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Copper(II) compounds of some rigid dinucleating *bis*-amine–*bis*-imidazole ligands

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Abstract

The Mannich condensation of formaldehyde with some amines and imidazoles rendered three *bis*-(amine–imidazole) ligands in a simple one pot reaction. Although these ligands are formally dinucleating, the copper(II) ions are held far apart, as shown by the Xray structures of five copper(II) compounds obtained with these ligands. Consequentially, these copper(II) compounds behave magnetically mononuclear.

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1. Introduction

Imidazoles are encountered in natural systems as part of histidine residues in active sites containing various transition metal ions. To model such active sites of metalloproteins, a range of artificial ligands containing imidazole groups derivatised in the 4(5) position are needed. Quite elaborate procedures exist [1,2] to synthesize such ligands, but the availability of a relatively simple synthetical procedure would really fulfill this need. This requirement is met by the Mannich condensation [3], an easy reaction utilising basic reagents like formaldehyde, amines and imidazoles [4–6] as well as pyrazoles [7]. In this paper three new rigid dinucleating *bis*-(amine–imidazole) ligands, synthesized via a Mannich condensation (see Fig. 1), and the single crystal Xray structures of five copper(II) compounds are reported.

Previous reports [8,9] dealt with two analogous ligands, derivatives of imidazole with aminopropane and glycine, respectively.

2. Experimental

All starting materials were commercially available and used as purchased. ^{1}H NMR spectra were obtained on a Jeol JNM-FX (200 MHz) FT NMR spectrometer (δ 0–21 ppm).

X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer with a Golden Gate Single Reflection Diamond ATR (4000–300 cm^{-1}). Ligand-field spectra in the Near Infrared and Visible region were obtained by solid state reflectance on a Perkin–Elmer Lambda 900 spectrophotometer using MgO as a reference.

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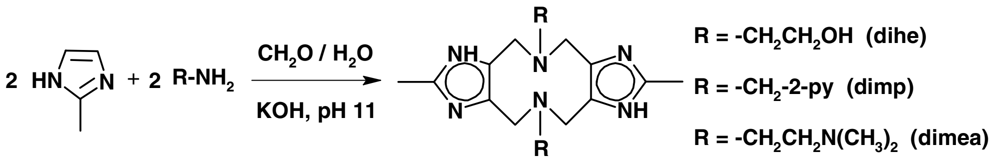

Fig. 1. Mannich synthesis of the ligands.

2.1. Synthesis of the ligands

In all cases 2-methylimidazole was reacted with a primary amine and formaldehyde at pH 11 to a cyclic compound, as depicted in Fig. 1. The overall concentration of 2-methylimidazole must be lower than 1 mol/L otherwise a 1:1 condensation product is also formed in rather large quantities instead of mostly the 2:2 condensation product.

2.1.1. *2,8-Dimethyl-5,11-di-(hydroxyethyl)-1,4,5,6,7,10,11,12-octahydroimidazo[4,5h]-imidazo[4,5c][1,6] diazecine, dihe*

About 3.05 g (50 mmol) ethanolamine and 8.12 g (100 mmol) formaldehyde (37% in water) were slowly added simultaneously but separately to 4.11 g (50 mmol) 2-methylimidazole in 70 ml water. The pH was adjusted to 11 with KOH, after which the solution was refluxed for 24 h during which a suspension formed. This suspension was filtered and washed with water.

^{1}H NMR (D_2O/HCl): δ 2.43 (s) im-CH_3, 3.47 (t) N-CH_2, 3.83 (t) CH_2-OH, 4.39 (s) im-CH_2N.

The other ligands were synthesised in an analogous way.

2.1.2. *2,8-Dimethyl-5,11-di-(2-methylpyridine)-1,4,5,6,7,10,11,12-octahydroimidazo[4,5-h]imidazo[4,5-c][1,6]-diazecine, dimp*

^{1}H NMR (D_2O/HCl): δ 1.42 (s) im-CH_3, 2.61 (s) im-CH_2-N, 3.35 (s) N-CH_2-py, 6.78 (m) py(5), 6.91 (d) py(3), 7.34 (m) py(4), 7.59 (t) py(6). *Anal.* Calc. for dimp · $2H_2O$: C, 62.05; H, 6.94; N, 24.12. Found: C, 62.07; H, 6.99; N, 24.13%.

2.1.3. *2,8-Dimethyl-5,11-di-(dimethylethyleneamine)-1,4,5,6,7,10,11,12- octahydroimidazo[4,5-h]imidazo [4,5-c][1,6]diazecine, dimea*

^{1}H NMR (MeOD): δ 2.33 (s) im-CH_3, 2.33 (s) N-$(CH_3)_2$, 2.60 (t) Me_2-N-CH_2, 2.98, (t) NCH_2, 3.32 (s) im-CH_2-N. *Anal.* Calc. for dimea · $2H_2O$: C, 56.58; H, 9.50; N, 26.39. Found: C, 56.92; H, 9.82; N, 26.00%.

2.2. Synthesis of the coordination compounds

The coordination compounds have been prepared by adding water/methanol solutions of the appropriate copper(II) salts to ligand solutions, while maintaining a ligand to metal ion ratio of 1:2.

Analytical data for the obtained coordination compounds:

$[Cu_2(dihe)Cl_4](H_2O)_2$ (**1**) for $C_{16}H_{30}N_6Cu_2O_4Cl_4$: Calc.: C, 30.06; H, 4.73; N, 13.14; Cu, 19.88; Cl, 22.18. Found: C, 30.19; H, 4.50; N, 13.13; Cu, 19.50; Cl, 21.58%.

$[Cu_2(dimp)Cl_4](H_2O)_2$ (**2**) for $C_{24}H_{32}N_8Cu_2O_2Cl_4$: Calc.: C, 39.30; H, 4.40; N, 15.28; Cu, 17.33; Cl, 19.33. Found: C, 39.21; H, 4.58; N, 15.29; Cu 16.99; Cl, 19.24%.

$[Cu_2(dimea)(NO_3)_2(MeOH)_2](NO_3)_2$ (**3**) for $C_{22}H_{44}N_{12}Cu_2O_{14}$: Calc.: C, 31.92; H, 5.36; N, 20.31. Found: C, 31.94; H, 5.33; N, 20.15%.

$[Cu_2(dimea)Cl_2(H_2O)_2]Cl_2(H_2O)_2$ (**4**) for $C_{20}H_{44}N_8Cu_2O_4Cl_4$: Calc.: C, 32.93; H, 6.08; N, 15.36; Cu, 17.42; Cl, 19.44. Found: C, 33.00; H, 6.02; N, 15.33; Cu, 16.99; Cl, 19.62%.

$[Cu_2(dimea)Br_2(H_2O)_2]Br_2(H_2O)_2$ (**5**) for $C_{20}H_{44}N_8Cu_2O_4Br_4$: Calc.: C, 26.48; H, 4.89; N, 12.35; Cu, 14.01; Br, 35.23. Found: C, 26.59; H, 4.99; N, 12.32; Cu, 13.71; Br, 35.32%.

2.3. Crystal structure determinations

Single crystals were mounted on a glass fiber using the oil drop method [10] and measured with a Rigaku AFC-7S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and $\omega/2\theta$ scans. Data reduction was performed using the TEXSAN [11] package. The intensity data were corrected for Lorentz and polarisation effects and for absorption. All non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The structure was solved using direct methods SHELXS-97 [12]. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0740P)^2 + 0.6717P]$ where $P = (F_o^2 + 2F_c^2)/3$ was adopted. The refinement method was full-matrix least squares on F^2 using the SHELXL-97 [13] package.

Crystal and refinement data of $[Cu_2(dihe)Cl_4](H_2O)_2$ (**1**), $[Cu_2$ $(dimp)Cl_4](H_2O)_2$ (**2**), $[Cu_2(dimea)(NO_3)_2(MeOH)_2](NO_3)_2$ (**3**), $[Cu_2(dimea)Cl_2(H_2O)_2]Cl_2(H_2O)_2$ (**4**), and $[Cu_2(dimea)Br_2(H_2O)_2]Br_2(H_2O)_2$ (**5**) are collected in Table 1.

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