Role of metal center in reactions of polynuclear nickel(II) and cobalt(II) trimethylacetates with 8-amino-2,4-dimethylquinoline

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The reactions of 8-amino-2,4-dimethylquinoline (L) (**1**) with polynuclear nickel(II) and cobalt(II) hydroxotrimethylacetato complexes under anaerobic conditions were studied. The nonanuclear cluster $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ gave the mononuclear complex $Ni(\eta^2\text{-}L)(\eta^2\text{-}OOCCMe_3)_2$ (**2**). The tetranuclear complex $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ produced the mononuclear complex $Ni(\eta^2\text{-}L)(\eta^2\text{-}OOCCMe_3)(OOCCMe_3)L$ (**3**). At room temperature, the cobalt-containing polynuclear trimethylacetates, *viz*., the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ and the tetranuclear complex $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$, were transformed into the trinuclear cobalt(II) complex $Co_3(\mu_3\text{-}OH)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}L)_2(OOCCMe_3)$ (**4**). Meanwhile, at 80 °C these compounds generated the binuclear cobalt(III) complex $Co_2(\mu_2\eta^2\text{-}(HN)C_9NMe_2)_2(\mu\text{-}OOCCMe_3)(L)(OOCCMe_3)_3$ (**5**). The structures of the resulting compounds were established by X-ray diffraction analysis. Compounds **2—4** exhibit the antiferromagnetic spin-spin exchange coupling, whereas compound **5** is diamagnetic.

Key words: 8-amino-2,4-dimethylquinoline, cobalt complexes, nickel complexes, X-ray diffraction analysis.

It is known[1—6] that 2,2´-dipyridyl and *o*-phenanthroline readily form stable metallocycles with transition metal atoms without undergoing essential transformations. Organic aromatic 1,2-diamines are also often used as ligands that form the coordination spheres about transition metal atoms. However, because of the high chemical activity of the amino groups, which readily undergo oxidative dehydrogenation, new organic fragments, *viz*., the products of inner-sphere transformations of amines, can also be generated.[7—13] The N-donor 8-amino-2,4-dimethylquinoline ligand (**1**) combines both functions, containing the pyridine ring and amino group. The geometry of this bifunctional donor center gives promise that not only chelate metal fragments but also polynuclear structures with bridging ligands may be prepared.

In the present study, we examined the reactions of diamine **1** with polynuclear nickel(II) and cobalt(II) hydroxotrimethylacetato complexes under anaerobic conditions.

Results and Discussion

Molecule **1** contains the amino group, which is prone to oxidation. Hence, the reactions were carried out under an inert atmosphere in anhydrous solvents. It appeared that, in spite of the identical reaction conditions, the results of the reaction of compound **1** with polynuclear nickel trimethylacetate clusters depend on the compositions and structures of the latter. The reaction with the nonanuclear cluster $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ afforded the mononuclear cluster $LNi(OOCCMe_3)_2$ of composition 1 : 1, (**2**, L is 8-amino-2,4-dimethylquinoline), whereas the reaction with the tetranuclear complex $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ gave rise to the mononuclear complex $L_2Ni(OOCCMe_3)_2 \cdot 0.5C_6H_6$ (**3**) (Scheme 1).

X-ray diffraction study of complex **2** showed that the Ni atom in this complex is coordinated only by one che-

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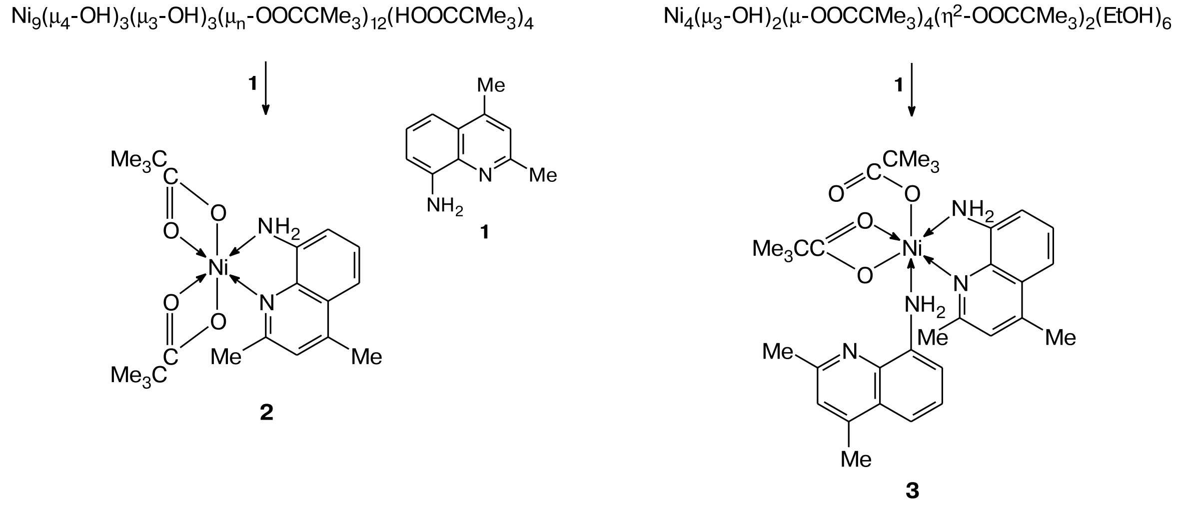
Scheme 1



Reagents and conditions: **1** : Ni = 1 : 1, C_6H_6, Ar, 20 °C.

late-bound aminoquinoline molecule (Ni—N(amine), 2.0484(18) Å; Ni—N(quinoline), 2.0807(17) Å) and two chelate-bound trimethylacetate anions (Ni—O, 2.0804(17)—2.1210(17) Å) (Fig. 1, Table 1). The structurally similar dipyNi(OOCCMe$_3$)$_2$ complex has been prepared earlier by thermolysis of the (dipy)$_2$Ni$_2$(μ-H$_2$O)$_2$(OOCCMe$_3$)$_4$ complex.[5] Complex **3** contains two ligand molecules coordinated in different fashions, *viz.*, the monodentate (Ni—N(amine), 2.270(4) Å) and bidentate chelate-bound aminoquinoline (Ni—N(amine), 2.056(4) Å; Ni—N(quinoline), 2.088(4) Å) molecules. The Me$_3$CCOO groups are also characterized by different modes of coordination, *viz.*, one group is terminal (Ni—O(1), 2.033(7) Å) and another group is chelate-bound (Ni—O(3), 2.117(3) Å; Ni—O(4), 2.160(3) Å) (Fig. 2, Table 2).

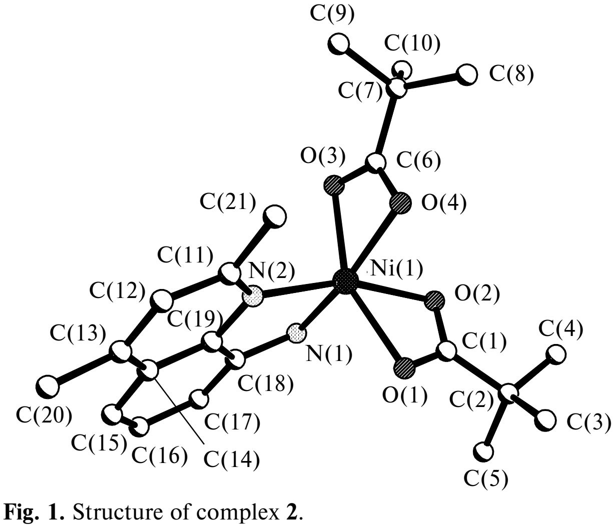


Fig. 1. Structure of complex **2**.

Compounds **2** and **3** were characterized by electronic absorption spectra (EAS) of solutions in acetonitrile and diffuse reflectance spectra (DRS) of polycrystalline samples (Fig. 3, Table 3). The fact that EAS and DRS for each compound are identical in the number and energy positions of the main absorption bands indicates that compounds **2** and **3** retain their structures in solution. The

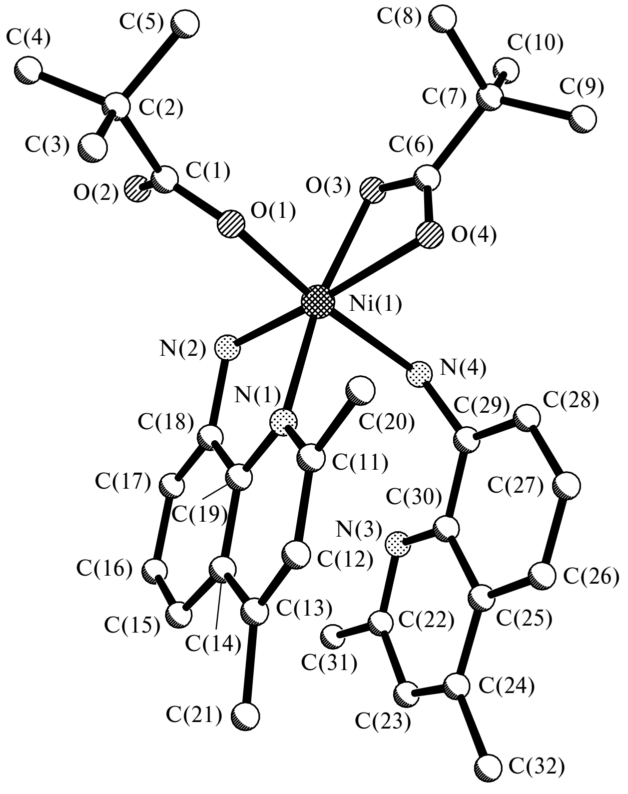


Fig. 2. Structure of complex **3**.

Table 1. Selected geometric parameters of complex **2**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Ni(1)—O(1)	2.121(2)	O(1)—Ni(1)—O(2)	62.16(6)	O(2)—Ni(1)—N(2)	161.13(7)
Ni(1)—O(2)	2.115(2)	O(1)—Ni(1)—O(3)	154.20(7)	O(3)—Ni(1)—O(4)	63.45(6)
Ni(1)—O(3)	2.081(2)	O(1)—Ni(1)—O(4)	98.70(6)	O(3)—Ni(1)—N(1)	102.00(7)
Ni(1)—O(4)	2.090(2)	O(1)—Ni(1)—N(1)	93.08(7)	O(3)—Ni(1)—N(2)	101.73(7)
Ni(1)—N(1)	2.048(2)	O(1)—Ni(1)—N(2)	100.96(7)	O(4)—Ni(1)—N(1)	164.50(7)
Ni(1)—N(2)	2.087(2)	O(2)—Ni(1)—O(3)	96.67(6)	O(4)—Ni(1)—N(2)	105.25(7)
		O(2)—Ni(1)—O(4)	86.64(6)	N(1)—Ni(1)—N(2)	82.17(7)
		O(2)—Ni(1)—N(1)	90.01(7)		

Table 2. Selected geometric parameters of complex **3**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Ni(1)—O(1)	2.033(3)	O(1)—Ni(1)—O(3)	91.6(1)	O(3)—Ni(1)—N(4)	84.7(1)
Ni(1)—O(3)	2.117(3)	O(1)—Ni(1)—O(4)	87.8(1)	O(4)—Ni(1)—N(1)	110.2(1)
Ni(1)—O(4)	2.160(3)	O(1)—Ni(1)—N(1)	93.6(1)	O(4)—Ni(1)—N(2)	168.2(1)
Ni(1)—N(1)	2.088(4)	O(1)—Ni(1)—N(2)	96.4(1)	O(4)—Ni(1)—N(4)	86.7(1)
Ni(1)—N(2)	2.056(4)	O(1)—Ni(1)—N(4)	174.4(1)	N(1)—Ni(1)—N(2)	80.6(1)
Ni(1)—N(4)	2.270(4)	O(3)—Ni(1)—O(4)	61.8(1)	N(1)—Ni(1)—N(4)	89.5(1)
		O(3)—Ni(1)—N(1)	170.3(1)	N(2)—Ni(1)—N(4)	88.7(1)
		O(3)—Ni(1)—N(2)	106.9(1)		

following absorption regions can be distinguished in EAS of solutions of complexes **2** and **3**: very intense absorption bands *A*, *B*, *C*, and *D* in the UV and near-UV regions, which belong to charge-transfer transitions (CTT), and low-intensity transitions in the region of a broad ($\Delta_{1/2}$ > 9000 cm^{-1}) low-energy band *E*, which has a complex multiplet structure (particularly, in the spectrum of compound **3** with the symmetry C_{2v} of the metal chromophore *cis*-$[NiN_2O_4]$). According to the EAS for octahedral Ni^{II} complexes[14] and our spectroscopic data on binuclear nickel carboxylate complexes,[15] the absorption in the region of the band *E* is associated with ligand field transitions (LFT) (see Table 1), whose resolution depends on the donor environment about the metal atom and effective symmetry of the metal chromophore. The coordinated 8-amino-2,4-dimethylquinoline molecules (L) in compounds **2** and **3** (one chelate-bound ligand L in complex **2** and mono- and bidentate-coordinated ligands L in complex **3**) are responsible for the character of electron transitions in the charge-transfer region (bands *A*, *B*, *C*, and *D*) (see Table 3). According to the published data on the charge-transfer spectra for transition metal complexes containing coordinated ligands, such as 2,2´-bipyridine, bipyrazine, *o*-phenanthroline, *o*-phenylenediamine, *etc.*,[14,16,17] absorption in the region of the bands *B* and *C* in the EAS of compounds **2** and **3** results from both the intraligand $\pi \rightarrow \pi^*$ transitions of the ligand L and the ligand→metal charge-transfer transitions (LMCT) $\pi(L) \rightarrow d\pi^*(M)$ and $\pi(L) \rightarrow d\sigma^*(M)$ (bands *C* and *B*, respectively). The absorption intensity in the region of the band *A* is determined primarily by the $\sigma(L) \rightarrow d\pi^*(M)$ LMCT. Apparently, the medium-intensity band in the near-UV region (band *D*) is associated with the metal→ligand charge-transfer transitions (MLCT) $d(M) \rightarrow \pi^*(L)$ by analogy with the position of this type of transitions in the spectra of related complexes.[14,16,17]

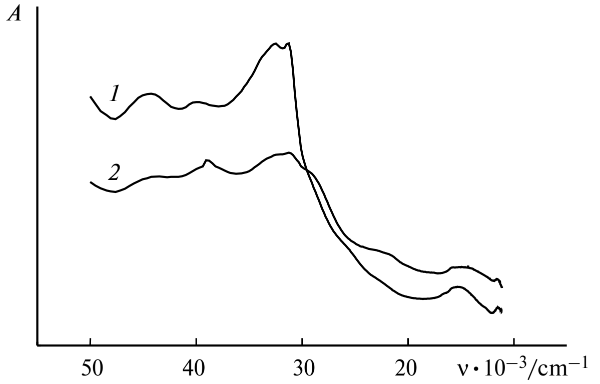


Fig. 3. Diffuse reflectance spectra of polycrystalline samples of the Ni^{II} complexes: *1*, compound **2**; *2*, compound **3**.

In spite of the mononuclear structure, complexes **2** and **3** exhibit antiferromagnetic properties at helium temperatures due, apparently, to intermolecular interactions (Fig. 4). It should be noted that we have observed an analogous effect[18] for the nickel(II) pivalate mononuclear complexes with aniline and propargylamine.

Although complexes **2** and **3** differ in the number of molecules **1** and their mode of coordination, the N-donor

Table 3. Positions ($\nu \cdot 10^{-3}$/cm^{-1}) and intensities (ε/L mol^{-1} cm^{-1}) of the bands in the electronic spectra of compounds **2** and **3**

2			**3**			Band	Transition
DRS $\nu \cdot 10^{-3}$	EAS of solution in MeCN		DRS $\nu \cdot 10^{-3}$	EAS of solution in MeCN			
	$\nu \cdot 10^{-3}$	ε		$\nu \cdot 10^{-3}$	ε		
	13.89 sh	21					
	14.92 sh	26					LFT $^3A_{2g} \to {}^3T_{2g}$(F), $^3T_{1g}$(F), $^1E_g(^1D)$, $^3T_{1g}$(P)
15.34	15.87	27	15.20	14.79	104	*E*	
	17.48	18					
	23.58 sh	44	22.83 sh	22.94 sh	142		
26.60 sh	29.24	1124	28.74 sh	30.30 sh	3680		
31.25	31.65 sh	3391	31.25	31.45	4600	*D*	MLCT d(M)$\to\pi^*$(L)
32.47	33.78	3992	33.33 sh	32.68	4265		
	39.68	$1.45 \cdot 10^4$	39.06	39.37	$2.73 \cdot 10^4$	*C*	LMCT π(L)$\to$dπ^*(M) π(L)$\to$dσ^*(M)
41.67	42.74	$2.18 \cdot 10^4$	43.48	42.74	$2.54 \cdot 10^4$	*B*	CTT π(L)$\to\pi^*$(L)
47.60	47.62	$2.43 \cdot 10^4$		46.30 inflect	$2.62 \cdot 10^4$		
				47.61	$2.87 \cdot 10^4$	*A*	LMCT σ(L)$\to$dπ^*(M)
	49.02 sh	$2.37 \cdot 10^4$		49.02 sh	$2.58 \cdot 10^4$		

Note: sh is a shoulder, inflect is an inflection.

ligand retains its composition and overall geometry. Apparently, the difference in the composition of compounds **2** and **3** results from the fact that the reaction with the tetranuclear complex gave rise to the second product (in ~50% yield), which is highly soluble even in alkanes. According to the IR spectroscopic data, this compound contains nickel atoms, hydroxo groups, and trimethylacetate anions but is devoid of the coordinated molecules of **1**. As a result, in the presence of the same amount of the starting ligand per metal atom, the L : carboxylate ratio was higher in the former complex, which is reflected in the compositions of the final reaction products.

Unlike the nickel derivatives, cobalt(II) trimethylacetates, *viz.*, the polynuclear complex

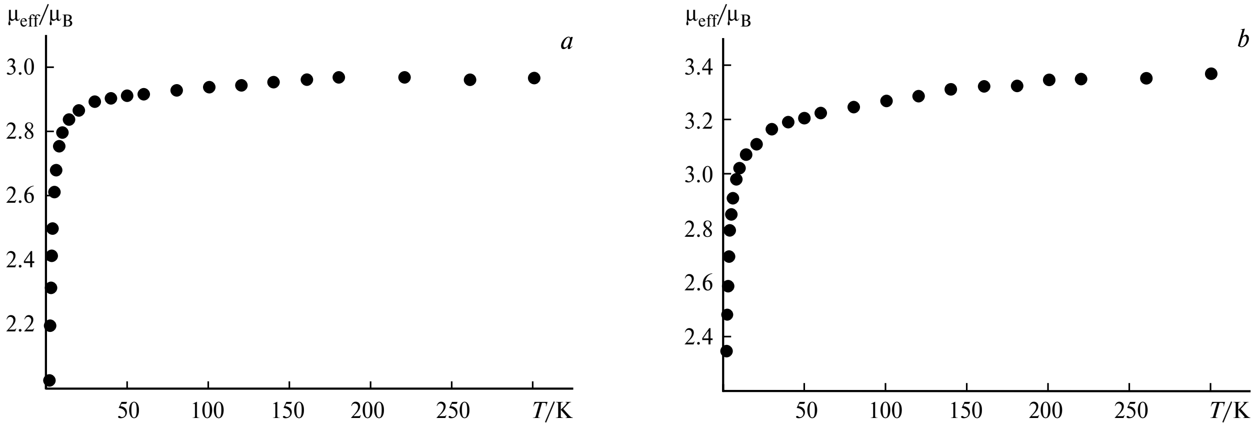


Fig. 4. Temperature dependences of the effective magnetic moments (μ_{eff}) for complexes **2** (*a*) and **3** (*b*).

$[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ and the tetranuclear cluster $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$, gave the trinuclear complex $Co_3(\mu_3\text{-}OH)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}L)_2(\eta\text{-}OOCCMe_3) \cdot C_6H_6$ (**4**) (Scheme 2, Fig. 5, Table 4) under analogous conditions (20 °C, benzene, **1** : Co = 1 : 1). X-ray diffraction study demonstrated that three metal atoms in complex **4** (Co...Co, 3.145(1)—3.454(1) Å) are linked through the tridentate-bridging hydroxo group (Co—O(OH), 1.985(10)—2.098(10) Å) and four bridging carboxylate anions (Co—O, 1.924(13)—2.094(13) Å). In the molecule of complex **4**, only two cobalt atoms are in an octahedral environment and contain the chelate-bound ligand L in the inner sphere (Co(2)—N(amine), 2.248(18) Å; Co(2)—N(quinoline), 2.15(2) Å). The third metal atom is in a tetrahedral environment and is coordinated only by carboxylate groups (Co(1)—O(7), 1.992(12) Å). One of these groups is terminal and is stabilized through the short intramolecular bond between the H atom of the hydroxo group and the O atom of the trimethylacetate anion (OH...H, 2.10 Å; O—H, 0.85 Å; O(8)—O(11), 2.76(6) Å).

In spite of the involvement of the Co^{II} ions in spin-orbital coupling,[19,20] the temperature dependence of the effective magnetic moment for complex **4** is more likely to correspond to the antiferromagnetic exchange (Fig. 6, μ_{eff} = 7.24—5.56 μ_B (300—2 K)).

The situation changed when the reactions of the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ or the tetranuclear cluster $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ with **1** were carried out with heating. In spite of the anaerobic conditions, these reactions afforded the diamagnetic binuclear complex $Co_2(\mu_2\eta^2\text{-}L)_2(\mu\text{-}OOCCMe_3)(\eta\text{-}L)(OOCCMe_3)_3 \cdot C_6H_6$ (**5**) (see Scheme 2) in which some amino groups are deprotonated and the Co atoms are in the oxidation state of +3. As a result, two new bridging chelate ligands are formed in which the tetrahedral nitrogen atoms of two amido groups are bound to both metal atoms

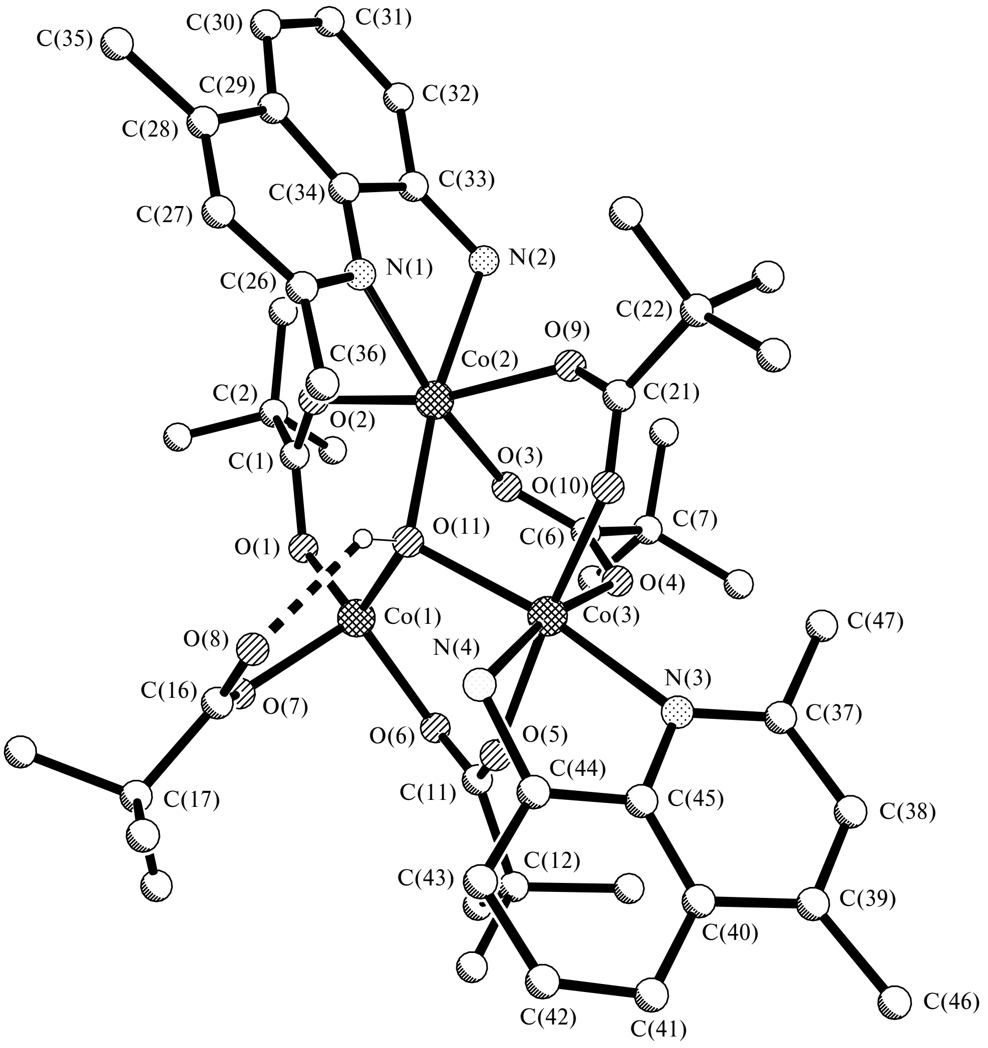
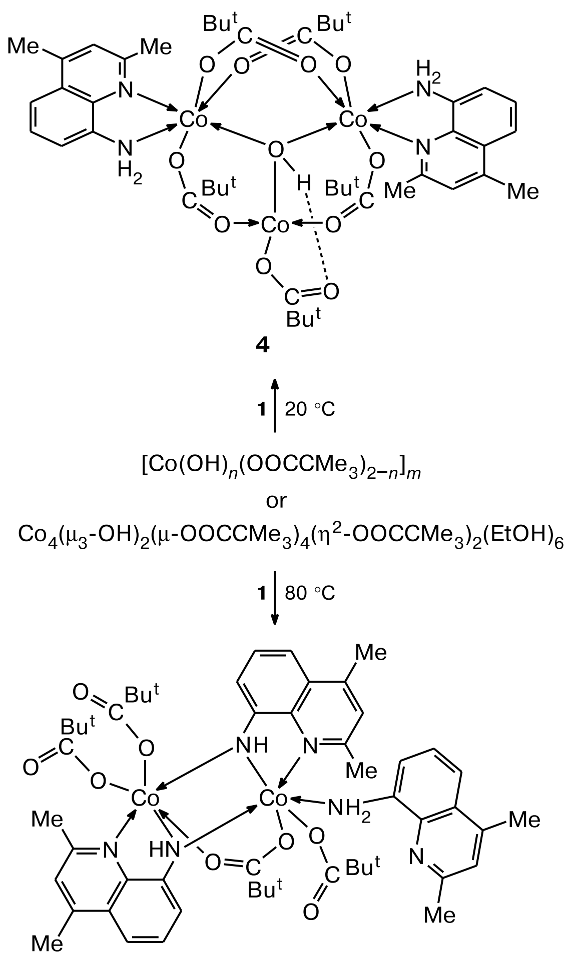


Fig. 5. Crystal structure of complex **4**.

Scheme 2



4

$[Co(OH)_n(OOCCMe_3)_{2-n}]_m$

or

$Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$

5

Reagents and conditions: 1 : Co = 1 : 1, C_6H_6, Ar.

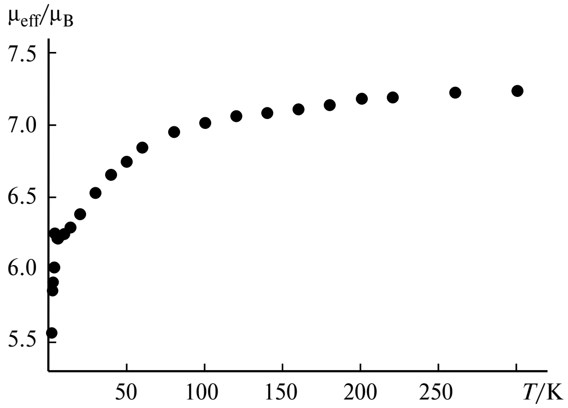


Fig. 6. Temperature dependence of the effective magnetic moment (μ_{eff}) for complex **4**.

(Co...Co, 2.8485(13) Å; Co(1)—N(NH), 1.953(5) Å; Co(2)—N(NH), 1.910(6) Å; Co—N(quinoline), 1.985(6) Å) (Fig. 7, Table 5). In molecule **5**, the Co^{III} atoms are nonequivalent. The distorted octahedral environment about the Co(1) atom is completed with two terminal trimethylacetate anions (Co—O, 1.939(4)—1.945(4) Å), whereas the Co(2) atom is bound to only one terminal trimethylacetate group (Co—O, 1.956(5) Å) and one monodentate-coordinated neutral aminoquinoline molecule (Co—N(amine), 2.024(5) Å). Noteworthy are the very short metal—ligand distances in complex **5**, which are typical of Co^{III} derivatives in an octahedral environment with the stable 18-electron configuration.[21,22] For example, the Co—N bonds in molecule **5** containing N-donor ligands are, on the average, 0.16 Å and 0.28 Å shorter (for Co—N(quinoline) and Co—N(amine), respectively) than the analogous bonds in molecule **4** containing the octahedral Co^{II} atoms.

Table 4. Selected geometric parameters of complex **4**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Co(1)—O(1)	1.92(1)	O(1)—Co(1)—O(6)	107.1(6)	O(3)—Co(2)—N(1)	165.0(7)	O(5)—Co(3)—O(10)	170.9(5)
Co(1)—O(6)	1.98(1)	O(1)—Co(1)—O(7)	106.3(5)	O(3)—Co(2)—N(2)	90.6(6)	O(5)—Co(3)—O(11)	90.9(5)
Co(1)—O(7)	1.99(1)	O(1)—Co(1)—O(11)	120.1(5)	O(9)—Co(2)—O(11)	96.9(5)	O(5)—Co(3)—N(3)	86.1(6)
Co(1)—O(11)	1.99(1)	O(6)—Co(1)—O(7)	101.5(5)	O(9)—Co(2)—N(1)	88.7(7)	O(5)—Co(3)—N(4)	83.4(5)
Co(2)—O(2)	2.08(1)	O(6)—Co(1)—O(11)	119.4(5)	O(9)—Co(2)—N(2)	78.2(6)	O(10)—Co(3)—O(11)	95.1(5)
Co(2)—O(3)	2.09(1)	O(7)—Co(1)—O(11)	99.5(5)	O(11)—Co(2)—N(1)	111.7(7)	O(10)—Co(3)—N(3)	86.6(6)
Co(2)—O(9)	2.05(1)	O(2)—Co(2)—O(3)	87.2(5)	O(11)—Co(2)—N(2)	171.7(6)	O(10)—Co(3)—N(4)	89.5(5)
Co(2)—O(11)	2.06(1)	O(2)—Co(2)—O(9)	164.9(6)	N(1)—Co(2)—N(2)	75.1(8)	O(11)—Co(3)—N(3)	168.0(5)
Co(2)—N(1)	2.15(2)	O(2)—Co(2)—O(11)	98.1(5)	O(4)—Co(3)—O(5)	88.9(5)	O(11)—Co(3)—N(4)	93.3(5)
Co(2)—N(2)	2.25(2)	O(2)—Co(2)—N(1)	87.6(7)	O(4)—Co(3)—O(10)	97.4(5)	N(3)—Co(3)—N(4)	74.8(6)
Co(3)—O(4)	2.09(1)	O(2)—Co(2)—N(2)	86.7(6)	O(4)—Co(3)—O(11)	93.5(5)	Co(1)—O(11)—Co(2)	102.2(5)
Co(3)—O(5)	2.09(1)	O(3)—Co(2)—O(9)	92.8(5)	O(4)—Co(3)—N(3)	98.1(6)	Co(1)—O(11)—Co(3)	107.1(5)
Co(3)—O(10)	2.07(1)	O(3)—Co(2)—O(11)	82.9(5)	O(4)—Co(3)—N(4)	169.9(5)	Co(2)—O(11)—Co(3)	112.5(5)
Co(3)—O(11)	2.10(1)						
Co(3)—N(3)	2.18(2)						
Co(3)—N(4)	2.14(1)						

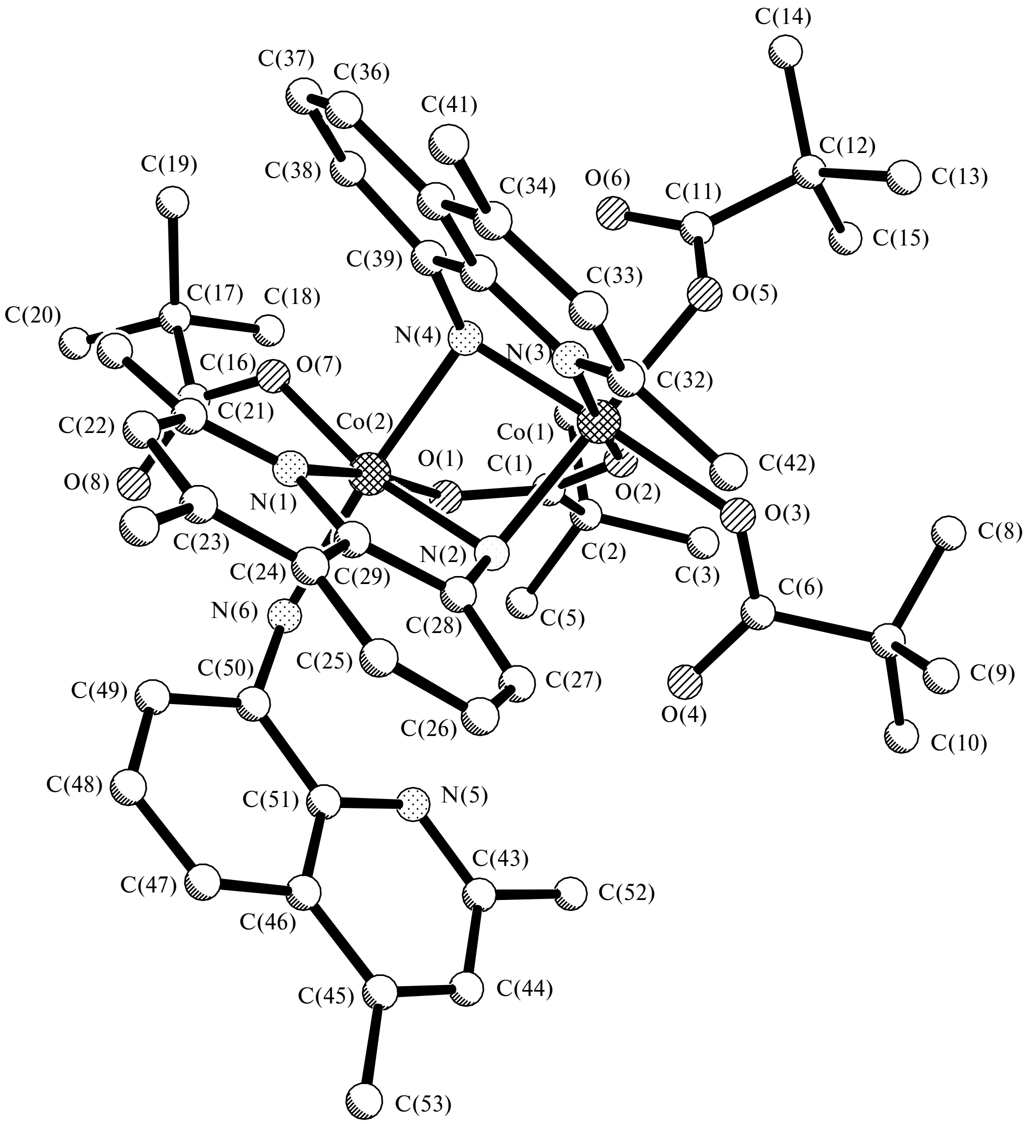


Fig. 7. Crystal structure of complex **5**.

Table 5. Selected geometric parameters of complex **5**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Co(1)...Co(2)	2.849(1)	O(2)—Co(1)—O(3)	85.3(2)	N(2)—Co(1)—N(4)	84.1(2)	O(7)—Co(2)—N(1)	101.9(2)
Co(1)—O(2)	1.907(5)	O(2)—Co(1)—O(5)	87.5(2)	N(3)—Co(1)—N(4)	85.5(2)	O(7)—Co(2)—N(2)	168.4(2)
Co(1)—O(3)	1.945(4)	O(2)—Co(1)—N(2)	88.0(2)	Co(1)—Co(2)—O(1)	81.1(1)	O(7)—Co(2)—N(4)	86.8(2)
Co(1)—O(5)	1.939(4)	O(2)—Co(1)—N(3)	173.9(2)	Co(1)—Co(2)—O(7)	125.9(1)	O(7)—Co(2)—N(6)	94.1(2)
Co(1)—N(2)	1.953(5)	O(2)—Co(1)—N(4)	90.1(2)	Co(1)—Co(2)—N(1)	97.6(2)	N(1)—Co(2)—N(2)	85.1(2)
Co(1)—N(3)	1.988(6)	O(3)—Co(1)—O(5)	86.1(2)	Co(1)—Co(2)—N(2)	43.1(2)	N(1)—Co(2)—N(4)	94.6(2)
Co(1)—N(4)	1.892(5)	O(3)—Co(1)—N(2)	94.3(2)	Co(1)—Co(2)—N(4)	41.4(2)	N(1)—Co(2)—N(6)	91.4(2)
Co(2)—O(1)	1.914(4)	O(3)—Co(1)—N(3)	99.3(2)	Co(1)—Co(2)—N(6)	135.5(2)	N(2)—Co(2)—N(4)	83.3(2)
Co(2)—O(7)	1.956(5)	O(3)—Co(1)—N(4)	175.1(2)	O(1)—Co(2)—O(7)	84.6(2)	N(2)—Co(2)—N(6)	95.1(2)
Co(2)—N(1)	1.985(6)	O(5)—Co(1)—N(2)	175.4(2)	O(1)—Co(2)—N(1)	172.7(2)	N(4)—Co(2)—N(6)	173.6(2)
Co(2)—N(2)	1.910(6)	O(5)—Co(1)—N(3)	88.7(2)	O(1)—Co(2)—N(2)	89.2(2)	Co(1)—N(2)—Co(2)	95.0(2)
Co(2)—N(4)	1.963(5)	O(5)—Co(1)—N(4)	95.2(2)	O(1)—Co(2)—N(4)	89.2(2)	Co(1)—N(4)—Co(2)	95.3(2)
Co(2)—N(6)	2.024(5)	N(2)—Co(1)—N(3)	95.8(2)	O(1)—Co(2)—N(6)	84.6(2)		

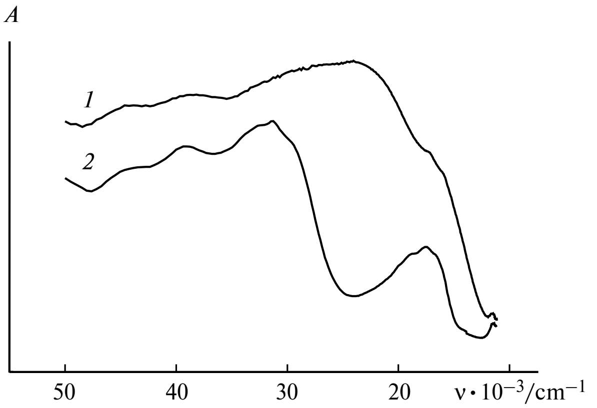


Fig. 8. Diffuse reflectance spectra of polycrystalline samples of the Co^{II} complexes: *1*, compound **5**; *2*, compound **4**.

The structural differences between complexes **4** and **5** are manifested in DRS of these compounds (Fig. 8). The spectrum of compound **4** is better resolved both in the UV and visible regions compared to the spectrum of compound **5**. The EAS for these compounds in solutions are given in Table 6. The spectrum of compound **5** in acetonitrile agrees well with its DRS, which indicates that this compound retains its structure in solution. By contrast, the blue-violet color of compound **4** is retained only in a solution in benzene (during the measurement of the spectrum), whereas a solution in acetonitrile turned a steady brown color. A comparison of the results obtained in the present study provides evidence that complex **4** in acetonitrile in the presence of atmospheric oxygen underwent transformations accompanied by changes in the geometry of the metal fragment (transformation of the trinuclear complex into the binuclear structure).

Hence, the polynuclear nickel and cobalt pivalates differ noticeably in their behavior in the reactions with ligand **1**. The results of the reactions with nickel derivatives are determined primarily by the **1** : carboxylate anion ratio, giving rise to mononuclear complexes with the high-spin Ni^{II} atom in an octahedral environment, which is typical of the behavior of nickel in such systems.[4,5] The reactions of **1** with polynuclear cobalt trimethylacetates are accompanied by destruction of their metal cores to form tri- or binuclear complexes. However, the structures of the final products are determined by the reaction temperature. Compound **4** contains cobalt atoms both in octahedral and tetrahedral environments, which is rather typical of cobalt in such ligand-deficient systems.[23,24] It should be noted that, in spite of the absence of an external oxidizing agent under the conditions of the thermal reaction, the cobalt atom and molecule **1** (in compound **5**) were oxidized. In this case, the carboxylate anion can be the only oxidizing agent. We observed an analogous situation upon oxidation of the N-Ph-*o*-phenylenediamine molecules coordinated to the Co^{II} atoms under inert conditions.[25]

Table 6. Positions ($\nu \cdot 10^{-3}/\text{cm}^{-1}$) and intensities ($\varepsilon$/L mol^{-1} cm^{-1}) of the bands in the electronic spectra of compounds **3** and **4**

Compound **4** (blue-violet)					Compound **5** (brown)		
EAS of solution in MeCN (brown)		EAS of solution in C_6H_6 (blue-violet)		DRS $\nu \cdot 10^{-3}$	DRS $\nu \cdot 10^{-3}$	EAS of solution in MeCN (brown)	
$\nu \cdot 10^{-3}$	ε	$\nu \cdot 10^{-3}$	ε			$\nu \cdot 10^{-3}$	ε
48.54 sh	$3.91 \cdot 10^4$				49.02	49.50	$9.78 \cdot 10^4$
47.17	$4.46 \cdot 10^4$	Absorption of					
43.10	$3.65 \cdot 10^4$	the solvent		43.86 sh	44.84	43.10	$7.84 \cdot 10^4$
39.37	$4.08 \cdot 10^4$			39.06	38.91	40.16 sh	$6.21 \cdot 10^4$
		33.78	5889				
		32.68	6060				
31.45	66.61	31.35	6186	31.25			
(br. band)		30.49 sh	4874	29.94 sh	29.15	30.58	$1.46 \cdot 10^4$
		29.94 sh	4535				
					26.53 sh	26.53 sh	$1.10 \cdot 10^4$
		23.58 inflect	224		24.33	25.00 sh	7194
						19.45 sh	1516
19.01	333	18.66	226	18.87 sh			
17.54	335	17.24	273	17.54	18.05 sh	17.24 sh	663
16.67 sh	301	16.45	245	16.67 sh	16.21 sh		
				15.15 sh			
14.49 sh	60	14.49 sh	29	13.90 sh			
12.19 sh	8			11.49	11.44		

Experimental

All syntheses of the complexes were carried out in an inert atmosphere with the use of anhydrous solvents. The starting Ni^{II} and Co^{II} hydroxotrimethylacetato complexes were synthesized according to known procedures.[15,26] The IR spectra of the complexes were measured on a Specord M80 instrument in KBr pellets. The electronic absorption spectra of solutions of complexes **2—5** and diffuse reflectance spectra of polycrystalline samples of these complexes were recorded on a Specord M400 spectrophotometer. The concentration of the solutions was ~10^{-3} mol L^{-1}. The measurements were carried out with the use of 1.0—0.1-cm quartz cells. The static magnetic susceptibility χ'_M was measured on a SQUID MPMS-5S Quantuim Design magnetometer in the temperature range of 300—2 K. The effective magnetic moments μ_{eff} were calculated according to the equation:

$$\mu_{eff} = (8\chi'_M T)^{1/2}.$$

Syntheses of complexes 2—5. η^2-8-Amino-2,4-dimethylquinolinoditrimethylacetatonickel(II), $Ni(\eta^2\text{-}L)(\eta^2\text{-}OOCCMe_3)_2 \cdot 0.5C_6H_6$ (2). Benzene (20 mL) was added to a mixture of $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ (0.2 g, 0.091 mmol) and 8-amino-2,4-dimethylquinoline (0.13 g, 0.77 mmol), and the reaction mixture was stirred under argon at 20 °C for 15 min until the reagents were completely dissolved. The reaction solution was concentrated at 0.1 Torr (20 °C) to 10 mL and then kept at ~20 °C for 24 h. The pale-green crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried in an argon flow. The yield of $\mathbf{2} \cdot 0.5C_6H_6$ was 0.3 g (79% with respect to the starting amount of Ni). Found (%): C, 60.5; H, 6.7; N, 5.7. $C_{24}H_{33}N_2NiO_4$. Calculated (%): C, 60.99; H, 6.99; N, 5.93. IR (KBr), ν/cm^{-1}: 3304 w, 3208 w, 3184 w, 3136 w, 2960 s, 2928 m, 2864 w, 1664 m, 1608 s, 1576 m, 1528 v.s, 1512 v.s, 1488 s, 1432 v.s, 1360 s, 1224 s, 1176 m, 1088 m, 1032 w, 984 w, 904 s, 816 m, 776 m, 760 w, 728 w, 608 s, 544 w, 528 w, 456 w, 408 m.

The crystals were suitable for X-ray diffraction analysis.

η^2-8-Amino-2,4-dimethylquinolino-η^1-8-amino-2,4-dimethylquinolino-η^2-trimethylacetatonickel(II), $Ni(\eta^2\text{-}L)(\eta^2\text{-}OOCCMe_3)(OOCCMe_3)L$ (3). Benzene (30 mL) was added to a mixture of $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ (0.3 g, 0.26 mmol) and 8-amino-2,4-dimethylquinoline (0.18 g, 1.04 mmol), and the reaction mixture was stirred under argon at 20 °C for 15 min until the reagents were completely dissolved. The reaction solution was concentrated at 0.1 Torr (20 °C) to 10 mL and then kept at ~20 °C for 24 h. The dark-green crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried in an argon flow. The yield of **3** was 0.18 g (28% with respect to the starting amount of nickel). Found (%): C, 63.7; H, 6.8; N, 9.3. $C_{32}H_{42}N_4NiO_4$. Calculated (%): C, 63.46; H, 6.94; N, 9.25. IR (KBr), ν/cm^{-1}: 3440 m, 3384 w, 3200 w, 3232 w, 3072 w, 2952 m, 2920 m, 2864 w, 1664 m, 1608 m, 1552 m, 1512 v.s, 1480 m, 1432 s, 1408 m, 1352 m, 1264 w, 1224 s, 1152 w, 1136 w, 1080 m, 1032 m, 1000 w, 968 w, 936 w, 896 m, 800 w, 792 w, 760 s, 720 w, 664 w, 632 w, 600 s, 552 m, 488 m, 408 m.

The crystals were suitable for X-ray diffraction analysis.

Bis(η^2-8-amino-2,4-dimethylquinolino)tetra(μ_2-*O,O′*-trimethylacetato)(trimethylacetato)(μ_3-hydroxo)tricobalt(II), $Co_3(\mu_3\text{-}OH)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}L)_2(\eta\text{-}OOCCMe_3) \cdot C_6H_6$ (4). Benzene (30 mL) was added to a mixture of $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (0.27 g, 1.04 mmol per formula unit $Co(OOCCMe_3)_2$) or $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ (0.3 g, 0.26 mmol) and 8-amino-2,4-dimethylquinoline (0.18 g, 1.04 mmol), and the reaction mixture was stirred under argon at 20 °C for 15 min until the reagents were completely dissolved. The reaction solution was concentrated at 0.1 Torr (20 °C) to 10 mL and then kept at ~20 °C for 24 h. The blue-violet crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried in an argon flow. The yield of $\mathbf{4} \cdot C_6H_6$ was 0.32 g (82% with respect to the starting amount of cobalt). Found (%): C, 56.9; H, 6.9; N, 5.3. $C_{53}H_{76}N_4Co_3O_{11}$. Calculated (%): C, 56.69; H, 6.77; N, 4.99. IR (KBr), ν/cm^{-1}: 3276 m, 3196 m, 3156 m, 3092 w, 3072 w, 3036 w, 2960 s, 2924 s, 2868 m, 1684 w, 1600 v.s, 1548 s, 1480 v.s, 1416 v.s, 1372 s, 1360 s, 1260 m, 1224 v.s, 1176 m, 1156 w, 1100 m, 1036 m, 984 w, 936 w, 900 s, 872 w, 808 s, 792 s, 760 s, 728 m, 680 v.s, 604 w, 536 m, 416 m.

The crystals were suitable for X-ray diffraction analysis.

η^1-8-Amino-2,4-dimethylquinolino-bis(μ-*N,N*-η^2-8-amido-2,4-dimethylquinolino)-(μ-trimethylacetato)trimethylacetatodicobalt(III), $Co_2(\mu_2\eta^2\text{-}L)_2(\mu\text{-}OOCCMe_3)(\eta\text{-}L)(OOCCMe_3)_3 \cdot C_6H_6$ (5). Benzene (30 mL) was added to a solution of $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (0.24 g, 0.94 mmol per formula unit $Co(OOCCMe_3)_2$ or $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ (0.27 g, 0.23 mmol) and 8-amino-2,4-dimethylquinoline (0.16 g, 0.94 mmol), and the reaction mixture was stirred under argon at 80 °C for 15 min until the reagents were completely dissolved. The reaction solution was concentrated at 0.1 Torr (60 °C) to 10 mL and then kept at ~20 °C for 24 h. The brown crystalline compound that precipitated was separated from the solution by decantation, washed with cold pentane, and dried in an argon flow. The yield of $\mathbf{5} \cdot C_6H_6$ was 0.29 g (58% with respect to the starting amount of cobalt). Found (%): C, 63.0; H, 6.6; N, 7.8. $C_{59}H_{76}N_6Co_2O_8$. Calculated (%): C, 63.49; H, 6.81; N, 7.53. IR (KBr), ν/cm^{-1}: 3424 w, 3312 w, 3264 w, 2960 m, 2920 m, 2864 m, 1672 m, 1592 v.s, 1568 v.s, 1520 m, 1480 s, 1444 m, 1392 s, 1352 s, 1336 v.s, 1264 w, 1212 v.s, 1112 m, 968 w, 880 w, 800 w, 752 m, 688 w, 640 w, 616 w, 560 m, 504 w, 464 w, 424 w, 408 w.

The crystals suitable for X-ray diffraction analysis were prepared by a slow decrease in solubility of compound **5** in a benzene solution through absorption of a hexane vapor. For this purpose, a Schlenk vessel containing a solution of the complex and a flask containing hexane were linked by a tube and the system was evacuated until the hexane started to boil and then kept at 20 °C for 72 h.

X-ray diffraction study. The X-ray diffraction data sets for complexes **2—5** were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 K (for **2** and **3**), 140 K (for **4** and **5**), ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) with the use of a standard procedure.[27] The semiempirical absorption correction was applied.[28] The crystallographic parameters and details of the structure refinement of all structures are listed in Table 7.

Table 7. Crystallographic parameters of the complexes

Parameter	$\mathbf{2}\cdot0.5C_6H_6$	**3**	$\mathbf{4}\cdot C_6H_6$	$\mathbf{5}\cdot C_6H_6$
Empirical formula	$C_{24}H_{33}N_2NiO_4$	$C_{32}H_{42}N_4NiO_4$	$C_{53}H_{76}N_4Co_3O_{11}$	$C_{59}H_{76}N_6Co_2O_8$
Molecular weight	472.23	605.41	1121.97	1115.11
Space group	$P\bar{1}$	*Pbca*	$P2_1/n$	$P2_1/n$
a/Å	9.744(3)	24.109(8)	12.317(12)	12.7542(19)
b/Å	10.814(3)	9.456(4)	18.73(2)	13.963(2)
c/Å	12.152(4)	26.528(9)	24.25(2)	31.521(5)
α/deg	106.181(7)	90	90	90
β/deg	100.880(7)	90	91.47(4)	96.553(5)
γ/deg	99.405(7)	90	90	90
V/Å^3	1175.6(6)	6047(4)	5593(9)	5576.8(15)
Z	2	8	8	4
ρ_{calc}/g cm^{-3}	1.334	1.330	1.331	1.331
μ/cm^{-3}	0.857	0.684	0.938	0.654
Radiation	Mo-Kα (λ = 0.71073 Å)			
$\theta/2\theta$ scan range/deg	1.80—30.7	1.75—29.97	1.37—26.94	1.60—30.02
Number of measured reflections	7185	12646	9123	12624
Number of reflections with $I > 4.0\sigma$	5604	5627	6191	6723
R_1	0.0503	0.0688	0.0698	0.0716
wR_2	0.1349	0.1454	0.1295	0.1499

The structures of all complexes were solved by direct methods with the use of the SHELXS97 program package[29] and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms (positions of the H atoms were kept fixed with $U_H = 0.08^2$) using the SHELXL97 program package.[30] The selected geometric parameters of the complexes are given in Tables 1, 2, 4, and 5.

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