Synthesis of Phenoxo-bridged Dicopper(II) Complexes of *N*-(2-Aminoalkyl)salicylaldimines and Their Use in the Formation of Monohalogeno-complexes and Non-symmetrical Quadridentate Schiff-base Complexes †

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Phenoxo-bridged dicopper(II) complexes, $[Cu_2L^1{}_2][ClO_4]_2{\cdot}2H_2O$, of *N*-(2-aminoethyl)salicylaldimine (HL^1) and its analogues have been synthesised by a high dilution method. These compounds react with *p*-substituted *o*-acylphenols and 1,3-diketones to form non-symmetrical quadridentate Schiff-base complexes. The phenoxo-bridge in $[Cu_2L^1{}_2][ClO_4]_2{\cdot}2H_2O$ can be split by strong nucleophiles, yielding the monomeric compounds $[CuL^1(X)]$ (X = Cl, Br, I, N_3, or NCS). Similar reactions occur with $[Cu_2L^7{}_2][ClO_4]_2{\cdot}2H_2O$, where HL^7 is the reduced version of HL^1.

Although chromium(III),[1] cobalt(III),[2] and iron(III) [3] complexes of the tridentate ligand *N*-(2-aminoethyl)salicylaldimine (HL^1) have been structurally characterised, copper(II) complexes have so far remained unexplored. We report here preparation of the oxo-bridged compounds $[Cu_2L^1{}_2][ClO_4]_2{\cdot}2H_2O$ (1'a) and analogues as well as of complexes of 2-(2′-aminoethylaminomethyl)phenol (HL^7), the saturated derivative of HL^1. We also demonstrate that the complex (1a) is a useful precursor for the generation of non-symmetrical quadridentate Schiff-base complexes and the mononuclear compounds $[CuL^1(X)]$ (X = Cl, Br, I, N_3, or NCS).

Experimental

Physical Measurements.—The equipment used was as reported earlier.[4] *X*-Band e.s.r. spectra of polycrystalline specimens were recorded at room temperature on a Varian XL-E109 spectrometer.

Preparations.—*Complexes* (1a)—(1c). To a boiling methanol solution (500 cm^3) of the sodium salt of salicylaldehyde or 2-acetyl-4-methylphenol (5 mmol) was quickly added a methanol–water (1 : 1) solution (20 cm^3) of $Cu(ClO_4)_2{\cdot}6H_2O$ (7.5 mmol) and 1,2-diaminoethane or 1,3-diaminopropane (7.5 mmol). The resulting solution was heated under reflux for 2 h and then filtered. The filtrate was reduced to *ca.* 100 cm^3 on a rotary evaporator and again filtered. After further concentration of the filtrate to 50 cm^3 it was set aside for crystallisation. The crystalline product obtained after standing overnight was recrystallised from methanol–water (1 : 1); yield 90%.

Complexes (2a)—(2d). To a methanol solution (30 cm^3) of an appropriate complex (1) (2 mmol) were added salicylaldehyde or a *p*-substituted *o*-acylphenol (4 mmol) and triethylamine (4 mmol). The solution was refluxed for 3 h and then concentrated to half its original volume. Crystals which separated on slow evaporation of the solution were collected by filtration and washed several times with water to remove any unreacted dimeric species. The compounds were recrystallised from methanol.

$[CuL^6]{\cdot}H_2O$ {H_2L^6 = N-[2-(1′-*Methyl*-3′-*oxobutylideneamino*)*ethyl*]*salicylaldimine*} (3). Starting from (1a) and acetylacetone (Hacac) this compound was prepared in the same way as described above. However, in this case some $[Cu(acac)_2]$ first crystallised out from the solution and was removed by filtration. The product that remained in solution deposited on further concentration of the filtrate. It was recrystallised from methanol.

$[CuL^1(X)]{\cdot}nH_2O$ (4a)—(4e). Dried and finely ground alkali-metal salt [LiCl for (4a), NaBr for (4b), NaI for (4c), and NaN_3 for (4d)] or NH_4NCS [for (4e)] (10 mmol) was added to a solution of complex (2a) (1 mmol) in dry methanol (100 cm^3). The mixture was refluxed for 4 h, filtered, and the filtrate concentrated to 40 cm^3. After standing overnight, the crystals which deposited were collected by filtration, washed with cold methanol, and dried *in vacuo*.

$Na(L^7)$ (5). This compound was prepared by condensing salicylaldehyde with 1,2-diaminoethane and then reducing with $NaBH_4$ following a similar reaction reported [5] for 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and 1,2-diaminoethane.

$[Cu_2L^7{}_2][ClO_4]_2{\cdot}2H_2O$ (6). The salt $Na(L^7)$ (0.38 g, 2 mmol) was dissolved in methanol (50 cm^3) and a methanol solution (10 cm^3) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.93 g, 2.5 mmol) was added with stirring. The solution was refluxed for 1 h, filtered, and concentrated to *ca.* 20 cm^3. The crystalline product which deposited on standing was collected by filtration and recrystallised from methanol.

The complexes $[CuL^7(Cl)]{\cdot}H_2O$ (7) and $[CuL^8]{\cdot}H_2O$ {H_2L^8 = 2-[2′-(*o*-hydroxybenzylideneamino)ethylaminomethyl]phenol} (8) were prepared in the same way as described for (4) and (2) respectively. Analytical data for the compounds are given in the Table.

Results and Discussion

The high dilution reaction described here affords the binuclear copper(II) complexes (1a)—(1c) in almost quantitative yield. The usefulness of these as precursors for several other interesting compounds is shown in Scheme 1. Similar reactions carried out to a limited extent for complex (6) are outlined in Scheme 2.

In dry methanol the azido- (4d) and thiocyanato- (4e) complexes behave as non-electrolytes, but partial dissociation

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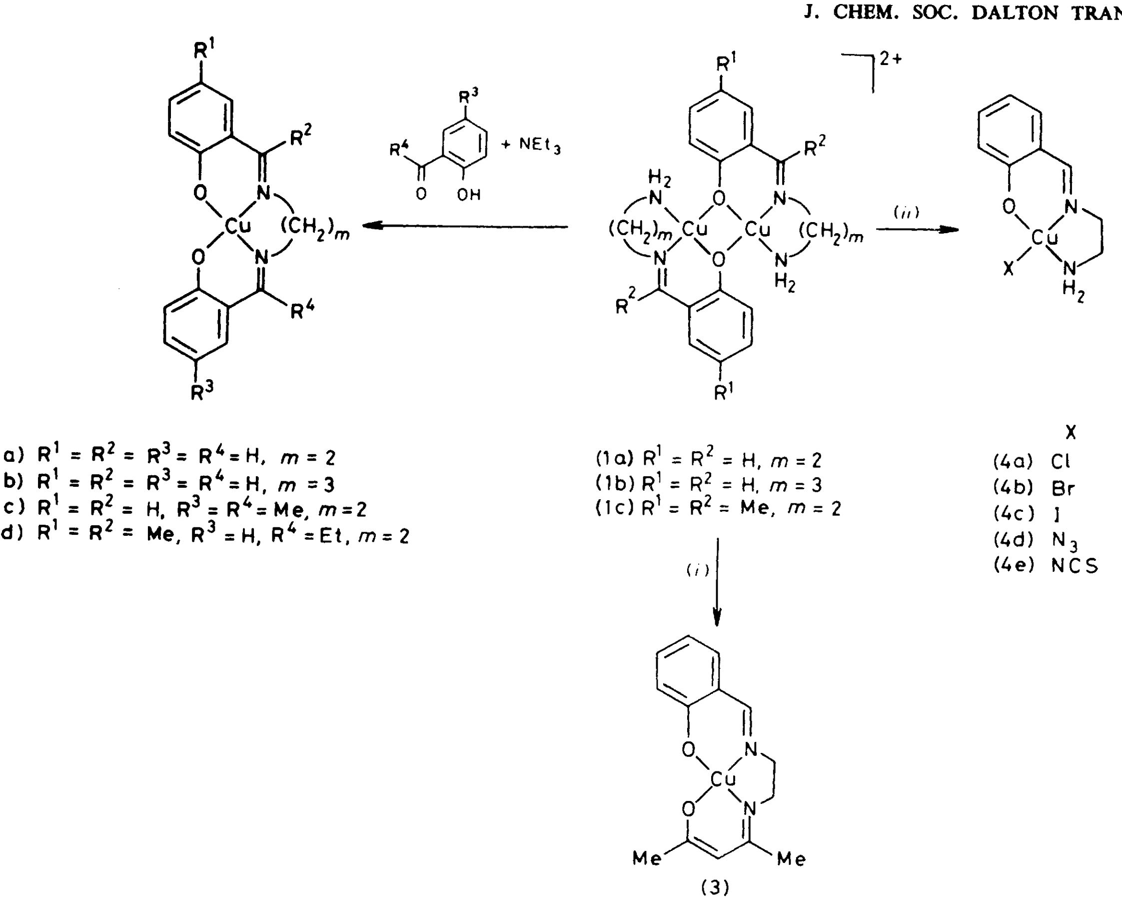
† *Non-S.I. unit employed*: B.M. ≈ 9.27×10^{-24} A m^2.

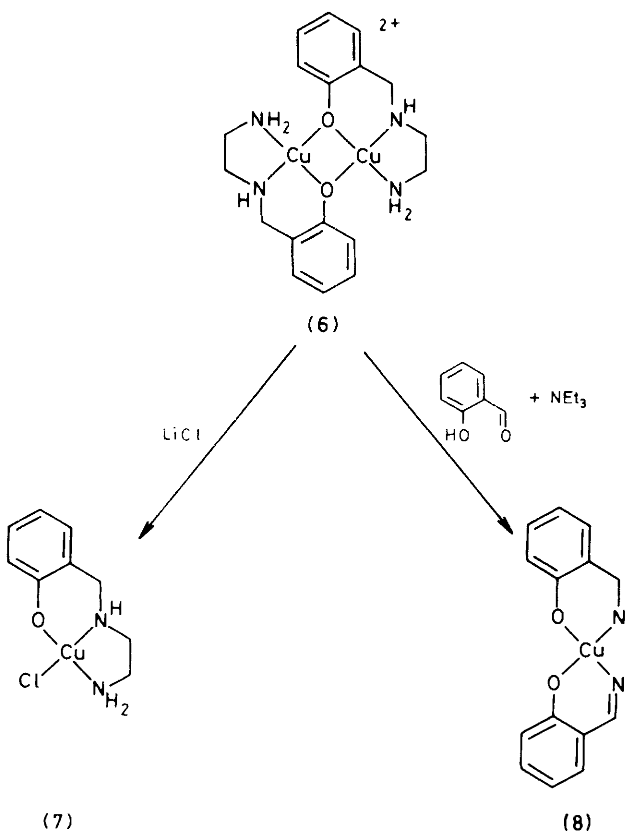


Scheme 1. (*i*) $m = 2$, Hacac; (*ii*) $m = 2$, NaX or NH_4X

Table. Analytical, magnetic, and electronic spectral data for the complexes

	Analysis (%) [a]					
Complex	C	H	N	Cu	$\mu_{eff.}$[b]/B.M.	ν [c]/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})
(1a) $[Cu_2L^1_2][ClO_4]_2\cdot 2H_2O$	31.3 (31.4)	3.55 (3.75)	8.0 (8.15)	18.35 (18.45)	1.1	27 400 (10 200), 17 240 (290)
(1b) $[Cu_2L^2_2][ClO_4]_2\cdot 2H_2O$ [d]	33.65 (33.5)	4.0 (4.2)	8.0 (7.8)	17.6 (17.75)	1.18	27 780 (11.300), 16 950 (245)
(1c) $[Cu_2L^3_2][ClO_4]_2\cdot 2H_2O$ [e]	35.65 (35.5)	4.8 (4.55)	7.4 (7.5)	17.2 (17.05)	1.05	27 030 (10 000), 17 090 (220)
(2c) $[CuL^4]\cdot H_2O$ [f]	57.3 (57.5)	5.5 (5.3)	7.3 (7.45)	17.0 (16.9)	1.85	27 030 (9 550), 18 020 (330)
(2d) $[CuL^5]$ [g]	62.0 (62.25)	5.9 (5.7)	7.2 (7.25)	16.25 (16.5)	2.1	27 030 (9 650), 18 180 (330)
(3) $[CuL^6]\cdot H_2O$			8.4 (8.6)	19.6 (19.5)	2.0	28 570 (3 000), 17 700 (90), 13 990 (35)
(4a) $[CuL^1(Cl)]\cdot H_2O$	38.3 (38.55)	4.8 (4.65)	9.75 (10.0)	22.5 (22.7)	2.0	15 750 [h]
(4b) $[CuL^1(Br)]\cdot H_2O$	24.3 [i] (24.6)		8.8 (8.65)	19.5 (19.6)	2.0	16 000 [h]
(4c) $[CuL^1(I)]\cdot H_2O$	33.8 [j] (34.2)		7.3 (7.55)	17.0 (17.1)	1.8	16 810 [h]
(4d) $[CuL^1(N_3)]$	40.5 (40.2)	4.25 (4.1)	25.7 (26.05)	23.8 (23.65)	2.05	16 390 [h]
(4e) $[CuL^1(NCS)]\cdot H_2O$			14.15 (13.9)	21.2 (21.0)	1.95	16 670 [h]
(6) $[Cu_2L^7_2][ClO_4]_2\cdot 2H_2O$	30.8 (31.2)	4.5 (4.35)	8.25 (8.1)	18.2 (18.35)	1.05	26 670 (1 570), 17 240 (250)
(7) $[CuL^7(Cl)]\cdot H_2O$	12.8 [k] (12.55)		10.1 (9.9)	22.4 (22.55)	2.1	16 260 [h]
(8) $[CuL^8]\cdot H_2O$			8.15 (8.0)	17.9 (18.15)	1.95	17 240 [h]

[a] Calculated values are in parentheses. [b] At 300 K. [c] In MeCN unless stated otherwise. [d] HL^2 = *N*-(3-Aminopropyl)salicylaldimine. [e] HL^3 = *N*-(2-Aminoethyl)-α,5-dimethylsalicylaldimine. [f] H_2L^4 = *N*-[2-(α′,5′-Dimethylsalicylideneamino)ethyl]salicyaldimine. [g] H_2L^5 = *N*-[2-(α′,5′-Dimethylsalicylideneamino)ethyl]-α-ethylsalicylaldimine. [h] In Nujol mull. [i] % Br. [j] % I. [k] % Cl.



Scheme 2.

occurs for the halogeno-complexes (4a)—(4c) and increases with incremental addition of water. The existence of a monomer–dimer equilibrium, $[Cu_2L^1_2]^{2+} + 2X^- \rightleftharpoons 2[CuL^1(X)]$, has been verified by spectrophotometric titrations.

The room-temperature magnetic moments (Table) of complexes (1a)—(1c) and (6) lie in the range 1—1.2 B.M. and are consistent with their dimeric formulations. In the remaining cases the observed moments (1.9—2.1 B.M.) probably indicate monomeric compositions, although weak dimeric interaction cannot be ruled out in the absence of low-temperature data.

The i.r. spectra of complexes (1a)—(1c) exhibit stretching vibrations due to ν(N–H) (3 300—3 100 cm^{-1}), ν(C=N) (1 640—1 610 cm^{-1}), ν(C $\cdots$ O) (*ca.* 1 530 cm^{-1}), and ionic perchlorate (*ca.* 1 100 and 620 cm^{-1}). Compounds (2a)—(2d) and (3) show no sign of ν(N–H), but display characteristic C=N and C $\cdots$ O stretches. In complexes (6) and (7) where the azomethine group has been reduced the band due to ν(C $\cdots$ O) is no longer present, however this reappears in (8) which contains both amine and azomethine groups. The azido-complex (4d) is characterised by a single antisymmetric stretch due to $\nu_3(N_3^-)$ at 2 060 cm^{-1}, thus showing the absence of an azide bridge. The lack of a SCN bridge is also evident in complex (4e) which displays a ν(C≡N) vibration at 2 070 cm^{-1} indicating metal–nitrogen bonding.[6]

All of the complexes exhibit a *d–d* band at 640—550 nm and another band around 370 nm (Table). The absorption occurring at 370 nm seems to be due to both π–π^* transitions of C=N chromophores and ligand to metal charge transfer [compare (1a) and (6)]. It may be noted that the intensities of the *d–d* band of the mononuclear complexes (2), (5), and (8) are stronger relative to those of the binuclear compounds (1) and (6). This is reminiscent of the weaker intensities in bis-(bidentate *trans*-planar Schiff-base)copper(II) complexes compared to *cis*-planar quadridentate systems.[7]

The complexes $[CuL^1(X)]\cdot nH_2O$ (4a)—(4e) exhibit three different types of e.s.r. spectra. The chloro-(4a) and bromo-(4b) complexes have broad isotropic spectral features [g = 2.11 (4a) and 2.115 (4b)], the iodo-(4c) and thiocyanato-(4e) complexes display spectra with axial symmetry [g = 2.204, $g_\perp$ = 2.069 (4c); $g_\parallel$ = 2.24, $g_\perp$ = 2.076 (4e)], and the spectrum of the azido-complex (4d) shows rhombic symmetry (g_3 = 2.184, g_2 = 2.114, and g_1 = 2.068). None of these compounds exhibits $\Delta M_s = \pm 2$ transitions at half field (*ca.* 1 600 G).

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