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Ditopic bis(oxazolines): Synthesis and structural studies of zinc(II), copper(II) and nickel(II) complexes

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ABSTRACT

The synthesis, crystal structures, magnetic and spectroscopic properties of zinc(II), nickel(II) and copper(II) dinuclear complexes **2**–**4** of a novel dinucleating polyoxazoline ligand **1** are reported. X-ray analysis revealed that the three complexes are centrosymmetric dinuclear species with an overall S shape, the bisoxazoline moieties pointing toward the aromatic core of the molecule. Magnetic susceptibility measurements suggest that there is a very weak exchange interaction between the copper or nickel ions in complexes **3** and **4**.

1. Introduction

Because of their features, oxazolines are among the most widely used ligands in asymmetric catalysis and coordination chemistry [1]. They are readily accessible, stable and offer a simple and straightforward way to efficiently control the chiral environment around the metal [2]. These advantages constitute the base for the development of efficient enantioselective catalytic systems and now successful ligands incorporating an oxazoline include bisoxazolines, trisoxazolines or oxazoline ligands with an additional donating element [3].

More recently, there have been growing interests to form potentially dinucleating oxazoline-based ligands, the goal being the development of bifunctional or recyclable catalysts [4]. Thus, chiral ditopic azabis(oxazoline) ligands have shown interest in cobalt-catalyzed enantioselective conjugate reduction [5], cyclopropanation [6], or Henry reaction [7]. However, in all these cases, the coordination chemistry of the related ligand has not been investigated and information about it would be instructive.

In recent years, we have been exploring the coupling of an additional 'sidearm' to the bridging carbon atom of bisoxazoline by using simple synthetic strategies. Thus, we found that monolithiated methyl-bis(oxazolinyl)methane was easily functionalized with the appropriate electrophile [8]. We now have investigated the reactivity with biselectrophile giving rise to a new type of ditopic oxazoline-based ligand, called DiBox. In the present paper, we have synthesized zinc, copper and nickel complexes bearing DiBox as ditopic ligand. All these complexes were characterized by standard analytical methods and their molecular structures were determined by X-ray crystallography, revealing an S conformation of the complexes. The magnetic study suggests a very weak antiferromagnetic interaction between the paramagnetic ions (Cu and Ni complexes).

2. Experimental

2.1. General details

All manipulations were carried out under an inert gas atmosphere of dry nitrogen using standard Schlenk techniques, unless notified. Solvents were purified and dried by standard methods. All reagents were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz and were referenced using the residual proton solvent (^{1}H) or carbon solvent (^{13}C) resonance. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. Mass spectra and elemental analysis were recorded by the analytical service of the Chemistry Department. 1,1-Bis[4,4-dimethyl-1,3-oxazolin-2-yl]ethane was synthesized according to literature procedure [9]. Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. The susceptibility measurements were performed in the 300 to 1.8 K temperature range with an applied field of 5 kOe. Magnetization

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measurements at different fields at a given temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants.

2.2. Synthesis of the ligand **1**

To a solution of bis[4,4-dimethyl-1,3-oxazolin-2-yl]ethane (1.06 g, 4.8 mmol) in THF (30 mL) was added dropwise ^{n}BuLi (3.0 mL, 4.8 mmol, 1.6 M in hexanes) at −78 °C and the mixture was stirred for 15 min. 1,4-Bis(bromomethyl)benzene (596 mg, 2.26 mmol, 0.47 equiv.) was then added and the resulting solution was stirred for additional 12 h at room temperature. Dichloromethane was added and the organic phase was washed with aqueous ammonium chloride and then dried with Na_2SO_4 and concentrated in vacuo. Flash column chromatography (methanol/ethyl acetate) afforded 0.66 g of DiBox (53%) as off-white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.03 (s, 4H), 3.92 (s, 8H, O–C*H*$_2$–), 3.21 (s, 4H), 1.37 (s, 6H), 1.25 (s, 12H, C(C*H*$_3$)(CH_3)), 1.19 (s, 12H, C(CH_3)(C*H*$_3$)). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.3 (O–*C*=N), 134.9, 130.1, 79.3 (O–CH_2–), 67.1 (*C*(CH_3)$_2$), 42.8 (*C*H$_2$), 41.6(*C*H$_2$), 28.2 (C(*C*H$_3$)(CH_3)), 28.0 (C(CH_3)(*C*H$_3$)), 21.2 (*C*H$_3$). *Anal.* Calc. for $C_{32}H_{46}N_4O_4$ (550.73): C, 69.79; H, 8.42; N, 10.17. Found: C, 69.68; H, 8.46; N, 10.08%. MS (ES): *m*/*z* (%) 551.361 [M$^+$+1] (1 0 0). FT-IR (cm^{-1}): 1666 (C=N).

2.3. Synthesis of [(DiBox)($ZnCl_2$)$_2$] **2**

$ZnCl_2$ (49 mg, 0.36 mmol) and DiBox (100 mg, 0.18 mmol) were dissolved in dry methanol (25 mL) under nitrogen and the solution was stirred at room temperature for one night. After filtration and evaporation to dryness, the resulting white solid was washed with pentane (2 × 15 mL). Recrystallization from acetone/methanol afforded complex **2** as colorless crystals (118 mg, 80% yield).

^{1}H NMR (DMSO, 300 MHz) δ: 7.12 (s, 4H), 4.29 (d, *J* = 7.5 Hz, 4HO–CH*H*–), 4.19 (d, *J* = 7.5 Hz, 4HO–C*H*H–), 3.30 (s, 4H, C*H*$_2$), 1.60 (s, 6H, C*H*$_3$), 1.39 (s, 12H, C(C*H*$_3$)(CH_3)), 1.28 (s, 12H, C(CH_3)(C*H*$_3$)). The ^{13}C NMR was not recorded due to its low solubility. MS (ESI): *m*/*z* (%) 845.1 [M+Na]$^+$ (4), 787.1 [M−Cl]$^+$ (10), 687.2 [M−$ZnCl_2$+1]$^+$ (18), 551.4 [M−2($ZnCl_2$)+1]$^+$ (1 0 0). *Anal.* Calc. $C_{32}H_{46}Cl_4N_4O_4Zn_2$ (823.36): C, 46.68; H, 5.63; N, 6.80. Found: C, 46.59; H, 5.72; N, 6.72%. FT-IR (cm^{-1}): 1659 (C=N).

2.4. Synthesis of [(DiBox)($NiBr_2$)$_2$] **3**

$NiBr_2(PPh_3)_2$ (134 mg, 0.18 mmol) and ligand **1** (50 mg, 0.09 mmol) were dissolved in dry dichloromethane (10 mL) under nitrogen and the solution was stirred at room temperature for one night. After filtration and evaporation to dryness, the resulting purple solid was washed several times with diethyl ether. Recrystallization from diethyl ether/methanol afforded complex **3** in quantitative yield.

MS (ESI): *m*/*z* (%) 851.4 [M−(2Br+Na)]$^+$ (5), 551.3 [M−2($NiBr_2$)+1]$^+$ (1 0 0). *Anal.* Calc. $C_{32}H_{46}Br_4N_4Ni_2O_4$ (987.73): C, 38.91; H, 4.69; N, 5.67. Found: C, 38.86; H, 4.75; N, 5.59%. FT-IR (cm^{-1}): 1663 (C=N).

2.5. Synthesis of (DiBox)[Cu(OAc)$_2$]$_2$ **4**

Cu(OAc)$_2$ (67 mg, 0.37 mmol) and ligand **1** (100 mg, 0.18 mmol) were dissolved in methanol (15 mL) under nitrogen and the solution was stirred at room temperature for 1 h. After filtration and evaporation to dryness, the resulting blue solid was washed three times with pentane. Recrystallization from diethyl ether/dichloromethane afforded complex **4** in quantitative yield.

MS (ESI): *m*/*z* (%) 869.4 [M−(OAc)+Na+1]$^+$ (1 0), 853.4 [M−2(OAc)+Na+1]$^+$ (1 5), 551.4 [M−2Cu(OAc)$_2$+1] (1 0 0). *Anal.* Calc. $C_{40}H_{58}Cu_2N_4O_{12}$ (914.00): C, 52.56; H, 6.40; N, 6.13. Found: C, 51.47; H, 6.28; N, 5.96%. FT-IR (cm^{-1}): 1659 (C=N), 1590 (acetate).

2.6. X-ray crystal structures for compounds **2**·2(CH_3OH), **3** and **4**·2(H_2O)

Suitable crystals of **2**·2(CH_3OH) were obtained as colorless prisms from $(CH_3)_2CO$/MeOH. Suitable crystals of **4**·2(H_2O) were obtained as turquoise-blue blocks from CH_2Cl_2/Et_2O. Suitable crystals of **3** were obtained as purple prisms from MeOH/Et_2O. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fiber and placed in a low-temperature N_2 stream.

Compound **2**·2(CH_3OH) and **4**·2(H_2O): X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 36 mm. The cell parameters were determined (Denzo software) from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure [10].

Compound **3**: X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software) [11] from reflections taken from three sets of 12 frames, each at 10 s exposure.

The structures were solved by Direct methods using the program SHELXS-97 [12]. The refinement and all further calculations were carried out using SHELXL-97 [13]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters, except for the water molecule (**4**) and for the OH group of the methanol molecule (**2**) where the H-atoms were located from Fourier difference maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. For complexes **2**·2(CH_3OH) and **4**·2(H_2O), a semi-empirical absorption correction was applied using the MULscanABS routine in PLATON [14]; transmission factors: T_{min}/T_{max} = 0.581/0.899 and 0.574/0.737, respectively. For complex **3**, a semi-empirical absorption correction was applied using SADABS in APEX2 [10]; transmission factors: T_{min}/T_{max} = 0.270/0.471.

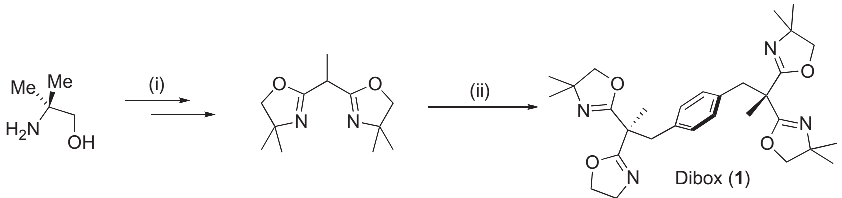
3. Results and discussion

3.1. Ligand synthesis

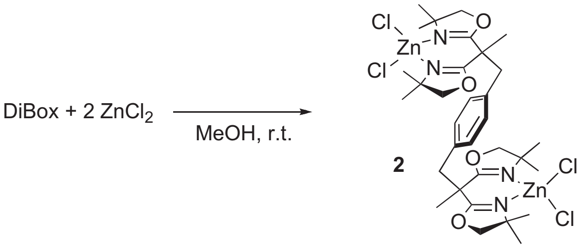
The ditopic bis(oxazoline) DiBox was obtained in one step starting from methyl-bis(oxazolinyl)methane derivative [9]. Deprotonation with ^{n}BuLi followed by reaction with 1,4-bis(bromomethyl)benzene gave the desired ligand in 53% yield (Scheme 1). Spectroscopic data are consistent with the proposed structure for **1**. The product was also characterized by X-ray diffraction. However, the preliminary X-ray data obtained were of insufficient quality for a refinement of the structure; only the basic connectivities were verified (see supporting information for details).

3.2. Synthesis and characterization of dinuclear complexes **2**–**4**

The reaction of $ZnCl_2$ with half- equivalent of DiBox ligand in methanol results in the formation of air-stable, dinuclear complex **2** (Scheme 2). The formation of the complex was confirmed by NMR spectroscopy, IR spectroscopy and mass spectrometry. In particular, the IR spectrum indicates that the oxazolines are coordi-



Scheme 1. Synthesis of the ditopic ligand DiBox **1**. Reaction conditions: (i) Ref. [8]; (ii) ^{n}BuLi, THF, −78 °C then bis(bromomethyl)benzene (0.5 equiv.), r.t. overnight (53% yield).



Scheme 2. Synthesis of the dinuclear zinc complex **2**.

nated to the Zn center (slight coordination shift of $\nu_{(CN)}$ band of 7 cm^{-1}). The complexation is also highlighted by the ^{1}H NMR spectra, which displays an AB quartet, assigned to the protons of the methylene of the oxazoline ring (J = 7.5 Hz).

An X-ray diffraction study of complex **2** established its structural details. Fig. 1 displays its molecular structure along with the principal bond lengths and angles. The crystallographic data are shown in Table 1. It crystallizes in the triclinic space group $P\bar{1}$. The zinc atoms adopt a tetrahedral coordination with Zn–N bond length average of 2.032(3) Å and Zn–Cl bond length average of 2.238(11) Å. They both are within the range found for related bisox complexes reported in the literature [15]. The six-membered ring moieties form a nearly planar metallacycle and the Zn atom deviates from the N(1)–C(3)–C(11)–C(8)–N(2) plane by 0.233(2) Å. Interestingly, the molecule is a centrosymmetric dinuclear species and the overall shape resembles the letter S with the bisoxazoline moieties pointing toward the aromatic core and the apical methyl groups pointing to the outside of the molecule. As a result, the Zn(1)–Zn(1)′ distance was found to be only 8.9627 (6) Å, which is relatively short if you consider the possibility to have a more extended linear arrangement of the ligand.

The reaction of the Dibox ligand **1** with 2 equivalents $(Ph_3P)_2NiBr_2$ in dichloromethane led to the purple, stable and isolable dinuclear nickel complex **3** in quantitative yield (Scheme 3). IR and mass spectrometry confirmed the formation of the expected dinuclear complex. Recrystallization from MeOH/diethyl ether led

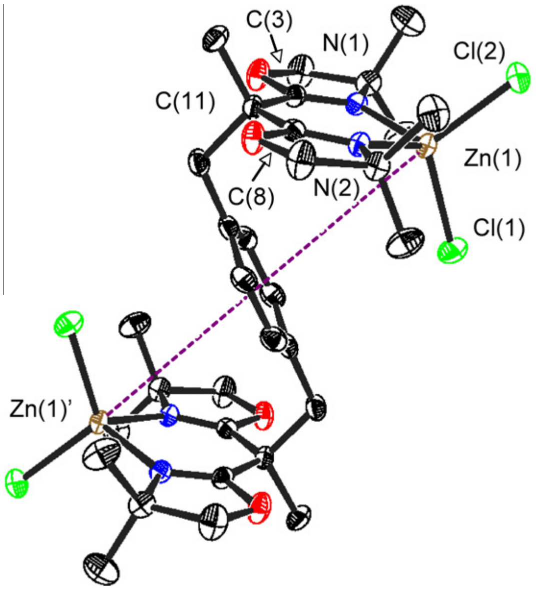
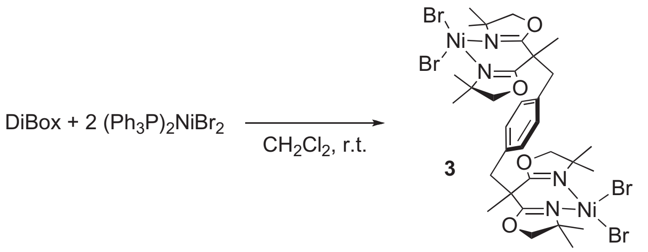


Fig. 1. Molecular structure of dinuclear zinc complex **2** (ellipsoids are drawn at 50% probability level). Selected bond lengths (Å) and angles (°): Zn(1)–Cl(1), 2.2457(6); Zn(1)–Cl(2), 2.2295(6); Zn(1)–N(1), 2.0296(16); Zn(1)–N(2), 2.0336(17); Cl(1)–Zn(1)–Cl(2), 113.50(2); N(1)–Zn(1)–N(2), 90.72(7); Zn(1)–N(1)–C(3)–C(11), 5.4(3); N(1)–C(3)–C(11)–C(8), 3.0(3); Zn(1)–Zn(1)′, 8.9627(6). Symmetry transformation used to generate equivalent atoms: ′−x + 1, −y + 1, −z + 1. H atoms have been omitted for clarity.

Table 1
X-ray experimental data of compounds **2**, **3** and **4**.

	$\mathbf{2}\cdot 2(CH_3OH)$	**3**	$\mathbf{4}\cdot 2(H_2O)$
Formula	$C_{34}H_{54}Cl_4N_4O_6Zn_2$	$C_{32}H_{46}Br_4N_4Ni_2O_4$	$C_{40}H_{62}Cu_2N_4O_{14}$
Molecular weight (g mol^{-1})	887.35	987.79	950.02
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.7656(4)	8.2890(2)	9.3476(2)
b (Å)	9.3900(3)	17.2633(4)	9.8673(3)
c (Å)	12.9860(7)	14.6589(4)	13.6214(5)
α (°)	102.371(3)	90.00	69.069(2)
β (°)	105.910(2)	105.6990(10)	71.417(2)
γ (°)	93.728(2)	90.00	73.661(2)
V (Å^3)	995.30(8)	2019.37(9)	1092.21(6)
Z	1	2	1
ρ_{calc}(g cm^{-3})	1.480	1.625	1.444
F(0 0 0)	462	988	500
Crystal size(mm)	0.38 × 0.18 × 0.15	0.36 × 0.20 × 0.18	0.40 × 0.30 × 0.12
μ (mm^{-1})	1.520	4.927	1.043
Temperature (K)	173(2)	173(2)	173(2)
θ minimum–maximum	1.68–27.47	1.86–30.03	1.65–27.47
Dataset [h,k,l]	−11/10,−12/ 12,−14/16	−11/11,−24/ 23,−20/20	−12/12,−12/ 12,−17/15
Wavelength (Å)	0.71073	0.71073	0.71073
Radiation		Mo Kα graphite monochromated	
Number of data measurements	4547	5888	4985
Number of data with $I > 2\sigma(I)$	4068	4651	4484
Number of variables	236	213	286
R_1	0.0305	0.0346	0.0372
wR_2	0.0852	0.0793	0.1036
Goodness-of-fit (GOF)	1.198	1.041	1.146
Largest peak in final difference (eÅ^3)	0.482	1.763	0.543
Color	colorless	purple	blue



Scheme 3. Synthesis of the dinuclear nickel complex **3**.

to single crystals for X-ray diffraction studies (Fig. 2). The complex **3** crystallizes in the monoclinic space group $P2_1/c$ and the arrangement of the dinuclear species is identical to complex **2**. The nickel atoms adopt a tetrahedral coordination with Ni–N bond length average of 1.975(6) Å and Ni–Br bond length average of 2.37(2) Å [16]. The six-membered ring moieties is boat shaped and the nickel atom deviates from the N(1)–C(3)–C(8)–N(2) plane by 0.460(4) Å. As a result, the metal-metal distance is significantly longer than the previous zinc complex (11.3411(7) Å versus 8.9627(6) Å).

Finally, we investigated the coordination chemistry of the ligand with copper(II) acetate. Thus, reacting half equivalent of Dibox with $Cu(OAc)_2$ in methanol lead to complex **4** as a turquoise-blue powder in nearly quantitative yield (Scheme 4). Recrystallization from methanol/diethyl ether gave single crystals of sufficient quality for X-ray diffraction study (Fig. 3). The complex **4** crystallizes in the triclinic space group $P\bar{1}$ and the overall shape of the complex is matching with previous complexes **2** and **3**. The geometry around copper atoms is distorted octahedral with two acetate oxygen atoms and the nitrogen atoms in equatorial positions and two oxygen atoms in axial positions (Cu–N bond distance average 2.01(2) Å and equatorial Cu–O bond distance average 1.979(2) Å, and axial Cu–O bond distance average 2.55(3) Å). The O_{eq}–Cu–O_{eq} and the O_{ax}–Cu–O_{ax} angles are 87.76(7)° and 141.44(6)°, respectively, the N–Cu–N angle being 90.92(7)° [17]. The six-membered ring metallacycle is relatively flat akin to complex **2** and the intramolecular metal–metal distance is 9.4315(5) Å.

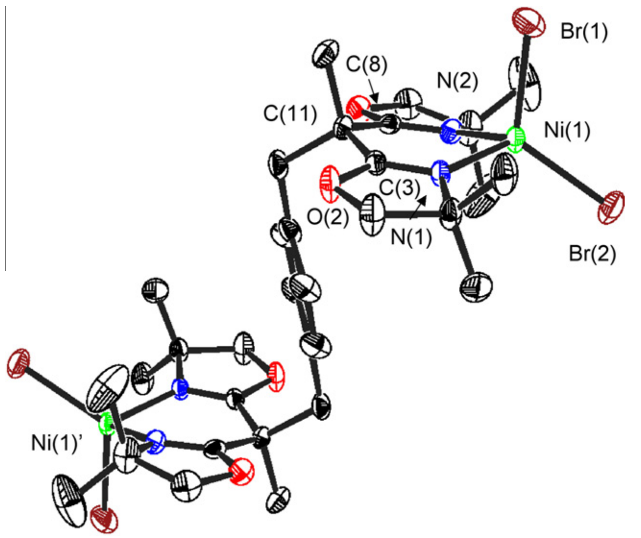
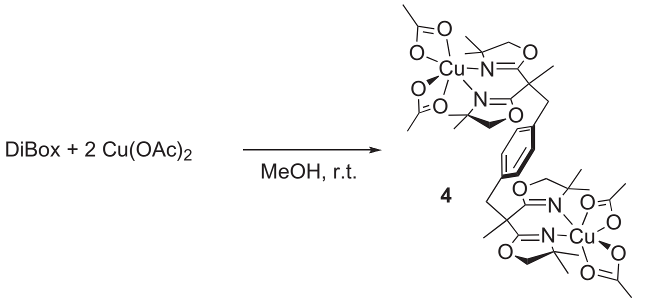


Fig. 2. Molecular structure of dinuclear nickel complex **3** (ellipsoids are drawn at 50% probability level). Selected bond lengths (Å) and angles (°): Ni(1)–Br(1), 2.3830(5); Ni(1)–Br(2), 2.3505(4); Ni(1)–N(1), 1.9704(19); Ni(1)–N(2), 1.979(2); Br(1)–Ni(1)–Br(2), 120.413(18); N(1)–Ni(1)–N(2), 90.05(8); Ni(1)–N(2)–C(8)–C(11), −9.0(4); N(2)–C(8)–C(11)–C(3), −16.4(4); Ni(1)–N(1)–C(3)–O(2), −172.36(18); Ni(1)–Ni(1)′, 11.3411(7). Symmetry transformation used to generate equivalent atoms: ′ −x + 2, −y + 1, −z + 1. H atoms have been omitted for clarity.



Scheme 4. Synthesis of the dinuclear copper complex **4**.

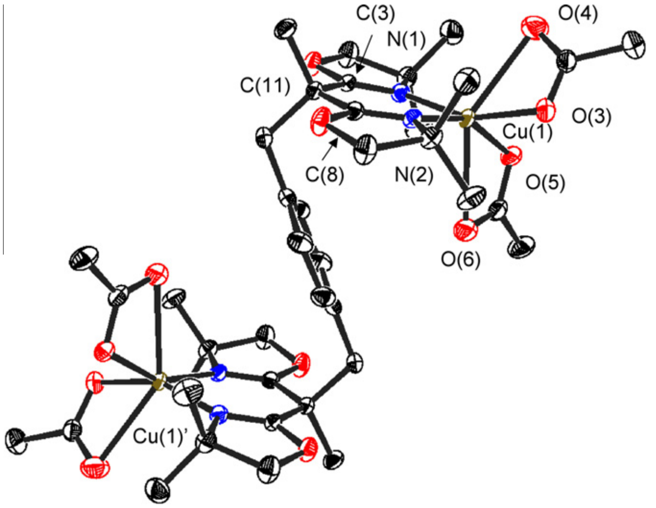


Fig. 3. Molecular structure of dinuclear copper complex **4** (ellipsoids are drawn at 50% probability level). Selected bond lengths (Å) and angles (°): Cu(1)–N(1), 1.9978(17); Cu(1)–N(2), 2.0196(17); Cu(1)–O(3), 1.9777(16); Cu(1)–O(4), 2.5304(18); Cu(1)–O(5), 1.9800(16); Cu(1)–O(6), 2.5707(18); O(4)–Cu(1)–O(6), 141.44(6); O(3)–Cu(1)–O(5), 87.76(7); N(1)–Cu(1)–N(2), 90.92(7); Cu(1)–N(1)–C(3)–C(11), 10.9(3); N(1)–C(3)–C(11)–C(8), −4.7(3); Cu(1)–Cu(1)′, 9.4315(5). Symmetry transformation used to generate equivalent atoms: ′ −x, −y, −z + 1. H atoms have been omitted for clarity.

3.3. Magnetic properties

Given the unusual S shape of the complexes, it was interesting to study the magnetic interaction between the spin-carriers, possibly relayed by the aromatic cycle in-between. The Curie constants, $C = 2.74\ \mathrm{emu\ K\ mol^{-1}}$ for **3** and $C = 0.83\ \mathrm{emu\ K\ mol^{-1}}$ for **4**, determined from the fit of the data using the Curie–Weiss law, are in good accordance with the expected values for two Ni(II) ions ($2.42\ \mathrm{emu\ K\ mol^{-1}}$ assuming $g = 2.2$) and for two Cu(II) ions ($0.83\ \mathrm{emu\ K\ mol^{-1}}$ assuming $g = 2.1$), respectively (Fig. 4) [18].

For both compounds the χT product remains almost constant, down to about 80 K and 20 K for **3** and **4**, respectively. Then it decreases slightly upon decreasing the temperature down to $1.67\ \mathrm{emu\ K\ mol^{-1}}$ and $0.75\ \mathrm{emu\ K\ mol^{-1}}$ at 1.8 K for **3** and **4**, respectively, indicating the occurrence of very weak antiferromagnetic interactions.

Neglecting all possible intermolecular interactions, the $\chi T = f(T)$ curves can be fit using the following spin Hamiltonian where all parameters have their usual meaning and the spin operator **S** is defined as $\mathbf{S} = \mathbf{S}_{M1} + \mathbf{S}_{M2}$ (where M = Ni or Cu) [19]:

$$\mathcal{H} = -J\mathbf{S}_{M1}\mathbf{S}_{M2} + g\beta H\mathbf{S}$$

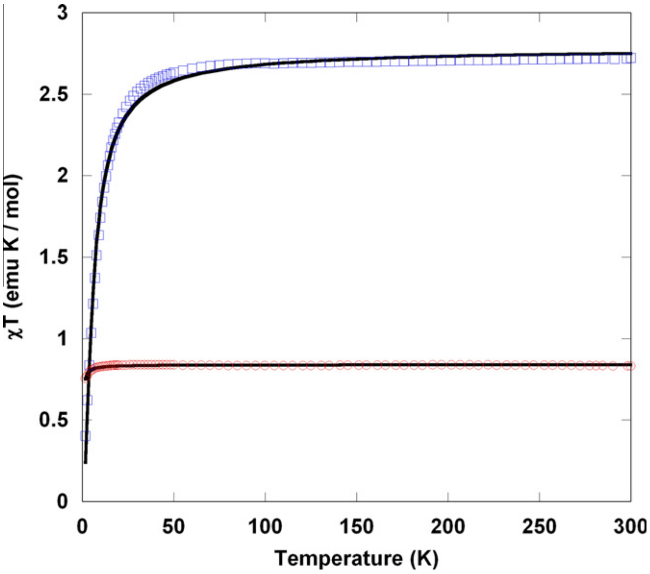


Fig. 4. $\chi T = f(T)$ for **3** (open squares) and **4** (open circles), full black lines: best fit considering intra and inter-dimer interactions for **3** and only intra-dimer interaction for **4** (see text).

The fit leads the following values for **3** and **4**, respectively: $J = -3.5(1)\ \mathrm{cm}^{-1}$, $g = 2.36(2)$ and $J = -0.48(2)\ \mathrm{cm}^{-1}$, $g = 2.11(2)$ with good agreement factors $R = 2.7 \times 10^{-4}$ and $R = 1.7 \times 10^{-5}$, respectively.[1]

Yet considering the structure (and above all the M–M distances), it does not seem reasonable to neglect interdimer interaction (for **3** the intradimer Ni–Ni distance is 11.34 Å whereas the smallest interdimer Ni–Ni distance is 7.82 Å, for **4** the intradimer Cu–Cu distance is 9.43 Å and the smallest interdimer Cu–Cu distance is 7.64 Å). Therefore, one has to consider intermolecular interactions in the fitting procedure.

For **3**, the fit performed using a mean-field approach leads $J = -3.3(3)\ \mathrm{cm}^{-1}$, $g = 2.36(2)$ and $zJ = -0.2(1)\ \mathrm{cm}^{-1}$ with a good agreement factor $R = 2.9 \times 10^{-4}$. Nevertheless, the hypothesis underlying the use of the mean-field approach ($zJ \ll J$) is actually hardly fulfilled. Therefore the present fit can just give very approximate values of the interactions. For **4**, considering the weakness of the (supposed) intramolecular interaction, the mean field approach is clearly not applicable.

The complete and careful fit of the magnetic properties would require a full analysis of the 3D arrangement of the dimers within the crystal, which is clearly beyond the scope of this study. DFT calculations would also enable to understand more clearly the exchange pathways within the dimers, for instance determining the spin density distribution in the ground state, in order to precise the possible role of the aromatic cycle in-between the two paramagnetic metals [20].

4. Conclusion

In conclusion, we have shown that methyl-bis(oxazolinyl)methane was easily converted into ditopic oxazoline-based ligand. The coordination chemistry of the new ligand with zinc, nickel and copper was investigated and the structures were determined by X-ray crystallography revealing an S conformation of the complexes. Finally, the magnetic studies suggest a very weak antiferromagnetic interaction between the ions (Cu and Ni). Further work will focus on the development of chiral ditopic oxazoline-based ligands and their use in asymmetric catalysis.

Acknowledgments

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[1] R is defined as $R = \frac{\sum \chi_{\mathrm{exp}} - \chi_{\mathrm{calc}}}{\sum \chi^2_{\mathrm{exp}}}$.