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A Novel Type of Tetranuclear Cluster with the Trinucleating Ligand 1,2-Bis(benzimidazol-2-yl)-1-hydroxyethane. Crystal and Molecular Structure of $Ni(HRSL)_2(CF_3SO_3)_2$ and $[Cu_4(SL)_4(NO_3)_2(EtOH)](NO_3)_2(EtOH)_3(H_2O)_2$; Spectroscopy and Magnetism of these and Related Transition Metal Compounds

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Abstract

A number of nickel, copper and zinc compounds with the tridentate chelating ligand 1,2-bis(benzimidazol-2-yl)-1-hydroxyethane (abbreviated HL, and HSL or HRSL for the *S* isomer and the *RS* mixture, respectively) is described. The ligand forms mononuclear complexes of general formula $M(HRSL)_2$(anion)$_2$ for all metal ions and a variety of anions, both for the racemic mixture of ligands (*R,S*) and – in a few cases – for the chiral (*S*) ligand. A dinuclear species of formula $[CuCl(RSL)](H_2O)_2Cl_2$ appears to be formed with a bridging ligand and a bridging chloride anion, again both for the chiral and the (*S*) forms of the ligands. Tetranuclear species are formed only for copper nitrate and copper perchlorate, with formula $[Cu_4(RSL)_4]$(anion)$_4$(EtOH)$_x$. Crystal structures have been solved for a monomeric and for a tetrameric species.

The compound $[Cu_4(SL)_4(NO_3)_2(EtOH)](NO_3)_2(EtOH)_3(H_2O)_2$ (**I**) crystallizes in the orthorhombic space group $P2_12_12$ with cell dimensions a = 28.633(9), b = 18.599(4), c = 15.509(8) Å and Z = 4. The crystal structure has been determined from X-ray diffraction data by direct and Fourier methods and refined by full-matrix least-squares techniques to a conventional R value of 0.077 for 3046 independent reflections. The compound consists of a tetrameric distorted cubane-type Cu_4O_4 core formed by four copper(II) and four triply bridging oxygen atoms of SL^- ligands with Cu–Cu distances of 3.069(4)–3.734(4) Å. Each copper(II) atom has a distorted octahedral environment, two oxygen and two nitrogen atoms of three SL ligands forming the equatorial coordination with Cu–O and Cu–N bonds of 1.95(1)–2.03(2) Å. The axial sites are occupied by SL oxygen, ethanol or nitrate oxygen atoms with Cu–O distances varying from 2.56(2) to 2.93(2) Å.

$Ni(HRSL)_2(CF_3SO_3)_2$ (**II**) crystallizes in the monoclinic space group $C2/c$, with a = 21.985(3), b = 11.786(2), c = 14.816(2) Å, β = 94.67(1)°, Z = 4 (i.e. four HRL units and four HSL units). The nickel(II) ion is octahedrally coordinated by 2 oxygen atoms and 4 nitrogen atoms in a *cis* geometry. Ni–N distances are 2.04–2.06 Å, whereas Ni–O = 2.15 Å. The octahedral coordination *cis* angles vary from 75 to 101°. The spectroscopic properties of the monomeric species agree with a strong tridentate chelating behaviour, in agreement with the somewhat distorted geometry found for the Ni(II) triflate. In fact the ligand field spectra show two groups of $Ni(HRSL)_2$ compounds, with slightly but significantly different ligand field parameters. No $Ni(HSL)_2^{2+}$ salts could be isolated.

The magnetic properties of the (supposed) dimer and the tetramers are in agreement with expectation for a dimer of dimers, since the Cu(II) ions have pairwise strong interactions.

Introduction

During the last decade a variety of benzimidazole-type chelating ligands has been prepared and studied in their coordinating behaviour [1, 2]. Most of these studies have been inspired by bioinorganic questions, and the wish to mimic the active sites of metalloproteins. Many metalloproteins use imidazole ligands of histidine side chains and especially copper and zinc almost always use two or more of these ligands in their metalloproteins [3].

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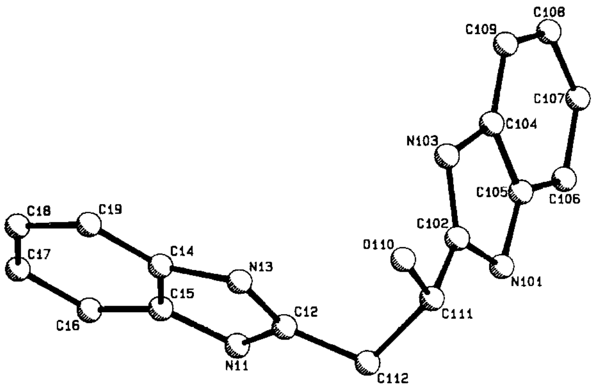

Fig. 1. Structure of the ligand HSL and the atomic numbering used.

It is also known that many copper proteins contain more than one metal ion at the active site, because the protein is bridging the metals, either by a bridging ligand or by another exogeneous ligand. However, in many cases this dimer or cluster formation has not yet been proven for the proteins. The metal site in copper and zinc proteins usually is also chiral, because the surrounding proteins side-chain ligands are chiral. This is known to facilitate chiral recognition in biological systems [4].

Continuing our earlier studies, we have now prepared a chiral, chelating benzimidazole-type ligand, i.e. 1,2-bis(benzimidazol-2-yl)-1-hydroxyethane (abbreviated HRSL). The ligand structure and numbering are given in Fig. 1. At carbon-111 a chiral center is present, allowing the study of – apart from the (*R,S*) mixture – the (*R*) and (*S*) isomers of this ligand. Molecular models of this ligand have made clear that tridentate mononuclear chelation should be possible, both with neutral and dehydronated (at OH) ligand. However, tridentate dinuclear chelating, with dehydronation of the alcohol oxygen, appeared to be difficult, without creating large steric strain. Therefore a study was undertaken with the metal ions Ni(II), Zn(II) (both likely to favor monomeric species) and with Cu(II) (a metal ion likely to form dimers or higher aggregates). The present paper describes the results, which prove that the ligand indeed is versatile, allowing both monomeric and oligomeric metal species. With certain copper salts, a novel type of tetranuclear species has been observed, which will be described in detail, including the magnetic properties.

Experimental

Starting Materials

Metal(II) salts, L-malic acid and DL-malic acid were used as commercially available without further purification.

The ligand 1,2-bis(benzimidazol-2-yl)-1-hydroxyethane was synthesized according to Taffs *et al.* [5]. The white solid, which was almost insoluble in most organic solutions was characterized by elemental analysis, NMR and mass spectroscopy.

Yield 50%. *Anal.* Found: C, 69.3; H, 4.9; N, 19.1. Calc. for $C_{16}N_4H_{14}O$: C, 69.1; H, 5.1; N, 20.1%. ^{1}H NMR spectrum measured in $(CD_3)_2SO$: 3.25–3.65 ppm (m, 2H); 5.36–5.45 ppm (q, 1H); 7.07–7.56 ppm (m, 4H). Optical activity for HSL measured in acetic acid: $[\alpha]_D^{25} = -101.2$ ($C = 2,8$) and $(CD_3)_2SO$: $[\alpha]_D^{25} = -2.75$ ($C = 1,2$).

The ligands are called HSL and HRSL, respectively. After dehydronation the abbreviations are SL and RSL, respectively.

Synthesis of the Coordination Compounds

The ligand was slurried in ethanol or methanol. This mixture was added to the metal salt (0.001 mol) dissolved in ethanol or methanol to obtain the compounds $M(HL)_2$ or M(L). When adding carefully the metal salt mixture to the ligand slurry, purple $M(L)_2$ compounds were obtained. Upon standing at room temperature the powder or crystals were formed. All compounds are listed in Table 1, together with some of their analytical and spectroscopic data. See also 'Supplementary Material'.

Physical and Analytical Measurements

Metal analyses were carried out by standard complexometric titrations and atomic absorption spectroscopy. C, H, N analyses were carried out by the Microanalytical Laboratory of University College, Dublin, Republic of Ireland. Infrared spectra were obtained as KBr pellets (4000–200 cm^{-1}) on a Perkin-Elmer 580B spectrophotometer. Ligand field spectra were obtained by the diffuse-reflectance method on solid powders on a Perkin-Elmer 330 spectrophotometer. EPR spectra of the powdered compounds were recorded at room and liquid nitrogen temperatures with a Varian E-3 spectrometer operating at X-band frequencies (9 GHz). Optical measurements were carried on a PE 141 polarimeter. Magnetic susceptibilities were measured routinely on a local Faraday balance (77–300 K). In one case a complete set of data (4–400 K) was collected on a squid magnetometer at the University of New Orleans (courtesy of Prof. Dr C. J. O'Connor).

X-ray Data Collection and Structure Determination of $[Cu_4(SL)_4(NO_3)_2(EtOH)](NO_3)_2(EtOH)_3(H_2O)_2$

A blue crystal of the title compound used for data collection had dimensions of 0.25 × 0.30 × 0.50 mm. Crystal data and relevant information about the data collection and refinement have been summarized in Table 2. The data were corrected for Lorentz and polarization effects and absorption from empirical ϕ-scan data. The structure was solved by direct and

TABLE 1. Stoichiometry and spectroscopy of the compounds with HRSL and HSL

Formula	Colour	Spectroscopic and magnetic characteristics					
		UV–Vis maxima ($cm^{-1} \times 10^3$)			EPR data		Maximum in χ (K)
					g values	$A_\parallel$ (Gauss)	
$Cu_2Cl(SL)(H_2O)_{1/2}Cl_2$	green	13.4			imp[a]		220
$Cu_2(RSL)Cl(H_2O)_2Cl_2$	green	13.3			imp[a]		>400[g]
$CuCl_2(HRSL)_2(H_2O)_2$	purple	15.0	18.0	2.05	2.25	(175)	none
$CuCl_2(HSL)_2(H_2O)_4$	purple	15.2	18.3	2.04	2.25	(175)	none
$Cu(HRSL)_2(NO_3)_2$	purple	14.7	17.8	2.05	2.26	(170)	none
$Cu(HSL)_2(NO_3)_2(H_2O)_4$	purple	15.0	18.1	2.03	2.23	(185)	none
$Cu(HRSL)_2(ClO_4)_2(H_2O)_4$	purple	14.5	17.7	2.05	2.26	(170)	none
$Cu(HSL)_2(ClO_4)_2(H_2O)_2$	purple	14.9	17.8	2.04	2.25	(170)	none
$Cu(RSL)(NO_3)(H_2O)$	blue	14.6			imp[c]		235
$Cu(SL)(NO_3)(EtOH)$	blue	15.3			imp[d]		225[h]
$Cu(RSL)(ClO_4)(H_2O)$	blue	15.0			imp[e]		250
$Cu(SL)(ClO_4)(H_2O)$	blue	14.6			imp[f]		300
$Zn(HSL)_2(ClO_4)_2(H_2O)_3$	white	$[\alpha]_D^{25} = -183.2$ ($C = 1.3$)					
$Zn(HSL)_2(BF_4)_2(H_2O)_3$	white	$[\alpha]_D^{25} = -179.9$ ($C = 2.0$)					
$Ni(HRSL)_2Cl_2(H_2O)$	blue	10.3	17.3	26.9			
$Ni(HRSL)_2Br_2$	blue	10.3	17.2	26.8			
$Ni(HRSL)_2(NO_3)_2$	blue	10.3	17.2	26.8			
$Ni(HRSL)_2(BF_4)_2$	blue	9.8	16.8	26.4			
$Ni(HRSL)_2(ClO_4)_2(H_2O)_2$	blue	9.9	16.9	26.4			
$Ni(HRSL)_2(CF_3SO_3)_2$	blue	9.8	16.8	26.3[j]			

[a–f]Only small paramagnetic impurities are visible. [g]Studies in the 4–400 K region; parameters from best fit are: $g = 2.27$, $-J/k$ = 343 and 0.5% magnetic impurity. [h]X-ray structure solved of the product that contains only HSL. [j]X-ray structure solved.

TABLE 2. Crystal and diffraction data of $[Cu_4(SL)_4(NO_3)_2(EtOH)](NO_3)_2(EtOH)_3$ (I) and $Ni(HRSL)_2(CF_3SO_3)_2$ (II)

	Compound I	Compound II
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12$	$C2/c$
a (Å)	28.633(9)	21.895(3)
b (Å)	18.599(4)	11.786(2)
c (Å)	15.509(8)	14.816(2)
β (°)	90	94.67(1)
V	8259(6)	3826(1)
Z	4	4
D(calc.) (g cm^{-3})	1.473	1.586
Molecular weight	1831.7	913.44
Diffractometer	Nicolet P3	CAD-4
Scan type	ω	$\omega/2\theta$
Radiation	Mo Kα	Ni-filtered Cu Kα
μ (cm^{-1})	11.0	25.3
θ range (°)	2–24	70
h, k, l range	0:32, 0:21, 0:17	−26:26; 0:14; −18:0
Standard reflections	2	2
Unique reflections	7130	3997
Significant reflections	3046($I > 3\sigma(I)$)	1882($I > 2.5\sigma(I)$)
No. variables	388	313
R	0.077	0.12
R_w	0.082	0.13

Fourier methods using the SHELXS-86 and SHELX-76 programs [6, 7] on a Vax 8650 computer. Least-squares refinement with anisotropic temperature factors for Cu atoms and isotropic for the other atoms yielded the final $R = 0.077$ and $R_w = 0.082$, with $w = 1/\sigma^2(F_o)$. All phenyl groups (C–C = 1.395 Å and C–C–C = 120°) and three disordered ethanol molecules were refined as rigid groups. Final positional parameters are given in Table 3 together with U_{eq} values. Scattering factors, including anomalous dispersion correction, were taken from the literature [8].

Structure Determination and Refinement of $[Ni(HRSL)_2](CF_3SO_3)_2$

Crystal data and numerical details of the structure determination are listed in Table 2. X-ray data were collected for a blue crystal (0.15 × 0.28 × 0.33 mm) sealed in a Lindemann glass capillary. Unit-cell parameters were derived by least-squares from the diffractometer setting angles at minimum reflection profile width (*vide infra*) of 24 reflections in the range $9 < \theta < 16°$. The space group was determined from the observed systematic absences as *Cc* or *C2/c*. The lattice was checked for the presence a higher symmetry with the program LEPAGE [9]. The two reference reflections showed no decay during the 73 h of X-ray exposure time. Reflection profiles were found to be highly structured. The A-vector method

TABLE 3. Fractional atomic coordinates (×10^4) and thermal parameters for [$Cu_4(SL)_4(NO_3)_2(EtOH)](NO_3)_2(EtOH)_3(H_2O)_2$ (**2**)

Atom	x	y	z	U^a (Å^2)
Cu(1)	−2213(1)	2021(2)	3174(2)	0.033
Cu(2)	−1214(1)	2024(2)	2389(2)	0.035
Cu(3)	−2196(1)	3262(1)	1842(2)	0.033
Cu(4)	−1401(1)	3567(2)	3118(2)	0.035
O(110)	−1881(5)	1865(8)	2088(9)	0.031
O(210)	−1556(5)	2137(7)	3480(9)	0.028
O(310)	−2096(5)	3431(8)	3070(10)	0.040
O(410)	−1512(5)	3364(8)	1913(10)	0.034
N(11)	−3258(7)	1110(10)	1734(13)	0.041
N(13)	−2812(7)	1667(10)	2677(12)	0.041
N(101)	−2192(8)	1803(11)	−188(13)	0.051
N(103)	−2177(7)	2764(9)	726(11)	0.032
N(21)	−115(8)	1949(13)	4104(14)	0.056
N(23)	−597(7)	2095(11)	2962(13)	0.044
N(201)	−1433(8)	2876(12)	5632(14)	0.053
N(203)	−1400(7)	3438(10)	4362(12)	0.039
N(31)	−3541(7)	3758(10)	2595(13)	0.050
N(33)	−2881(7)	3443(10)	1967(13)	0.042
N(301)	−2732(7)	3309(10)	5078(12)	0.038
N(303)	−2451(7)	2455(10)	4259(12)	0.029
N(41)	−126(9)	4151(13)	2113(15)	0.071
N(43)	−723(7)	3854(10)	2945(12)	0.036
N(401)	−864(7)	2828(11)	−31(13)	0.042
N(403)	−1007(7)	2194(10)	1168(12)	0.043
C(12)	−2810(9)	1271(12)	1958(16)	0.041
C(14)	−3291(6)	1805(8)	2898(9)	0.030
C(15)	−3561(6)	1429(8)	2300(9)	0.048
C(16)	−4046(6)	1415(8)	2381(9)	0.064
C(17)	−4261(6)	1779(8)	3060(9)	0.066
C(18)	−3992(6)	2155(8)	3658(9)	0.056
C(19)	−3507(6)	2168(8)	3577(9)	0.049
C(102)	−2128(9)	2049(14)	672(16)	0.042
C(104)	−2229(7)	3041(7)	−110(12)	0.033
C(105)	−2267(7)	2453(7)	−665(12)	0.059
C(106)	−2347(7)	2563(7)	−1542(12)	0.068
C(107)	−2390(7)	3260(7)	−1865(12)	0.077
C(108)	−2352(7)	3847(7)	−1311(12)	0.078
C(109)	−2272(7)	3738(7)	−433(12)	0.067
C(111)	−2015(8)	1520(13)	1331(15)	0.034
C(112)	−2406(9)	962(14)	1511(17)	0.045
C(22)	−569(8)	1936(13)	3800(14)	0.034
C(24)	−142(8)	2212(10)	2683(10)	0.046
C(25)	149(8)	2132(10)	3398(10)	0.063
C(26)	629(8)	2235(10)	3313(10)	0.083
C(27)	819(8)	2418(10)	2514(10)	0.104
C(28)	528(8)	2498(10)	1799(10)	0.091
C(29)	47(8)	2395(10)	1883(10)	0.066
C(202)	−1395(9)	2821(12)	4752(16)	0.039
C(204)	−1443(7)	3958(7)	5007(12)	0.043
C(205)	−1466(7)	3603(7)	5798(12)	0.056
C(206)	−1516(7)	3997(7)	6558(12)	0.084
C(207)	−1543(7)	4754(7)	6527(12)	0.079
C(208)	−1520(7)	5100(7)	5735(12)	0.085
C(209)	−1470(7)	4706(7)	4975(12)	0.059
C(211)	−1393(8)	2086(13)	4355(14)	0.034
C(212)	−950(10)	1688(14)	4424(18)	0.050
C(32)	−3071(9)	3719(14)	2464(17)	0.044
C(34)	−3269(6)	3106(9)	1485(9)	0.036
C(35)	−3670(6)	3370(9)	1888(9)	0.050
C(36)	−4110(6)	3218(9)	1546(9)	0.071
C(37)	−4149(6)	2801(9)	802(9)	0.078
C(38)	−3748(6)	2537(9)	399(9)	0.063
C(39)	−3309(6)	2690(9)	740(9)	0.033
C(302)	−2527(8)	3146(12)	4309(14)	0.030
C(304)	−2618(6)	2150(6)	5001(11)	0.032
C(305)	−1802(6)	2693(6)	5521(11)	0.045
C(306)	−3013(6)	2520(6)	6304(11)	0.053
C(307)	−3042(6)	1804(6)	6567(11)	0.069
C(308)	−2858(6)	1261(6)	6047(11)	0.044
C(309)	−2646(6)	1434(6)	5264(11)	0.051
C(311)	−2391(8)	3723(13)	3722(15)	0.033
C(312)	−2804(10)	4118(13)	3275(17)	0.050
C(42)	−585(11)	4034(15)	2178(18)	0.057
C(44)	−353(8)	3883(11)	3455(9)	0.046
C(45)	25(8)	4048(11)	2924(9)	0.071
C(46)	473(8)	4098(11)	3273(9)	0.085
C(47)	543(8)	3981(11)	4152(9)	0.098
C(48)	164(8)	3815(11)	4683(9)	0.103
C(49)	−284(8)	3766(11)	4334(9)	0.056
C(402)	−1046(10)	2834(15)	819(19)	0.052
C(404)	−821(7)	1738(7)	583(12)	0.053
C(405)	−718(7)	2126(7)	−163(12)	0.044
C(406)	−502(7)	1785(7)	−858(12)	0.071
C(407)	−389(7)	1057(7)	−807(12)	0.072
C(408)	−492(7)	669(7)	−61(12)	0.076
C(409)	−708(7)	1010(7)	634(12)	0.067
C(411)	−1255(8)	3547(13)	1181(15)	0.038
C(412)	−898(9)	4112(14)	1362(17)	0.045
O(1)	−1239(8)	639(11)	2512(15)	0.083
O(2)	−2174(9)	422(13)	9448(16)	0.095
O(3)	−4134(15)	4356(26)	3699(29)	0.203
O(4)	−926(14)	4044(22)	8945(24)	0.178
O(5)	−2204(8)	4619(12)	1574(15)	0.085
O(6)	−1825(12)	5670(20)	1606(25)	0.174
O(7)	−1683(8)	4938(12)	2667(14)	0.079
O(8)	−1930(7)	565(11)	3670(14)	0.069
O(9)	−2156(9)	−177(12)	4635(16)	0.088
O(10)	−2059(11)	−504(17)	3361(21)	0.136
O(11)	−4456(16)	630(24)	10612(32)	0.194
O(12)	−4469(13)	683(20)	9288(26)	0.153
O(13)	−4969(16)	1208(21)	9933(23)	0.179
O(14)	−314(18)	2498(30)	6128(35)	0.219
O(15)	150(12)	1661(18)	5807(22)	0.145
O(16)	−154(15)	1620(22)	7088(28)	0.193
O(17)	−3474(9)	348(12)	208(15)	0.095
O(18)	−1286(15)	1722(24)	6913(30)	0.219
N(1)	−1935(9)	5054(14)	2004(17)	0.067
N(2)	−2057(9)	−16(16)	3901(18)	0.072
N(3)	−4532(22)	886(34)	9944(44)	0.198
N(4)	−142(20)	2028(33)	6391(37)	0.172

(continued)

TABLE 3. *(continued)*

Atom	x	y	z	U^a (Å^2)
C(1)	−849(8)	157(11)	2651(15)	0.223
C(2)	−967(8)	−577(11)	2201(15)	0.286
C(3)	−1737(19)	144(28)	9348(32)	0.140
C(4)	−1596(21)	−416(29)	10039(35)	0.167
C(5)	−4150(15)	4859(26)	4413(29)	0.467
C(6)	−4178(15)	4439(26)	5267(29)	0.802
C(7)	−535(14)	4340(22)	8469(24)	0.354
C(8)	−398(14)	3821(22)	7737(24)	0.294

$^a U = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ for the copper atoms.

[10] was used during data collection to minimize the profile width. Data were corrected for Lp but not for absorption. The structure was solved with Patterson methods (SHELXS-86 [6]) and refined on F by full matrix least-squares techniques (SHELX-76 [7]). Hydrogen atoms were introduced at calculated positions and refined with fixed geometry with respect to their carrier atoms. The triflate anion showed significant disorder and was refined with a disorder model using bond restraints. Non-hydrogen atoms were refined with anisotropic thermal parameters and H atoms with two common isotropic thermal parameters. Final positional parameters are listed in Table 4. Scattering factors were taken from ref. 11 and corrected for anomalous effects from ref. 12. A final difference map did not show features other than absorption artefacts near Ni and residual disorder peaks in the triflate region. The relatively high final R value is attributed to the poor crystal quality and anionic disorder problems. Geometry calculations and the preparation of the thermal motion ellipsoid plot were done with the program PLATON [13]. The calculations were carried out on a MicroVax-II.

TABLE 4. Final coordinates and equivalent isotropic thermal parameters and their e.s.d.s in parentheses for $[Ni(HRSL)_2](CF_3SO_3)_2$

Atom	x	y	z	U_{eq} (Å^2)
Ni	1/2	0.2019(3)	3/4	0.038(1)
O(110)	0.4285(4)	0.0782(7)	0.7537(6)	0.044(3)
N(11)	0.3387(6)	0.393(1)	0.7463(9)	0.061(5)
N(13)	0.4280(5)	0.312(1)	0.7353(7)	0.048(4)
N(101)	0.4379(5)	0.110(1)	0.9945(7)	0.045(4)
N(103)	0.4930(5)	0.176(1)	0.8863(7)	0.040(3)
C(12)	0.3766(5)	0.303(1)	0.7646(9)	0.044(4)
C(14)	0.4248(6)	0.421(1)	0.6887(9)	0.046(5)
C(15)	0.3715(7)	0.468(1)	0.697(1)	0.057(6)
C(16)	0.353(1)	0.574(2)	0.658(1)	0.090(9)
C(17)	0.399(1)	0.621(2)	0.610(1)	0.082(8)
C(18)	0.4538(9)	0.575(1)	0.602(1)	0.067(6)
C(19)	0.4707(6)	0.468(1)	0.6404(9)	0.049(5)
C(102)	0.4439(6)	0.133(1)	0.9025(9)	0.041(4)
C(104)	0.5304(7)	0.187(1)	0.9712(8)	0.052(5)
C(105)	0.4936(7)	0.146(1)	1.0360(9)	0.048(5)
C(106)	0.5130(8)	0.147(1)	1.1276(9)	0.060(6)
C(107)	0.5718(8)	0.187(2)	1.149(1)	0.069(6)
C(108)	0.6089(9)	0.229(2)	1.084(1)	0.072(7)
C(109)	0.5880(7)	0.228(1)	0.992(1)	0.056(6)
C(111)	0.3934(6)	0.102(1)	0.8313(9)	0.047(5)
C(112)	0.3499(6)	0.200(1)	0.8131(9)	0.053(5)
Disordered triflate anion (major form)				
S(1)	0.3006(10)	0.0511(14)	0.1194(9)	0.15(2)*
F(31)	0.1950(6)	−0.0251(16)	0.0495(10)	0.16(1)
F(32)	0.2696(8)	−0.045(2)	−0.0344(10)	0.20(1)
F(33)	0.2663(9)	−0.1511(15)	0.0818(15)	0.20(1)
O(131)	0.3601(9)	0.009(3)	0.114(2)	0.09(2)*
O(132)	0.276(2)	0.039(4)	0.2041(15)	0.20(3)*
O(133)	0.282(3)	0.1574(13)	0.083(4)	0.36(7)*
C(31)	0.2541(8)	−0.048(2)	0.0480(15)	0.12(1)

Starred atoms denote disordered atoms with population 0.59(6). $U_{eq} = 1/3[\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \vec{a}_i \cdot \vec{a}_j]$.

Results and Discussion

General Observations

All compounds of this study are listed in Table 1, together with their colours and with some spectroscopic and magnetic data. Elemental analyses were performed for all compounds (C, H, Cu, Ni, Cl, N) and the results agree with the formulae in Table 1. See 'Supplementary Material'.

It is surprising that no pure solid compounds of the HSL ligand could be obtained for the nickel compounds. Apparently the chiral species $Ni(HSL)_2^{2+}$ always requires a $Ni(HRL)_2^{2+}$ to crystallize. No solid compounds at all could be obtained for Co(II) and Mn(II), neither with HRSL nor with HSL. As shown in Table 1 by the specific rotation, the zinc compounds indeed only show the presence of the S isomer (HSL). When starting from HRSL in the case of Zn(II) salts, only products with no specific rotation were obtained.

The IR spectra of all compounds with the same stoichiometry are almost the same, apart from the anion vibrations. The IR spectra for the RS and the S products also hardly differ, indicating that only the coordination modes for the ligands are the same. The small differences observed for the several compounds undoubtedly have to do with small geometric (and as a result also) lattice water differences. Detailed spectral and magnetic data are discussed below, after the description of the crystal structures.

Structure of the Tetramer (I)

The compound consists of the tetrameric distorted cubane-type Cu_4O_4 cores formed by four copper and four triply bridging oxygen atoms of SL ligands with

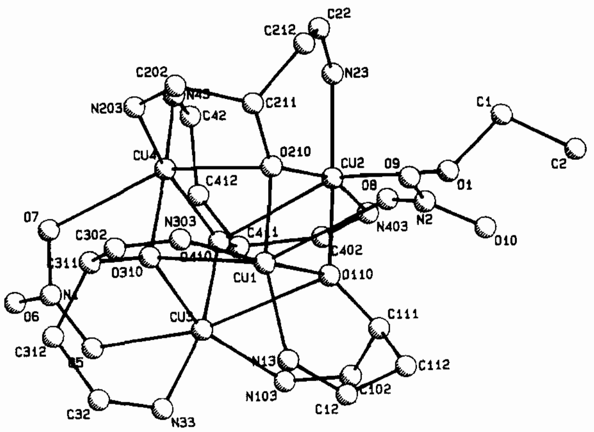

Fig. 2. Structure of the tetrameric unit in I. Most of the non-coordinating ligand atoms have been omitted for clarity.

four short Cu–Cu distances of 3.069–3.131 and two long ones of 3.699 and 3.732 Å. The basic structure has been depicted in Fig. 2. Further, one may consider the Cu_4O_4 core as derived from two Cu_2O_2 dimers, which are linked into the tetrameric unit by four SL ligand oxygen atoms with Cu–O distances of 2.65–2.78 Å. Within the two dimers Cu–O bonds are 1.95–2.01 Å. Relevant bond lengths and angles are given in Table 5. They appear as normal for Cu(II) [14]. A recent structure determination of Piggott *et al.* [15] of a dinuclear Cu(II) compound containing only one benzimidazole group and a bridging alcoholic group, also shows very similar distances around Cu(II) and in the Cu–O–Cu bridge (angles between 101 and 105°).

The coordination of each copper atom is distorted octahedral with two nitrogen and two oxygen atoms

TABLE 5. Interatomic distances (Å) and angles (°) around the copper atoms for I

Cu(1)–O(110)	1.96(1)	Cu(3)–O(310)	1.95(2)
Cu(1)–O(210)	1.95(1)	Cu(3)–O(410)	1.97(2)
Cu(1)–N(13)	1.99(2)	Cu(3)–N(33)	1.98(2)
Cu(1)–N(303)	1.99(2)	Cu(3)–N(103)	1.97(2)
Cu(1)–O(310)	2.65(2)	Cu(3)–O(110)	2.78(1)
Cu(1)–O(8)	2.93(2)	Cu(3)–O(5)	2.56(2)
Cu(2)–O(110)	1.99(1)	Cu(4)–O(310)	2.01(2)
Cu(2)–O(210)	1.97(1)	Cu(4)–O(410)	1.93(2)
Cu(2)–N(23)	1.98(2)	Cu(4)–N(43)	2.03(2)
Cu(2)–N(403)	2.01(2)	Cu(4)–N(203)	1.94(2)
Cu(2)–O(410)	2.74(1)	Cu(4)–O(210)	2.75(1)
Cu(2)–O(1)	2.58(2)	Cu(4)–O(7)	2.76(2)
Cu(1)–Cu(2)	3.108(4)	Cu(3)–Cu(4)	3.069(4)
Cu(1)–Cu(3)	3.098(4)	Cu(3)–Cu(2)	3.732(4)
Cu(1)–Cu(4)	3.699(4)	Cu(4)–Cu(2)	3.131(4)

Cu(1)–O(110)–Cu(2)	104.0(7)	Cu(3)–O(310)–Cu(4)	101.6(7)
Cu(1)–O(210)–Cu(2)	105.0(7)	Cu(3)–O(410)–Cu(4)	103.7(7)
O(110)–Cu(1)–O(210)	75.9(6)	O(310)–Cu(3)–O(410)	77.6(7)
O(110)–Cu(1)–N(13)	92.1(7)	O(310)–Cu(3)–N(33)	92.2(7)
O(110)–Cu(1)–O(310)	91.9(5)	O(310)–Cu(3)–O(110)	88.2(5)
O(110)–Cu(1)–O(8)	87.4(6)	O(310)–Cu(3)–O(5)	90.1(7)
O(210)–Cu(1)–N(303)	94.6(7)	O(410)–Cu(3)–N(103)	93.8(8)
O(210)–Cu(1)–O(310)	77.5(5)	O(410)–Cu(3)–O(110)	76.1(5)
O(210)–Cu(1)–O(8)	76.8(6)	O(410)–Cu(3)–O(5)	85.6(7)
N(13)–Cu(1)–N(303)	99.6(8)	N(33)–Cu(3)–N(103)	98.6(8)
N(13)–Cu(1)–O(310)	114.4(6)	N(33)–Cu(3)–O(110)	112.3(6)
N(13)–Cu(1)–O(8)	91.9(7)	N(33)–Cu(3)–O(5)	86.2(8)
N(303)–Cu(1)–O(310)	72.1(7)	N(103)–Cu(3)–O(110)	70.7(6)
N(303)–Cu(1)–O(8)	104.4(7)	N(103)–Cu(3)–O(5)	108.8(7)
O(8)–Cu(1)–O(310)	153.7(5)	O(5)–Cu(3)–O(110)	161.5(6)
O(210)–Cu(2)–O(110)	74.9(6)	O(410)–Cu(4)–O(310)	77.1(7)
O(210)–Cu(2)–N(23)	93.0(7)	O(410)–Cu(4)–N(43)	94.7(7)
O(210)–Cu(2)–O(410)	88.8(5)	O(410)–Cu(4)–O(210)	89.0(5)
O(210)–Cu(2)–O(1)	91.7(7)	O(410)–Cu(4)–O(7)	83.5(6)
O(110)–Cu(2)–N(403)	94.9(7)	O(310)–Cu(4)–N(203)	92.3(8)
O(110)–Cu(2)–O(410)	76.9(5)	O(310)–Cu(4)–O(210)	74.1(6)
O(110)–Cu(2)–O(1)	80.9(7)	O(310)–Cu(4)–O(7)	79.5(6)
N(23)–Cu(2)–N(403)	98.6(6)	N(43)–Cu(4)–N(203)	99.3(7)

(continued)

TABLE 5. *(continued)*

N(23)–Cu(2)–O(410)	109.8(7)	N(43)–Cu(4)–O(210)	115.8(6)
N(23)–Cu(2)–O(1)	93.3(8)	N(43)–Cu(4)–O(7)	90.2(7)
N(403)–Cu(2)–O(410)	72.2(6)	N(203)–Cu(4)–O(210)	71.3(7)
N(403)–Cu(2)–O(1)	103.5(7)	N(203)–Cu(4)–O(7)	111.5(7)
O(1)–Cu(2)–O(410)	156.9(6)	O(7)–Cu(4)–O(210)	153.5(6)

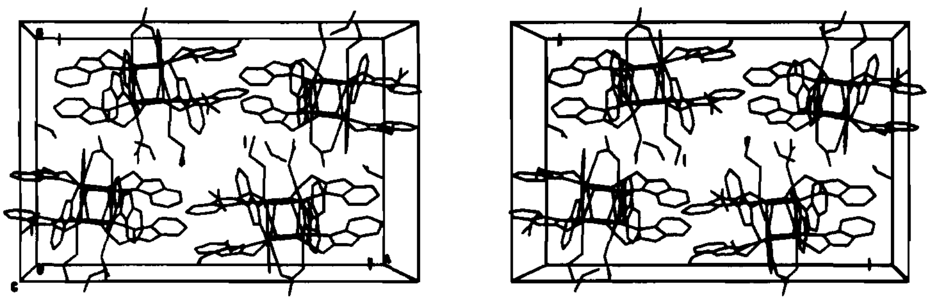

Fig. 3. Stereo packing diagram of the tetrameric compound I.

of the three SL ligands forming the equatorial coordination. One axial site of each copper atom is occupied by a SL oxygen atom. The other axial sites are completed by ethanol (Cu(2)) and nitrate Cu(1), Cu(3) and Cu(4)) oxygen atoms. The nitrate ion coordinated to Cu(3) and Cu(4) acts in addition as a bridging group with Cu(3)–O(5) and Cu(4)–O(7) distances of 2.56 and 2.76 Å, respectively. The average deviation of equatorial O(110), O(210), N(13) and N(303) atoms with regard to the mean plane is 0.20 Å. The corresponding values for Cu(2), Cu(3) and Cu(4) atoms are 0.19, 0.22 and 0.22 Å. The copper atoms lie practically in the mean planes, the deviations being between 0.05(1) and 0.11(1) Å.

Moreover, the complex structure shows a set of hydrogen bonds involving all ethanol molecules, water molecules, nitrate ions and the non-coordinated nitrogen atoms of the SL ligands. Several N...O and O...O distances from 2.63–3.00 Å occur. A packing diagram has been depicted in Fig. 3.

Structure of the Monomer (II)

The monoclinic unit cell contains four cations, two of the $Ni(HSL)_2$ complex, two of the $Ni(HRL)_2$ complex, and eight disordered triflate anions. The cations have two-fold crystallographic symmetry. Cation layers at $z = 0$ and $z = \frac{1}{2}$ alternate with anion layers at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. All O–H and N–H functions bridge through hydrogen bonds to the oxygen atoms of the triflate anions thus linking anions and cations into an infinite two-dimensional network parallel to the *bc* plane. A thermal motion ellipsoid plot of the cation is shown in Fig. 4. Data about the geometry are given in Table 6. No unusual distances are observed.

Spectroscopy and Magnetism

The ligand field spectra of the copper compounds (see Table 1) are not very informative about the precise geometry; however, the combination with the EPR spectra for the compounds with stoichiometry $Cu(ligand)_2(anion)_2$ suggests a square planar based geometry, with at least a CuN_4 chromophore. However, the ligand field peak at about 15 000 cm^{-1} clearly indicates a significant axial ligand interaction [16]; in this case the axial interactions most likely originate from the alcohol oxygens of the ligand, just as found in the Ni(II) triflate. The electron paramagnetic resonance spectra and the susceptibility of the other compounds of Cu(II), indicate a structure that is at least dimeric. Although it is quite likely that the other compounds of stoichiometry Cu(L)(anion) have a tetrameric structure, this cannot be proven from the present data alone. Unfortunately, other crystal structures could not be solved. The magnetic susceptibility of $Cu_2(RSL)Cl(H_2O)Cl_2$, a compound with an unusual stoichiometry, was measured in great detail (2–400 K) and shows a maximum above room temperature (the susceptibility increases up to 400 K, the limiting temperature before the onset of decomposition). The $2J$ value of -340 cm^{-1} strongly suggests a bridging ligand and, probably, also a bridging Cl^- ligand.

The ligand field spectra of the Ni(II) compounds nicely agree with an octahedrally based geometry with a chromophore NiN_4O_2 [16], just as found in the X-ray structure. A very interesting observation is the fact that the compounds with the anions Cl, Br and NO_3 have slightly different ligand field maxima than those with the ClO_4, BF_4 and CF_3SO_3 anions (see Table 1). The origin for this difference is likely

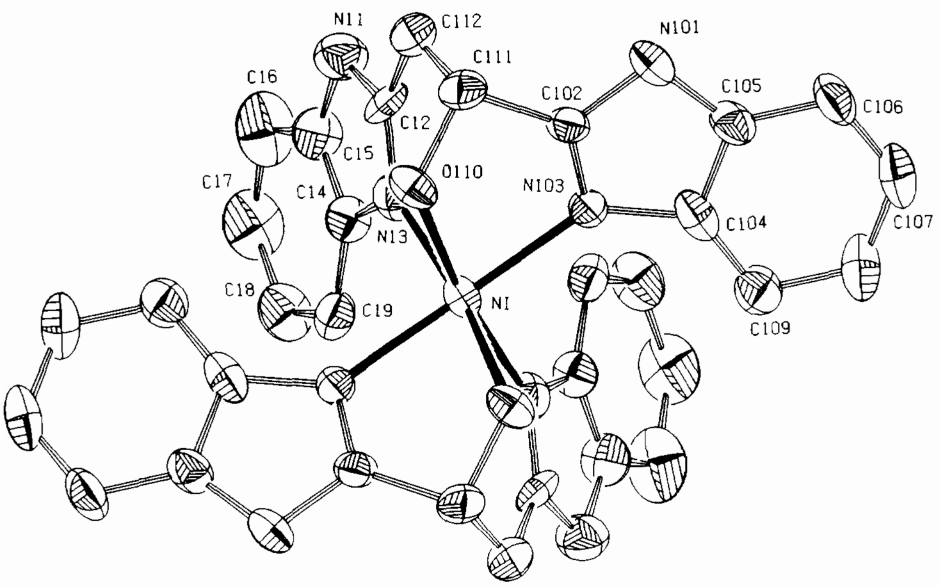

Fig. 4. Structure of the molecular unit in **II**; thermal ellipsoids drawn at the 30% probability level; only the *R* isomer has been drawn for clarity.

TABLE 6. Bond distances (Å) and angles (°) for $[\mathrm{Ni(HRSL)_2}](\mathrm{CF_3SO_3})_2$

Ni–O(110)	2.149(9)	C(14)–C(19)	1.40(2)
Ni–N(13)	2.04(1)	C(15)–C(16)	1.43(2)
Ni–N(103)	2.06(1)	C(16)–C(17)	1.38(3)
O(110)–C(111)	1.46(2)	C(17)–C(18)	1.34(3)
N(11)–C(12)	1.36(2)	C(18)–C(19)	1.41(2)
N(11)–C(15)	1.38(2)	C(102)–C(111)	1.51(2)
N(13)–C(12)	1.25(2)	C(104)–C(105)	1.39(2)
N(13)–C(14)	1.46(2)	C(104)–C(109)	1.36(2)
N(101)–C(102)	1.41(2)	C(105)–C(106)	1.39(2)
N(101)–C(105)	1.39(2)	C(106)–C(107)	1.39(2)
N(103)–C(102)	1.23(2)	C(107)–C(108)	1.39(2)
N(103)–C(104)	1.45(2)	C(108)–C(109)	1.39(2)
C(12)–C(112)	1.55(2)	C(111)–C(112)	1.51(2)
C(14)–C(15)	1.31(2)		

O(110)–Ni–O(110′)	94.5(4)	N(101)–C(105)–C(106)	129(1)
O(110)–Ni–N(13)	82.6(4)	C(104)–C(105)–C(106)	121(1)
O(110)–Ni–N(13′)	171.8(4)	C(105)–C(106)–C(107)	116(1)
O(110)–Ni–N(103)	76.1(4)	C(106)–C(107)–C(108)	123(1)
O(110)–Ni–N(103′)	92.1(4)	C(107)–C(108)–C(109)	122(2)
O(110′)–Ni–N(13)	171.8(4)	C(104)–C(109)–C(108)	116(1)
O(110′)–Ni–N(103)	92.1(4)	O(110)–C(111)–C(102)	101(1)
N(13)–Ni–N(13′)	101.3(5)	O(110)–C(111)–C(112)	112(1)
N(13)–Ni–N(103)	94.6(4)	C(102)–C(111)–C(112)	111(1)
N(13)–Ni–N(103′)	96.3(4)	C(12)–C(112)–C(111)	115(1)
N(13′)–Ni–N(103)	96.3(4)	N(11)–C(12)–N(13)	115(1)
N(103)–Ni–N(103′)	162.8(5)	N(11)–C(12)–C(112)	117(1)
Ni–O(110)–C(111)	108.9(7)	N(13)–C(14)–C(15)	109(1)
C(12)–N(11)–C(15)	105(1)	N(13)–C(14)–C(19)	126(1)
Ni–N(13)–C(12)	129(1)	N(13)–C(12)–C(112)	128(1)
Ni–N(13)–C(14)	128.1(8)	C(15)–C(14)–C(19)	125(1)
C(12)–N(13)–C(14)	103(1)	N(11)–C(15)–C(14)	107(1)
C(102)–N(101)–C(105)	103(1)	N(11)–C(15)–C(16)	129(2)
Ni–N(103)–C(102)	112.9(9)	C(14)–C(15)–C(16)	124(2)

(continued)

TABLE 6. *(continued)*

Ni–N(103)–C(104)	138.8(9)	C(15)–C(16)–C(17)	111(2)
C(102)–N(103)–C(104)	108(1)	C(16)–C(17)–C(18)	126(2)
N(101)–C(102)–N(103)	115(1)	C(17)–C(18)–C(19)	122(2)
N(101)–C(102)–C(111)	120(1)	C(14)–C(19)–C(18)	112(1)
N(103)–C(104)–C(105)	104(1)		
N(103)–C(104)–C(109)	133(1)		
N(103)–C(102)–C(111)	125(1)		
C(105)–C(104)–C(109)	123(1)		
N(101)–C(105)–C(104)	110(1)		

$' = 1 - x, y, \frac{3}{2} - z$.

related to the fact that the first three anions are known to act as strong hydrogen bond acceptors, whereas the other three anions are very weak hydrogen bond acceptors. Such a hydrogen bonding is likely to disturb the ligand field around the metal, resulting in a different ligand field splitting parameter. This hydrogen bonding difference is confirmed by the IR spectra, which are the same in the mid-IR region (apart from anion bands) and different in the area above 3000 cm^{-1} where the N–H and O–H stretching vibrations occur. However, it cannot be excluded that other factors, like a different geometry, contribute also to the spectral differences.

Concluding Remarks

The results described in the present paper have shown that the ligand 1,2-bis(benzimidazol-2-yl)-1-hydroxyethane (HRSL), which exists in two chiral isomers (HSL and HRL), can coordinate as a tridentate ligand, yielding both monomeric and oligomeric complexes. The ligand usually dehydronates with bridging between two or more ligand, losing the hydrogen at the alcoholic group and allowing the oxygen atom to bridge between two or three metal ions. In that case strongly exchange coupled dimers (or even tetramers) are formed. In the case of neutral ligands magnetically isolated, monomeric complexes are formed. It appears that complexes are most easily obtained with the HRSL ligand (mixture). With the chiral isomeric HSL only a few complexes could be isolated in the solid state.

Supplementary Material

Tables giving analytical data, positional parameters and isotropic temperature factors of the hydrogen atoms for both structures, anisotropic parameters of the non-hydrogen atoms and calculated and observed structure factors are available from the authors on request.

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