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First helical zinc(II) complex with a salen ligand

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The structure of a tetra-coordinated zinc(II) complex with a salen ligand was determined for the first time; unexpectedly, the complex was an interesting 2:2 metal-to-ligand complex.

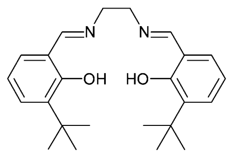
Salen (*N*,*N*′-bis(salicylidene)-1,2-ethylenediamine)-type ligand complexes of transition metals have been extensively studied mainly because of their ability to catalyze various reactions.[1] In recent years, properties of interest in materials science, such as their nonlinear optical (NLO) properties, have been investigated energetically.[2] On the other hand, salen complexes of main group elements have been much less investigated,[3] although they have been known to photoluminesce for a long time.[4] Recent studies,[5] in which it was reported that a zinc(II) complex with a salicylideneamine ligand exhibited electroluminescence as well as photoluminescence, indicate that zinc(II)-salen complexes may also be interesting compounds from the standpoint of materials science.

The first study concerning the structure of a zinc(II)–salen complex was done by Hall and Moore in 1966.[6] They found a five-coordinate complex, in which the zinc(II) ion was co-ordinated by four donor atoms of salen and one water molecule. They also described the existence of a more stable anhydrous form, but found that crystalline products could only be grown when they contained extra solvent molecules, either pyridine or water. Surprisingly, there have been no reports concerning the structure of anhydrous zinc(II)–salen complexes prior to the present study. The structure of a five-coordinated zinc(II)–salen complex, in which the zinc(II) ion is coordinated by pyridine, was not reported until 2002 by Reglinski *et al.*[7] They also isolated a zinc(II)–salen complex containing no solvent but did not determine its structure.

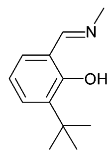
One of the reasons for the difficulty of crystallisation of anhydrous zinc(II)–salen complexes can be ascribed to the ability of salen oxygen atoms to coordinate to another metal ion even after chelation.[8] Therefore, to block this tendency we introduced a tertiary butyl group in the positions adjacent to the hydroxyl groups, that is the 3- and 3′-positions of salen ($H_2\mathbf{L}^1$). This same strategy had been successful in allowing us to crystallise another salicylidene–metal complex which had been resistant to crystallisation.[9] Another merit of introducing a tertiary butyl group into the ligand is the well-known effect of an increase in solubility resulting in some experimental advantage.

The synthesis of zinc(II) complex with this ligand ($\mathbf{L}^1$) is shown below. The ligand $H_2\mathbf{L}^1$ was prepared by mixing 3-*tert*-butyl-2-hydroxybenzaldehyde and a half equivalent of ethylenediamine in methanol at 60 °C and filtering the resulting crystals after cooling. Then, $H_2\mathbf{L}^1$ was dissolved in abs. methanol and an equivalent of zinc(II) acetate dihydrate and an excess of triethylamine added. After cooling, yellow needles were obtained. The product was then recrystallized from acetonitrile to give yellow block crystals† (yield 58%), which fluoresced bright bluish green in the solid state. In the crystal state, this complex was very stable under air.

A single crystal was suitable for X-ray analysis.‡ The solid structure of the complex is shown in Figure 1. Unexpectedly, the compound was found to be a helical 2:2 complex. No helical complexes which have salen as the basic ligand structure were known prior to this discovery, although many other helical complexes are known.[10] The coordination geometries around the two zinc(II) ions are distorted tetrahedra. The distance between the two zinc(II) ions is 3.825 Å, and the two zinc(II) ions are not crystallographically equivalent to each other. The asymmetry of the solid structure is probably caused by the crystal packing. Evidence for this comes from ^1H and ^{13}C NMR spectra which show that the molecule has four equivalent parts. Compared with the structure of the control compound $[Zn\mathbf{L}^2_2]$‡§ (Figure 2), the coordination geometries of $[Zn_2\mathbf{L}^1_2]$ are very similar except that the angle N(1)–Zn(1)–N(2) is smaller than the angle O(1)–Zn(1)–O(2) in $[Zn\mathbf{L}^2_2]$. The ^1H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of $[Zn_2\mathbf{L}^1_2]$ shows that the ^1H–^1H geminal coupling of the methylene group is 12.8 Hz, which is in accord with maintenance of the helical structure in $CDCl_3$ solution. This amount of geminal coupling was still observed at higher temperatures (328 K). Why was the helical structure formed? Zinc(II) ion prefers tetrahedral coordination as observed in $[Zn_2\mathbf{L}^2_2]$ to square planar coordination. Thus, in the absence of some coordinating molecules as pyridine or water, 2:2 metal/ligand complex would be more stable than 1:1



$H_2\mathbf{L}^1$



$H\mathbf{L}^2$

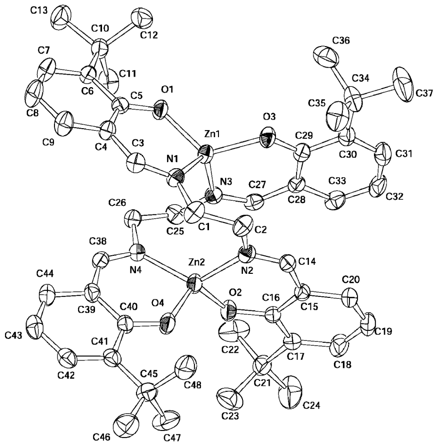


Fig. 1 ORTEP diagram of $[Zn_2\mathbf{L}^1_2]$. Thermal ellipsoids for the non hydrogen atoms were drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond length: Zn1–O1 1.912(2) Å; Zn1–O3 1.902(2) Å; Zn1–N1 2.000(2) Å; Zn1–N3 2.000(2) Å; Zn2–O2 1.902(2) Å; Zn2–O4 1.911(2) Å; Zn2–N2 2.001(3) Å; Zn2–N4 1.995(2) Å. Selected bond angles: O1–Zn1–O3 120.91(9)°; O1–Zn1–N1 96.21(9)°; O1–Zn1–N3 108.83(9)°; O3–Zn1–N1 115.99(10)°; O3–Zn1–N3 96.76(9)°; N1–Zn1–N3 119.60(10)°; O2–Zn2–O4 117.36(9)°; O2–Zn2–N2 96.95(9)°; O2–Zn2–N4 116.46(10)°; O4–Zn2–N4 95.72(10)°; N2–Zn2–N4 124.9(1)°.

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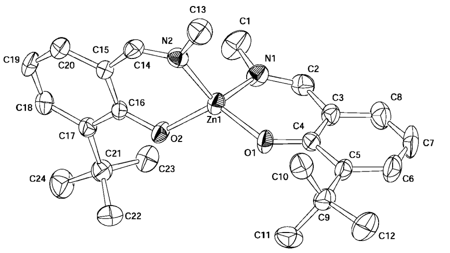

Fig. 2 ORTEP diagram of $[Zn\mathbf{L}^2{}_2]$. Thermal ellipsoids for the non hydrogen atoms were drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond length: Zn1–O1 1.905(2) Å; Zn1–O2 1.921(2) Å; Zn1–N1 1.988(2) Å; Zn1–N2 1.997(2) Å. Selected bond angles: O1–Zn1–O2 122.20(8)°; O1–Zn1–N1 96.41(8)°; O1–Zn1–N2 119.43(9)°; O2–Zn1–N1 108.29(9)°; O2–Zn1–N2 94.62(8)°; N1–Zn1–N2 116.97(10)°.

complex, in which the donor atoms cannot be placed tetrahedrally.

The distinguishing characteristic of $[Zn_2\mathbf{L}^1{}_2]$ is that two pairs of parallel aromatic planes exist, the distance between the parallel planes being very short (Figure 3(a)). The distances of N1–N4 and N2–N3, which are almost equivalent to the interplanar distances, are 3.284 and 3.217 Å, respectively. This is due to the shortness of the linker ethylene group. Besides this intramolecular stacking, a comparable intermolecular stacking is observed (Figure 3(b)). Since other zinc(II)–salicylideneamine complexes have been reported to show both photoluminescence and electroluminescence,[5] it is of interest to investigate the relationship between the helical stacked structure and the optical properties of helical zinc(II)–salicylideneamine complex found in the present work. To our knowledge, there have been no studies of the relationship between the structural and the optical properties of a helical chromophore. The absorption and emission spectra of $[Zn_2\mathbf{L}^1{}_2]$ (λ_{abs} = 382 nm, λ_{em} = 473 nm) in acetonitrile are shifted toward longer wavelength compared with $[Zn\mathbf{L}^2{}_2]$ (λ_{abs} = 370 nm, λ_{em} = 456 nm). This bathochromic shift is due to intramolecular stacking. A larger difference between these two complexes was observed in the crystal fluorescence. The crystal fluorescence of $[Zn_2\mathbf{L}^1{}_2]$ was bluish green ($\lambda_{em,crystal}$ = 488 nm) while that of $[Zn\mathbf{L}^2{}_2]$ was blue ($\lambda_{em,crystal}$ = 440 nm). Moreover, when the crystals were crushed to powder, the fluorescence was shifted to 474 nm. Transition of crystal structure may have been induced by applying stress to the crystal. This result indicates that the intermolecular stacking is an important factor of the remarkable bathochromic shift in the fluorescence. These optical properties are being studied in more detail.

In summary, we have determined the first structure of an anhydrous zinc(II) complex with a salen-type ligand. This complex is of great interest for several reasons; (1) this is the first example of a 2:2 salen–metal complex, although most chemists have considered the four donor atoms of salen ligand to coordinate to the same metal ion. Our result implies that there may exist as yet unknown helical structures for other zinc(II)–salen complexes. (2) The complex $[Zn_2\mathbf{L}^1{}_2]$ is one of the simplest known helical complexes with a short synthetic scheme. Helical structures in general are attracting the attention of many chemists,[11] because research into helicate chemistry is not only to understand fundamental principles of recognition and self-assembly processes, but also to search for new supramolecular functional devices.[12] (3) The complex $[Zn_2\mathbf{L}^1{}_2]$ is potentially of interest because their solid fluorescence wavelength ($\lambda_{em,max}$) is about 50 nm longer than that of the half complex analogue $[Zn\mathbf{L}^2{}_2]$. Additionally, they are expected to have electroluminescence. Following our discovery we expect various applications of helical zinc(II)–salen complex derivatives in supramolecular chemistry, materials science and nanoarchitectonics.

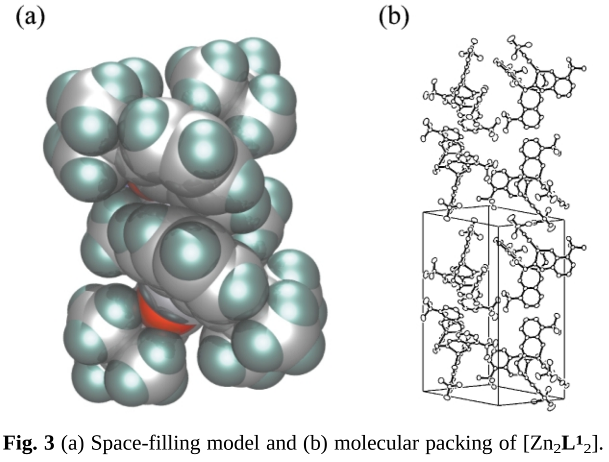

Fig. 3 (a) Space-filling model and (b) molecular packing of $[Zn_2\mathbf{L}^1{}_2]$.

Notes and references

† Elemental analysis: found(calc.) for $[Zn_2\mathbf{L}^1{}_2]$: C, 64.91(64.94); H, 6.78(6.81); N, 6.21(6.31)%. ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 36H, *t*Bu), 3.72 (d, 4H, J = 12.8 Hz, CH_2), 4.00 (d, 4H, J = 12.8 Hz, CH_2), 6.47 (t, 4H, J = 7.3 Hz, H^5), 6.52 (dd, 4H, J = 7.3, 1.9 Hz, H^4), 7.35 (dd, 4H, J = 7.3, 1.9 Hz, H^6), 7.69 (s, 4H, CH=N). IR (KBr): ν = 2955m, 1606s [ν(C=N)], 1538s, 1409s, 1227w, 1186m, 1146s, 1087w cm^{-1}. ESI-MS (CH_3CN): m/z = 885 ($[Zn_2\mathbf{L}^1{}_2 + H]^+$).

‡ *Crystal data* for $[Zn_2\mathbf{L}^1{}_2]$: $C_{48}H_{60}N_4O_4Zn_2$, M = 887.79; monoclinic, a = 11.3432(3), b = 16.2924(3), c = 24.2065(6) Å, β = 90.9037(5)°, V = 4510.0(2) Å^3, T = 193 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo–Kα) = 11.10 cm^{-1}, 40713 reflections measured, 10256 unique (R_{int} = 0.055), $R1$ = 0.0365, Rw = 0.0853 ($F^2 > 1.5\sigma(F^2)$). $[Zn\mathbf{L}^2{}_2]$: $C_{24}H_{32}N_2O_2Zn$, M = 445.91; monoclinic, a = 13.7768 (5), b = 12.8301(5), c = 14.3708(6) Å, β = 111.446(2)°, V = 2364.3(2) Å^3, T = 193 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo–Kα) = 10.59 cm^{-1}, 23471 reflection measured, 5383 unique (R_{int} = 0.045), $R1$ = 0.0380, Rw = 0.0677 ($F^2 > 1.5\sigma(F^2)$. CCDC 201549 and 201550. See http://www.rsc.org/suppdata/cc/b3/b301099f/ for crystallographic data in .cif or other electronic format.

§ The control compound $[Zn\mathbf{L}^2{}_2]$ was prepared by mixing 3-*tert*-butyl-2-hydroxybenzaldehyde (2.0 eq.), methylamine (8.0 eq.) and zinc(II) acetate dihydrate (1.0 eq.) in abs. methanol at room temperature. The precipitate was recrystallized from acetonitrile to give a light yellow crystal (yield 26%). Elemental analysis: found(calc.) for $[Zn\mathbf{L}^2{}_2]$: C, 64.74(64.64); H, 7.18(7.23); N, 6.14(6.28)%. ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 18H, *t*Bu), 3.34 (s, 2H, NCH_3), 6.55 (t, 2H, J = 7.5 Hz, H^5), 7.00 (dd, 2H, J = 7.5, 1.8 Hz, H^4), 7.34 (dd, 2H, J = 7.5, 1.8 Hz, H^6), 8.19 (s, 2H, CH=N). IR (KBr): ν = 2955m, 1627s [ν(C=N)], 1594s, 1543s, 1426s, 1404s, 1314m, 1231w, 1185m, 1150m, 1093w, 1027w cm^{-1}.

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