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Stable N-heterocyclic carbene derivatives of copper(I) and silver(I) containing radical anion redox active ligands

**Irina N. Meshcheryakova, Kseniya V. Arsenyeva, Georgy K. Fukin,
Vladimir K. Cherkasov and Alexandr V. Piskunov***

*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603950
Nizhny Novgorod, Russian Federation. E-mail: pial@iomc.ras.ru*

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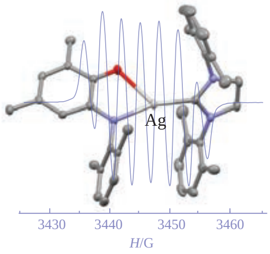
N-Heterocyclic carbene is a versatile ligand for the preparation of copper(I) and silver(I) derivatives bearing the radical anion forms of redox active *o*-benzoquinone and *o*-iminobenzoquinone. The paramagnetic three-coordinated copper(I) and silver(I) *o*-benzosemiquinone and *o*-iminobenzosemiquinone complexes were prepared and characterized by EPR spectroscopy and X-ray diffraction analysis.



Keywords: N-heterocyclic carbene, copper(I), silver(I), redox active ligand, *o*-benzosemiquinone, *o*-iminobenzosemiquinone, X-ray diffraction.

N-Heterocyclic carbenes (NHCs) are promising ligands for the design of catalytically active compounds.[1] Due to their good σ-donating property, NHCs can form stronger bonds with metals to prevent catalyst decomposition. A new direction in the chemistry of NHC complexes is the synthesis of hybrid ligand systems containing a phenolate function along with a carbene fragment.[2] Recent studies have demonstrated the activity of such compounds in heteroallene activation,[3] olefin polymerization,[4] ROMP processes,[5] lactide polymerization,[6] trifluoromethylation,[7] coupling of epoxides with CO$_2$[8] and transamidation reactions.[9] Moreover, compounds with the hybrid ligands can form paramagnetic derivatives due to the redox activity of a phenolate fragment.[10] Another way to the preparation of paramagnetic carbene metal compounds is the use of *o*-benzoquinone-like radical anions along with NHC ligands.[11] The introduction of a redox active ligand into the carbene metal complexes can be promising for their use. The paramagnetic radical anions of *o*-benzoquinone or related ligands are convenient spin labels in the metal coordination sphere.[12] The EPR spectra of *o*-benzosemiquinone species contain information on the structure of metal coordination spheres in solution and make it possible to study such processes as the complex dissociation, the exchange of neutral ligands, solvation, the expansion of the coordination sphere and intramolecular metal–ligand electron transfer.[12,13]

The NHC derivatives of copper(I) and silver(I) can actively participate in catalytic transformations such as conjugate addition, carbene transfer, [3 + 2] cycloaddition, allylic alkylation, diboration and cross-coupling reactions.[14] We used a sterically hindered N-heterocyclic carbene and 3,6-di-*tert*-butyl-*o*-benzoquinone or 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone as redox active ligands to prepare paramagnetic copper(I) and silver(I) NHC complexes.

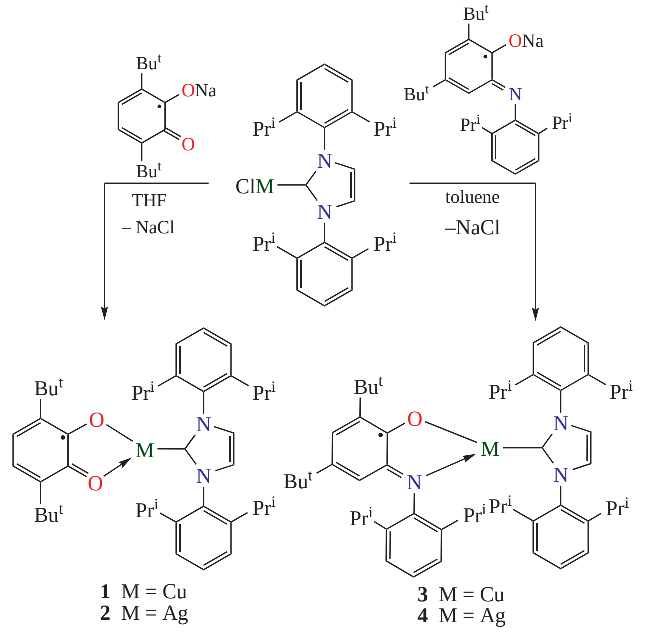
The paramagnetic *o*-benzosemiquinone copper(I) and silver(I) derivatives were stabilized due to complexation with neutral donor ligands, such as phosphines, arsines, carbon monoxide, 1,5-cyclooctadiene, diphenylacetylene, *etc.*[13(*d*),15(*a*)] The copper(I) and silver(I) *o*-benzosemiquinone complexes have been studied in solution by EPR spectroscopy.[13(*d*),15] A few paramagnetic silver(I) derivatives are highly unstable and quickly decompose in solution.[15(*a*),(*d*)] A related tetra(triphenylphosphine)disilver(I) rhodizonate was synthesized and examined using X-ray diffraction.[16]

The individual copper(I) compounds isolated and characterized by X-ray diffraction are mainly tetracoordinated,[17] and stable three-coordinated copper(I) complexes can be prepared using bulky phosphine ligands such as 2-biphenyl derivatives.[18]

Stable three-coordinated paramagnetic copper(I) and silver(I) *o*-benzosemiquinone and *o*-iminobenzosemiquinone derivatives **1**–**4** were obtained by an exchange reaction between an *o*-benzoquinone or *o*-iminobenzoquinone monosodium salt and copper(I) or silver(I) chloride containing coordinated N-heterocyclic carbene in a THF or toluene solution (Scheme 1). All attempts to synthesize related gold(I) derivatives were unsuccessful. The interaction of an NHC–AuCl precursor with *o*-benzoquinone or *o*-iminobenzoquinone monosodium salts led to a rapid redox process with the formation of unreduced organic ligands and fine gold even at low temperatures (–50 °C).

The complexes were isolated as green (**1**, **3** and **4**) or violet (**2**) fine crystalline powders.[†] Copper(I) derivatives **1** and **3** are stable both in a solid state and in solution under anaerobic conditions. Crystalline silver(I) compounds **2** and **4** can be stored under anaerobic conditions and in the absence of direct sunlight for a long time. However, they decompose in a few days in solutions with the precipitation of metal powder. Note that complexes **2** and **4** are the first examples of paramagnetic silver(I) compounds, which can be isolated in a crystalline state and characterized. Moreover, derivative **3** is a unique copper(I) compound bearing a radical anion *o*-iminobenzosemiquinone ligand. All previously known copper *o*-iminobenzosemiquinolate complexes are bonded with Cu^{II} ions,[19] while Cu^{I} compounds were augmented with unreduced forms of *o*-iminoquinones.[20]

[†] See details in Online Supplementary Materials.



Scheme 1

The complexes are paramagnetic both in solution and in a solid state. The hyperfine structure of X-band EPR spectra measured in THF (**1**, **3**) or toluene (**2**, **4**) at 25 °C is well resolved and caused by the interaction of an unpaired electron with the magnetic nuclei of redox active ligands (^{1}H, 99.98%, $I = 1/2$, $\mu_N = 2.7928$, ^{14}N, 99.63%, $I = 1$, $\mu_N = 0.4037$)[21] and the metal center (^{63}Cu, 69.17%, $I = 3/2$, $\mu_N = 2.2233$, ^{65}Cu, 30.83%, $I = 3/2$, $\mu_N = 2.3817$ or ^{107}Ag, 51.84%, $I = 1/2$, $\mu_N = 0.1135$, ^{109}Ag, 48.16%, $I = 1/2$, $\mu_N = 0.1305$)[21] (Figures 1 and 2).

As noted above, the EPR spectra parameters of *o*-benzosemiquinone derivatives are sensitive to changes in the coordination sphere of the metal center.[12,13(*d*)] Data on copper(I) *o*-benzosemiquinonates allowed us to make conclusions on relations between the geometry of complexes and hyperfine splitting constants in their EPR spectra. In particular, tetracoordinated copper(I) compounds were characterized by hyperfine coupling constants a_i(Cu) of about 10–12 G.[12,13(*b*)–(*d*),15] In three-coordinated derivatives, this parameter was about 3–5 G.[12,13(*d*),18] The hyperfine coupling constants a_i(^{63}Cu) and a_i(^{65}Cu) of the EPR spectrum of copper(I) *o*-benzosemiquinolate **1** are 3.1 and 3.3 G, respectively. Thus, the copper atom in complex **1** is three-coordinated and not additionally solvated by THF molecules. The EPR spectrum parameters of silver(I) complex **2** are similar to those of unstable silver(I) *o*-benzosemiquinolates.[15(*a*),(*d*)] Note that the hyperfine splitting on metal centers in the EPR spectra of derivatives **2** and **4** was twice as high as that in the case of related dioxolene complexes **1** and **3**. The presence of a nitrogen atom in paramagnetic ligands promotes spin density transfer from the redox active ligand to the metal. Such a behavior can be clearly confirmed by a comparison of the EPR spectra parameters of related three-coordinated *o*-benzosemiquinolate[22] and *o*-iminobenzosemiquinolate[23] derivatives of tin(II) and lead(II).

Another reason can be a change in the coordination node geometry (see below). Silver iminosemiquinonate is asymmetric with no symmetry planes passing through the C–Ag bond (the C–Ag–O and C–Ag–N angles are 123.13 and 146.62°, respectively). In contrast, two orthogonal planes pass through the C–Cu bond in copper *o*-semiquinonate (the dihedral angles are close to 90°). The C–Cu–O bond angles are almost identical (137.90 and 141.78°). The efficiency of spin density transfer can be determined by these differences in geometry.

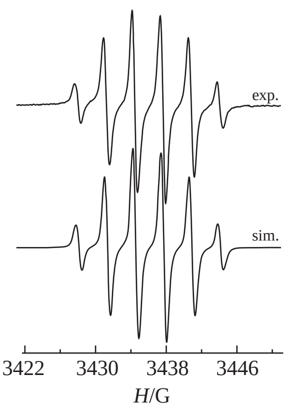


Figure 1 Experimental (THF, 25 °C) X-band EPR spectrum of **1** (exp.) and its simulation (sim.).

The molecular structures of **1** and **4** were determined by single-crystal X-ray diffraction analysis[‡] (Figures 3 and 4, respectively). Two independent molecules **4A** and **4B** are in an asymmetric unit cell of **4**. They have similar geometric characteristics and differ in the angles between carbene and o-iminobenzosemiquinone planes (63.56° for **4A** and 78.66° for **4B**).[†] Further discussion of the structure of **4** is carried out on the example of **4A** molecule. The unit cell of **1** contains 1.5 disordered toluene molecules per molecule of the complex.

According to the X-ray diffraction data, metal atoms in **1** and **4** have planar trigonal coordination environments formed by the heteroatoms of chelate redox active ligands and the carbon atoms of N-heterocyclic carbene. Copper compound **1** is a rare example of three-coordinated copper(I) *o*-benzosemiquinonate complexes characterized by X-ray diffraction. At the same time, **4** is the first example of structurally characterized silver(I) compounds containing an *o*-benzoquinone radical anion ligand. The sums of bond angles at the metal atoms in **1** and **4** are 360.00 and 359.69°, respectively; the copper atom lies in the O(1)O(2)C(15) plane while the silver atom deviates from the O(1)N(1)C(27) plane by 0.05 Å. The Cu–O bond lengths[†] [2.016(2) and 2.032(2) Å] are typical of *o*-benzosemiquinone copper(I) derivatives.[17,18] The Ag(1)–O(1) [2.3997(18) Å] and Ag(1)–N(1) [2.176(2) Å] distances are slightly greater than the sums of covalent radii of the elements (1.98 and 1.99 Å,[26] respectively). Note that *o*-iminosemiquinonate metal complexes are usually characterized by an inverse ratio of M–N and M–O bond lengths when the metal–oxygen distance is much shorter than the metal–nitrogen distance.[27] A significant elongation of the M–O bond in comparison with the M–N one was previously observed only in three-coordinated *o*-iminosemiquinonate mercury(II) derivatives.[28] The Cu(1)–C(15) [1.861(3) Å] and Ag(1)–C(27) [2.091(3) Å] bond lengths are

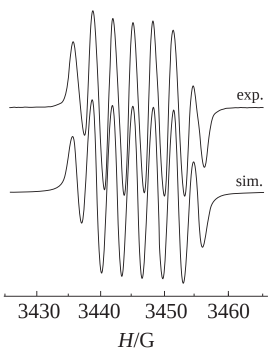


Figure 2 Experimental (toluene, 25 °C) X-band EPR spectrum of **4** (exp.) and its simulation (sim.).

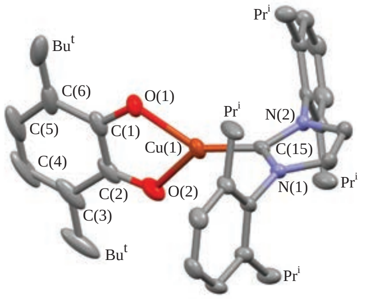


Figure 3 Molecular structure of **1**·1.5PhMe with 50% probability ellipsoids. The toluene molecules, methyl groups of *tert*-butyl and isopropyl substituents and H atoms are omitted for clarity.

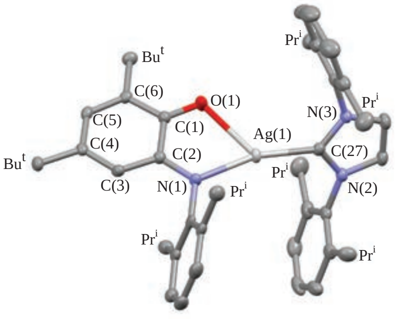


Figure 4 Molecular structure of **4** with 50% probability ellipsoids. The methyl groups of *tert*-butyl and isopropyl substituents and H atoms are omitted for clarity.

within a normal range of Cu–C and Ag–C metal–carbene bonds.[14(*a*)] The distribution of bond lengths in redox active ligands clearly indicates the radical anion character, which is typical of *o*-benzosemiquinonate and *o*-iminobenzosemiquinonate metal complexes.[29]

In summary, the use of N-heterocyclic carbene as a neutral ligand allowed us to obtain the rare examples of stable paramagnetic three-coordinated copper(I) and silver(I) complexes based on the radical anion forms of *o*-benzoquinone and *o*-iminobenzoquinone. Silver compounds of this type were isolated and structurally characterized for the first time. Paramagnetic complexes were analyzed by EPR spectroscopy and X-ray diffraction study.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.013.

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[‡] The X-ray suitable crystals were obtained after the storage of solutions at room temperature in a mixture of toluene–hexane (1 : 1) or diethyl ether–hexane (1 : 2) for **1** and **4**, respectively. The unit cell of **1** contains 1.5 toluene molecules per molecule of the complex. X-ray diffraction data were collected using an Agilent Xcalibur diffractometer and MoKα radiation (λ = 0.71073 Å). Data processing was carried out with the CrysAlis$^{\rm Pro}$ software.[24] The structures of **1** and **4** were solved by a direct method and refined by a full-matrix least squares method using the SHELX software package.[25] All non-hydrogen atoms were refined anisotropically. All of H atoms were placed in calculated positions and refined in the riding-model with $U(H)_{\rm iso} = 1.2U_{\rm eq}$ of their parent atoms [$U(H)_{\rm iso} = 1.5U_{\rm eq}$ for methyl groups].

Crystal data for **1**·1.5PhMe. $C_{51.50}H_{68}CuN_2O_2$, M = 810.61, monoclinic, space group $P2_1/c$, at 100(2) K: a = 12.8386(7), b = 17.1306(6) and c = 22.0254(13) Å, β = 105.705(6)°, V = 4663.3(4) Å^3, Z = 4, $d_{\rm calc}$ = = 1.155 g cm^{-3}. A dark green single crystal (0.230 × 0.200 × 0.080 mm) was selected and intensities of 56480 reflections were collected (μ = 0.508 mm^{-1}, $2\theta_{\rm max}$ = 50.052°). After absorption corrections, 8237 independent reflections ($R_{\rm int}$ = 0.0658) were used for the structure solution and refinement. Final R factors R_1 = 0.0586 [for reflections with $I > 2\sigma(I)$], wR_2 = 0.1385 (for all reflections). GOF 1.004.

Crystal data for **4**. $C_{53}H_{73}AgN_3O$, M = 876.01, triclinic, space group $P\bar{1}$, at 120(2) K: a = 12.5916(2), b = 17.0385(5) and c = 23 .9726(6) Å, α = 87.404(2)°, β = 87.581(2)°, γ = 71.584(2)°, V = 4872.6(2) Å^3, Z = 4, $d_{\rm calc}$ = 1.194 g cm^{-3}. A dark green single crystal (0.380 × 0.220 × 0.100 mm) was selected and the intensities of 60217 reflections were collected (μ = 0.452 mm^{-1}, $2\theta_{\rm max}$ = 50.052°). After merging of equivalence and absorption corrections, 17176 independent reflections ($R_{\rm int}$ = 0.0363) were used for the structure solution and refinement. Final R factors R_1 = 0.0386 [for reflections with $I > 2\sigma(I)$], wR_2 = 0.0840 (for all reflections). GOF 1.034.

CCDC 2006344 and 2006345 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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