

Catecholato complexes of cobalt and nickel with 1,4-disubstituted-1,4-diazabutadiens-1,3 and 1,2-bis(diphenylphosphino)ethane

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MS received 03 June 2014; revised 19 September 2014; accepted 24 September 2014

Abstract. Divalent cobalt and nickel form four-coordinate complexes with sterically hindered 3,6-di-*tert*-butylcatecholato dianion (3,6-DBCat) and neutral bidentate 1,4-disubstituted-1,4-diazabutadiens-1,3 (DAB). Structural study of (1,4-di-*tert*-butyl-1,4-diazabutadiene-1,3)(3,6-di-*tert*-butyl-catecolato)nickel and (1,4-bis-(2,6-di-*iso*-propylphenyl)-2,3-dimethyl-1,4-diazabutadiene-1,3)(3,6-di-*tert*-butyl-catecolato)cobalt indicates square-planar environment of metals. Chemical one-electron oxidation of nickel complexes proceeds through catecholato ligand and leads to *o*-semiquinonato adducts. EPR spectral parameters indicate preservation of square-planar configuration after oxidation. Complexes (DAB)M(Cat) (M = Ni, Co) undergo neutral ligand substitution reactions.

Keywords. Catecholates; diazabutadienes; cobalt; nickel; ligand exchange; oxidation; structural study.

1. Introduction

A feature of catecholato ligands is their ability to undergo easy one-electron oxidation forming semiquinones.^{1,2} Reversible one-electron oxidation accompanied by structural transformation occurring in a complex molecule leads to equilibrium of two isomers differing by charge distribution between metal and ligand. This phenomenon is called valent tautomerism or redox-isomerism.^{3–6} In the case of copper, the redox-isomeric transformation was observed on complexes containing 1,4-disubstituted-1,4-diazabutadiens-1,3 as neutral ancillary ligand and catecholato as redox active ligand (scheme 1). Basing on the general consideration of the theory of ligand field splitting, the authors⁴ have proposed that reversible electron transfer is accompanied by structural transformation. Square-planar geometry was attributed to catecholato derivative of copper (II) whereas the distorted tetrahedral was attached to semiquinonato complex of copper (I). Sterical hindrances of both DAB and SQ-ligands

and semiquinonato acceptor properties influence the equilibrium position.

Cobalt and nickel are the predecessors before copper in the first row of transition metals. The aim of this work is synthesis of similar complexes of cobalt and nickel and searching for new complexes demonstrating reversible intramolecular electron transfer in solution.

We have found two structurally characterized diazabutadiene nickel catecholates: (1,4-bis-(2,6-di-*iso*-propylphenyl)-2,3-dimethyl-1,4-diazabutadiene-1,3)(3,4,5,6-Cl₄-catecolato)nickel and (1,4-bis-(2,6-di-methylphenyl)-2,3-dimethyl-1,4-diazabutadiene-1,3)(3,4,5,6-Cl₄-catecolato)nickel which were used as precursors for olefin polymerization catalysts.⁷ Reversible interconversion of redox isomers was observed in complex (N,N'-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediamino)nickel cation.⁸ It is the equilibrium between Ni(III)-phenolato form of complex (at low temperature) and Ni(II)-phenoxyl radical one (at ambient temperature). Several examples of mono-catecholato complexes of cobalt and nickel with phosphines (PMe₃, dppe) have been already described.^{9,10} There are also some examples of chemical control of electronic state of nickel complexes with catecholato ligand.^{11,12}

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Scheme 1. Copper valent tautomers interconversion (DAB = 1,4-diazabutadiene-1,3; SQ and Cat = anion-radical and dianion of substituted o-quinone respectively).

2. Experimental

2.1 General considerations

Cobalt(II) chloride, nickel tetracarbonyl, amines, dppe, diacetil, glyoxal water solution (40%), were received from commercial sources (Aldrich, Fluka). 3,6-Di-*tert*-butyl-*o*-quinone-1,2 was obtained according to known procedures.¹³ Solvents were carefully dried and in most cases were degassed before using. Diazabutadiens were obtained according to known procedures.¹⁴ EPR spectra were recorded on “Bruker ER-200 SRC”, IR - on “Specord M-80”. X-ray structural studies were performed on “Smart Apex” (Bruker AXS). The most synthetic procedures were carried out in evacuated ampoules.

2.2 Synthesis and characterization of diazabutadiene-catecholato nickel complexes

General procedure: Nickel tetracarbonyl (1 mmol) was condensed into evacuated frozen ampoule (of approximately 200 mL volume) containing 1 mmol of 3,6-di-*tert*-butyl-*o*-quinone + 1 mmol corresponding diazabutadiene in 50 mL of degassed toluene. Ampoule was slowly warmed at ~30°C for half an hour and at ~80°C during the next two hours. It was necessary to freeze and evacuate ampoule periodically every ten minutes for removing CO. Resulting solution was allowed to stay for a night at -10°C. Crystalline solid was filtered, washed with light petroleum and dried under vacuum. Yields and properties are listed below.

2.2a (1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)nickel (**1**): Green solid. Slowly decomposes in air. Yield 45%. Anal. (%) Found: C 64.80; H 9.02; Ni 13.07. $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}_2\text{Ni}$ Calc.: C 64.43; H 8.95; Ni 13.20. IR (Nujol), ν , cm^{-1} : 1600 w, 1555, 1540, 1540, 1410 s, 1400 s, 1370 s, 1325 w, 1280 w, 1265 s, 1250 s, 1210 s, 1150 w, 1100 w, 1030 w, 985 s, 960 w, 945 m, 875 m, 830 w, 795, 785 m, 700 s, 655 m, 615 m, 545 w, 520 w.

2.2b (1,4-bis-(2,6-di-*iso*-propylphenyl)-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)nickel (**2**): Dark green airstable crystals. Yield 65%. Anal. (%) Found: C

72.94; H 8.79; Ni 8.95. $\text{C}_{40}\text{H}_{56}\text{N}_2\text{O}_2\text{Ni}$ Calc.: C 73.28; H 8.55; Ni 9.01. IR (Nujol, cm^{-1}): 1590 w, 1550 w, 1370 m, 1360 m, 1320 s, 1305 s, 1275 s, 1260 s, 1210 s, 1180 s, 1040 s, 985 s, 940 m, 870 m, 860 m, 785 s, 750 s, 700 s, 655 s, 620 m, 595 m, 515 m, 490 w.

2.2c (2,3-dimethyl-1,4-bis-(2,6-di-*iso*-propylphenyl)-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)nickel (**3**): Dark green airstable crystals. Yield 80%. Anal. (%) Found: C 73.48; H 8.70; Ni 8.85. $\text{C}_{42}\text{H}_{60}\text{N}_2\text{O}_2\text{Ni}$ Calc.: C 73.79; H 8.78; Ni 8.64. IR (Nujol, cm^{-1}): 1595 w, 1580 w, 1505 s, 1405 s, 1370 m, 1345 s, 1320 s, 1305 s, 1275 s, 1215 s, 1065 w, 985 s, 950 m, 890 w, 880 w, 835 w, 785 m, 740 m, 715 w, 705 w, 655 w, 620 m, 515 w.

2.2d (1,4-bis-(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)nickel (**4**): Dark green air stable solid. Yield 55%. Anal. (%) Found: C 70.50; H 7.71; Ni 10.56. $\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_2\text{Ni}$ Calc.: C 70.73; H 7.42; Ni 10.80. IR (Nujol), ν , cm^{-1} : 1720, 1600, 1555, 1460, 1360, 1320 s, 1305 s, 1245, 1205 s.

2.2e (2,2'-dipyridine)(3,6-di-*tert*-butyl-catecholato)nickel (**5**) from $\text{Ni}(\text{CO})_4$: Blue-grey air sensitive solid. Yield 42%. Anal. (%) Found: C 65.87; H 6.45; Ni 13.96. $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2\text{Ni}$ Calc.: C 66.24; H 6.49; Ni 13.49. IR (Nujol, cm^{-1}): 1615 w, 1605 m, 1420 s, 1290 m, 1280 m, 1255 m, 990 m, 950 m, 785 s, 770 s, 730 m, 655 w, 625 w.

2.2f (2,2'-dipyridine)(3,6-di-*tert*-butyl-catecholato)nickel (**5**) from $(\text{DME})\text{NiCl}_2$: $(\text{DME})\text{NiCl}_2$ was obtained by treatment of nickel powder by bromine in DME. Dithallium 3,6-di-*tert*-butyl-catecholate (prepared from 3,6-di-*tert*-butyl-*o*-benzoquinone (0.11 g, 0.5 mmol) as it is described below) was added to the suspension containing $(\text{DME})\text{NiCl}_2$ (0.11 g, 0.5 mmol) and 2,2'-bipyridine (0.078 g, 0.5 mmol) in THF (50 mL). The mixture was warmed (~80°C) and shaken during one hour, filtered and concentrated. After the *n*-hexane addition, dark microcrystalline solid was formed. It was filtered, washed with light petroleum and dried under vacuum. Yield 30%.

2.2g (1,2-bis(diphenylphosphino)ethane)(3,6-di-*tert*-butyl-catecholato)nickel* toluene (**6**): [1,2]-bis(diphenylphosphino)ethane nickel(II) chloride was obtained analogously to known procedure.¹⁵ The mixture of commercial $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (13.2 g, 0.08 mol) in 40 mL

H₂O with acetic acid (140 mL) was added to warm solution of 1,2-bis(diphenylphosphino)ethane (31.8 g, 0.08 mol) in acetic acid (570 mL) with stirring. Reaction mixture was allowed to stay for ten hours. Pink-brown crystals were filtered, washed with cold acetic acid and dried in vacuum. Yield: 40.1 g (95%).

Suspension of di-thallium-3,6-di-*tert*-butyl-catecholate prepared from *o*-quinone (0.044 g, 0.2 mmol) as it is described below in THF (10 mL), was added to [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride (0.1 g, 0.2 mmol) in THF (40 mL) in evacuated ampoule. Reaction mixture was refluxed for one hour. Solvent was changed to the mixture toluene/CH₂Cl₂ (~10/1, 50 mL), the mixture was filtered; solution volume was reduced to one half. Dark green solid, formed after cooling, was filtered, washed with light petroleum and dried in vacuum. Yield: 0.068 g (53%). According to element analysis it contains toluene molecule as solvate. Anal.(%) Found: C 73.72; H 6.44; Ni 7.62; P 8.04. C₄₇H₅₂P₂O₂Ni Calc.: C 73.37; H 6.76; Ni 7.64; P 8.07. IR (Nujol), ν , cm⁻¹: 1595, 1485, 1440 s, 1410, 1275, 1255, 1190, 1110 s, 1035, 980, 940, 880, 830, 795, 745, 725 s, 710 s, 690 s, 660, 540, 480, 450.

2.3 Synthesis and characterization of diazabutadiene-catecholato cobalt complexes

2.3a General procedure: Evacuated ampoule containing 1 mmol of 3,6-di-*tert*-butyl-*o*-quinone in THF and excess of thallium amalgam (at least 10-fold excess of Tl) was shaken until the suspension colour became bright yellow. The light suspension of di-thallium catecholate was carefully decanted to another evacuated ampoule. Thallium amalgam was carefully washed several times by THF until the solution became colourless. (Attention! Di-thallium catecholate is extremely air sensitive.) United solutions of di-thallium catecholate were added to the mixture of corresponding diazabutadiene (α , α' -bpy, dppe) (1 mmol) and dry CoCl₂ (1 mmol) in THF. Reaction mixture was refluxed during one hour. Solvent was changed to toluene (or light petroleum). Solution was filtered, partly evaporated and allowed to stay at -10°C for a night. Resulting crystalline solid was filtered, washed by cold light petroleum and dried under vacuum. Yields and properties are listed below.

2.3b (1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)cobalt (7): Blue-grey crystals. Slowly decomposes in air. Yield 33%. Anal.(%) Found: C 64.70; H 9.22; Co 13.27. C₂₄H₄₀N₂O₂Co Calc.: C 64.41; H 9.01; Co 13.17. IR (Nujol, cm⁻¹):

1580 w, 1400 s, 1300 s, 1290 s, 1270 s, 1230 s, 1210 s, 1160 m, 1030 w, 990 s, 975 s, 960 s, 925 m, 890 m, 810 m, 790 s, 705 m, 680 m, 660 s, 560 w, 540 w, 505 w, 500 w, 455 w.

2.3c (1,4-bis-(2,6-di-*iso*-propylphenyl)-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)cobalt (8): Dark green crystals. Slowly decomposes in air. Yield 35%. Anal.(%) Found: C 73.16; H 8.78; Co 8.64. C₄₀H₅₆N₂O₂Co Calc.: C 73.29; H 8.55; Co 8.99. IR (Nujol, cm⁻¹): 1480, 1450 s, 1375, 1340 s, 1325, 1290 s, 1210, 1185, 1070, 980, 825, 800, 760 m, 710 m, 650, 625 m.

2.3d (2,3-dimethyl-1,4-bis-(2,6-di-*iso*-propylphenyl)-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)cobalt (9): Dark blue crystals. Slowly decomposes in air. Yield 30%. IR (Nujol, cm⁻¹): 1500 w, 1480 w, 1405 m, 1360 m, 1330 m, 1260 m, 1240 m, 1215, 980 s, 950 m, 890, 840, 790 m, 740 m, 720, 660, 625 m.

2.3e (1,4-bis-(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene)(3,6-di-*tert*-butyl-catecholato)cobalt (10): Dark blue air sensitive crystals. Yield 61%. Anal.(%) Found: C 71.00; H 7.37; Co 10.97. C₃₂H₄₀N₂O₂Co Calc.: C 70.73; H 7.42; Co 10.80. IR (Nujol), ν , cm⁻¹: 1675, 1630, 1605, 1555, 1460, 1360, 1345, 1325, 1300, 1275, 1260, 1210, 1200.

2.3f (2,2'-dipyridine)(3,6-di-*tert*-butyl-catecholato)cobalt (11): Recrystallized from DME. Brown airstable crystals. Yield 35%. Anal.(%) Found: C 66.37; H 6.55; Co 13.66. C₂₄H₂₈CoN₂O₂ Calc.: C 66.20; H 6.48; Co 13.53. IR (Nujol, cm⁻¹): 1605 m, 1585 w, 1575 w, 1405 s, 1365 w, 1285 m, 1270 m, 1260, 1225 m, 1205 m, 1160, 1145, 1025, 975 m, 940 m, 925 w, 780 w, 775 m, 765 m, 740 m, 700 w, 680 m, 660 m.

2.3g (Bis(diphenylphosphino)ethane)(3,6-di-*tert*-butyl-catecholato)cobalt: Preparation procedure is described in.¹⁶ IR (Nujol, cm⁻¹): 1595 w, 1440 v s, 1395 v s, 1285 w, 1260 s, 1250 s, 1190 m, 1150 w, 1105 m, 1030 w, 980 m, 940 w, 880 s, 810 w, 750 w, 735 v s, 695 v s, 680, 650 m, 525, 515 m, 495, 480 w.

2.4 Substitution reactions, general procedure

All the reactions of substitution of diazabutadiene ligands by dppe and 2,2'-bpy were carried out in the same manner. Toluene solutions of ligand and corresponding

Table 1. Crystallographic data and structure refinement details for **1** and **9**.

	1	9
Chemical formula	C ₂₄ H ₄₀ N ₂ NiO ₂	C ₄₅ H ₆₇ CoN ₂ O ₂
Formula weight	445.88	726.94
<i>T</i> /K	293	100
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
<i>a</i> /Å	32.220(6)	33.127(2)
<i>b</i> /Å	23.844(5)	12.6267(9)
<i>c</i> /Å	22.496(5)	25.1845(17)
β /°	133.81(3)	124.953(1)
<i>V</i> /Å ³	12472(4)	8634(1)
<i>Z</i>	20	8
<i>D_c</i> /Mg m ⁻³	1.189	1.118
μ /mm ⁻¹	0.797	0.433
<i>F</i> (000)	4832	3152
θ Range for collection/°	1.22–25.05	1.81–26.07
No. of reflns. colld.	11098	35915
No. of indep. reflns.	10891	8503
<i>R</i> (int)	0.0508	0.0685
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0359	0.0509
<i>wR</i> (all data)	0.1084	0.1377
GOF on <i>F</i> ²	0.940	1.008
Largest diff. peak and hole, eÅ ⁻³	0.061/–0.407	0.713 /–0.444

complex were mixed in evacuated ampoule and slightly warmed (~60°C). Hexane was slowly added until precipitation began. Ampoule was allowed to stay during the time necessary to observe the end of precipitation. Solid powder was washed by warm hexane and dried under vacuum. Products were identified by full coincidence of their IR spectra with corresponding IR spectra of the same complexes obtained independently by the other way.

2.5 X-ray crystallography

Diffraction data were collected on a Siemens P3/PC and Bruker-AXS Smart Apex I diffractometers with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) for **1** and **9** complexes, respectively. All structures were solved by direct methods and refined against *F*² on all data by full-matrix least squares with SHELXTL.¹⁷ Absorption correction was applied using SADABS.¹⁸ All non-hydrogen atoms were refined

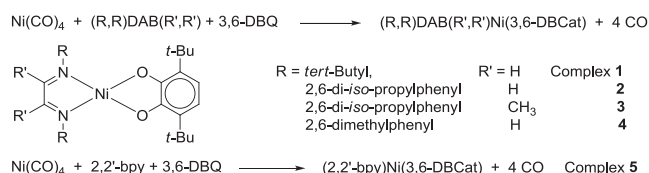
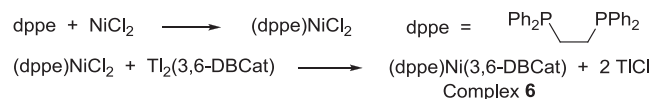
anisotropically. All hydrogen atoms in **1** and **9** were included in idealized positions and their *U*_{iso} values were set to ride on the *U*_{eq} values of the parent carbon atoms (*U*_{iso}(H) = 1.5*U*_{eq} for methyl carbons and 1.2*U*_{eq} for other carbons). Crystallographic data and structure refinement details are given in table 1. Asymmetric unit of **1** contains two independent molecules in common position and one molecule on C₂ axes. Asymmetric unit of **9** contains one disordered hexane molecule on C₂ axes.

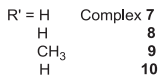
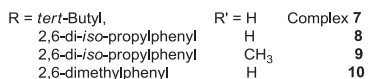
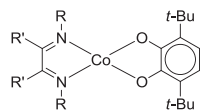
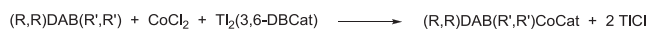
3. Results and Discussion

3.1 Synthesis and characterization of diazabutadiene-catecholato complexes of nickel and cobalt

Nickel compounds were synthesized by one-pot reaction of nickel tetracarbonyl with corresponding diazabutadiene or 2,2'-dipyridine and *o*-quinone (scheme 2).

The exception is catecholato complex with dppe (**6**) which was obtained by exchange reaction of nickel(II) chloride with dppe (scheme 3).

**Scheme 2.** Synthesis of diimine nickel catecholates.**Scheme 3.** Synthesis of catecholato nickel complex with 1,2-bis(diphenylphosphino)ethane.



Scheme 4. Synthesis of diimine cobalt catecholates.

Catecholato complexes of cobalt were obtained by exchange reaction of cobalt(II) chloride with thallium catecholate in the presence of diazabutadiene (scheme 4).

IR spectra of all complexes are typical for catecholato metal complexes and in general represent the superposition of IR-spectra of both organic fragments: coordinated neutral DAB- ligand and catecholato dianion (see experimental section).

Complex **1** was structurally characterized. Unit cell contains three independent molecules, in which geometries are very close. Each molecule has slightly distorted square-planar geometry. Nickel atom is surrounded by two oxygen atoms of catechol and two nitrogen atoms of diazabutadiene. Each ligand's fragment itself is close to planar. The planes of the ligands are twisted by an angle varying from 5.37 to 10.93°. The location of the axis of twist is distinct in each molecule. In one of the molecules it coincides with the molecular two-fold axis which is situated in the plane of complex. Naturally, in this molecule the distribution of bonds' lengths and angles are symmetrical, relative to this axis. General view of the complex molecule is presented in figure 1. Bond lengths for **1** and analogous distances for complexes described in literature are listed in the table 2.

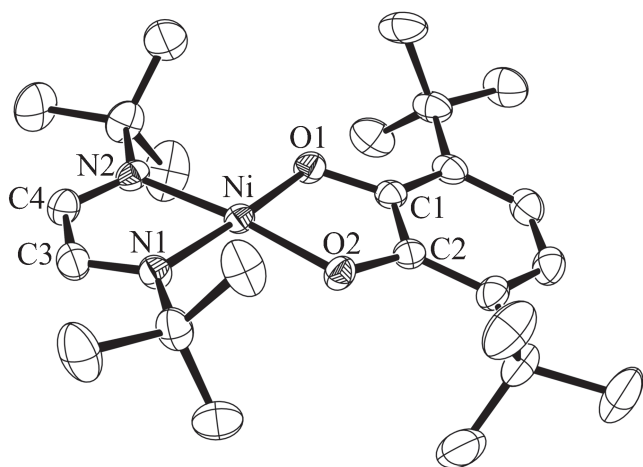


Figure 1. General view of complex **1** molecule. (30% of ellipsoids probabilities, hydrogen atoms are omitted for clarity, atoms numeration is arbitrary and corresponds to numeration in table 1).

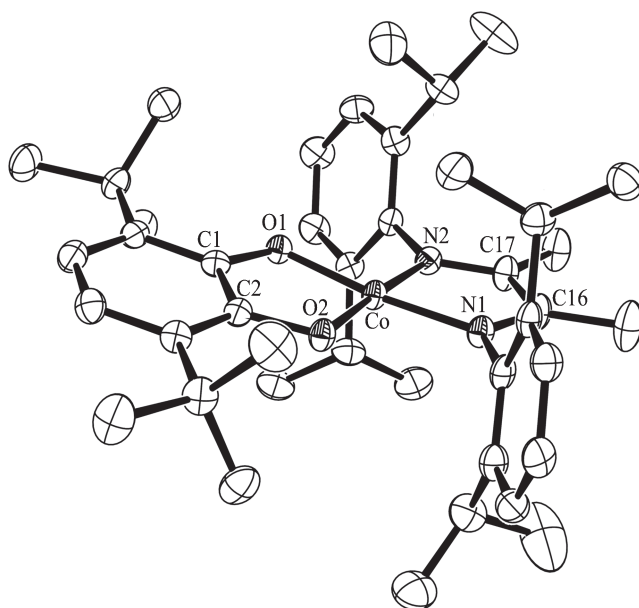


Figure 2. General view of complex **9** molecule. (50% of ellipsoids probabilities, hydrogen atoms are omitted for clarity).

Bond lengths of C-O and C1-C2 in chelate cycle of catecholato fragment characterize its valent state. It is known that these distances for anion-radical are in the range: C-O: 1.27–1.31 Å and C1-C2: 1.32–1.39 Å; for catecholato dianion: 1.31–1.35 Å and 1.36–1.42 Å respectively.¹⁹ In the case of **1** bond lengths (C-O: 1.352–1.357 Å; C1-C2: 1.397–1.410 Å) are typical for catecholato dianion coordination mode.

Bond length of C=N of diazabutadiene in **1** (1.260–1.275 Å) which are sensitive to ligand oxidation state are close to that, found for corresponding distances in coordinated neutral ligand in $(\text{tert-Bu})_2(\text{DAB})(\text{H,H})\text{NiBr}_2$: 1.275 Å.²⁰

Bond lengths of C3-C4 and Ni-N in catecholate complex **1** are slightly shorter than the same distances in corresponding dibromide: $(\text{tert-Bu})_2(\text{DAB})(\text{H,H})\text{NiBr}_2$: C-C 1.470 Å, Ni-N 1.996, 2.002 Å; and in free diazabutadiene: C-C 1.496 Å. It can be the consequence of the difference in the structures of complexes. $(\text{DAB})\text{NiBr}_2$ has distorted tetrahedral geometry. Square-planar configuration of **1** promotes π - π -interaction through the molecule skeleton. In the case of $\text{Ni}(3,6\text{-DBSQ})_2$, which molecule is square-planar, π - π -interaction results in strong anti-ferromagnetic coupling of unpaired electrons localized in ligands π -systems.²¹

Complex **9** was also structurally characterized. General view of complex molecule is presented in the figure 2. Selected bonds lengths are listed in the table 3. Unit cell of **9** contains the guest molecule of n-hexane.

Like **1**, complex **9** has square-planar coordination core. The geometry of each ligand's fragment is very

Table 2. Bond length intervals for complex **1** molecule (atoms numeration is arbitrary and corresponds to numeration in figure 1) and analogous distances for complexes described in literature.

Bond	Complex 1 range (Å)	(Me ₂ Ph)DAB(Me ₂)Ni(Cat-Cl ₄) ⁷ (Å)	(i-Pr ₂ Ph)DAB(Me ₂)Ni(Cat-Cl ₄) ⁷ (Å)
C-O	1.352–1.357	1.330/1.333	1.332/1.329
C=N	1.260–1.275	1.299/1.302	1.299/1.297
Ni-O	1.823–1.829	1.824/1.837	1.830/1.828
Ni-N	1.938–1.959	1.860/1.870	1.860/1.869
C1-C2	1.397–1.410	1.408	1.412
C3-C4	1.436–1.448	1.480	1.481

close to planar. Planes of ligands are slightly twisted. The angle between planes is 6.83°. Bond lengths in chelate ring of catecholato fragment are typical for catecholato-dianion coordination mode. Square-planar geometry is unusual for Co(II) compounds in such type of environment. Most of tetracoordinative cobalt(II) compounds with separated chelate ligands containing N- and O-atoms have distorted tetrahedron geometry. The exceptions are: bis-iminosemiquinonato complexes,^{22,23} catecholato cobalt with amino-pyridine,^{11,12} and a number of complexes, where salicylaldiminato ligands are connected by a bridge. Table 4 presents a number of Co-N and C=N bond lengths for close analogs - bis(salicylaldiminato)cobalt complexes of different symmetry. (Bonds lengths are cited from reference.²⁴) In distorted tetrahedron geometry Co-N and C=N bonds' lengths are in the ranges: 1.951–2.034 and 1.279–1.299 Å, whereas in distorted square-planar one they are: 1.849–1.883 and 1.284–1.309 Å respectively. It is evident that in tetrahedron, Co-N bonds are longer and C=N bonds are shorter than the same distances in square-planar coordination core. Square-planar geometry seems to be stabilized by π - back donation from filled d_{π} -orbitals of cobalt to empty anti-bonding π -orbitals of N-donor. As a consequence, it results in shortening of Co-N bond lengths and elongation of C=N distances. Bond lengths in **9** confirm this rule.

So, according to the presented data, diazabutadiene complexes of nickel and cobalt are catecholato derivatives of divalent metal ions with neutral diazabutadiens. Additional π - π bonding of diazabutadienes with metals is observed for both compounds **1** and **9**.

3.2 Some reactions of diazabutadiene-catecholato complexes of nickel and cobalt

Neutral ligands in diazabutadiene-catecholato complexes of cobalt and nickel undergo substitution reactions. Resulting compounds were isolated and characterized. The same products were obtained independently by exchange reactions. The identity of the complexes synthesized by different ways was confirmed by identity of their IR spectra.

1,2-Bis(diphenylphosphino)ethane (dppe) can substitute any DAB ligand in nickel catecholates **1–4** but only 1,4-di-(*tert*-Bu)-diazabutadiene in cobalt complex **7** (schemes 5, 6). Di-aryl-derived diazabutadiens in cobalt compounds are not being substituted. Resulting (dppe)Mcat compounds were synthesized independently by exchange reaction with catecholato thallium.

Diazabutadiene ligands undergo substitution reaction also upon action of stronger base 2,2'-bpy on both cobalt and nickel catecholates (scheme 7).

Complexes **1–6** undergo one-electron chemical oxidation by silver cation forming stable paramagnetic adducts which were studied by EPR in solution (scheme 8, figure 3). EPR spectral parameters are listed in table 5.

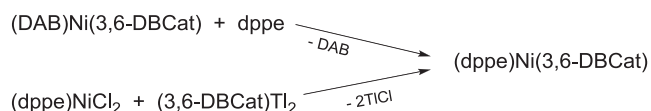
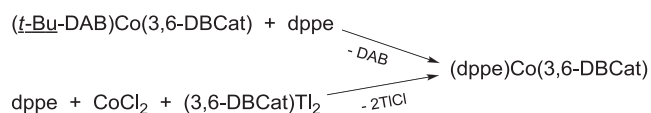
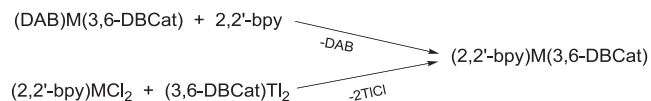
g-Factors and values of hyperfine coupling constants on protons of semiquinonato ligand indicate that unpaired electron is localized in π -system of semiquinonato fragment.³⁴ It means that nickel oxidative state remains unchanged but catecholato ligand undergoes oxidation. Small values of hyperfine coupling constants on ³¹P of dppe and the absence of hyperfine

Table 3. Selected bond lengths and angles of complex **9**.

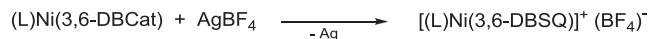
Bond	Distance (Å)	Bond	Distance (Å)	Atoms	Angles (°)
Co-N1	1.8743(16)	Co-O1	1.8066(13)	O1-Co-N1	173.66
Co-N2	1.8711(16)	Co-O2	1.8104(13)	O2-Co-N2	176.91
N1-C16	1.323(2)	O1-C1	1.364(2)	C1-O1-Co-N2	178.92
N2-C17	1.323(2)	O2-C2	1.359(2)	C2-O2-Co-N1	175.14
C16-C17	1.439(3)	C1-C2	1.406(3)	O1-Co-N2-C17	172.72
				O2-Co-N1-C16	177.64

Table 4. Selected bond lengths (Å) for several bis(salicylaldiminato)cobalt and **9**.

	Complex geometry, title and reference	Ligand 1		Ligand 2	
		Co-N	C=N	Co-N	C=N
Distorted tetrahedron	bis(salicylal-N-m-anisidinato)-cobalt(II) ²⁵	1.951	1.279	1.965	1.299
	bis(N-(2,6-dimethylphenyl)-salicylaldiminato-N,O)-cobalt(II) ²⁶	2.002	1.288	2.034	1.279
	bis(3- <i>tert</i> -butyl-N,5-dimethylsalicylaldiminato)-cobalt(II) ²⁷	1.975	1.286	1.966	1.288
Distorted square-planar	(R,R)-(N,N'-bis(2'-hydroxybenzylidene)-1,2-diaminocyclohexane-N,N',O,O')-cobalt(II) ²⁸	1.871	1.293	1.872	1.296
	(N,N'-(<i>o</i> -phenylene)-bis(salicylideneaminato))-cobalt(II) ²⁹	1.873	1.308	1.870	1.300
	N,N'-ethylene-bis(3- <i>tert</i> -butylsalicylideneiminato)-cobalt(II) ³⁰	1.849	1.289	1.849	1.289
	(N,N'-bis(3- <i>tert</i> -butyl-5-methylsalicylidene)-2,3-diamino-2,3-dimethylbutane)-cobalt(II) ³¹	1.860	1.293	1.860	1.293
	meso-(N,N'-cyclohexylene-bis(salicylideneiminato))-cobalt(II) ³²	1.881	1.305	1.883	1.284
	N,N'-bis(3,5-di- <i>tert</i> -butylsalicylidene-1,2-phenylenediamine)-cobalt(II) ³³	1.860	1.309	1.860	1.305
	Complex 9 (this work)	1.873/1.859	1.312/1.331		

**Scheme 5.** Substitution of DAB by dppe in catecholato nickel compounds and independent synthetic way to (dppe)Ni(3,6-DBCat).**Scheme 6.** Substitution of *t*-Bu-DAB by dppe in catecholato cobalt compound and independent synthetic way to (dppe)Co(3,6-DBCat).

M = Co, Ni

Scheme 7. Substitution of DAB by 2,2'bpy in nickel and cobalt catecholates and independent way to (2,2'bpy)M(3,6-DBCat), M=Ni, Co.**Scheme 8.** Oxidation of catecholato nickel complexes into corresponding semi quinonato cations.

coupling with ¹⁴N of DAB indicate that square-planar structure remains unchanged upon oxidation.^{34,35} EPR spectral parameters of cations do not depend on temperature and nature of diazabutadiene. It means that no redox-isomeric transformations occur. It should be mentioned that EPR spectral parameters of [(dppe)Ni(3,6-DBSQ)]⁺ cation coincide with those obtained by electrochemical oxidation of the same complex³⁶ and are similar to that obtained for analogous catecholates.¹⁰

Anisotropic EPR spectrum with axial symmetry of g-tensor was recorded for powder of **9** at T = 140 K. Hyperfine coupling with ⁵⁹Co nucleus was not detected. g-Tensor parameters: g_⊥ ≅ 1.90, g_∥ ≅ 3.36 indicate Co(II), d⁷ ground state to be low spin. No EPR

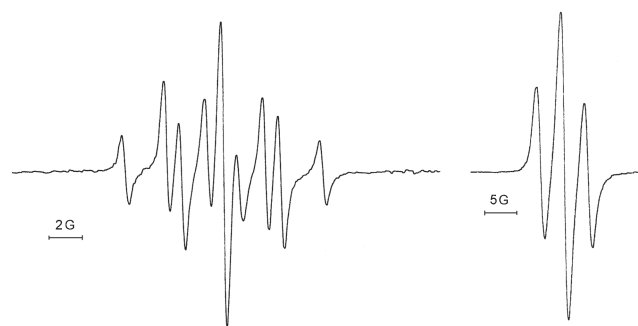
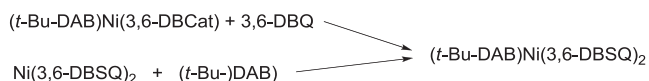
**Figure 3.** EPR spectra of cations [**6**]⁺ (left) and [**1**]⁺ (right) (CH₂Cl₂, 290 K).

Table 5. EPR spectral parameters of nickel semiquinonato cations.

Complex	g-factor	$a_i(^1\text{H})_{\text{SQ}}$, G	$a_i(^{31}\text{P})$, G
1 ⁺	2.0136	3.55	—
2 ⁺	2.0041	3.60	—
3 ⁺	2.0048	3.40	—
4 ⁺	2.0034	3.65	—
5 ⁺	2.0058	3.40	—
6 ⁺	2.0041	3.68	2.52

**Scheme 9.** Oxidative addition of *o*-quinone to nickel catecholate leads to bis-*o*-semiquinonato nickel compound.

spectra for cobalt(II) catecholate complexes in solution were observed in the temperature range of 77–300 K.

THF solution of (dppe)Co(3,6-DBCat) when exposed to air quickly changes its colour from brown to blue, which is typical for semiquinonate anion radical formation. n-Hexane addition causes colourless solid precipitation. IR spectrum of precipitate contains a very intensive band at $\nu = 1185 \text{ cm}^{-1}$, which can be attributed to $\nu_{\text{P}} = \text{O}$.

Oxidative addition of 3,6-DBQ to **1** leads to extending of nickel coordination sphere with simultaneous oxidation of catecholato ligand. Complex of the same composition can be obtained independently from bis(semiquinonato)nickel and diazabutadiene (scheme 9). Interaction of the complexes **2–4**, which have more sterically hindered DAB-ligand, with 3,6-DBQ is more complicated and will be the subject of a future publication.

Oxidative addition reaction of (dppe)Co(3,6-DBCat) with different *o*-quinones was used for synthesis of six-coordinated cobalt adducts containing *o*-quinonato fragments of different nature and consequently having different oxidative state.¹⁶

4. Conclusions

A number of new catecholato complexes of nickel and cobalt with diazabutadienes and 2,2'-bpy were synthesized. Structural study of two complexes indicated square-planar molecules containing divalent metals, catecholato-dianions and neutral diazabutadienes. Nickel complexes undergo chemical oxidation through catecholate ligand, forming semiquinonato nickel compounds. Square planar geometry remains unchanged upon oxidation.

Supplementary Information

CCDC-678237 (**1**) and CCDC- 678238 (**9**) contain the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk. Check CIF files are available at www.ias.ac.in/chemsci

Acknowledgements

The authors are thankful to L. Abakumova, N. Khamaletdinova and O. Kuznetcova for IR spectra recording. This work was supported by RFBR (grants: 13-03-97070), by Russian President Grant supporting scientific schools (NSh-271.2014.3), by Program of presidium of RAS № 18. This research was partly supported by the grant (the agreement of August 27, 2013 № 02.B.49.21.0003 between The Ministry of education and science of the Russian Federation and Lobachevsky State University of Nizhni Novgorod).

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