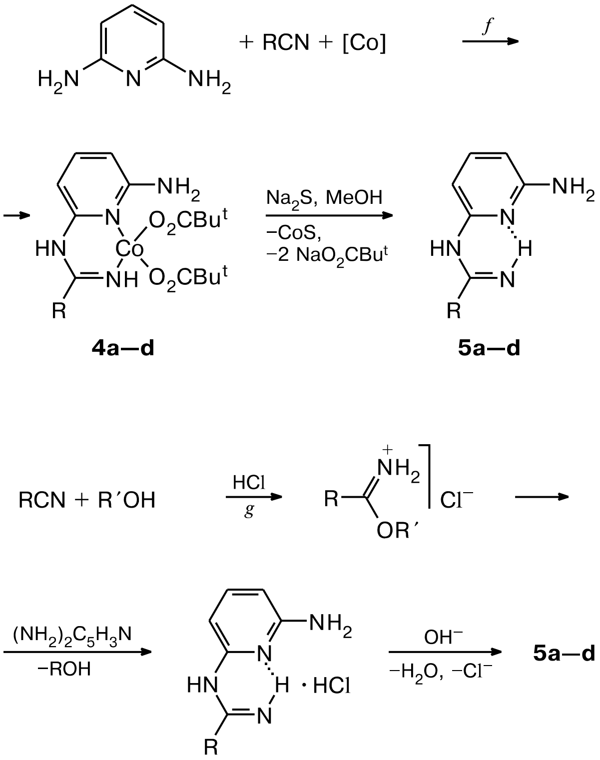
earlier,[29] have intermediate values between those found in the NH_2 groups of free 2,6-aminopyridine and this ligand coordinated through the pyridine nitrogen atom (see Table 1). An enhancement of the amide character of the NH_2 group due to imidoylation and/or coordination is, apparently, one of the factors responsible for the fact that the addition of nitrile to the second NH_2 group of 2,6-aminopyridine does not occur.

Molecules **4c** are linked to each other by the $N(3)—H...O(2)^{\#}$ and $N(3)^{\#}—H^{\#}...O(2)$ hydrogen bonds to form centrosymmetric dinuclear fragments. In addition to the difference in the structure of complexes **4a** and **4c** (tetrahedral and octahedral, respectively), these compounds differ in the molecular packing in the crystal lattice. The molecules of complex **4a** in the dinuclear fragments are parallel to each other and, in addition, these fragments are also parallel to each other, resulting in the formation of a layered structure.[29] In the crystal structure of **4c**, the molecules in the dinuclear fragments do not form parallel planes, and their packing mode is more similar to that of the complexes **4a** $\cdot$ $Bu^tCOOH \cdot 0.5C_6H_6$ and $[Ni(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Me)=\underline{N}H\}] \cdot \cdot MeCN$,[29] which also contain solvent molecules in the crystal lattice.

Liberation of amidines from complexes 4a—d. A series of 2,6-diaminopyridine derivatives, including amidines $NH_2(C_5H_3N)NHC(R)=NH$, are of interest also because they can exhibit antiparasitic activity.[34] These compounds can be prepared by the two-step Pinner synthesis from the corresponding heterocyclic amines and nitriles (Scheme 2, pathway *g*).[33,42] Amidines of this type (**5a—d**) are generated in the coordination sphere of cobalt complexes **4a—d**. Due to an increase in the efficiency of the reaction giving rise to amidines under microwave irradiation, it is advantageous to synthesize amidines $NH_2(C_5H_3N)NHC(R)=NH$ without the use of aggressive media in two steps (see Scheme 2, pathway *f*), which is an alternative route to these compounds.

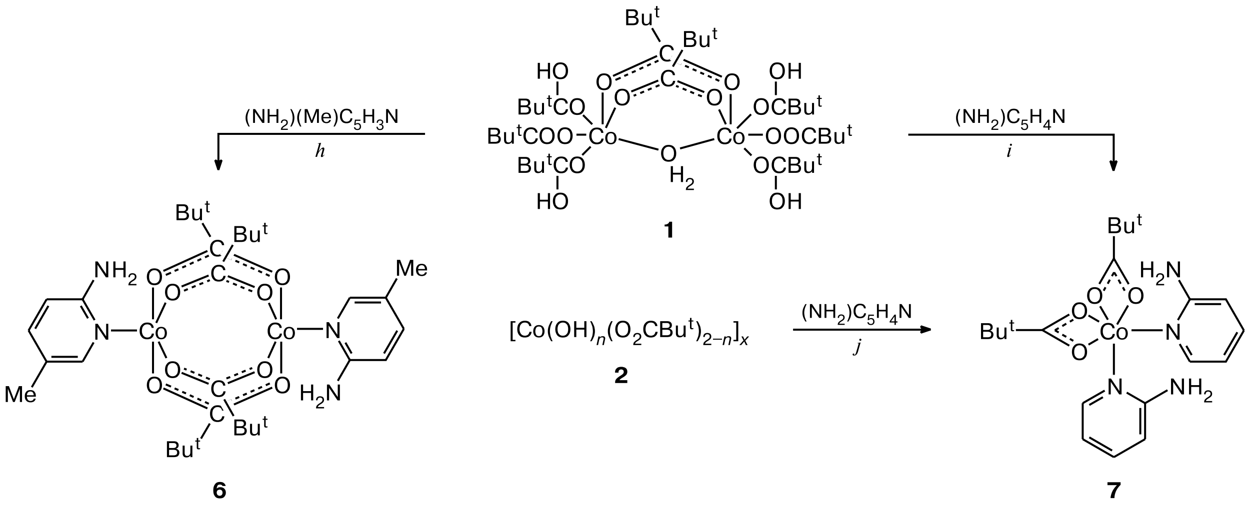
Amidines **5a—d** were liberated from a methanolic solution of complexes **4a—d** under the action of sodium sulfide (see Scheme 2, pathway *f*). The formation of free heterocycles **5a—d** was proved by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and electrospray mass spectrometry. The mass spectra of all compounds show peaks of the ion $[M + H]^+$ and the quasi-ion $[M + Na]^+$. It should be noted that the spectra of complexes **4a—d** contain also peaks corresponding to the ion of the amidine ligand $[L + H]^+$, whereas the molecular ion peaks of the complexes are not observed. The ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **5a—d** show signals of the pyridine ring and the nitrile residue, which are indicative of the addition of 2,6-diaminopyridine to RCN.

Scheme 2



Reactions of 2-aminopyridine with cobalt complexes in acetonitrile. To reveal the factors influencing the formation of coordinated *N*-(6-aminopyridin-2-yl)carboximidamides, we compared the reactivities of 2,6-diaminopyridine and 2-aminopyridine in the reactions with RCN in the presence of cobalt compounds **1** and **2** under microwave irradiation. The NH_2 groups in 2-aminopyridine and 2,6-diaminopyridine differ in the amide character, as evidenced by a comparison of the $NH_2—C_{arom}$ bond lengths and the $H—N—H...C_{arom}$ torsion angles (see Table 1). The NH_2 group in free monoaminopyridine has a more pronounced amide character compared to the analogous groups in 2,6-diaminopyridine. Unlike 2,6-diaminopyridine, 2-monoaminopyridines (2-amino-4-methylpyridine[30] and 2-aminopyridine) do not form amidine complexes of type **4** with compounds **1** and **2** in the reactions performed in acetonitrile both without microwave irradiation and under MWI. The reaction of polynuclear complex **2** with 2-amino-5-methylpyridine in acetonitrile performed under standard thermal conditions (in the absence of MWI) afforded Chinese-lantern-like complex **6** analogous to compound **3** as the major product (Scheme 3, reaction *h*).[30] The reactions of complexes **1** and **2** with 2-aminopyridine under more drastic conditions (MWI) also do not give a product of addition at the C≡N bond of nitrile; instead, other products with coordinated 2-aminopyridine are generated. For example, the reactions of dinuclear complex **1** and polynuclear complex **2** produced mononuclear cobalt complex **7** with two coordinated 2-aminopyridine molecules (see Scheme 3, the

Scheme 3



molar ratio of aminopyridine to cobalt is 2 : 1 (reaction *i*) and 1 : 1 (reaction *j*)).

In the IR spectrum of compound **7**, the bands characteristic of the free NH_2 group (ν(N—H), 3434, 3339, and 3227 cm^{-1}) are retained, whereas intense bands corresponding to stretching vibrations ν(C=N) are absent. These facts indicate that the NH_2 group does not interact with nitrile to form the amidine ligand.

Compound **7** was characterized by X-ray diffraction (Fig. 2). In complex **7**, the cobalt atom is coordinated by four oxygen atoms of two bidentate trimethylacetate ligands and two nitrogen atoms of two 2-aminopyridine ligands, which form an octahedral environment. The C—N bond lengths in the free NH_2 groups are 1.345(6) and 1.344(7) Å, which are comparable with the bond length in the free NH_2 group of compound **4c** (1.353(6) Å) and the corresponding bond lengths in cobalt,[42,43] nickel,[42] and zinc[44] complexes related to compound **7** (1.328—1.341 Å). The NH_2 group lies virtually in the plane of the aromatic ring. The H—N(4)—H...C(16) and H—N(2)—H...C(11) torsion angles are 163.7° and 159.5°, respectively, which is indicative of a pronounced amide character of this group. In the crystal structure, the molecules of complex **7** are linked to each other by the N(2)—H...O(3)$^{\#}$ and N(2)$^{\#}$—H$^{\#}$...O(3) hydrogen bonds to form centrosymmetric dinuclear fragments.

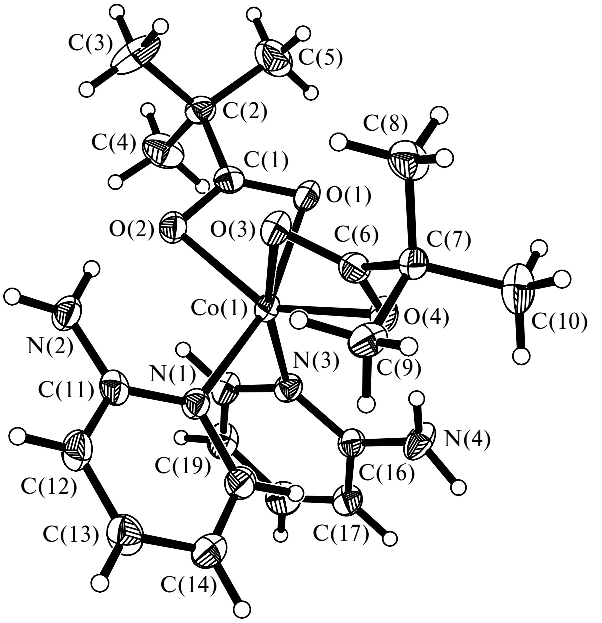


Fig. 2. Molecular structure of complex **7**.

Bond	N(2)—C(11)	N(4)—C(16)
d/Å	1.348(4)	1.342(4)

Therefore, in the present study we found that the use of MWI combined with coordination to the metal center makes it possible to prepare amidines starting from the inert Chinese-lantern-like complex $Co_2(O_2CBu^t)_4\{(NH_2)_2C_5H_3\underline{N}\}_2$ and acetonitrile, whereas an analogous reaction does not proceed when only coordination is used for activation. In addition, microwave irradiation leads to an increase in the efficiency of the reaction giving rise to *N*-(6-aminopyridin-2-yl)carboximidamides in the coordination sphere of cobalt, due to which amidines can be prepared by a two-step synthesis involving the formation of coordinated amidines followed by their isolation in the substitution reaction.

Experimental

Cobalt complexes **1** and **2** were synthesized according to a known procedure.[29,31] The microwave syntheses were carried out with the use of a specialized temperature-controlled Discover

LabMate laboratory focused-microwave oven (the maximum power was 300 W, and the frequency was 2.45 GHz) equipped with a stirring device. The IR spectra were measured in KBr pellets on a Nicolet magna 750 FT/IR instrument in the 4000—400 cm^{-1} region. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker-DPX 300 spectrometer at 20 °C. Electrospray mass-spectrometric analysis was carried out on a Bruker Esquire3000 instrument. All spectra were measured in the positive ion detection mode at *m/z* varying from 50 to 1200. The needle voltage was 3.0 kW, and dry nitrogen passing at a flow rate of 5 L min^{-1} was used as the drying and spraying gas. A methanolic solution of the compound ($2 \cdot 10^{-6}$ mol L^{-1}) under examination was injected at a rate of 6 μL min^{-1} directly into the mass spectrometer. The chamber temperature was 250 °C, and the voltage supplied to a separator was varied from 20 to 50 W.

Addition of 2,6-diaminopyridine to nitriles in cobalt pivalate complexes. Synthesis of the $[Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(R)=\underline{N}H\}]$ complexes (4a—d, R = Me, Et, Pr^n, or Ph). ***A.*** 2,6-Diaminopyridine (0.023 g, 0.212 mmol) was added with stirring to a solution of dinuclear complex **1** (0.050 g, 0.053 mmol) in hexane (2 mL). The resulting violet solution was immediately concentrated to dryness under a nitrogen stream at room temperature. The dry residue was dissolved in benzene (2 mL) with slight heating (40—50 °C). The solution was filtered off from the pivalate $[C_5H_3N(NH_2)_2](HO_2CBu^t)_2$ (**8**) that formed (this compound was identified by ^1H NMR and IR spectroscopy, see below). The filtrate was concentrated to 0.5 mL, nitrile RCN (R = Me or Et) (2 mL) was added, and the reaction mixture was subjected to microwave irradiation (30—40 W, the temperature was maintained at 90 °C) for 2 h. Then the homogeneous dark-violet solution was concentrated to 0.5 mL, benzene (4 mL) was added, and the solution was kept at 5 °C for 12 h. The dark-pink crystals of compound **4** that precipitated were filtered off, washed with benzene (2×1 mL), and dried in air at 25—27 °C. Compounds **4a** and **4b** were obtained in 11% yield.

B. The polymeric complex $[Co(O_2CBu^t)_{2-x}(OH)_x]_n$ (**2**) (0.100 g, 0.40 mmol) (the reagent ratio was calculated with the use of $x = 0.1$)[31] and 2,6-diaminopyridine (0.043 g, 0.40 mmol) were dissolved in nitrile RCN (R = Me, Et, Pr^n, or Ph) (3 mL). The resulting pink-violet solution was subjected to microwave irradiation for 15 min, 30 min, 1 h, 2 h, and 3 h (the yields are given below depending on the irradiation time). For Pr^nCN and MeCN, the resulting dark-violet solution was kept at room temperature. The dark-pink crystals that precipitated from the reaction mixture for 2 h were filtered off, washed with benzene (2×1.5 mL), and dried in air at room temperature for 1 day. To synthesize complexes with nitriles RCN (R = Et or Ph), the reaction mixture was cooled and concentrated *in vacuo* to 1 mL, and then benzene (5 mL) was added. The resulting violet solution was kept at 5 °C for 12 h, and the dark-pink crystals that precipitated were filtered off, washed with benzene (2×1.5 mL), and dried in air.

C. Products **4a** and **4c** were prepared by the reaction of the $Co_2(O_2CBu^t)_4\{H_2N(C_5H_3\underline{N})NH_2\}$ complex (**3**) (100 mg) with acetonitrile or butyronitrile, respectively, (5 mL) under microwave irradiation (2 h, 90 °C) (see Scheme 1, pathway *e*). The IR spectra of the products are identical to the IR spectra of the products prepared according to the method *B* (see Scheme 1, pathway *d*). The elemental analysis data for the compounds prepared according to these methods are identical. The yield of product **4a** synthesized by the latter method was 12%.

Bis-trimethylacetato[*N*-(6-amino-κ*N*-pyridin-2-yl)ethan-κ*N*-imidamide]cobalt(II), $Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Me)=\underline{N}H\}$ (4a). The yield of the product prepared according to the procedure *B* at 90° C was 10 (15 min), 15 (30 min), 20 (1 h), 30 (2 h), and 30% (3 h); at 80 °C, 20% (2 h). After refluxing for 2 h without the use of MWI (with the use of the same amounts of the starting compounds), the yield was 10%. Found (%): C, 49.26; H, 6.90; N, 13.40. $C_{17}H_{28}N_4CoO_4$. Calculated (%): C, 49.64; H, 6.86; N, 13.61. IR, 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 m-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.

Bis-trimethylacetato[*N*-(6-amino-κ*N*-pyridin-2-yl)propan-κ*N*-imidamide]cobalt(II), $Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Et)=\underline{N}H\}$ (4b). The yield of the product prepared according to the procedure *B* (2 h) was 20%. Found (%): C, 50.35; H, 7.16; N, 12.43. $C_{18}H_{30}N_4CoO_4$. Calculated (%): C, 50.82; H, 7.11; N, 13.17. IR, ν/cm^{-1}: 3422 m, 3346 m, 3236 m, 2960 m, 2931 m, 2871 m-w, 1637 s, 1587 m, 1557 s, 1529 s, 1482 m-s, 1457 s, 1411 m, 1360 m, 1258 m, 1224 m, 1093 w, 997 w, 806 m-w, 684 w, 611 w.

Bis-trimethylacetato[*N*-(6-amino-κ*N*-pyridin-2-yl)butan-κ*N*-imidamide]cobalt(II), $[Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Pr^n)=\underline{N}H\}]\cdot 0.5Pr^nCN$ (4c). The yield of the product prepared according to the procedure *B* (2 h) was 20%. Found (%): C, 52.76; H, 7.60; N, 12.85. $C_{19}H_{32}N_4CoO_4 \cdot 0.5PrCN$. Calculated (%): C, 53.21; H, 7.55; N, 13.30 IR, ν/cm^{-1}: 3410 m, 3346 m, 3235 m, 3057 w, 2964 m, 2931 m, 2874 m-w, 1632 s, 1587 m, 1555 s, 1537 s, 1484 m-s, 1457 s, 1420 m, 1361 m, 1259 m, 1227 m, 1192 m-w, 1155 m, 1093 w, 1030 w, 898 m-w, 808 m, 792 m-w, 670 w, 610 m, 538 w, 418 w.

Bis-trimethylacetato[*N*-(6-amino-κ*N*-pyridin-2-yl)benzene-κ*N*-carboximidamide]cobalt(II), $Co(O_2CBu^t)_2\{H_2N(C_5H_3\underline{N})NHC(Ph)=\underline{N}H\}$ (4d). The yield of the product prepared according to the procedure *B* (2 h) was 30%. Found (%): C, 57.59; H, 6.49; N, 10.91. $C_{22}H_{30}N_4CoO_4 \cdot 0.5C_6H_6$. Calculated (%): C, 58.59; H, 6.49; N, 10.93. IR, ν/cm^{-1}: 3426 m, 3352 m, 3223 m, 2959 m, 2931 m, 2864 m-w, 1625 s, 1587 s, 1557 s, 1482 m-s, 1455 m-s, 1415 m, 1361 m, 1225 m, 1113 m-w, 1031 w, 897 m-w, 791 m-w, 696 w, 611 w.

Isolation of amidines from complexes 4a—d (general procedure). A small excess of sodium sulfide (25 mg of $Na_2S \cdot 7H_2O$ in 2 mL of MeOH) was added to a solution of complex **4a—d** (40 mg) in methanol (1 mL). The black precipitate that formed was filtered off, the filtrate was removed under a nitrogen stream, and amidines **5b—d** were extracted from the reaction mixture with a 1 : 1 acetone—diethyl ether mixture. Amidine **5a** was not isolated from the reaction mixture because of poor solubility.

***N*-(6-Aminopyridin-2-yl)ethanimidamide, $H_2N(C_5H_3N)NHC(Me)=NH$ (5a).** MS (ESI), *m/z*: 151 $[M + H]^+$, 173 $[M + Na]^+$. The ^1H NMR spectrum was not recorded because of poor solubility of the compound in acetone-d_6.

***N*-(6-Aminopyridin-2-yl)propanimidamide, $H_2N(C_5H_3N)NHC(Et)=NH$ (5b).** MS (ESI), *m/z*: 165 $[M + H]^+$, 187 $[M + Na]^+$. ^1H NMR (acetone-d_6), δ: 8.76 (br.s, 1 H, HN=); 7.43 (d, 1 H, C(5)H); 7.34 (t, 1 H, C(4)H); 6.22 (d, 1 H, C(3)H); 5.20 (br.s, 3 H, NH, NH_2); 2.43 (q, 2 H, CH_2); 1.12 (t, 3 H, Me). ^{13}C NMR (acetone-d_6), δ: 181.18 (HN=C), 151.67 (C(2)), 139.77 (C(4)), 128.86 (C(6)), 104.02, 102.25 (C(3), C(5)), 28.59 (CH_2), 9.73 (Me).

***N*-(6-Aminopyridin-2-yl)butanimidamide, $H_2N(C_5H_3N)NHC(Pr^n)=NH$ (5c).** MS (ESI), *m/z*: 178 $[M + H]^+$, 202 $[M + Na]^+$. ^1H NMR (acetone-d_6), δ: 8.75 (br.s, 1 H, HN=); 7.44 (d, 1 H, C(5)H); 7.34 (t, 1 H, C(4)H); 6.24 (d, 1 H, C(3)H); 5.19 (br.s, 3 H, NH, NH_2); 2.40 (t, 2 H, CH_2); 1.66 (m, 2 H, CH_2); 0.96 (t, 3 H, Me). ^{13}C NMR (acetone-d_6), δ: 186.67 (C=N), 139.77 (C(4)), 103.98, 102.26 (C(3), C(5)), 39.48 (CH_2), 19.49 (CH_2), 13.96 (Me).

***N*-(6-Aminopyridin-2-yl)benzenecarboximidamide, $H_2N(C_5H_3N)NHC(Ph)=NH$ (5d).** MS (ESI), *m/z*: 213 $[M + H]^+$, 235 $[M + Na]^+$. ^1H NMR (acetone-d_6), δ: 8.75 (br.s, 1 H, HN=); 7.44 (d, 1 H, C(5)H); 7.34 (t, 1 H, C(4)H); 6.24 (d, 1 H, C(3)H); 5.19 (br.s, 3 H, NH, NH_2); 2.40 (t, 2 H, CH_2); 1.66 (m, 2 H, CH_2); 0.96 (t, 3 H, Me). ^{13}C NMR (acetone-d_6), δ: 186.67 (C=N), 139.39 (C(3)), 103.98, 111.41 (C(5)).

Reaction of 2-aminopyridine with cobalt pivalate complexes in acetonitrile. ***A.*** 2-Aminopyridine (0.020 g, 0.212 mmol) was added with stirring to a solution of dinuclear complex **1** (0.050 g, 0.053 mmol) in hexane (2 mL). The resulting cherry-violet solution was immediately concentrated to dryness under a nitrogen stream at room temperature. The dry residue was dissolved in benzene (2 mL) with slight heating (40—50 °C). The solution was filtered off from a small amount of a pale residue, the filtrate was concentrated to 0.5 mL, and acetonitrile (2 mL) was added. Then the reaction mixture was subjected to MWI for 2 h, the temperature being maintained at 90 °C. Then the homogeneous cherry-violet solution was kept at 5 °C for 12 h. The pink crystals of compound **6** that precipitated were filtered off, washed with benzene (2×1 mL), and dried in air at 25—27 °C. The yield was 20%.

B. Polymeric complex **2** (0.050 g, 0.200 mmol) and 2-aminopyridine (0.019 g, 0.200 mmol) were dissolved in MeCN (3 mL). The resulting pink-violet solution was subjected to MWI for 2 h. Then the dark pink-violet solution was kept at 5 °C. After 12 h, the pink crystals that precipitated from the reaction mixture were filtered off, washed with benzene (2×1.5 mL), and dried in air at room temperature for 1 day. The yield was 25%.

Bis(trimethylacetato)[bis-2,6-diamino-κ*N*-pyridine]cobalt(II), $Co(O_2CBu^t)_2(H_2NC_5H_4\underline{N})_2$ (7). Found (%): C, 52.96; H, 6.39; N, 12.09. $C_{22}H_{30}N_4CoO_4$. Calculated (%): 53.45; H, 6.73; N, 12.47. IR, ν/cm^{-1}: 3434 s, 3339 m-s, 3227 m, 2960 m, 2930 m, 2870 m-w, 1645 s, 1567 m-s, 1541 m-s, 1496 s, 1486 s, 1451 m-s, 1421 m, 1361 m, 1227m, 1158 m-w, 1008 m-w, 900 m, 770 m, 607 m-w.

2,6-Diaminopyridine bis(hydrotrimethylacetate), $[C_5H_3N(NH_2)_2](HO_2CBu^t)_2$ (8). IR, ν/cm^{-1}: 3435 m, 3160 m, 2974 m, 1656 s, 1619 m, 1410 m. ^1H NMR ($CDCl_3$), δ: 7.26 (t, 1 H, C(4)H); 5.86 (br.m, 2 H, C(3)H, C(5)H); 4.71 (br.s, 6 H, NH); 1.27 (s, 18 H, Me).

X-ray diffraction analysis. Single crystals of complexes **4c** and **7** were obtained directly from the reaction mixtures. X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The crystallographic data and the principal parameters of structure refinement for compounds **4c** and **7** are given in Table 2. The unit cell parameters were refined and the X-ray data were merged using the Denzo-Scalepack program package.[45] The structures were solved by direct methods using the SHELXS-97 program package[46] and refined using the SHELXL-97 program package[46] and the WinGX graphical interface.[47]

Table 2. Crystallographic data for complexes **4c** and **7**

Parameter	**4c**	**7**
Molecular formula	$C_{20.5}H_{34.5}CoN_{4.5}O_4$	$C_{20}H_{30}CoN_4O_4$
Molecular weight	466.96	449.41
T/K	120(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*
a/Å	25.311(2)	11.2306(5)
b/Å	12.7053(10)	23.6445(7)
c/Å	16.4422(10)	8.5436(4)
α/deg	90	90
β/deg	111.292(4)	102.668(4)
γ/deg	90	90
V/Å^3	4926.7(6)	2213.46(16)
Z	8	4
d_{calc}/mg m^{-3}	1.259	1.349
μ/mm^{-1}	0.728	0.80
Scan range/deg	4.47—25.00	2.05—25.30
Number of independent reflections (R_{int})	4163 (0.0684)	3993 (0.0637)
R_1 ($I \geq 2\sigma$)	0.0613	0.0415
wR_2 ($I \geq 2\sigma$)	0.1513	0.0809

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