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Formation of cobalt(III) cations with semiquinonediimine ligands

I. G. Fomina,[a] A. A. Sidorov,[a] G. G. Aleksandrov,[a] V. N. Ikorskii,[b]
V. M. Novotortsev,[a] S. E. Nefedov,[a] and I. L. Eremenko[a]★

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 952 1279. E-mail: ilerem@igic.ras.ru
[b]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489

The reactions of polynuclear cobalt(II) trimethylacetates $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$, $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$, or $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ with an excess of *N*-phenyl-*o*-phenylenediamine (**1**) in toluene followed by treatment with atmospheric oxygen afforded the diamagnetic complex $[Co\{\eta^2\text{-}(NPh)(NH)C_6H_4\}_2\{\eta^1\text{-}(NH_2)C_6H_4(NPhH)\}]^+(Me_3CCOO...H...OOCCMe_3)^-$ (**3**), whose cation contains the Co^{III} atom. The reaction of $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ with a deficient amount of diamine **1** in acetonitrile under an argon atmosphere gave rise to the antiferromagnetic ionic complex $[Co\{\eta^2\text{-}(NPh)(NH)C_6H_4\}_2MeCN]^+[Co_2(\mu_2,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2]^-\cdot 2MeCN$ (**4**), whose cation is an isoelectronic analog of the cation in complex **3**. The structures of the new compounds were established by X-ray diffraction analysis.

Key words: *N*-phenyl-*o*-phenylenediamine; cobalt(III), trimethylacetate complexes; semiquinonediimine, oxidative dehydrogenation, X-ray diffraction analysis.

Previously,[1—3] we have demonstrated that aromatic 1,2-diamines coordinated to transition metal atoms of the nickel subgroup are readily involved in oxidative dehydrogenation by atmospheric oxygen to form the stable $[C_6H_4(NH)(NR)]_2M$ fragment (M = Ni, Pd, or Pt) in which the M^{II} atoms are in a typical square-planar environment. *o*-Phenylenediamine and its *N*(R) derivatives (R = Ph (**1**), Me, H (**2**)) underwent oxidative dehydrogenation by $K_2[MX_4]$ (M = Pd, Pt; X = Cl^-, NO_2^-). The reactions proceeded *via* the formation of mononuclear metal(II) tetramine complexes.[3]

The reaction with trinuclear palladium trimethylacetate $Pd_3(\mu\text{-}OOCCMe_3)_6$ as the starting complex also gave rise to $[C_6H_4(NH)(NPh)]_2Pd$. However, this reaction afforded the trinuclear complex anion containing the chelate-bridging iminoimide groups, *viz.*, $\{Pd_3(OOCCMe_3)_4(\mu\text{-}OH)[\mu\text{-}N,N\text{-}\eta^2\text{-}N,N'\text{-}(N)(NPh)(C_6H_4)]_2\}^-$, as an intermediate.[4]

Oxidative dehydrogenation of *N*-phenyl-*o*-phenylenediamine (**1**) in the presence of the nonanuclear Ni^{II} cluster, *viz.*, $Ni_9(\mu_4\text{-}O)_3(\mu_3\text{-}OH)_3(HOOCCMe_3)_4(OOCCMe_3)_{12}$, is a more complicated process. This reaction yielded tetranuclear complexes with the monodentate- and chelate-coordinated L molecules, *viz.*, $L_2Ni_4(\mu_3\text{-}OH)_2(HOOCCMe_3)_4(\mu\text{-}OOCCMe_3)_6$ and $L_2Ni_4(\mu_3\text{-}OH)_2(MeCN)_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)_4$ (L = 1,2-$(NPhH)(NH_2)C_6H_4$), respectively, as intermediates. The formation of these intermediates is determined by the reaction conditions and the solvent nature. However, in the reactions performed under oxidation conditions and a ligand excess, these intermediates readily generated $[C_6H_4(NH)(NR)]_2Ni$ in high yields regardless of their structures.[5,6] The first step of oxidative dehydrogenation of *o*-phenylenediamine **2** involved the transformation of the nonanuclear cluster $Ni_9(\mu_4\text{-}O)_3(\mu_3\text{-}OH)_3(HOOCCMe_3)_4(OOCCMe_3)_{12}$ into a trinuclear complex with two unusual bridging *o*-phenylenediamine ligands. The latter complex underwent further transformation into the bis-semiquinonediimine mononuclear complex $[C_6H_4(NH)_2]_2Ni$ under the action of diamine in air.[7]

As a result, in spite of the different starting metal-containing reagents and paths of the transformation of coordinated aromatic 1,2-diamines, the reactions afforded bis-semidiimine complexes containing metals of the nickel triad in a square-planar coordination environment. Unlike these metals, the Co^{II} atom has one less electron. This fact allows one to vary the electronic structures of both the metal center and coordinated diamines. In the present study, we report the results of the exploration into oxidative dehydrogenation of diamine **1** in the presence of polynuclear cobalt(II) trimethylacetates.

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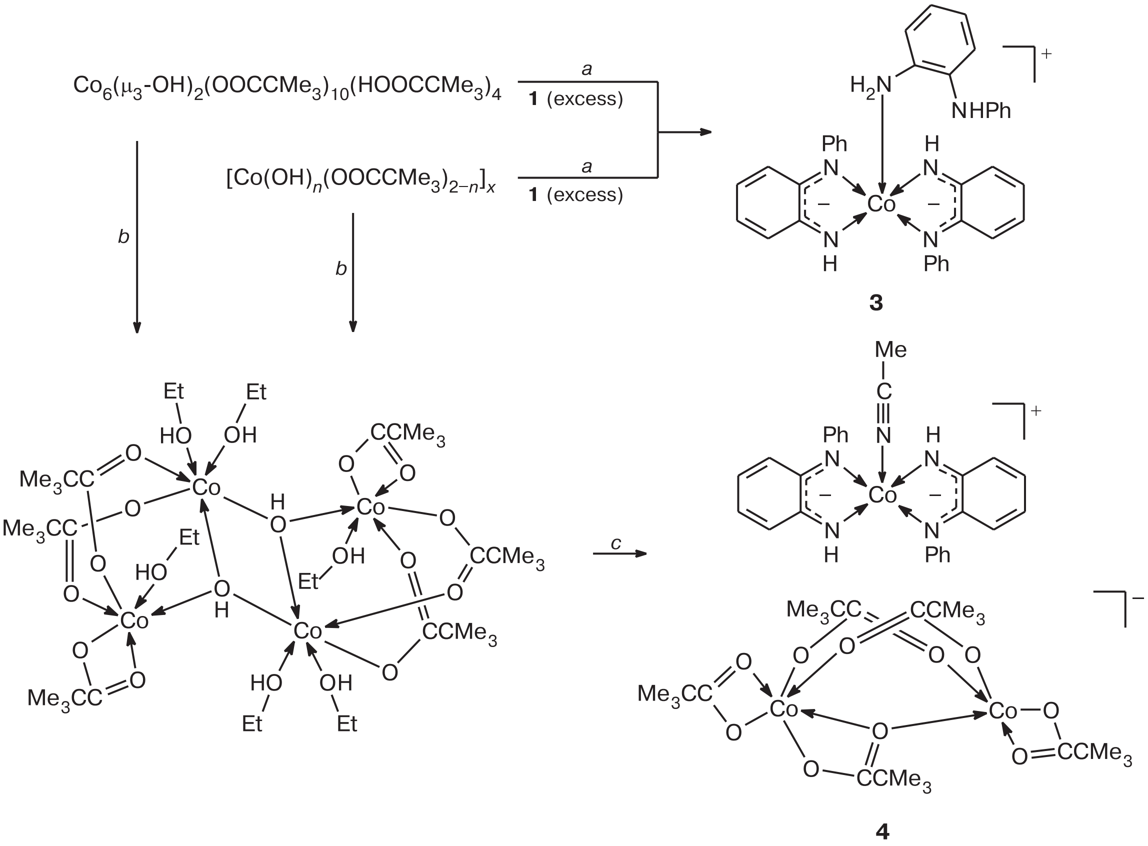
Scheme 1



Reagents and conditions: *a*. atmospheric O_2, toluene, 60 °C. *b*. atmospheric O_2, EtOH. *c*. [Co] : **1** = 2 : 1, MeCN, 60 °C, Ar.

Results and Discussion

We found that the reaction of the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (prepared by fusing $Co(OOCCH_3)_2 \cdot 4H_2O$ with excess pivalic acid at 165 °C) with an excess of diamine **1** in toluene under argon followed by slow oxidation of the reaction solution with atmospheric oxygen produced the diamagnetic ionic complex $[Co\{\eta^2\text{-}(NPh)(NH)C_6H_4\}_2\{\eta^1\text{-}(NH_2)C_6H_4(NPhH)\}]^+$ $(Me_3CCOO...H...OOCCMe_3)^-$ (**3**) (Scheme 1).

According to the X-ray diffraction data, the central Co^{III} atom in the cation of complex **3** (Fig. 1, Table 1) has a distorted tetragonal-pyramidal environment formed by five N atoms four of which are involved in two chelate-coordinated *o*-semiquinonediimine ligands. The angle between the planes of the ligands is 153.7(2)° (Co(1)—N(1), 1.915(4) Å; Co(1)—N(2), 1.839(5) Å; Co(1)—N(3), 1.911(4) Å; Co(1)—N(4), 1.861(5) Å). The fifth nitrogen atom belongs to the neutral ligand coordinated to the Co atom through the lone pair of the NH_2 group (Co(1)—N(5), 2.013(5) Å). The N—C and C—C bond lengths in this ligand have values typical of the nonoxidized benzoid form (N(5)—C(25), 1.436(6) Å; C(25)—C(30), 1.420(7) Å; C(30)—N(6), 1.410(7) Å).

The geometry of two planar semiquinonediimine fragments is characterized by shortened bonds in the five-membered nitrogen-containing metallocycle

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)—N(1)	1.915(4)	N(2)—Co(1)—N(4)	172.2(2)	N(3)—Co(1)—N(1)	160.05(18)
Co(1)—N(2)	1.839(5)	N(2)—Co(1)—N(3)	97.4(2)	N(2)—Co(1)—N(5)	94.9(2)
Co(1)—N(4)	1.861(5)	N(4)—Co(1)—N(3)	82.1(2)	N(4)—Co(1)—N(5)	92.8(2)
Co(1)—N(3)	1.911(4)	N(2)—Co(1)—N(1)	82.0(2)	N(3)—Co(1)—N(5)	105.11(18)
Co(1)—N(5)	2.013(5)	N(4)—Co(1)—N(1)	95.8(2)	N(1)—Co(1)—N(5)	94.79(18)

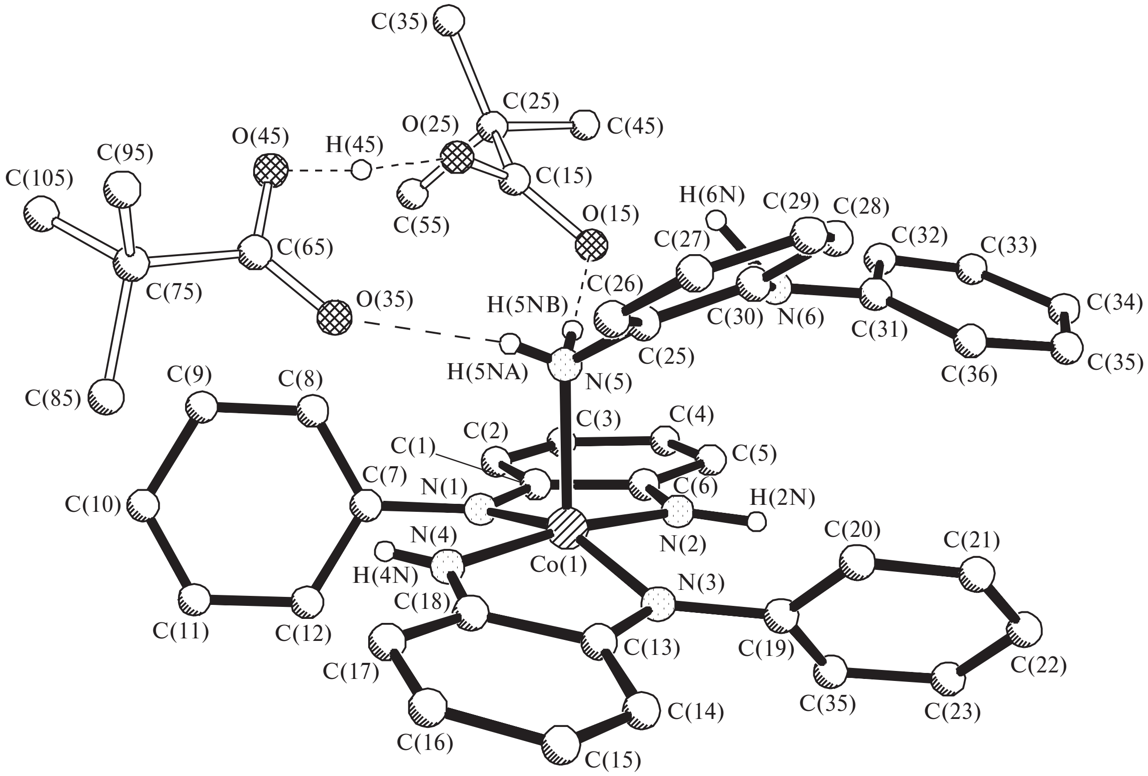


Fig. 1. Structure of complex **3**.

(N(1)—C(1), 1.339(7) Å; C(1)—C(6), 1.417(8) Å; C(6)—N(2), 1.354(7) Å; N(3)—C(13), 1.338(7) Å; C(13)—C(18), 1.444(8) Å; C(18)—N(4), 1.335(7) Å) and the alternation of short and long bonds in the phenylene ring (C(1)—C(2), 1.431(7) Å; C(2)—C(3), 1.358(8) Å; C(3)—C(4), 1.431(8) Å; C(4)—C(5), 1.379(8) Å; C(5)—C(6), 1.416(8) Å; C(13)—C(14), 1.429(8) Å; C(14)—C(15), 1.336(8) Å; C(15)—C(16), 1.420(9) Å; C(16)—C(17), 1.375(8) Å; C(17)—C(18), 1.425(8) Å). It should be noted that the phenyl substituents in cation **3** (like those in the above-mentioned bis-semidiimine complexes of Ni, Pd, and Pt**[1,2]**) are in *trans* positions. However, the metal atom in the cobalt-containing bis-semiquinonediimine fragment, unlike those in the square-planar $[C_6H_4(NH)(NR)]_2M$ complexes, substantially deviates (by 0.321(2) Å) from the plane through four N atoms. In the anion of complex **3** occurring as an associate $(Me_3CCOO...H...OOCCMe_3)^-$, the H atom is located at virtually equal distances from two acid residues (O(4s)...H(4s), 1.36(1) Å; O(2s)...H(4s), 1.23(1) Å). Two other O atoms of the carboxylate residue and the acid interact with the H atoms of the coordinated amino group of the neutral ligand through hydrogen bonds (O(3s)...H(5na), 2.03(1) Å; O(1s)...H(5nb), 1.84(1) Å) (see Fig. 1).

It appeared that the composition and structure of the starting polynuclear cobalt trimethylacetates have no effect on the character of the final reaction product obtained by oxidative dehydrogenation of diamine. Thus, the reactions with hexa- or tetranuclear cobalt(II) trimethylacetate hydroxo complexes, *viz.*, $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ or $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$, respectively, also afforded complex **3** in close yields. We failed to detect intermediates in all these reactions, unlike the above-mentioned analogous reactions with nickel trimethylacetate.

We suggested that the solvent and the ratio of reagents have to be changed for stabilization of the intermediates formed in the reaction of diamine **1** with polynuclear cobalt(II) carboxylates. It appeared that the reaction of $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ with *o*-phenylenediamine **1** taken in a ratio of [Co] : **1** = 2 : 1 (with respect to the Co atom) in MeCN under an atmosphere of argon gave rise to the antiferromagnetic ionic complex $[Co\{\eta^2\text{-}(NPh)(NH)C_6H_4\}_2MeCN]^+[Co_2(\mu_2,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2]^- \cdot 2MeCN$ (**4**) containing two solvent molecules (see Scheme 1). According to the X-ray diffraction data (Fig. 2, Table 2), the coordination environment about the central Co^{III} atom in the cation of compound **4** is formed by five N atoms. This coordination is analogous to that about the metal atom in the cation of complex **3**. Four N atoms in the coordination sphere of the Co^{III} atom (Co(3)—N(3), 1.856(4) Å; Co(3)—N(1), 1.861(4) Å; Co(3)—N(4), 1.898(4) Å; Co(3)—N(2), 1.905(4) Å) are involved in two *o*-semi-

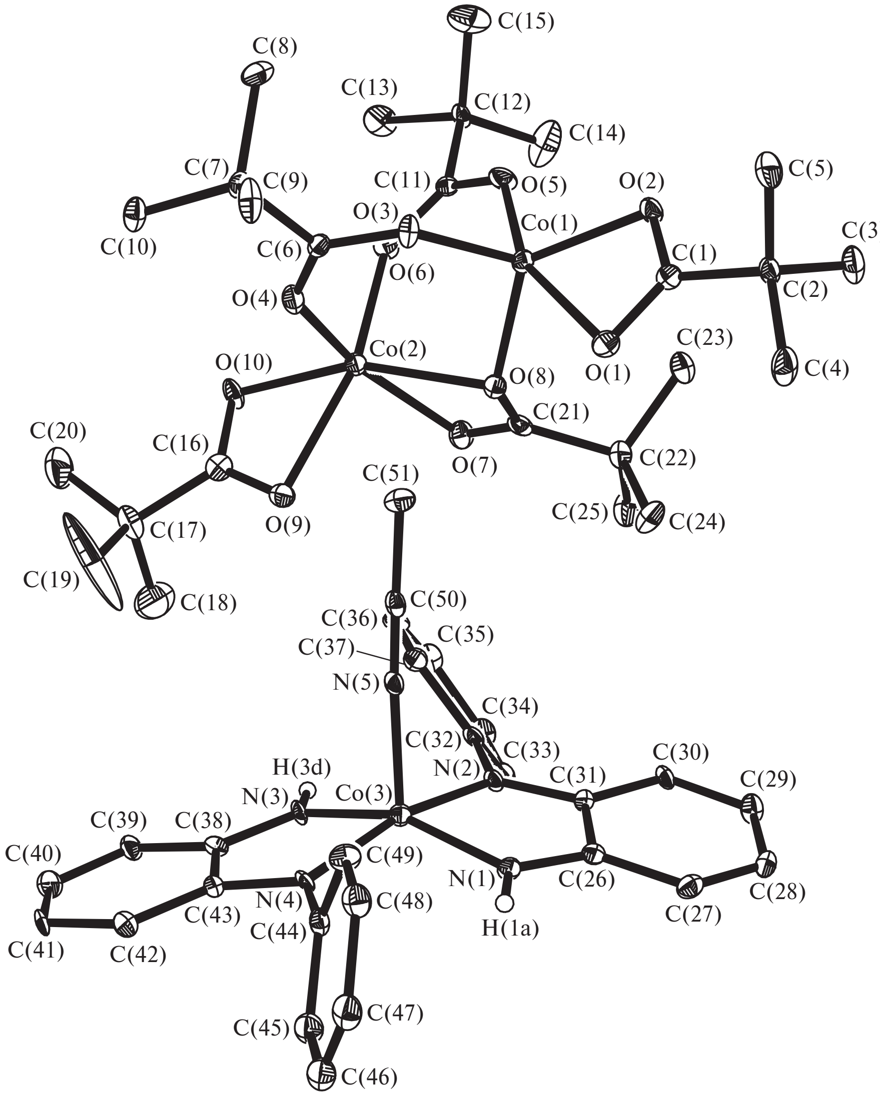


Fig. 2. Structure of complex **4**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **4**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)—O(2)	1.984(3)	O(2)—Co(1)—O(3)	115.0(1)	O(2)—Co(1)—O(5)	100.1(1)
Co(1)—O(5)	1.983(3)	O(2)—Co(1)—O(8)	127.9(1)	O(3)—Co(1)—O(5)	104.0(2)
Co(2)—O(4)	2.027(3)	O(3)—Co(1)—O(8)	107.0(1)	O(5)—Co(1)—O(8)	98.1(1)
Co(2)—O(7)	2.216(4)	O(4)—Co(2)—O(6)	95.9(1)	O(4)—Co(2)—O(7)	158.4(1)
Co(2)—O(9)	2.196(3)	O(4)—Co(2)—O(8)	98.7(1)	O(4)—Co(2)—O(9)	88.7(1)
Co(3)—N(1)	1.861(4)	O(4)—Co(2)—O(10)	95.2(1)	O(6)—Co(2)—O(7)	88.7(1)
Co(3)—N(3)	1.856(4)	O(6)—Co(2)—O(8)	95.8(1)	O(6)—Co(2)—O(9)	160.1(1)
Co(3)—N(5)	1.964(4)	O(6)—Co(2)—O(10)	98.6(1)	O(7)—Co(2)—O(8)	59.8(1)
Co(1)—O(3)	1.973(4)	O(7)—Co(2)—O(9)	94.1(1)	O(7)—Co(2)—O(10)	105.0(1)
Co(1)—O(8)	2.005(3)	O(8)—Co(2)—O(9)	102.7(1)	O(8)—Co(2)—O(10)	158.8(1)
Co(2)—O(6)	2.019(3)	O(9)—Co(2)—O(10)	61.6(1)	N(1)—Co(3)—N(2)	82.1(2)
Co(2)—O(8)	2.153(3)	N(1)—Co(3)—N(3)	155.9(2)	N(1)—Co(3)—N(4)	95.0(2)
Co(2)—O(10)	2.068(3)	N(1)—Co(3)—N(5)	101.5(2)	N(2)—Co(3)—N(3)	95.0(2)
Co(3)—N(2)	1.905(4)	N(2)—Co(3)—N(4)	165.8(2)	N(2)—Co(3)—N(5)	95.2(2)
Co(3)—N(4)	1.898(4)	N(3)—Co(3)—N(4)	81.9(2)	N(3)—Co(3)—N(5)	102.6(2)
		N(4)—Co(3)—N(5)	99.0(2)	Co(1)—O(8)—Co(2)	102.2(1)

quinonediimine ligands. The angle between the planes of the ligands is 153.7°. In the cation of complex **4**, the fifth N atom belongs to the coordinated MeCN molecule (Co(3)—N(5), 1.964(4) Å; N(5)—C(50), 1.146(6) Å; C(50)—C(51), 1.466(6) Å). The distribution of the C—N and C—C bond lengths in the identical symmetrically arranged five-membered chelate metallocycles with the *o*-semiquinonediimine ligands (N(1)—C(26), 1.316(6) Å; N(2)—C(31), 1.341(6) Å; C(26)—C(31), 1.440(6) Å) and the ration of short and long bonds in the six-membered carbon ring (C(26)—C(27), 1.435(7) Å; C(27)—C(28), 1.342(8) Å; C(28)—C(29), 1.429(7) Å; C(29)—C(30), 1.358(7) Å; C(30)—C(31), 1.421(7) Å; C(32)—C(33), 1.393(6) Å; C(32)—C(37), 1.398(7) Å) are analogous to those observed in complex **3**. In spite of the difference in the geometric characteristics of the neutral coordinated ligands in the cations of compounds **3** and **4** (**1** and MeCN, respectively), the metal atom in these compounds is characterized by the virtually identical deviation from the N_4 plane formed by the N atoms of the semidiimine ligands (0.305(2) Å in complex **4**).

Compound **4** contains the binuclear complex anion in which two cobalt(II) atoms are linked *via* three bridges, *viz*., two carboxylate ligands (Co(1)—O(3), 1.973(4) Å; Co(2)—O(4), 2.027(3) Å; O(3)—C(6), 1.272(6) Å; O(4)—C(6), 1.239(5) Å; and Co(1)—O(5), 1.983(3) Å; Co(2)—O(6), 2.019(3) Å; O(5)—C(11), 1.263(6) Å; O(6)—C(11), 1.253(6) Å) and one bridging O atom (Co(1)—O(8), 2.005(3) Å; Co(2)—O(8), 2.153(3) Å) of the chelate-bridging trimethylacetate ligand. The second O atom of the latter ligand is coordinated to the Co(2) atom (Co(2)—O(7), 2.216(4) Å; O(7)—C(21), 1.235(6) Å; O(8)—C(21), 1.305(6) Å) to form a chelate ring. Each Co atom bears the chelate-coordinated trimethylacetate ligand (Co(1)—O(2), 1.984(3) Å; Co(1)—O(1), 1.972(4) Å; O(1)—C(1), 1.241(6) Å; O(2)—C(1), 1.272(6) Å; and Co(2)—O(10), 2.068(3) Å; Co(2)—O(9), 2.196(3) Å; O(9)—C(16), 1.248(6) Å; O(10)—C(16), 1.274(6) Å). Hence, the binuclear anion contains the nonequivalent 17-electron five-coordinate and 19-electron six-coordinate Co atoms.

It can be assumed that it is the binuclear anion containing the high-spin Co^{II} atoms (S = 3/2) that is responsible for the magnetic properties of complex **4**. As can be seen from Fig. 3, the effective magnetic moment of the complex (for the overall molecule) is decreased from 6.45 to 4.34 μ_B in the temperature range of 300—2 K.

Oxidative dehydrogenation of diamine **2** with atmospheric oxygen in the presence of $Co(ClO_4)_2$, $Co(OAc)_2$, and $CoCl_2$ has been studied previously.[8] The bis-semiquinonediimine complex $[C_6H_4(NH)_2]_2Co$ containing the Co^{II} atom in a square-planar ligand environment was prepared only with the use of cobalt acetate. In spite of the presence of the unpaired electron on the metal atom, this complex remains mononuclear as distinct from the Pt^{III}-containing isoelectronic cation of composition $[C_6H_4(NH)_2]_2Pt$, which occurs as a dimer both in the crystal and in a solution in $CDCl_3$.[2] At the same time, the Co^{III}-containing mononuclear cations with the cobalt—bis-semiquinonediimine fragment, which are isoelectronic analogs of the cations in complexes **3** and **4**, were synthesized by the reactions of $Co(ClO_4)_2$ and $CoCl_2$, respectively, with diamine **2**. However, the latter reactions always required an oxidizing agent. The composition of the reaction products depends substantially on both the nature of the oxidizing agent and the synthesis conditions. The mechanism of formation of complex **4**, which contains the cation with the oxidized diamine ligands and the cobalt(III) atom, in an inert atmosphere remains to be elucidated. It can only be noted that the carbonyl groups of the trimethylacetate fragment are formally the only oxidizing agent present in the system. However, our attempts to isolate the products of reduction of the trimethylacetate ligands failed.

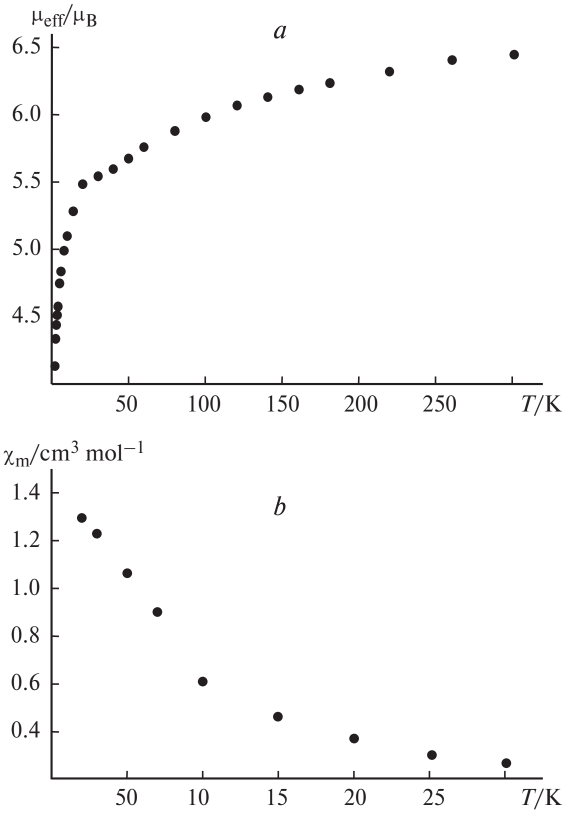


Fig. 3. Effective magnetic moment (μ_{eff}) (*a*) and static magnetic susceptibility (χ_m) (*b*) *vs*. the temperature for complex **4**.

Experimental

Complex **3** was synthesized in an inert atmosphere followed by slow bubbling of air through the reaction mixture. Complex **4** was prepared in the absence of O_2 under argon. In both cases, anhydrous solvents were used. The starting cobalt complexes were synthesized according to known procedures.[9] New compounds were synthesized with the use of *N*-phenyl-*o*-phenylenediamine (Fluka). The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. 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 moment μ_{eff} was calculated according to the equation

$$\mu_{eff} = (8\,\chi_m T)^{1/2}.$$

Complex $[Co\{\eta^2\text{-}(NPh)(NH)C_6H_4\}_2\{\eta^1\text{-}(NH_2)C_6H_4(NPhH)\}]^+(Me_3CCOO...H...OOCCMe_3)^-$ (3). The polymeric complex (0.40 g, 1.5 mmol based on the $Co(OOCCMe_3)_2$ formula unit), which was prepared by fusing $Co(OOCMe)_2 \cdot 4H_2O$ with excess pivalic acid, and *N*-phenyl-*o*-phenylenediamine (0.85 g, 4.6 mmol) were dissolved in toluene (60 mL) under argon upon heating to 60 °C. The resulting blue solution was kept at 5 °C for 2—3 days with a slow supply of atmospheric oxygen to the reaction vessel. The black-blue crystals that precipitated were washed with hexane and dried in air. The yield was 0.86 g (70%). Complex **3** was prepared according to an analogous procedure starting from $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ or $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ in yields of 82 and 77%, respectively. Found (%): C, 67.01; H, 6.80; N, 10.86. $C_{46}H_{51}CoN_6O_4$. Calculated (%): C, 68.13; H, 6.29; N, 10.40. IR, ν/cm^{-1}: 2980 w, 2965 w, 1670 m, 1645 s, 1590 s, 1545 w, 1520 s, 1475 s, 1460 m, 1440 s, 1400 m, 1355 m, 1340 s, 1305 m, 1270 m, 1220 w, 1185 m, 1170 w, 1145 w, 1125 w, 1100 w, 1075 w, 1025 w, 990 w, 960 w, 925 w, 885 w, 850 m, 830 m, 750 w, 690 s, 640 s, 580 m, 530 w, 510 w, 460 w.

Complex $[Co\{\eta^2\text{-}(NPh)(NH)C_6H_4\}_2MeCN]^+[Co_2(\mu_2,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2]^- \cdot 2MeCN$ (4). The $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ complex (0.2 g, 0.19 mmol) and *N*-phenyl-*o*-phenylenediamine (**1**) (0.068 g, 0.37 mmol) were dissolved in MeCN (50 mL) under argon upon heating to 60 °C. The resulting black-blue solution was kept at −5 °C for 12 h. The black-blue crystals that precipitated were washed with hexane and dried under argon. Compound **4** was obtained in a yield of 0.054 g (80% calculated for *N*-phenyl-*o*-phenylenediamine). Found (%): C, 56.89; H, 6.81; N, 7.79. $C_{55}H_{74}Co_3N_7O_{10}$. Calculated (%): C, 56.49; H, 6.33; N, 8.38. IR, ν/cm^{-1}: 3440 s, 2956 w, 1688 w, 1668 w, 1616 s, 1552 s, 1516 s, 1484 m, 1460 s, 1416 s, 1360 m, 1224 m, 1152 w, 952 w, 796 w, 696 w, 648 w, 624 m, 458 w, 424 w, 408 w.

X-ray diffraction study. The X-ray diffraction data for complex **3** were collected on a four-circle automatic Siemens R3/PC diffractometer (λ(Mo-Kα) radiation, λ = 0.71074 Å, *T* = 22 °C). The unit cell parameters were determined and refined using 24 equivalent reflections with 2θ < 24—28°. Three strong standard reflections with 0 < χ < 65° were monitored after each 100 reflections. The intensities of the standard reflections showed no decrease in the course of data collection, and therefore, the corresponding corrections were ignored. The experimental data for complex **4** were collected on a Bruker AXS SMART-1000 diffractometer equipped with a CCD detector (λ(Mo), graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max}$ = 60°) using a standard procedure.[10]

Table 3. Crystallographic parameters of complexes **3** and **4**

Parameter	Complex	
	3	**4**
Formula	$C_{46}H_{51}CoN_6O_4$	$C_{55}H_{74}Co_3N_7O_{10}$
Space group	*P*2(1)/*c*	$P\bar{1}$
a/Å	11.798(4)	12.457(2)
b/Å	18.041(6)	15.686(4)
c/Å	19.574(7)	17.477(3)
α/deg	90	110.15(2)
β/deg	96.36(3)	90.77(1)
γ/deg	90	111.13(1)
V/Å^3	4141(2)	2953.1(2)
Z	4	2
μ/mm^{-1}	0.465	0.891
d_{calc}/g cm^{-3}	1.301	1.316
θ/2θ scan range/deg	2—54	2—56
Number of measured reflections	6660	8066
Number of reflections with *I* > 4σ	3012	6533

The structures of complexes **3** and **4** 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 amino groups and imine fragments and the position of the proton in the RCOO...H...OOCR anion (in compound **3**) were located from difference Fourier syntheses and refined isotropically. All calculations were carried out with the use of the SHELX97 program package.[11] The main geometric parameters of complexes **3** and **4** are given in Tables 1 and 2, respectively. The crystallographic parameters and details of the structure refinement are listed in Table 3.

X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

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References

1. A. A. Sidorov and S. B. Katser, *Zh. Neorg. Khim.,* 1994, **39**, 860 [*Russ. J. Inorg. Chem.*, 1994, **39** (Engl. Transl.)].
2. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. O. Ponina, P. V. Danilov, T. A. Stromnova, I. P. Stolarov, S. B. Katser, S. T. Orlova, M. N. Vargaftic, I. I. Moiseev, and Yu. A. Ustynyuc, *J. Organomet. Chem.*, 1998, **551**, 171.
3. I. G. Fomina, S. S. Talismanov, A. A. Sidorov, Yu. A. Ustynyuk, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 494 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 515].

4. I. G. Fomina, A. A. Sidorov, G. G. Aleksandrov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *J. Organomet. Chem.*, 2001, **636**, 157.
5. A. A. Sidorov, P. V. Danilov, S. E. Nefedov, M. A. Golubnichaya, I. G. Fomina, O. G. Ellert, V. M. Novotortsev, and I. L. Eremenko, *Zh. Neorg. Khim.,* 1998, **43**, 930 [*Russ. J. Inorg. Chem.*, 1998, **43** (Engl. Transl.)].
6. A. A. Sidorov, S. A. Deomidov, S. E. Nefedov, I. G. Fomina, P. V. Danilov, V. M. Novotortsev, O. G. Volkov, V. N. Ikorskii, and I. L. Eremenko, *Zh. Neorg. Khim.,* 1999, **44**, 399 [*Russ. J. Inorg. Chem.*, 1999, **44** (Engl. Transl.)].
7. A. E. Malkov, G. G. Aleksandrov, V. N. Ikorskii, A. A. Sidorov, I. G. Fomina, S. E. Nefedov, V. M. Novotortsev, I. L. Eremenko, and I. I. Moiseev, *Koord. Khim.,* 2001, **27**, 677 [*Sov. J. Coord. Chem.,* 2001, **27** (Engl. Transl.)].
8. S.-M. Peng, C.-T. Chen, D.-S. Liaw, C.-I. Chen, and Y. Wang, *Inorg. Chim. Acta*, 1985, **101**, 31.
9. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, M. O. Ponina, S. M. Deomidov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1773 [*Russ. Chem. Bull.*, 1999, **48**, 1751 (Engl. Transl.)].
10. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison, WI, 1997.
11. G. M. Sheldrick, *SHELX97, Program for the Solution of Crystal Structures*, Göttingen University, Göttingen (Germany), 1997.

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