Synthesis and Characterization of Novel Ligands 1,2-Bis(salicylideneaminooxy)ethanes

Shigehisa Akine, Takanori Taniguchi, and Tatsuya Nabeshima*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

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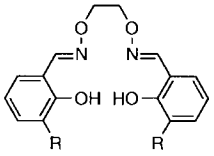
Novel ligands 1,2-bis(salicylideneaminooxy)ethanes were synthesized. They were much more stable against exchange reactions of aldehyde units than the corresponding salen derivatives. They form stable complexes with a copper(II) ion, whose structures were crystallographically determined. Spectroscopic and electrochemical studies indicated that the complexes have lower LUMO levels than salen analogues.

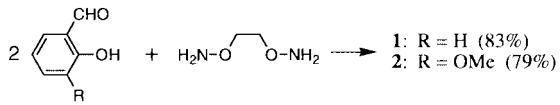
A series of *N*,*N*-bis(salicylidene)ethylenediamine[1] (H_2salen) derivatives have attracted much attention to many organic as well as inorganic chemists, because these ligands easily form complexes with various transition metals and some of them exhibit excellent catalytic activities for epoxidation, aziridination, etc.[2] Highly enantioselective reactions have been also achieved by the use of salen complexes. In addition, these salen-type units have also been employed to construct supramolecular structures containing transition metal ions.[3] Most of such ligands have two salicylideneamine units, but the linkage was limited to an alkylene (–CH=N–*C*–*X*–*C*–N=CH–) group due to the ease of preparation. Thus modification of a basic salen skeleton is very interesting and important. If an *O*-alkyl oxime moiety (–CH=N–O–$(CH_2)_n$–O–N=CH–) is used instead of a Schiff base, the larger electronegativity of oxygen atoms is expected to affect strongly the electronic properties of N_2O_2 coordination sphere,[4] which can lead to different and novel properties and structures of the resulted complexes. Several examples of an alkylated bis(salicylaldoxime) ligand were reported.[5] The ligating moieties are incorporated into a macrocyclic framework.[5b] But properties of the parent compounds were not thoroughly studied. In this paper, we report synthesis of 1,2-bis(salicylideneaminooxy)ethane (H_2salamo) **1** and methoxy derivative **2**, new ligands bearing two salicylidene moieties and two *O*-alkyloxime linkages. The spectroscopic properties and structures of copper(II) complexes are also reported.



1 (R = H): H_2salamo
2 (R = OMe): H_2(3-MeOsalamo)

The ligands **1** and **2** were prepared by the reaction of salicylaldehyde derivatives with 1,2-bis(aminooxy)ethane[6] in ethanol (Scheme 1), both of which were colorless crystals unlike yellowish H_2salen analogues. The ^{1}H NMR spectra showed a singlet at 8.25 ppm indicating the oxime bonds, and the signals of C=N carbon atoms were observed at 152 ppm in the ^{13}C NMR spectra. The C=N stretching absorption bands of **1** and **2** were observed at 1608 and 1606 cm^{-1}, respectively, in the IR spectra. The electronic absorption spectra of **1** and **2** showed π–π* bands at 362 and 372 nm, respectively. It is of note that there was no absorption around 400 nm, which is seen in the corresponding salen derivatives. The absorption is ascribed to the quinoid form of H_2salen.[7] X-ray crystallographic analysis of **2**[8] revealed all-*anti* conformation of the ethylenebis(oxynitrilo) bridge, which resulted in a planar structure with two salicylaldoxime units apart from each other (Figure 1).

Scheme 1.



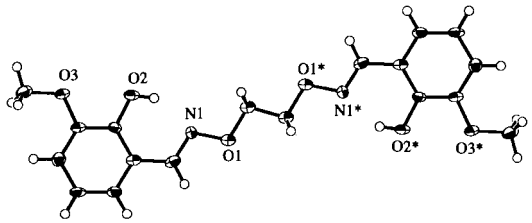


Figure 1. ORTEP drawing of ligand **2** (50% probability level). The molecule has a crystallographically imposed center of symmetry.

When ethanol solutions of **1** (or **2**) and copper(II) acetate were mixed, the color of the solution turned dark green. In the absorption spectra of Cu(salamo) and Cu(3-MeOsalamo), new absorption bands were observed at 641 and 632 nm, respectively, which were assigned to be the *d*–*d* transition of copper. These transition energies are smaller than those of the corresponding salen derivatives.

The cyclic voltammograms of the salamo derivatives in dimethyl sulfoxide showed irreversible waves as observed in other salen–Cu(II) complexes.[9] Thus, the first reduction potentials of the cathodic sweep were used for comparison. The potentials of the oxime complexes Cu(salamo) and Cu(3-MeOsalamo) were observed at –1.094 and –0.999 V, respectively, which were more positive than the corresponding salen derivatives (–1.190 V for Cu(salen) and –1.160 V Cu(3-MeOsalen)) (Table 1).

Table 1. Spectroscopic and electrochemical properties of Cu(II) complexes

compound	λ_{max}/nm (π-π*)^a	λ_{max}/nm (*d*-*d*)^a	E^1_{red}/V^b	E^2_{red}/V^b
Cu(salamo)	362 (9400)	641 (260)	–1.094	–
Cu(3-MeOsalamo)	372 (7400)	632 (300)	–0.999	–
Cu(salen)	356 (9800)	565 (270)	–1.190	–1.632
Cu(3-MeOsalen)	369 (7200)	570 (310)	–1.160	–1.587

^{a} Maximum absorpsion wavelength in absorption spectrum and molar extinction coefficient (in parenthesis) measured in methanol. ^{b} Reduction potential (vs. Ag/Ag$^+$) in the cathodic sweep of the cyclic voltammogram (1.0 mM solution in dimethyl sulfoxide in the presence of (n-Bu)$_4$NClO$_4$ (0.1 M)), working electrode, glassy carbon, counter electrode, Pt wire, scan rate, 100 mV/sec.

Such smaller transition energies and positively shifted reduction potentials of the salamo complexes may be explained by either the larger electronegativity of oxygen atoms or the difference of geometry around the copper atom (vide infra).

The structures of Cu(salamo)[10] and Cu(3-MeOsalamo)[11] were determined by X-ray crystallography, revealing that the tetracoordinate copper atom lies in the N_2O_2 coordination sphere (Figure 2). The copper atom of Cu(3-MeOsalamo) has a square planar geometry distorted tetrahedrally by 41.05(17)° (defined by the angle between two sets of N–Cu–O planes). Similar distortion was also observed for tetramethylene analogue Cu(salbn)[12] (42.8°), although shorter analogue Cu(saltn)[13] showed less distortion (20.1°).

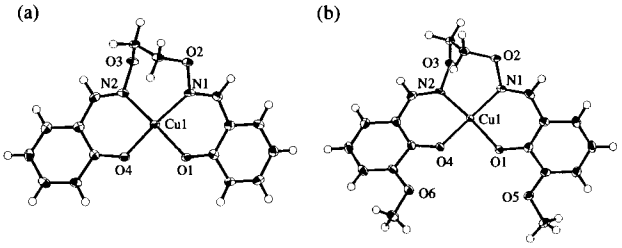


Figure 2. ORTEP drawings (50% probability level) of Cu(II) complexes. (a) Cu(salamo), selected bond lengths (Å): Cu1-O1 1.9515(17), Cu1-O4 1.9076(18), Cu1-N1 2.016(2), Cu1-N2 1.971(2). (b) Cu(3-MeOsalamo), selected bond lengths (Å): Cu1-O1 1.892(3), Cu1-O4 1.910(3), Cu1-N1 1.983(4), Cu1-N2 1.923(4).

On the other hand, Cu(salamo) was found to have a copper atom with a slightly pyramidalized square planar geometry. This structure may be stabilized by the intermolecular contacts (2.4269(18) Å) between copper and oxygen atoms to form a head-to-tail dimer (Figure 3). Similar interaction was observed for unsubstituted Cu(salen)[9,14] (2.415 Å for the distance of copper–oxygen).

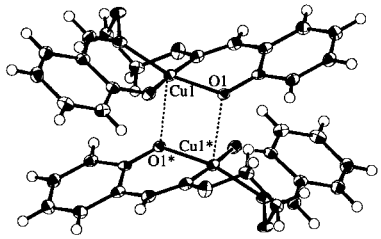
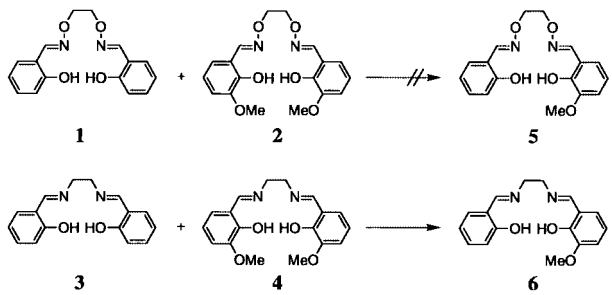


Figure 3. Crystal structure of Cu(salamo) showing the formation of a dimer. Distance of Cu1-O1*, 2.4269(18) Å.

Schiff bases are known to suffer imine exchange reactions, which sometimes make it difficult to construct more complicated systems consisting of different aldehyde units and diamine units.[15] Scrambling experiments showed high stability of oxime derivatives against the exchange of aldehyde units; no change occurred upon mixing the two oxime ligands **1** and **2** in $CDCl_3$ with about 0.1 equiv of water, while the corresponding imine ligands **3** and **4** gave a statistical mixture of **3**, **4**, and **6** under the same conditions (Scheme 2). This result suggests that an *O*-alkyl oxime moiety is much more useful to make supramolecular systems than a Schiff base moiety.

Further investigation on the synthesis and structures of other transition metal ions such as manganese, iron, cobalt, nickel, and zinc is now in progress.

Scheme 2.



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8 Crystallographic data for **2**: $C_{18}H_{20}N_2O_6$ (360.36), monoclinic, $P2_1/n$, a = 4.694(4), b = 14.616(6), c = 12.356(4) Å, β = 98.065(3)°, V = 839.3(9) Å^3, Z = 2, ρ_{calc} = 1.426 g/cm^3, unique reflections, 1482, R_1 = 0.0816 ($I > 2\sigma(I)$), wR_2 = 0.2330 (all data).[16]

9 M. M. Bhadbhade and D. Srinivas, *Inorg. Chem.*, **32**, 6122–6130 (1993).

10 Crystallographic data for Cu(salamo): $C_{16}H_{14}CuN_2O_4$ (361.83), monoclinic, $P2_1/n$, a = 12.833(2), b = 7.6517(10), c = 16.151(3) Å, β = 116.1807(10)°, V = 1423.3(4) Å^3, Z = 4, ρ_{calc} = 1.689 g/cm^3, unique reflections, 2506, R_1 = 0.0355 ($I > 2\sigma(I)$), wR_2 = 0.0960 (all data).[16]

11 Crystallographic data for Cu(3-MeOsalamo): $C_{18}H_{18}CuN_2O_6$ (421.88), monoclinic, $P2_1/n$, a = 8.0687(8), b = 11.1764(8), c = 18.990(3) Å, β = 93.3147(7)°, V = 1709.7(3) Å^3, Z = 4, ρ_{calc} = 1.639 g/cm^3, unique reflections, 3015, R_1 = 0.0502 ($I > 2\sigma(I)$), wR_2 = 0.1390 (all data).[16]

12 For the crystal structure of [*N*,*N'*-bis(salicylidene)-1,4-diaminobutane]copper(II), see: H.-H. Yao, J.-M. Lo, B.-H. Chen, and T.-H. Lu, *Acta Crystallogr.*, **C53**, 1012–1013 (1997).

13 For the crystal structure of [*N*,*N'*-bis(salicylidene)-1,3-diaminopropane]copper(II), see: a) M. G. B. Drew, R. N. Prasad, and R. P. Sharma, *Acta Crystallogr.*, **C41**, 1755-1758 (1985). b) R.-G. Xiong, B.-L. Song, J.-L. Zuo, X.-Z. You, and X.-Y. Huang, *Polyhedron*, **15**, 903–907 (1996).

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