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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

Contents

Experimental details

1. General information

All reagents were purchased from commercial sources and used without purification. 3,6-Di-*tert*-butyl-*o*-benzoquinone[1], 4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propylphenyl)-*o*-iminobenzoquinone[2], (NHC)CuCl[3], (NHC)AgCl[4] were synthesized according to reported procedures. Solvents were purified following standard methods[5]. All manipulations with solutions of complexes were performed under anaerobic conditions. The infrared spectra of complexes in the 4000–400 cm^{-1} range were recorded with an FSM 1201 Fourier-IR spectrometer in Nujol. EPR spectra were registered on a Bruker EMX spectrometer. Simulations of experimental EPR spectra were obtained using the WinEPR SimFonia v l.25 program (Bruker).

2. Synthesis

The solution of sodium *o*-benzosemiquinolate (which was prepared using 0.1 g (0.45 mmol) of *o*-benzoquinone according with known procedure[6] and was employed *in situ*) or sodium *o*-iminobenzosemiquinolate (which was prepared using 0.17 g (0.45 mmol) of *o*-iminobenzoquinone according with known procedure[6] and was employed *in situ*) in THF (20 ml) (in the case of compounds **1**, **3**) or toluene (20 ml) (in the case of complexes **2**, **4**) was added to the solution of (NHC)CuCl (0.22 g, 0.45 mmol) in THF (5 ml) or (NHC)AgCl (0.24 g, 0.45 mmol) in toluene (10 ml) with constant stirring. The formation of **1**-**4** was accompanied by a change in the color of the solution from blue to green (for **1**, **3** and **4**) or violet (for **2**). THF or toluene was removed under reduced pressure, and the residue was dissolved in diethyl ether (15 mL). The reaction mixture was separated from NaCl precipitate by filtration, the filtrate was concentrated to 10%, and the 10 ml of hexane was added. The following storage of solutions at -18° during few hours led to formation of microcrystalline products **1**-**4**, which were separated from mother liquor and dried in vacuo.

Complex **1**: the total yield of analytically pure product is 0.26 g (86 %). Anal. calc. for $C_{41}H_{56}CuN_2O_2$: C, 73.23 %; H, 8.39 %. Found: C, 73.48%; H, 8.54 %. IR (Nujol, KBr) cm^{-1}: 1593 m, 1570 m, 1550 m, 1545 m, 1490 vs, 1445 vs, 1405 s, 1364 m, 1354 m, 1339 s, 1330 s, 1310 w, 1275 m, 1257 w, 1235 w, 1214 m, 1200 w, 1180 w, 1115 m, 1105 m, 1080 m, 1060 m, 1042 w, 1025 w, 962 m, 953 s, 945 s, 820 s, 803 s, 760 s, 740 s, 700 w, 670 w, 654 s, 637 w, 550 w, 540 w, 497 w.

Complex **2**: the total yield of analytically pure product is 0.20 g (62 %). Anal. calc. for $C_{41}H_{56}AgN_2O_2$: C, 68.70 %; H, 7.88 %. Found: C, 68.93%; H, 7.96 %. IR (Nujol, KBr) cm^{-1}: 1580

w, 1500 vs, 1410 s, 1340 s, 1284 w, 1200 w, 1114 w, 1103 w, 1080 w, 1061 w, 1043 w, 950 s, 816 m, 805 s, 760 s, 743 m, 693 w, 670 w, 654 m, 637 w, 548 w, 525 w, 496 w, 475 w.

Complex **3**: the total yield of analytically pure product is 0.295 g (79 %). Anal. calc. for $C_{53}H_{73}CuN_3O$: C, 76.54 %; H, 8.85 %. Found: C, 76.79%; H, 9.03 %. IR (Nujol, KBr) cm^{-1}: 1487 m, 1395 m, 1354 m, 1311 w, 1285 w, 1264 w, 1240 s, 1204 w, 1168 w, 1142 w, 1027 w, 1018 m, 984 s, 940 m, 922 m, 869 m, 860 m, 814 m, 794 m, 790 m, 724 s, 700 w, 649 m, 616 w, 589 s, 558 w, 505 m, 481 m.

Complex **4**: the total yield of analytically pure product is 0.291 g (74 %). Anal. calc. for $C_{53}H_{73}AgN_3O$: C, 72.66 %; H, 8.40 %. Found: C, 72.85%; H, 8.57 %. IR (Nujol, KBr) cm^{-1}: 1580 m, 1509 w, 1482 s, 1446 s, 1405 m, 1366 m, 1352 m, 1328 m, 1306 w, 1274 w, 1248 m, 1215 w, 1198 w, 1180 w, 1164 w, 1115 m, 1100 w, 1080 w, 1060 w, 1044 w, 1023 w, 989 w, 944 m, 939 w, 908 m, 864 w, 857 m, 805 m, 793 m, 759 s, 749 m, 702 w, 690 w, 657 w, 644 w, 618 w, 603 w, 577 w.

3. EPR investigation

EPR spectra parameters for complexes **1-4** are:

1 - a_i (2^1H) = 3.30 G, a_i (^{65}Cu) = 3.30 G, a_i (^{63}Cu) = 3.10 G (g_i = 2.0047);

2 - a_i (2^1H) = 3.30 G, a_i (^{109}Ag) = 1.20 G, a_i (^{107}Ag) = 1.00 G (g_i = 2.0032);

3 - a_i (^{1}H) = 3.52 G, a_i (^{14}N) = 6.16 G, a_i (^{65}Cu) = 7.15 G, a_i (^{63}Cu) = 6.72 G (g_i = 2.0037);

4 - a_i (^{1}H) = 3.20 G, a_i (^{14}N) = 6.40 G, a_i (^{109}Ag) = 3.10 G, a_i (^{107}Ag) = 2.70 G (g_i = 2.0023).

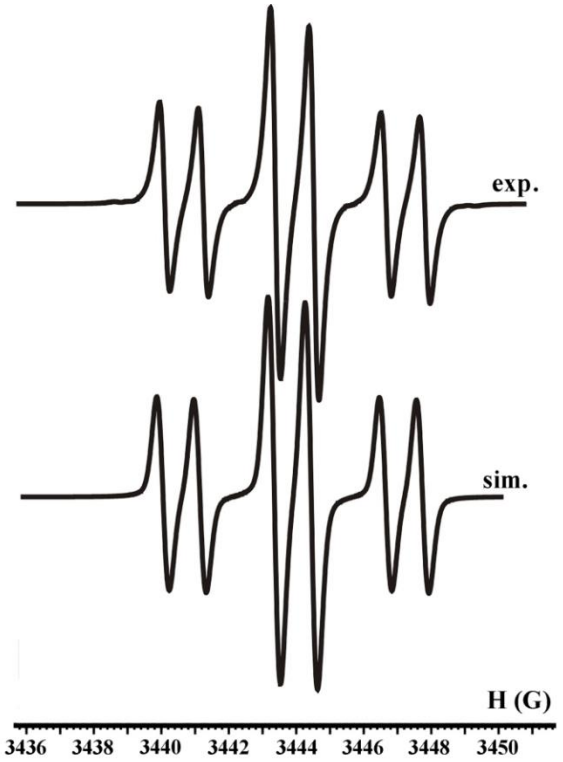

Figure S1. Experimental (toluene, 25º C) X-band EPR spectrum of **2** (exp.) and its computer simulation (sim.).

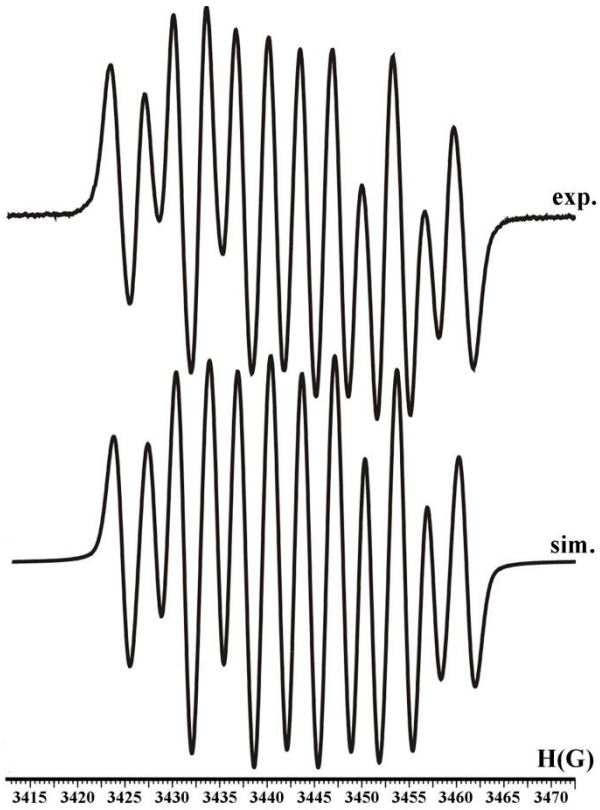

Figure S2. Experimental (THF, 25º C) X-band EPR spectrum of **3** (exp.) and its computer simulation (sim.).

4. Single-crystal X-ray diffraction analysis

X-ray diffraction data were collected by using an Agilent Xcalibur diffractometer and Mo-Kα radiation (λ = 0.71073 Å). Data processing and reduction were carried out with CrysAlisPro software[7]. Numerical absorption correction based on gaussian integration over a multifaceted crystal model was used. The structures of **1** and **4** were solved by direct method and refined by full-matrix least squares method using SHELX software package[8]. All non-hydrogen atoms are refined anisotropically. All of H atoms were placed in calculated positions and refined in the "riding-model" with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms ($U(H)_{iso} = 1.5U_{eq}$ for methyl groups).

The X-ray suitable crystals were obtained after storage of the solutions in a mixture of toluene/hexane (1:1) or diethyl ether/hexane (1:2) in the case of **1** and **4** respectively during the day at room temperature. The unit cell of **1** contains one and a half toluene molecules per molecule of the complex. The selected bond lengths and angles are presented in Table S1, the crystal data and some details of the data collection and refinement for **1**·1.5(toluene) and **4** are listed in the main text of the article. CCDC 2006344 (**1**·1.5(toluene)) and 2006345 (**4**) contain the supplementary crystallographic data for this paper. Copies of this information may be obtained

free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Table S1. Selected bond lengths (Å) and angles (º) for the compounds **1**·1.5($C_6H_5CH_3$) and **4**

Bond	**1**·1.5(toluene)	Bond	**4A**	**4B**
Cu(1)-O(1)	2.016(2)	Ag(1)-O(1)	2.3997(18)	2.442(2)
Cu(1)-O(2)	2.032(2)	Ag(1)-N(1)	2.176(2)	2.154(2)
Cu(1)-C(15)	1.861(3)	Ag(1)-C(27)	2.091(3)	2.074(3)
O(1)-C(1)	1.284(4)	O(1)-C(1)	1.261(3)	1.267(3)
O(2)-C(2)	1.278(4)	N(1)-C(2)	1.342(3)	1.329(3)
C(1)-C(2)	1.468(5)	C(1)-C(2)	1.467(4)	1.463(4)
C(2)-C(3)	1.446(5)	C(2)-C(3)	1.419(4)	1.422(4)
C(3)-C(4)	1.367(7)	C(3)-C(4)	1.370(4)	1.364(4)
C(4)-C(5)	1.408(7)	C(4)-C(5)	1.414(4)	1.418(4
C(5)-C(6)	1.368(6)	C(5)-C(6)	1.370(4)	1.372(4)
C(1)-C(6)	1.442(5)	C(1)-C(6)	1.445(4)	1.448(4)
Angles		Angles		
C(15)-Cu(1)-O(1)	137.90(11)	C(27)-Ag(1)-O(1)	123.13(8)	125.83(9)
C(15)-Cu(1)-O(2)	141.78(12)	C(27)-Ag(1)-N(1)	164.62(9)	163.07(9)
O(1)-Cu(1)-O(2)	80.32(10)	N(1)-Ag(1)-O(1)	71.94(7)	71.06(8)

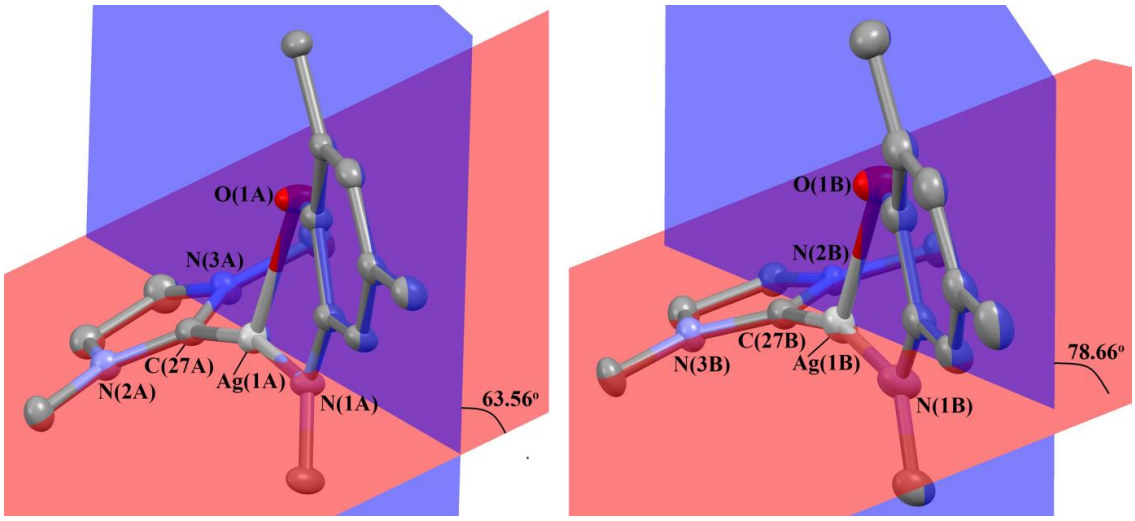

Figure S3. The views of **4A** (on the left) and **4B** (on the right) molecules showing the relative position of *o*-iminobenzosemiquinone and carbene planes. The H atoms, aryl and *tert*-butyl substituents are omitted for clarity.

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