Mendeleev Communications

Mendeleev Commun., 2026, **36**, 114–116

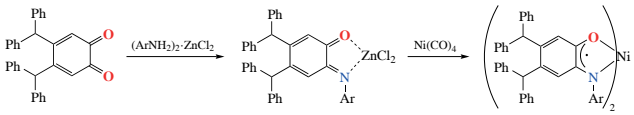
Zinc complex as a source of highly labile non-shielded *o*-iminoquinone

Tatiana N. Kocherova, Roman V. Rumyantcev, Viacheslav A. Kuropatov, Alexandr V. Piskunov* and Nikolay O. Druzhkov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603137 Nizhny Novgorod, Russian Federation. E-mail: pial@iomc.ras.ru

DOI: 10.71267/mencom.7864

Noval unstable *o*-iminobenzoquinone, namely, 3,4-dibenzhydryl-6-[(2,6-diisopropylphenyl)imino]cyclohex-2-en-1-one, bearing non-shielded chelating site was synthesized in the zinc coordination sphere as a neutral ligand. The bis-*o*-iminosemiquinonate Ni^{II} compound was prepared by the reaction of zinc *o*-iminoquinolate complex with $Ni(CO)_4$ and characterized by NMR spectroscopy and X-ray diffraction analysis.



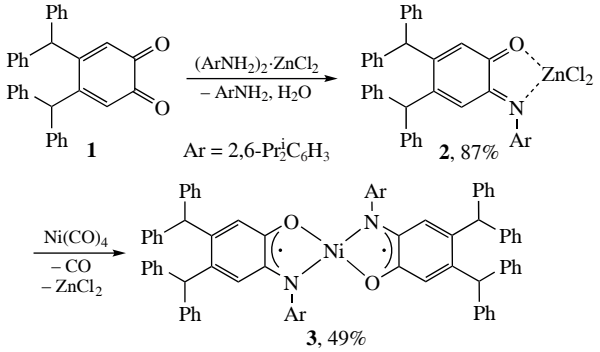
Keywords: zinc complexes, nickel complexes, redox-active ligand, *o*-iminoquinone, *o*-iminosemiquinone, X-ray diffraction.

o-Iminoquinones, like *o*-quinones, can serve as bidentate chelating ligands possessing a redox activity. Depending on the nature of the metal center and pendant ligands, *o*-iminoquinones in complexes are capable of coordinating as neutral,[1–4] radical anion (iminosemiquinone),[5–12] and dianionic (amidophenolate)[13–17] ligands; moreover, the interconversion between these redox forms can be realized directly in the coordination sphere of the metal ion.[18–21] Complexes with *o*-iminoquinone ligands have been studied much less in comparison with *o*-quinone ones for several reasons. One is that researchers usually restrict the preparation of such complexes to the use of stable *o*-aminophenols as precursors; as for *o*-quinone derivatives, they use both catechols and *o*-quinones as starting compounds. *o*-Iminoquinones are quite labile compounds; thus, even *N*-aryl-4,6-di-*tert*-butyl-*o*-iminoquinones bearing a substantial steric protection are prone to intramolecular cyclization[22,23] and subsequent dimerization.[22] However, the desired complexes are sometimes only accessible through the oxidative addition pathway, which should force the use of *o*-iminoquinones as starting compounds.

The vast majority of known complexes with *o*-iminoquinone ligands were prepared using substituted 3,5-di-*tert*-butyl-*o*-benzoiminoquinones.[24] Tertiary butyl substituents shield the coordination site and non-substituted positions of the aromatic ring from undesirable condensation reactions. The lability of benzodioxolene ligands in reduced states could be prevented by substitution of positions 4 and 5 of the quinonoid ring. Such a protection provides less steric loading for the coordination site of the ligand compared to 3,5-di-*tert*-butyl-substituted analogues, thereby making the coordination site of the ligand more accessible for large metallofragments or for bridging mode for binding of metal ions. In this work, essentially available[25] 4,5-bis(diphenylmethyl)cyclohexa-3,5-diene-1,2-dione **1** was chosen as the starting compound for imination.

The direct interaction of *o*-quinone **1** with 2,6-diisopropylaniline in the presence of formic acid proceeds with only moderate selectivity to give a mixture of products. In order to avoid side processes, we applied a preparative technique for the protection of the coordination site with $ZnCl_2$. Recently we have shown[26] that usage of zinc(II) adducts allows previously inaccessible non-shielded iminoquinones to be prepared under mild conditions. Using this approach, we succeeded in imination of *o*-quinone **1** directly in the coordination sphere of the neutral complex of 2,6-diisopropylaniline with zinc chloride $(2,6\text{-}Pr^i_2C_6H_4NH_2)_2 \cdot ZnCl_2$ (Scheme 1). In this way, complex **2** was prepared by stirring *o*-quinone **1** suspensions and $(2,6\text{-}Pr^i_2C_6H_4NH_2)_2 \cdot ZnCl_2$ in diethyl ether for 8 h. Then, it was isolated as a light brown precipitate. Instrumental analyses confirmed the substitution of one oxo group in the quinone ligand with the imino function as a result of condensation of the amino group of 2,6-diisopropylaniline with the carbonyl group of *o*-quinone **1** in the coordination sphere of the Zn^{II} ion.

According to the X-ray crystallography data, the zinc atom in complex **2** is coordinated by chelating *o*-iminoquinone ligand and two chlorine anions (Figure 1).† The O(1)–C(1) [1.232(3) Å] and N(1)–C(2) [1.295(3) Å] bond lengths in the OCCN-fragment



Scheme 1

† *Crystal data for* **2**. $C_{44}H_{41}Cl_2NOZn \cdot C_7H_8 \cdot 0.125\,H_2O$, M = 830.43, triclinic, space group $P\bar{1}$, 100 K, a = 10.4603(3), b = 13.2962(4) and c = 17.2575(6) Å, α = 67.710(3)°, β = 84.999(3)°, γ = 89.898(3)°, Z = 2, V = 2211.12(14) Å^3, d_{calc} = 1.247 g cm^{-3}, $F(000)$ = 870. A brown crystal with a size of 0.23×0.21×0.15 mm was selected, and intensities of 27803 reflections were collected with an Oxford Xcalibur Eos diffractometer (Mo-K_α radiation, ω-scan technique and λ = 0.71073 Å).

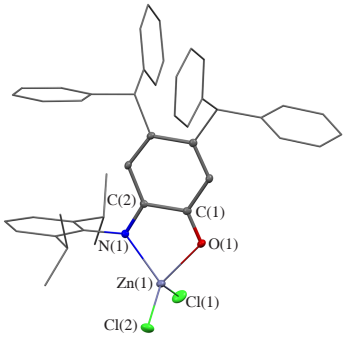


Figure 1 Molecular structure of complex **2**. Thermal ellipsoids are shown with a 30% probability. Hydrogen atoms are omitted for clarity.

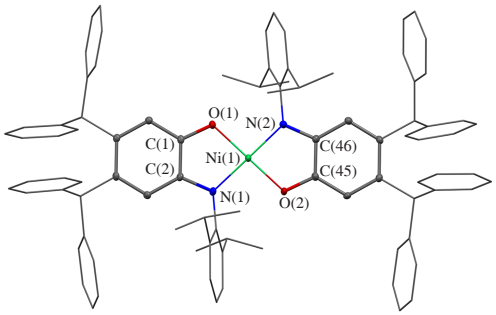


Figure 2 Molecular structure of complex **3**. Thermal ellipsoids are shown with a 30% probability. Hydrogen atoms are omitted for clarity.

indicate the neutral charge of the ligand.[27] The distinct alternation of single and double bonds in the six-membered ring also confirms this fact (see Online Supplementary Materials, Table S1). The Zn–O [2.0783(16) Å] and Zn–N [2.095(2) Å] distances in complex **2** are in good agreement with the values for the previously reported[2] complex of the 4,6-di-*tert*-butyl-*N*-aryl-substituted *o*-iminobenzoquinone ligand with ZnI_2. On the basis of the τ_4' value (0.82), the zinc atom in complex **2** adopts a distorted tetrahedral geometry.[28,29] The mutual arrangement of the phenyl substituents of the ligand completely excludes the possibility of intramolecular π···π interactions.

An attempt to obtain free *o*-iminoquinone by hydrolysis of complex **2** with potassium oxalate failed due to the lability of the desired compound (its formation could be detected only by TLC). Luckily, zinc complex **2** could be used as a source of the new *o*-iminoquinone in neutral form in further reactions. Thus, the reaction of **2** with $Ni(CO)_4$ in THF gives bis-iminosemiquinonate Ni^{II} complex **3** in a 49% yield (see Scheme 1).

The molecular structure of complex **3** is shown in Figure 2.† Unlike complex **2**, the metal atom in **3** adopts almost ideal square planar geometry (τ_4' = 0.01).[28,29] According to the lengths of the C–C [1.413(4), 1.413(4) Å], O–C [1.313(3), 1.315(3) Å], and N–C [1.355(3), 1.356(3) Å] bonds in the OCCN fragment, both ligands in complex **3** exist in the radical anion form.[27] The lengths of M–O and M–N bonds in complex **3** are significantly shorter compared to complex **2** (see Table S1), despite the similarity of the ionic radii of zinc and nickel.[33] Correspondingly, the nickel center adopts a formal oxidation state of +2. This is consistent with the square-planar geometry for the Ni ion bearing a d^8 electron configuration. Thus, the structure of complex **3** is similar to the related nickel(II) *o*-iminoquinone complexes.[34,35] The IR spectrum (see Online Supplementary Materials, Figure S2) shows a shift of the absorption bands of carbonyl and imine groups to a longer wavelength region compared to the spectrum of complex **2** (Figure S1), indicating the elongation of C–O and C–N bonds. The ^{1}H NMR spectrum of complex **3** exhibits a multidirectional paramagnetic shift of signals compared to original complex **2** (Figures S3, S5).

In summary, new *o*-iminoquinone, 3,4-dibenzhydryl-6-[(2,6-diisopropylphenyl)imino]cyclohex-2-en-1-one unstable in its free form, was obtained as a ligand in the coordination sphere of zinc. This zinc complex could be used as a source of this *o*-iminoquinone ligand in unreduced form. The reaction of this zinc complex with $Ni(CO)_4$ indicates that there is an opportunity to use it in oxidative addition reactions for preparation of iminosemiquinonate metal complexes by the interactions with low-valence metal species.

The study was financially supported by the Russian Science Foundation (grant no. 22-13-00351-P). This work was carried out using the equipment of the Collective Use Center 'Analytical Center IOMC RAS'.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7864.

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After merging of equivalence and absorption corrections, 8700 independent reflections (R_{int} = 0.0485) were used for the structure solution and refinement. Final *R* factors are R_1 = 0.0419 [for reflections with $F2 > 2\sigma(F2)$] and wR_2 = 0.0870 (for all reflections); *S* = 1.049; and the largest diffraction peak and hole are 0.360 and –0.340 e Å^{-3}, respectively.

Crystal data for **3**. $C_{88}H_{82}N_2NiO_2 \cdot (C_4H_8O)$, *M* = 1402.47, monoclinic, space group $P2_1/c$, 100 K, *a* = 17.3354(3), *b* = 35.4135(7) and *c* = 13.4218(3) Å, $\alpha = \gamma = 90°$, β = 104.993(2)°, *Z* = 4, *V* = 7959.2(3) Å^3, d_{calc} = 1.170 g cm^{-3}, *F*(000) = 2992. A green crystal with a size of 0.75×0.46×0.22 mm was selected, and intensities of 163579 reflections were collected with an Oxford Xcalibur Eos diffractometer (Mo-K_α radiation, ω-scan technique, and λ = 0.71073 Å). After merging of equivalence and absorption corrections, 16278 independent reflections (R_{int} = 0.0776) were used for the structure solution and refinement. Final *R* factors are R_1 = 0.0699 [for reflections with $I > 2\sigma(I)$] and wR_2 = 0.1596 (for all reflections); *S* = 1.123; and the largest diffraction peak and hole are 0.797 and –0.522 e Å^{-3}, respectively.

Data collection, cell refinement, data reduction, and absorption corrections were carried out using CrysAlisPro.[30] Empirical absorption correction using spherical harmonics was implemented in the SCALE3 ABSPACK scaling algorithm. Both compounds were solved by the dual method[31] and were refined on F^2_{hkl} using the SHELXTL package.[32] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except the water H-atoms in **3** were placed in calculated positions and were refined using a riding model [U_{iso}(H) = 1.5U_{eq}(C) for CH_3 groups and U_{iso}(H) = 1.2U_{eq}(C) for other groups]. In turn, the hydrogen atoms of the water molecule were located from difference Fourier maps and were refined with geometrical (DFIX) and displacement parameter [U_{iso}(H) = 1.2U_{eq}(O)] constraints.

CCDC 2407494 (**2**) and 2407495 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

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Received: 1st July 2025; Com. 25/7864