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Dinuclear Complexes Derivatives of *N,N'*-Ethylenebis(2-hydroxyacetophenoneimine)-(mesalen) and 1,3-Bis-(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$). The Crystal and Molecular Structure of Cu(mesalen)Zn($bhppH_2$)$_2$

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Abstract

The copper and nickel complexes of mesalen (mesalen = *N,N'*-ethylenebis-(2-hydroxyacetophenoneimine) have been used as ligands to form binuclear complexes with the bis(1,3-bis-(2-hydroxyphenyl)-1,3-propanedionate)metal(II) complexes, M'(bhpp-H_2)$_2$, where M' = Ni(II), Zn(II) and Mn(II). The structure of Cu(mesalen)Zn($bhppH_2$)$_2$ was determined from single-crystal X-ray diffraction methods. The complex consists of a four coordinated copper atom in a distorted planar environment and Zn in a distorted octahedron. Crystal data for Cu(mesalen)-Zn($bhppH_2$)$_2$, space group, $P\bar{1}$, $Z = 2$, $a = 11.779(6)$, $b = 13.796(10)$, $c = 17.913(5)$ Å, $\alpha = 62.85(8)°$, $\beta = 73.51(3)°$, $\gamma = 71.57(9)°$, $V = 2421.3$ Å^3. The magnetic properties of these complexes have been studied using magnetic susceptibility measurements in the range 300–77 K.

Introduction

Polynuclear transition-metal compounds are of interest because they provide the means to study (i) multielectron redox reactions, (ii) magnetic exchange interactions, and (iii) possible activation of small substrate molecules and ions between the metal centers. With the aim of obtaining heterotrinuclear complexes we have been studying a trinucleating ligand, 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$) [1–3], which presents two types of reacting sites, one more reactive and placed in the center (the β-diketone moiety), and two less reactive and placed outerly (the β-ketophenol moieties). This ligand yields isomerically pure mononuclear complexes permitting, consequently, the synthesis of, otherwise difficult to obtain, MM'M linear trinuclear compounds [4, 5].

On the other hand, this ligand has enabled the production of simple mononuclear alkaline and alkaline-earth metal complexes such as NEt_4 Li(bh-ppH_2)$_2$ [6], and M($bhppH_2$)$_2$ (M = Mg, Ca, Sr, Ba) [7]; a behaviour comparable to this is only found in solution by fluorine substituted β-diketones, dipivaloylethane and diisobutyrylmethane [8]. These results suggested the possibility of obtaining heterodinuclear compounds such as those found by Drago [9], Sinn [10] and coworkers with hexafluoroacetylacetone, and *N,N'*-ethylenebis-(2-hydroxypropiophenoneiminato-*N,O*(2–) M(II) complexes. One of the major problems we envisaged was the bulkier nature of the hydroxyphenol groups compared to that of the trifluoromethyl.

The present paper concentrates on the dinuclear MM' transition metal (M = M' or different) complexes based on $bhppH_3$ and mesalen ligands ($bhppH_3$ = 1,3-bis(2-hydroxyphenyl)-1,3-propanedione, mesalen = *N,N'*-ethylenebis(2-hydroxyacetophenoneimine). In particular, the crystal and molecular structure of Cu(mesalen) Zn($bhppH_2$)$_2$·$2H_2CCl_2$ is described as well as the magnetic susceptibility properties of several M(mesalen)M'($bhppH_2$)$_2$ complexes measured in the range 300–77 K.

Experimental

General

The ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione($bhppH_3$) was obtained according to a reported method [11] by a Claisen condensation of 2-hydroxyacetophenone and methyl salycylate, M(mesalen) (M = Cu, Ni) (mesalen = *N,N'*-ethylenebis(2-hydroxyacetophenoneimine)) was obtained according to a procedure reported by Sinn *et al.* [10]. M'($bhppH_2$)$_2$

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(M′ = Ni, Zn, Mn) were obtained following the procedure given in ref. 2. Solvents were reagent grade and were used as received.

Synthesis of Compounds M(mesalen)M′(bhppH$_2$)$_2$ (M = Ni, Cu; M′ = Ni, Zn, Mn)

To a warm solution of M(mesalen) (M = Ni, Cu) (0.5 mmol) in CH_2Cl_2 (20 ml), solid M′(bhpp-H$_2$)$_2$ (0.5 mmol) (M′ = Ni, Zn, Mn) was added under a nitrogen atmosphere and the resulting mixture was allowed to reflux for 2 h. The resulting solution was refrigerated at 5 °C for several hours to give crystalline solids of M(mesalen)M′(bhppH$_2$)$_2$ which were collected by filtration, washed with a small amount of CH_2Cl_2 and dried *in vacuo* (yield = 50%).

Anal. For M = Cu and M′ = Ni. Found: C, 62.4; H, 4.2; N, 3.1. Calc. for $C_{48}H_{40}N_2O_6CuNi$: C, 62.19; H, 4.32; N, 3.02%.

For M = Cu and M′ = Zn. Found: C, 61.1; H, 4.3; N, 3.1. Calc. for $C_{48}H_{40}N_2O_6CuZn$: C, 61.74; H, 4.29; N, 3.00%.

For M = Cu and M′ = Mn. Found: C, 62.0; H, 4.3; N, 3.1. Calc. for $C_{48}H_{40}N_2O_6CuMn$: C, 62.44; H, 4.39; N, 3.03%.

For M = Ni and M′ = Ni. Found: C, 62.7; H, 4.4; N, 3.2. Calc. for $C_{48}H_{40}N_2O_6NiNi$: C, 62.51; H, 4.34; N, 3.04%.

For M = Ni and M′ = Zn. Found: C, 61.4; H, 4.3; N, 3.3. Calc. for $C_{48}H_{40}N_2O_6NiZn$: C, 62.06; H, 4.31; N, 3.02%.

Attempts to Synthesize M(mesalen)Cu(bhppH$_2$)$_2$ (M = Cu, Ni)

The reaction of M(mesalen) (M = Cu, Ni) with Cu(bhppH$_2$)$_2$ in a manner similar to that reported for the other MM′ complexes, although reaction conditions were varied, yielded unreacted starting materials. When M(mesalen) was reacted with suspended $CuCl_2 \cdot 2H_2O$ in CH_2Cl_2 a highly insoluble black solid was obtained, that did not react further upon addition of bhppH$_3$.

Physical Measurements

Elemental analyses of the newly prepared complexes were performed in our microanalytical laboratory using a Perkin-Elmer 240 microanalyzer. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer as KBr pellets. Magnetic measurements were made on a Faraday type equipment in the 300–77 K temperature range. The balance was calibrated with standard Hg(Co(SCN)$_4$). Pascal Tables and our own measures were used for diamagnetic corrections as will be discussed later, but no attempts were made to introduce TIP corrections.

X-ray Diffraction

Well formed red prismatic crystals of $H_{40}ZnCuC_{48}N_2O_{10} \cdot 2H_2CCl_2$ were grown from CH_2Cl_2 solution and included into epoxy adhesive because of their instability in air.

Crystal data: $M = 2207.3$, triclinic, $a = 11.779(6)$, $b = 13.796(10)$, $c = 17.913(5)$ Å, $\alpha = 62.88(8)$, $\beta = 73.51(3)$, $\gamma = 71.57(9)°$, $V = 2421.3$ Å^3; $D_x = 1.51$ g cm^{-3}; $Z = 2$; $F(000) = 1.130$; μ(Mo Kα) = 12.28 cm^{-1} crystal size 0.3 × 0.1 × 0.1 mm.

There were no systematic absences, space group $P\bar{1}$. Cell parameters were obtained from fitting 25 high angle independent reflexions and refining the orientation matrix and unit cell parameters by least-squares method. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer at 294 K.

Intensity Data Collection

Scan width $1.0 + 0.35 \tan \theta$; standard reflection $0\,\bar{3}\,\bar{2}$; decay of standard 0.98%, reflections measured 8794, with 2θ range = 1–50°. Independent reflections considered observed 4487 with $I \geqslant 3\sigma(I)$.

The intensities were corrected for Lorentz and polarization effects. The reflections were measured at the azimuth position corresponding to a minimum absorption using an imaginary crystal with finite but small thickness having an infinitely large surface area (flat psi mode).

The positions of heavy atoms could not be found correctly using direct methods. The automated Patterson-search procedure was performed with the Rotsearch [12] program in two steps: a two dimensional angular scan to determine the orientation of the Zn–Cu pairs (estimated Zn–Cu distance = 3.06 Å) applying the rotation function and a subsequent full-symmetry translation search using the τ-function [13]. The remaining atoms were located from successive F_o synthesis.

Five cycles of full-matrix least-squares refinement on positional and isotropic thermal parameters with constrained benzene rings give a crystallographic R factor of 0.17. In this and subsequent refinement cycles the quantity minimized was $\Sigma w(\Delta F)^2/\Sigma w F_o^2$ where $w = 1/\sigma^2(F) + 0.03066 F_o^2$, and $\sigma(F)$ is derived from counting statistics. Anisotropic thermal parameters were now introduced for non-hydrogen atoms and four cycles of full-matrix least-squares refinement reduced R to 7.5 and R_w to 7.9. The hydrogen atoms were introduced in calculated positions. In the refinement we included two molecules of CH_2Cl_2 for the complex, which were located by difference Fourier synthesis. The Program system employed for refinement is SHELX-76 [14], XANADU [15] for geometric calculations, and PLUTO [16] for drawings. The scattering factors were those of International Tables of X-ray Crystallography [17]. The atomic coordinates with equivalent temperature factors are listed in Table I; the bond distances and angles are shown in Tables II and III. On a final difference Fourier synthesis the maximum and

TABLE I. Final Positional Parameters ($\times 10^4$) for Non-hydrogen Atoms in $H_{40}CuZnC_{48}N_2O_{10} \cdot 2H_2CCl_2$ and Equivalent Temperature Factors (A^2) with e.s.d.s in Parentheses

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Zn	960(1)	1880(1)	2027(1)	4.51
Cu	883(1)	3609(1)	269(1)	4.97
O1	708(4)	296(4)	2563(3)	4.90
O2	−320(4)	2179(4)	2972(3)	5.12
O3	2306(4)	1592(4)	2649(3)	4.87
O4	2368(4)	1530(4)	1116(3)	5.14
O5	−99(8)	2562(8)	1065(8)	5.01
O6	1026(8)	3650(8)	1273(8)	5.83
O7	1343(5)	−1361(4)	2209(4)	7.69
O8	−1446(6)	3779(5)	3366(4)	10.98
O9	2679(4)	1003(4)	−110(3)	6.01
O10	2350(5)	1475(5)	4056(3)	7.63
C1	−1855(6)	3028(6)	4126(5)	7.32
C2	−2604(7)	3420(6)	4745(5)	9.21
C3	−3063(7)	2686(6)	5541(5)	8.69
C4	−2761(6)	1590(6)	5727(5)	7.55
C5	−2025(6)	1184(6)	5126(4)	5.79
C6	−1601(5)	1901(5)	4313(4)	5.06
C7	−810(5)	1470(5)	3654(4)	4.23
C8	−640(5)	342(5)	3826(4)	4.93
C9	79(5)	−197(5)	3287(4)	4.29
C10	159(5)	−1377(5)	3540(4)	4.77
C11	815(6)	−1921(5)	3000(5)	5.60
C12	920(7)	−3018(6)	3237(5)	7.64
C13	382(7)	−3660(6)	4046(6)	9.67
C14	−298(7)	−3146(6)	4574(6)	10.14
C15	−359(6)	−2024(5)	4340(5)	7.44
C16	3526(6)	1545(5)	3763(4)	5.52
C17	4166(6)	1455(6)	4351(5)	7.37
C18	5366(6)	1527(6)	4093(5)	8.18
C19	5938(6)	1689(6)	3273(5)	7.67
C20	5317(6)	1749(6)	2699(5)	6.67
C21	4101(5)	1650(5)	2943(4)	4.65
C22	3432(5)	1648(5)	2341(4)	4.49
C23	4012(5)	1668(5)	1548(4)	4.57
C24	3478(5)	1612(5)	964(4)	4.26
C25	4189(5)	1605(5)	144(4)	4.51
C26	5315(5)	1928(5)	−201(4)	5.59
C27	5982(6)	1872(6)	−934(5)	6.44
C28	5560(6)	1539(6)	−1413(4)	6.49
C29	4459(6)	1224(5)	−1093(4)	5.73
C30	3761(5)	1273(5)	−346(4)	5.04
C31	1686(6)	4238(5)	1329(5)	5.81
C32	1607(6)	4153(5)	2146(5)	6.97
C33	2321(7)	4701(6)	2302(6)	10.05
C34	3021(7)	5371(6)	1616(6)	10.86
C35	3036(7)	5488(6)	814(6)	9.92
C36	2389(6)	4925(5)	629(5)	6.49
C37	2494(6)	5115(5)	−245(5)	7.38
N38	1915(5)	4658(5)	−461(4)	6.17
C39	3236(6)	5901(6)	−941(6)	10.12
C49	1881(7)	4965(6)	−1366(5)	8.28
C40	−616(5)	2006(5)	839(4)	5.20
C41	−1352(5)	1350(5)	1504(5)	6.11
C42	−1968(6)	746(6)	1358(5)	7.23
C43	−1837(6)	830(6)	561(6)	9.12
C44	−1107(8)	1482(8)	−143(8)	8.00
C45	−465(8)	2079(8)	9(8)	5.86
C46	303(8)	2699(8)	−727(8)	6.75
N47	804(8)	3395(8)	−716(8)	6.32
C48	605(8)	2522(8)	−1538(8)	11.98
C50	1667(8)	4001(8)	−1489(8)	8.51
Cl1	5041(4)	5689(4)	2741(3)	13.20
Cl2	3634(5)	4435(4)	4253(3)	15.50
C51	5005(8)	4380(7)	3460(7)	14.33
Cl3	4036(5)	1145(4)	6709(4)	15.31
Cl4	3079(6)	3331(5)	6569(4)	22.88
C52	2941(8)	2318(7)	6392(7)	17.82

TABLE II. Bond lengths (A) with e.s.d.s in parentheses

O1–Zn	2.029(5)	C17–C16	1.406(13)
O2–Zn	2.018(5)	C21–C16	1.390(9)
O3–Zn	2.034(6)	C18–C17	1.374(10)
O4–Zn	2.071(5)	C19–C18	1.372(11)
O5–Zn	2.106(2)	C20–C19	1.386(14)
O6–Zn	2.201(1)	C21–C20	1.402(9)
O4–Cu	2.827(4)	C22–C21	1.509(12)
N38–Cu	1.936(6)	C23–C22	1.378(9)
N47–Cu	1.947(2)	C24–C23	1.409(12)
O5–Cu	1.919(1)	C25–C24	1.467(9)
O6–Cu	1.882(2)	C26–C25	1.409(9)
C51–Cl1	1.679(9)	C30–C25	1.416(12)
C51–Cl2	1.823(10)	C27–C26	1.343(10)
C52–Cl3	1.696(9)	C28–C27	1.395(14)
C52–Cl4	1.631(15)	C29–C28	1.378(10)
C9–O1	1.285(7)	C30–C29	1.372(10)
C7–O2	1.281(6)	C32–C31	1.392(13)
C11–O7	1.337(8)	C36–C31	1.403(8)
C1–O8	1.345(8)	O6–C31	1.337(9)
C2–C1	1.407(12)	C33–C32	1.445(15)
C6–C1	1.381(10)	C34–C33	1.380(10)
C3–C2	1.391(9)	C35–C34	1.365(16)
C4–C3	1.339(11)	C36–C35	1.432(15)
C5–C4	1.387(11)	C37–C36	1.437(14)
C6–C5	1.388(8)	N38–C37	1.288(13)
C7–C6	1.506(10)	C39–C37	1.494(10)
C8–C7	1.401(10)	C49–N38	1.487(11)
C9–C8	1.408(10)	C50–C49	1.546(10)
C10–C9	1.457(9)	C41–C40	1.380(8)
C11–C10	1.399(11)	C45–C40	1.405(8)
C15–C10	1.376(8)	O5–C40	1.357(9)
C12–C11	1.346(10)	C42–C41	1.408(14)
C13–C12	1.393(10)	C43–C42	1.346(14)
C14–C13	1.361(13)	C44–C43	1.402(7)
C15–C14	1.389(11)	C45–C44	1.430(2)
C22–O3	1.293(7)	C46–C45	1.435(1)
C24–O4	1.287(8)	N47–C46	1.286(2)
C30–O9	1.336(9)	C48–C46	1.505(2)
C16–O10	1.349(9)	C50–N47	1.521(1)

TABLE III. Bond Angles (°) with e.s.d.s in Parentheses

O2-Zn-O1	88.6(2)	C20-C21-C16	117.9(8)
O3-Zn-O1	97.4(2)	C22-C21-C16	120.5(6)
O3-Zn-O2	91.1(2)	C22-C21-C20	121.6(6)
O4-Zn-O1	91.2(2)	C21-C22-O3	114.1(6)
O4-Zn-O2	175.7(2)	C23-C22-O3	124.4(7)
O4-Zn-O3	84.7(2)	C23-C22-C21	121.4(6)
O5-Zn-O1	98.6(2)	C24-C23-C22	125.3(6)
O5-Zn-O2	99.7(2)	C23-C24-O4	123.1(6)
O5-Zn-O3	160.9(1)	C25-C24-O4	115.9(7)
O5-Zn-O4	84.6(1)	C25-C24-C23	121.0(5)
O6-Zn-O1	169.2(2)	C26-C25-C24	122.8(8)
O6-Zn-O2	93.8(1)	C30-C25-C24	120.8(6)
O6-Zn-O3	93.1(1)	C30-C25-C26	116.4(6)
O6-Zn-O4	87.3(1)	C27-C26-C25	122.2(9)
O6-Zn-O5	70.6(1)	C28-C27-C26	121.2(7)
N47-Cu-N38	89.5(2)	C29-C28-C27	117.9(7)
O5-Cu-N38	175.6(2)	C30-C29-C28	122.0(9)
O6-Cu-N38	93.8(2)	C25-C30-O9	122.2(6)
O6-Cu-O5	81.9(1)	C29-C30-O9	117.6(8)
Cl2-C51-Cl1	107.8(5)	C29-C30-C25	120.2(6)
Cl4-C52-Cl3	113.7(8)	C36-C31-C32	120.7(8)
C9-O1-Zn	128.4(5)	O6-C31-C32	115.1(5)
C7-O2-Zn	127.8(4)	O6-C31-C36	124.2(8)
C2-C1-O8	118.0(7)	C33-C32-C31	120.8(6)
C6-C1-O8	122.9(7)	C34-C33-C32	118.6(10)
C6-C1-C2	119.0(6)	C35-C34-C33	119.6(10)
C3-C2-C1	120.7(7)	C36-C35-C34	124.1(7)
C4-C3-C2	119.5(8)	C35-C36-C31	116.1(8)
C5-C4-C3	120.7(6)	C37-C36-C31	125.5(9)
C6-C5-C4	121.1(7)	C37-C36-C35	118.3(6)
C5-C6-C1	118.7(7)	N38-C37-C36	121.7(6)
C7-C6-C1	119.6(5)	C39-C37-C36	120.7(9)
C7-C6-C5	121.5(6)	C39-C37-N38	117.5(9)
C6-C7-O2	116.3(6)	C37-N38-Cu	128.3(5)
C8-C7-O2	124.7(6)	C49-N38-Cu	109.2(6)
C8-C7-C6	119.0(5)	C49-N38-C37	122.3(6)
C9-C8-C7	126.2(5)	C50-C49-N38	111.6(5)
C8-C9-O1	123.5(6)	C45-C40-C41	120.8(8)
C10-C9-O1	116.0(6)	O5-C40-C41	114.2(7)
C10-C9-C8	120.5(5)	O5-C40-C45	125.0(4)
C11-C10-C9	121.8(5)	C42-C41-C40	120.3(8)
C15-C10-C9	121.4(7)	C43-C42-C41	118.9(7)
C15-C10-C11	116.7(6)	C44-C43-C42	123.7(9)
C10-C11-O7	121.1(6)	C45-C44-C43	117.3(5)
C12-C11-O7	116.7(7)	C44-C45-C40	119.0(3)
C12-C11-C10	122.2(6)	C46-C45-C40	126.1(3)
C13-C12-C11	120.5(8)	C46-C45-C44	114.9(1)
C14-C13-C12	118.6(7)	N47-C46-C45	121.8(1)
C15-C14-C13	120.5(7)	C48-C46-C45	121.2(1)
C14-C15-C10	121.2(8)	C48-C46-N47	116.9(1)
C22-O3-Zn	128.7(4)	C50-N47-C46	121.0(1)
C24-O4-Zn	128.2(6)	N47-C50-C49	109.0(3)
C17-C16-O10	116.1(6)	Cu-O5-Zn	94.8(1)
C21-C16-O10	122.8(8)	C40-O5-Zn	127.4(2)
C21-C16-C17	121.0(6)	C40-O5-Cu	123.7(3)
C18-C17-C16	119.1(7)	Cu-O6-Zn	92.8(2)
C19-C18-C17	120.8(9)	C31-O6-Zn	128.6(3)
C20-C19-C18	120.1(7)	C31-O6-Cu	126.3(3)
C21-C20-C19	120.8(7)		

minimum electron densities are +0.60 e Å^{-3} located near to the metal atoms.

Results and Discussion

General Chemistry

Interaction of unsolvated M′(bhppH$_2$)$_2$ with M(mesalen) in CH$_2$Cl$_2$ yields crystalline solids with the molecular formula M(mesalen)M′(bhppH$_2$)$_2$. The general sequence of reactions starting from M′(bhppH$_2$)$_2$·SS′ is indicated in the following schema:

$$\mathrm{M'(bhppH_2)_2 \cdot SS'} \xrightarrow{\Delta} \mathrm{M'(bhppH_2)_2} \qquad (1)$$

$$\mathrm{M'(bhppH_2)_2 + M(mesalen)} \xrightarrow[\mathrm{CH_2Cl_2}]{} \mathrm{M(mesalen)M'(bhppH_2)_2} \qquad (2)$$

The desolvation reaction (1) is necessary to provide empty positions in the coordination sphere of the M′ metal to be occupied by the phenoxy groups of the M(mesalen) moiety . If the solvation molecules were not removed the reaction would not occur. A similar situation happens when Cu(bhppH$_2$)$_2$ is used. This compound is obtained as such directly from synthesis and it is believed that the copper exhibits a highly stable square planar coordination. Interaction with M(mesalen) would imply a move out of the plane of the β-diketone moiety consequently not favouring the reaction.

Description of the Structure of Cu(mesalen)Zn(bhppH$_2$)$_2$

The compound Cu(mesalen)Zn(bhppH$_2$)$_2$ belongs to the triclinic system, space group $P\bar{1}$. Figure 1 shows schematically the coordination environment about both metal ions. Selected interatomic distances and angles are compiled in Tables II and III. Positional parameters are indicated in Table I.

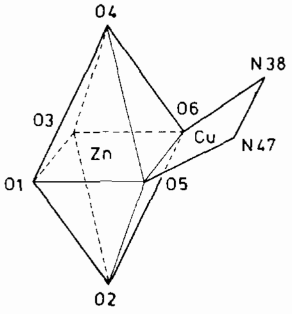

Fig. 1. Schematic coordination environment about the zinc and copper atoms.

The molecular structure as determined by X-ray diffraction methods consists of a six-coordinate zinc atom and a four-coordinate copper atom. The octahedron and square share one edge formed by the two

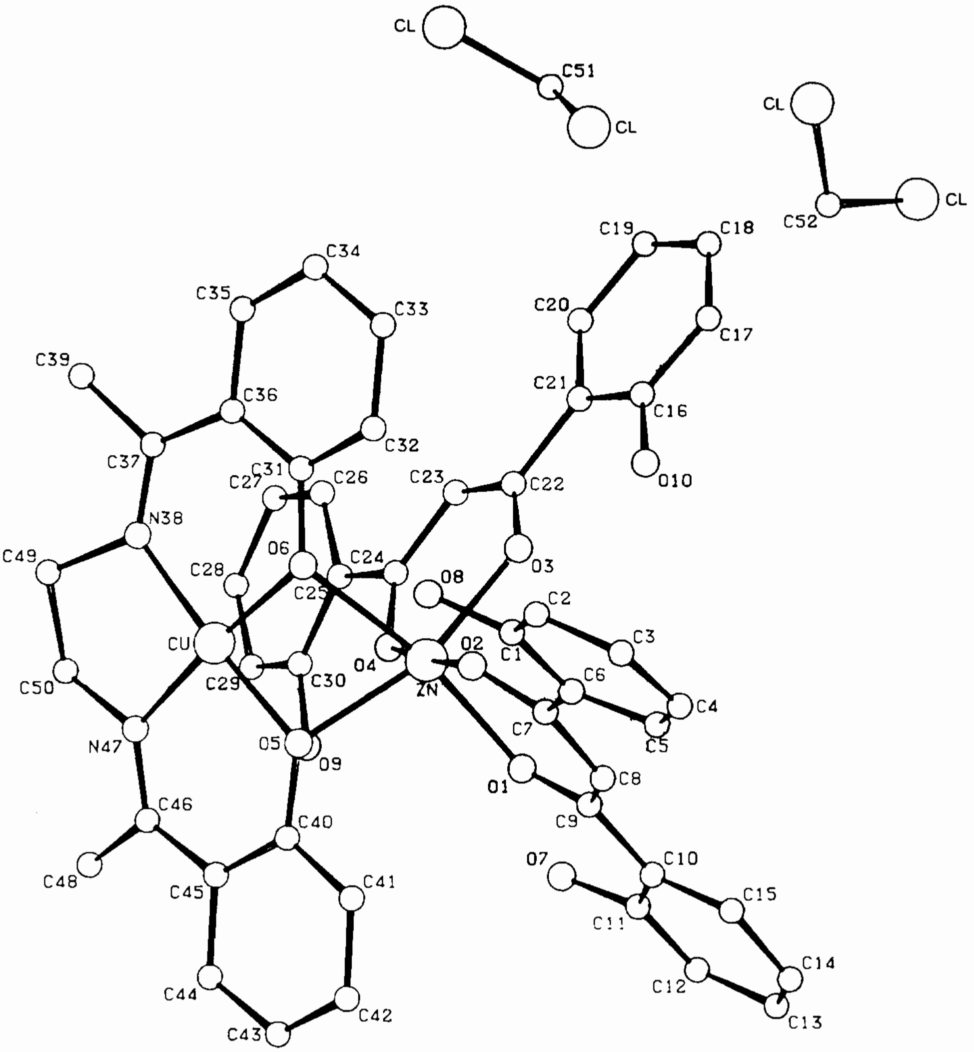

Fig. 2. Molecular structure of Cu(mesalen)Zn(bhppH$_2$)$_2$ and the atom labelling scheme.

phenolic oxygen atoms of the mesalen moiety. Two CH_2Cl_2 molecules are packed with the dinuclear molecules in the crystalline structure (Fig. 2).

The copper atom is in a slightly distorted square-planar environment, the Cu–O5, Cu–O6 distances being shorter than the Cu–N38, Cu–N47 distances. All five atoms are basically in the same plane, the copper atom deviating only –0.0419 Å from the best plane through the O5, O6, N38, N47, and Cu atoms. All phenolic groups of the mesalen moiety are essentially planar and coplanar with the Cu plane.

The zinc atom is in a distorted octahedral coordination. The distances Zn–O1, Zn–O2, Zn–O3 are almost identical with an average value of 2.027 Å. The distances Zn–O4, Zn–O5, Zn–O6 are larger but not identical. The largest is Zn–O6 (2.201 Å), followed by Zn–O5 (2.106 Å) and Zn–O4 (2.071 Å). Notice that the largest Zn–O6 distance is in correspondence with the shortest Cu–O6; the same occurs with the Zn–O5 and Cu–O5 distances as could be expected. The bhppH$_2$ moiety is essentially planar as has been proved to occur in mononuclear complexes with this ligand [18].

The Cu plane defined by O5, O6, N38, N47, Cu and the Zn plane defined by O1, O3, O5, O6, Zn form a dihedral angle of 49.66°, similar values are found in analogous complexes reported in the literature [10]. The O4 atom is separated by 2.827 Å from the Cu atom. This distance does not correspond to a normal Zn–O bond, however it is short enough to indicate some kind of bonding interaction between these two atoms. Consequently, the coordination about the Cu atom cannot be explained as simply as a square-planar pyramid. The Zn– Cu distance is 2.966 Å excluding the possibility of any significant metal–metal bonding.

Magnetic Properties

Nimesalen $Zn(bhppH_2)_2$ shows a diamagnetic behaviour as could be expected from a Ni(II) ion in a square-planar environment and a Zn(II) ion. This compound exhibits a diamagnetic susceptibility of -144.1×10^{-6} emu/mol very close to the value that can be calculated from the Pascal Tables [19] so we have used this measure, averaged in the interval 300–77 K, as a diamagnetic correction for the other compounds taking into account the different metal ions present in the complexes.

The compounds $Cu(mesalen)Zn(bhppH_2)_2$ and $Ni(mesalen)Ni(bhppH_2)_2$ have only one paramagnetic centre in the molecule and the magnetic measurements confirm it.

The complex $Cu(mesalen)Zn(bhppH_2)_2$ exhibits a Curie–Weiss behaviour in the temperature range studied (300–77 K). The magnetic moments are temperature independent and their average value is 2.1 BM. The g-value, calculated from the Curie constant assuming one paramagnetic ion per molecule and a spin value of ½ is 2.0. This behaviour is characteristic of planar Cu(II) complexes without Cu–Cu interactions [20, 21].

The compound $Ni(mesalen)Ni(bhppH_2)_2$ also shows a Curie–Weiss behaviour in the temperature range tested (300–77 K). The average magnetic moment is temperature independent and its value is 3.2 BM. The g-value, calculated from the Curie constant assuming only one paramagnetic centre per molecule and a spin value of 1, is 2.02. These values are characteristic of octahedral Ni-(II) complexes without magnetic interactions [20, 21].

The compounds $Cu(mesalen)Ni(bhppH_2)_2$ and $Cu(mesalen)Mn(bhppH_2)_2$ have two paramagnetic centres in the molecule and their magnetic behaviour could be more complicated.

The compound $Cu(mesalen)Ni(bhppH_2)_2$ shows a Curie–Weiss behaviour in the temperature range tested. The Curie Paramagnetic Temperature, θ, is -67.7 K. This large negative value could be explained by assuming antiferromagnetic interactions between both metal ions in the molecule. This is so since Cu(II) (D_{4h}) and Ni(II) (O_h) have a non-degenerate ground state and a no spin-orbit contribution to the θ constant could be expected [21].

The compound $Cu(mesalen)Mn(bhppH_2)_2$ also shows a Curie–Weiss behaviour in the temperature range tested (300–77 K). The Curie Paramagnetic Temperature, θ, is -8.7 K and as in the last compound this value indicates an antiferromagnetic interaction between Cu and Mn ions in the molecule [21]. From the Curie constant, a g-value for the Mn ion of 1.97 can be calculated, assuming a g-value of 2.0 for the Cu(II) ion.

IR spectra of $M(mesalen)M'(bhppH_2)_2$

The IR spectra of these dinuclear complexes are different to those of the starting M(mesalen) compounds. However they present great similarities with those of $M'(bhppH_2)_2$. One of the most remarkable differences is found in the band at 1590 cm^{-1}, with increased intensity with respect to the same observed in $M'(bhppH_2)_2$. This fact is attributed to the additional appearance in this position of the ν(C=N) band.

Supplementary Material

Thermal parameters, least-square planes and listing of structure factors for the compound are available from the authors on request.

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References

1 F. Teixidor, A. Llobet, L. Escriche and J. Casabo, *Polyhedron, 3,* 1017 (1984).
2 F. Teixidor, A. Llobet, L. Escriche and J. Casabo, *Polyhedron, 4,* 215 (1985).
3 F. Teixidor, A. Llobet, J. Casabo and S. Bordas, *Thermochim. Acta, 79, 315 (1984).*
4 R. L. Lintvedt, B. A. Schoenfelner, C. Cercarelli and M. D. Glick, *Inorg. Chem., 23,* 2867 (1984).
5 F. J. Rietmeijer, G. A. Van Albada, R. A. G. De Graaff, J. G. Haasnoot and J. Reedijk, *Inorg. Chem., 24,* 3597 (1985).
6 F. Teixidor, A. Llobet, J. Casabo, X. Solans, M. Font-Altaba and M. Agullo, *Inorg. Chem., 24,* 2315 (1985).
7 F. Teixidor, T. Flor and J. Casabo, *Inorg. Chim. Acta, 118,* 125 (1986).
9 B. B. Martin and D. F. Martin, *J. Inorg. Nucl. Chem., 41,* 1503 (1979).
9 N. B. O'Bryan, Z. O. Maier, I. C. Paul and R. S. Drago, *J. Am. Chem. Soc.,* 6640 (1973).
10 C. J. O'Connor, D. P. Freyley and E. Sinn, *Inorg. Chem., 18,* 1077 (1979).
11 F. Eiden and H. D. Schweizer, *Synthesis,* 511 (1974).
12 J. Rius, 'ROTSEARCH', program for crystal structure determination using fragments of known geometry, Instituto 'Jaime Almera' C.S.I.C. Barcelona, Spain, 1986.
13 J. Rius and C. Miravitlles, *Acta Crystallogr., Sect. A,* 1986, in press.
14 G. M. Sheldrick, 'SHELX-76', program for crystal structure determination, University of Cambridge, U.K., 1976.
15 P. Roberts and G. M. Sheldrick, 'XANADU', program for crystallographic calculations, University of Cambridge, U.K., 1975.
16 W. D. S. Motherwell and W. Clegg, 'PLUTO-78', program for plotting molecular crystal structures, 1978.
17 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (present distributor D. Reidel, Dordrecht), 1974, p. 149.

18 X. Solans, M. Font-Altaba, J. L. Brianso, A. Llobet, F. Teixidor and J. Casabo, *Acta Crystallogr., Sect. C, 39,* 1512 (1983).

19 F. E. Mabbs and D. J. Machin, 'Magnetism and Transition Metals Complexes', Chapman and Hall, London, 1973.

20 R. L. Carlin and A. J. van Duyneveldt, 'Magnetic Properties of Transition Metal Compounds', Springer, New York, 1977.

21 R. L. Carlin, 'Magnetochemistry', Springer, New York, 1986.