

Synthesis and structure of mixed metal tetradentate Schiff base complexes containing copper(II) and zinc(II) ions – Stabilisation of a supramolecular structure[†]

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Abstract : The tetradentate copper(II) Schiff base complexes, Cu(SALEN) and Cu(5-BrSALEN), underwent facile reactions with zinc perchlorate hexahydrate, Zn(ClO₄)₂·6H₂O resulting excellent complex formations. Solid compounds of formula [CuL]₂Zn(H₂O)₂(ClO₄)₂·2CuL [where CuL = *N,N'*-ethylenebis(salicylideneiminato)copper(II), Cu(SALEN); *N,N'*-ethylenebis(5-bromosalicylideneiminato)copper(II), Cu(5-BrSALEN)] were isolated as powdery solid materials. The complexes are characterized by magnetic, spectroscopic and electrochemical properties. X-Ray crystallographic structure analysis performed on [Cu(SALEN)]₂Zn(H₂O)₂(ClO₄)₂·2Cu(SALEN) (1) showed it to crystallize in monoclinic space group, C2/c with Z = 4, and a = 28.3450(10), b = 10.4330(3), c = 23.7993(9) Å, β = 111.073(3)°. The copper(II) ions are in distorted square planar coordination whereas the central Zn^{II} ion is bound to two water molecules and to four oxygen atoms of the two Cu(SALEN) Schiff base complex molecules in a distorted octahedral fashion. The structure consists of two perchlorate ions and two further molecules of Cu(SALEN) complexes.

Keywords : Copper(II), zinc(II), tetradentate Schiff base, supramolecular structure.

Introduction

Schiff bases in general and salen-type Schiff bases in particular are often regarded as “prevalent ligands”¹. Salen-type N₂O₂ Schiff base ligands coordinate to various types of transition metal ions in a tetradentate fashion to produce stable complexes. Many such complexes have found a profound role to play in homogeneous catalysis²⁻⁶. Recently the salen structures have also emerged as highly useful building blocks for supramolecular structures⁷⁻¹⁰, some other applications and materials¹¹⁻¹³ and molecular sensors^{14,15}. The crystal and molecular structure of the heterometallic gadolinium complexes in which the gadolinium(III) ions are coordinated to two copper(II) salicylaldiminato complexes stabilising^{16,17} a novel trinuclear Cu₂Gd unit and that such complex molecules also consist of two additional salicylaldiminato copper(II) complexes are reported. With a view to stabilize more of

such mixed metal complexes reactions of various tetradentate salicylaldiminato copper(II) complexes with various metal perchlorate hydrates have been performed. The investigations involving the reactions with Zn(ClO₄)₂·6H₂O however ended up with the isolation of heterometallic zinc complexes in which Zn^{II} ions are also found to be coordinated to two copper(II) salicylaldiminato complexes yielding a Cu₂Zn triangular unit consisting of two additional salicylaldiminato copper complexes as integral part of the complex molecules stabilizing a supramolecular structure similar to the Cu-Gd complexes. Synthetic details and details of all physicochemical studies of these and a number of other different but related complexes are in progress.

Experimental

The tetradentate Schiff bases (TSBH₂) were prepared

[†]Dedicated to Professor Dr. H. Vahrenkamp on the occasion of his 70th birthday.

by the usual method of condensation of salicylaldehyde/5-bromosalicylaldehyde with ethylenediamine in 2 : 1 molar ratios in refluxing ethanol.

The copper(II) tetradentate Schiff base (CuTSB) complexes $[N,N'$ -ethylenebis(salicylaldiminato)]copper(II), Cu(SALEN) and $[N,N'$ -ethylenebis(5-bromosalicylaldiminato)]copper(II), Cu(5-BrSALEN) were prepared as reported earlier¹⁸. Crystalline zinc(II) perchlorate hexahydrate, $Zn(ClO_4)_2 \cdot 6H_2O$ (Aldrich) and all other chemicals were of reagent grade and were used as purchased. Solvents were dried and distilled before use. Room temperature magnetic susceptibilities were measured on a Sherwood Scientific Ltd., Cambridge, UK magnetometer fitted with a Magnetic susceptibility balance Magway MSB MK1 with $Hg[Co(SCN)_4]$ used as standard. Microanalysis of C, H, N were performed on a Perkin-Elmer 2400 Series II CHN analyzer. Copper contents were estimated on a Perkin-Elmer atomic absorption spectrometer. Electronic spectra were recorded on a Shimadzu UV-Vis 1601 spectrophotometer. A Perkin-Elmer FTIR Paragon 1000 spectrometer was used to record the infra red spectra. ESR spectra were recorded on a EPR E-112X spectrometer. The electrochemical measurements were made using a par mode 273 potentiostat with a platinum wire as auxiliary electrode and an aqueous saturated calomel electrode as the reference electrode in a three electrode configurations. A REOO74 x-y recorder was used to trace the voltammograms. All electrochemical measurements were performed under nitrogen atmosphere at 298 K and were uncorrected for junction potentials. The ESR spectra were recorded at room temperature and at liquid nitrogen temperature (77 K) using 100 KHz modulation of the magnetic field. DPPH was used as the internal reference.

Preparation of the heterometallic complexes :

1 mmol of $Zn(ClO_4)_2 \cdot 6H_2O$ dissolved in 30 ml acetonitrile was added to the Cu(TSB) complexes (3.5 mmol) dissolved in 70 ml dichloromethane under constant stirring at room temperature and the mixtures were then refluxed for two hours. Filtered off when hot, the clear filtrate on cooling yielded dark crystalline solid which were collected by filtration, washed successively with acetonitrile and dichloromethane and finally dried *in vacuo*.

Caution! Perchlorate salts and perchlorate salts of metal complexes are potentially explosive. Although not exper-

rienced any incident they should be handled with extreme care.

$\{[Cu(SALEN)]_2Zn(H_2O)_2\}(ClO_4)_2 \cdot 2Cu(SALEN)$ (1) :

Yield, 0.75 g (47%); dark red; m.p. 249 °C; paramagnetic, μ_{eff} , 3.48 B.M. (298 K) (Found : C, 47.14; H, 3.68; N, 7.08; Cu, 15.18. Calcd. for $C_{64}H_{60}N_8O_{18}Zn_1Cu_4Cl_2$: C, 47.46; H, 3.73; N, 6.92; Cu, 15.69%); FT-IR : $\nu(C=N)$, 1634(vs); $\nu(C-O)$ (phenolic), 1340; $\nu_{as}(ClO_4^-)$, 1105(vs); $\delta_{as}(ClO_4^-)$, 621(m); δ (out-of-plane C-H (phenol) deformation), 789(m), 774(s), 758(s); $\nu(Co-N)$, 530(m); $\nu(Co-O)$, 471(m) cm^{-1} ; λ_{max} (log ϵ) : 277 (4.60), 358 (4.25), 562 (2.63).

$\{[Cu(5-BrSALEN)]_2Zn(H_2O)_2\}(ClO_4)_2 \cdot Cu(5-BrSALEN)$ (2) :

Yield, 0.81 g (42%); red; m.p. 284 °C; paramagnetic, μ_{eff} , 3.66 B.M. (298 K) (Found : C, 39.45; H, 2.85; N, 5.66; Cu, 12.98. Calcd. for $C_{64}H_{56}N_8O_{18}Zn_1Cu_4Cl_2Br_4$: C, 39.72; H, 2.92; N, 5.79; Cu, 13.13%) : FT-IR : $\nu(C=N)$, 1630(vs); $\nu(C-O)$ (phenolic), 1332; $\nu_{as}(ClO_4^-)$, 1102(vs); $\delta_{as}(ClO_4^-)$, 622(m); δ (out-of-plane C-H (phenol) deformation), 782(m), 770(s), 754(s); $\nu(Co-N)$, 527(m); $\nu(Co-O)$, 461(m) cm^{-1} ; λ_{max} (log ϵ) : 276 (4.12), 367 (4.10), 552 (2.39).

Results and discussion

Cu(SALEN) dissolved in dichloromethane showed facile reaction with $Zn(ClO_4)_2 \cdot 6H_2O$ dissolved in acetonitrile at room temperature. The reaction mixture was allowed to reflux for 2 h to ensure completion of the reaction whereby the relatively large complex molecule comprising of four copper atoms and a zinc atom, $\{[Cu(SALEN)]_2Zn(H_2O)_2\}(ClO_4)_2 \cdot 2Cu(SALEN)$ (1) gets stabilized. Similar reaction of Cu(5-BrSALEN) with $Zn(ClO_4)_2 \cdot 6H_2O$ as well yielded similar tetracoppermonozinc complex, $\{[Cu(5-BrSALEN)]_2Zn(H_2O)_2\}(ClO_4)_2 \cdot 2Cu(5-BrSALEN)$ (2). The products were isolated as dark red (1) and pinkish red (2) powdery solid.

Yields, m.p., results of elemental analysis, room temperature magnetic moment values, spectroscopic data of the complexes are presented in the Experimental section.

Infrared spectra :

The infrared spectra (IR) of the tetradentate Schiff bases and their metallic complexes has long been the subject of much discussion¹⁹ which with some deviations are grossly applicable in these complexes also.

The IR spectra showed strong absorptions at 1635–1615 cm^{-1} assignable to $\nu(\text{C}=\text{N})$ vibrations²⁰ which remained nearly unchanged from that observed for the precursor complexes Cu(TSB) (dianion of the tetradentate Schiff bases). The $\nu(\text{C}-\text{O})$ phenolic bands appeared around 1340–1300 cm^{-1} were shifted more appreciably than in Cu(TSB) precursor complexes. The shift was again more appreciable compared to what were observed for free Schiff bases and was attributed to the coordination of phenolic oxygen to both the metal centres^{21,12} indicative of a strong reduction of the C–O bond order due to complexation. Besides there were bands due to $\nu(\text{C}=\text{C})$, $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{N})$ which complicated the exact assignments of all the bands. The medium but sharp bands at 780–760 cm^{-1} were assigned as the out-of-plane C–H deformation of the phenyl ring. Presence of strong bands in the range 1110–1080 cm^{-1} (antisymmetric stretch) and medium but sharp bands at 627–621 cm^{-1} (antisymmetric bend) indicated the presence of uncoordinated perchlorate ion^{23,24}. The $\nu(\text{Cu}-\text{N})$ and $\nu(\text{Cu}-\text{O})$ vibrations were observed at 540–530 cm^{-1} and 480–470 cm^{-1} respectively.

Magnetic data :

Room temperature magnetic moment (μ_{eff}) values observed for the complexes (**1**, **2**) corresponded well to the values expected for magnetically isolated copper(II) complexes (see Experimental)^{16–24}. ESR spectra of the complexes (**1**) and (**2**) in DMF solution at room temperature showed an isotropic signal with four line hyperfine structure ($g_{\text{iso}} = 2.10$ – 2.12 , $A_{\text{iso}} = 80$ – 85 G). Such ESR spectra are characteristic of magnetically diluted copper(II). At liquid nitrogen temperature the spectra showed an axial pattern but on the g_{\parallel} component is superposed a multiline hyperfine structure.

Electronic spectra :

The electronic spectra of the Cu_4Zn complexes (**1**, **2**) showed two intense bands in the near ultraviolet region assignable to $\pi \rightarrow \pi^*$ and ligand ($\sigma_{\text{L}} \rightarrow \text{metal}$ (e_{g}) charge transfer transitions^{25,26} respectively. Both the bands appeared at shorter wavelengths (at 270–280 nm and 350–370 nm) compared to those observed for the precursor tetradentate Schiff base complexes of copper(II). Complexes (**1**, **2**) showed a distinct medium intensity band at nearly the same wavelength (560–570 nm) as those of the precursor complexes assignable to the $d-d$ transitions which

probably contained several transitions in the $3d$ levels predominantly the $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions²⁶.

Cyclic voltammetry :

Cyclic voltammetric studies [solvent, acetonitrile, supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, $\sim 10^{-3}$ M; $E^0 = 0.5 (E_{\text{pa}} + E_{\text{pc}})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively, $\Delta E_{\text{p}} = (E_{\text{pa}} - E_{\text{pc}})$ in mV, scan rate 50 mV s^{-1}] performed with these compounds showed involvement of a quasireversible process with E^0 ($\Delta E_{\text{p}} = 1.11$ V (100) and 1.10 V (100) observed for (**1**) and (**2**) respectively.

Crystal structure analysis of $\{[\text{Cu}(\text{SALEN})]_2\text{Zn}(\text{H}_2\text{O})_2\}(\text{ClO}_4)_2 \cdot 2\text{Cu}(\text{SALEN})$ (**1**) :

One of the dark brown crystals of about $0.3 \times 0.2 \times 0.2$ mm size was mounted in a sealed glass capillary and measured at room temperature on a Nonius Kappa CCD-diffractometer using graphite monochromatised $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS97²⁷ and structure refinement on F^2 was carried out with SHELXL97²⁸. For molecular graphics ORTEP III²⁹ was used (Figs. 1 and 2). The crystal turned out to belong to the monoclinic space group $C2/c$ with $Z = 4$ and $a = 28.3450(10)$, $b = 10.4330(3)$, $c = 23.7993(9)$ Å, $\beta = 111.073(3)$, $V = 6567.3(4)$ Å³. Solution and refinement of the crystal structure revealed the composition of the crystal as $\{[\text{Cu}(\text{SALEN})]_2\text{Zn}(\text{H}_2\text{O})_2\}(\text{ClO}_4)_2 \cdot 2\text{Cu}(\text{SALEN})$ (**1**) cocrystal.

The final R_1 value for a structure model showing composition (**1**) is 0.0495. It should be noted that a similar molecular constellation has been found in $\{[\text{Cu}(\text{SALEN})]_2\text{Gd}(\text{H}_2\text{O})_3\}[\text{ClO}_4]_3 \cdot 2[\text{Cu}(\text{SALEN})] \cdot 1/2\text{C}_2\text{H}_5\text{NO}_2$ cocrystals¹⁶.

In (**1**), Zn^{2+} is coordinated bidentally by two $[\text{Cu}(\text{SALEN})]$ molecules and by two “monoatomic” ligands which we assigned to two $\text{O}(\text{H}_2\text{O})$ atoms. The cation shows two-fold rotational (crystallographic) symmetry. The Zn coordination polyhedron defined by 2×2 O atoms of the $[\text{Cu}(\text{SALEN})]$ ligands and the two additional O (H_2O) ligands is a distorted octahedron (see Fig. 1). The Zn–O (water) distance of 2.054(3) Å is in the range of distances found, e.g. in hexahydrate-zinc complexes^{30,31}. The two independent Zn–O(SALEN) distances [2.075(3) and 2.242(3) Å] differ by remarkable 0.167(3) Å. Similar

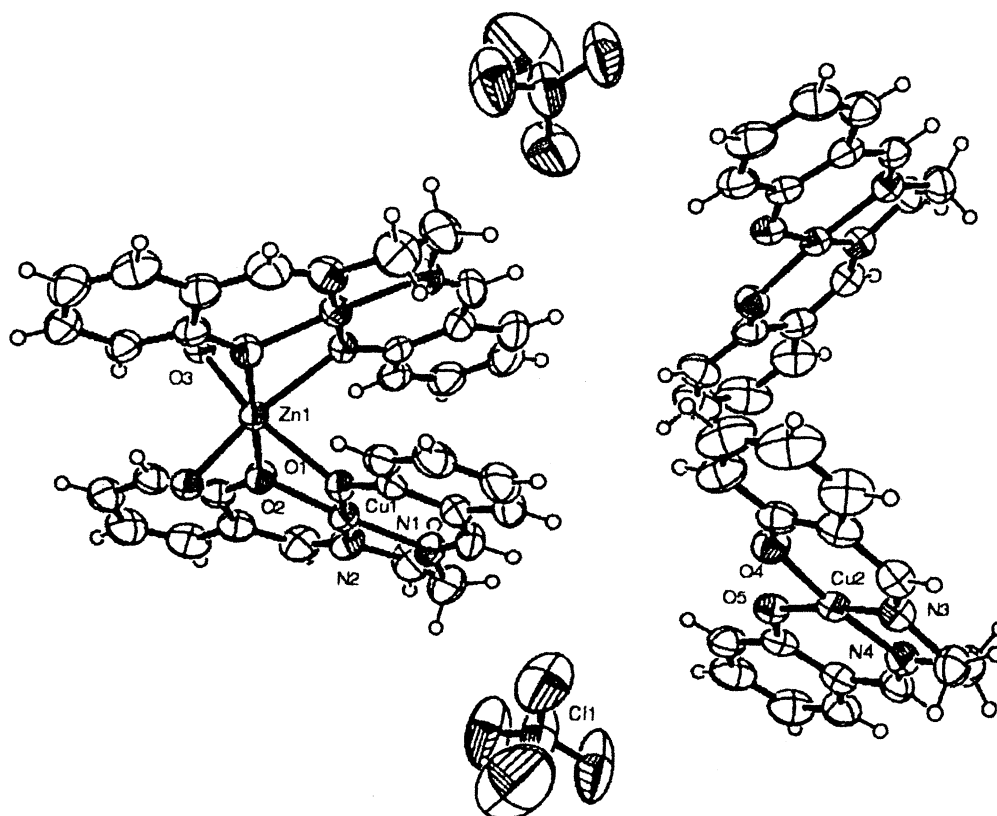


Fig. 1. Molecular structure of the compound (1).

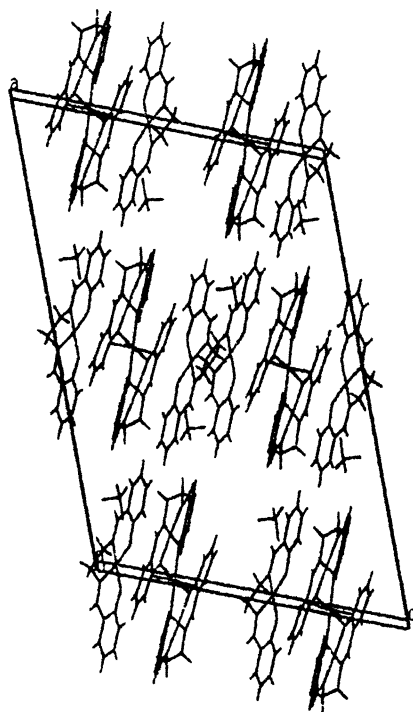


Fig. 2. Stereoview of the unit cell of the compound (1).

Table 1. Crystal data and structure refinement for (1)

Empirical formula	$C_{64}H_{60}Cl_2Cu_4N_8O_{18}Zn$
Formula weight	1619.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $C2/c$
Unit cell dimensions	$a = 28.3450(10)$ Å $b = 10.4330(3)$ Å $c = 23.7993(9)$ Å $\beta = 111.073(3)^\circ$
Volume	$6567.3(4)$ Å ³
Z, calculated density	4, 1.638 mg/m ³
Absorption coefficient	1.794 mm ⁻¹
$F(000)$	3296
Crystal size	$0.3 \times 0.2 \times 0.2$ mm
θ range for data collection	1.54 to 26.57°
Limiting indices	$-35 < h < 35$, $-13 < k < 13$, $-26 < l < 27$
Reflections collected/unique	61725/6852 [$R(int) = 0.0414$]
Completeness to $\theta = 27.08$	100%

Table-1 (contd.)

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7523 and 0.6532
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6852/0/439
Goodness-of-fit on F^2	1.135
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0495$, $wR2 = 0.1386$
R indices (all data)	$R1 = 0.079$, $wR2 = 0.1690$
Largest diff. peak and hole	1.222 and $-0.654 \text{ e}\text{\AA}^{-3}$

Table 2. Selected bond lengths (Å) and bond angles (°) for (1)

Bond lengths :			
Zn(1)-O(1)	2.242(4)	C(7)-N(2)	1.279(7)
Zn(1)-O(2)	2.075(3)	C(8)-N(2)	1.488(8)
Zn(1)-O(3)	2.054(3)	C(9)-N(1)	1.467(8)
Cu(1)-O(1)	1.888(4)	C(10)-N(1)	1.264(8)
Cu(1)-O(2)	1.902(3)	C(23)-N(4)	1.263(6)
Cu(1)-N(1)	1.900(5)	C(24)-N(4)	1.467(6)
Cu(1)-N(2)	1.907(5)	C(25)-N(3)	1.468(6)
Cu(2)-O(4)	1.907(3)	C(26)-N(3)	1.264(6)
Cu(2)-O(5)	1.907(3)		
Cu(2)-N(3)	1.924(4)		
Cu(2)-N(4)	1.919(4)		
Bond angles :			
O(3)-Zn(1)-O(2)	91.26(12)	O(2)-Cu(1)-N(2)	93.60(17)
O(5)-Cu(2)-O(4)	90.33(14)	O(2)-Zn(1)-O(1)	72.96(12)
O(5)-Cu(2)-N(4)	92.97(15)	O(1)-Cu(1)-N(1)	95.68(18)
O(4)-Cu(2)-N(4)	174.05(15)	N(1)-Cu(1)-O(2)	175.51(17)
O(5)-Cu(2)-N(3)	173.50(15)	O(1)-Cu(1)-N(2)	178.15(17)
O(4)-Cu(2)-N(3)	92.80(16)	N(1)-Cu(1)-N(2)	85.2(2)
N(4)-Cu(2)-N(3)	84.41(17)	O(1)-Cu(1)-O(2)	85.40(12)
O(3)-Zn(1)-O(1)	155.47(11)		

differences have been observed¹⁶ where Gd-O(SALEN) distances range from 2.30 to 2.44 Å. Cu-O (1.888–1.907 Å) and Cu-N (1.900–1.924 Å) distances in the neutral molecules as well as in the Zn complex are in the lower halves of the ranges reported for other structures containing [Cu(SALEN)] molecules (Cu-O : 1.89–1.94 Å; Cu-N : 1.90–1.97 Å)^{32–35}.

In addition to the regions occupied by the [Cu(SALEN)] molecules and the complex cation, a third region showed a number of peaks which were finally interpreted as two close-by positioned Cl atoms of weight 0.5 surrounded by 7 O atoms of weight 0.5 and two more O atoms of weight 0.25 thus leading to the sum formula ClO_4 . The smaller Cl-O distances in this model are in the range 1.15

to 1.50 Å. Attempts to replace the model by two “rigid body” tetrahedral $[\text{ClO}_4]^-$ ions of weights 0.5 (with Cl-O = 1.40 Å) led to higher $R1$ (= 0.066) value and to three remaining residual peaks corresponding to O atoms of weights 0.25 to 0.5. It should be noted that anisotropic refinement of the two Cl atoms led to large displacement parameters in the Cl→Cl direction, thus, more than two rigid-body $[\text{ClO}_4]^-$ ions would probably be necessary to model the electron density in a satisfactory manner.

As corresponding models would imply fractional O atoms carrying only few electrons, the “free atoms” model was retained instead.

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35. All details of structure analyses and the tables for observed and calculated structure factors may either be obtained from the authors or from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; E-mail : deposit@ccdc.cam.ac.uk (CCDC No. 742549).