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Synthesis and Crystal Structure of Linear Chain Homotetranuclear Complexes with N_3^-

Raif Kurtaran,^{1,*} Kaan Cebesoy Emregül,²
Cengiz Arıcı,³ Filiz Ercan,³ Vincent J. Catalano,⁴
and Orhan Atakol²

¹Department of Chemistry, Faculty of Arts and Sciences,
Balıkesir University, Balıkesir, Turkey

²Department of Chemistry, Faculty of Sciences, University of
Ankara, Tandoğan, Ankara, Turkey

³Department of Engineering Physics, Hacettepe University,
Beytepe, Ankara, Turkey

⁴Department of Chemistry, University of Nevada, Reno,
Nevada, USA

ABSTRACT

Mononuclear copper(II) complexes, Cu(L) [N,N'-bis(salicylidene)-1,3-propanediaminato]copper(II), and Cu(LDM) [N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato]copper(II), were prepared from the ONNO type ligands N,N'-bis(salicylidene)-1,3-diaminopropane

*Correspondence: Raif Kurtaran, Department of Chemistry, Faculty of Arts and Sciences, Balıkesir University, 10100 Balıkesir, Turkey; E-mail: atakol@science.ankara.edu.tr.

(H₂L) and N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-diaminopropane (H₂LDM). These mononuclear complexes were transformed into tetranuclear complexes, [(S)Cu(L)Cu(N₃)₂]₂ and [(S)Cu(LDM)Cu(N₃)₂]₂ (S are solvent molecules, DMSO, DMF, THF, dioxan), with N₃⁻ and Cu(II) ions. All complexes were characterized by elemental analyses and IR spectroscopy. A molecular model of the complex [(DMSO)Cu(L)Cu(N₃)₂] was obtained by single crystal x-ray diffraction methods.

INTRODUCTION

It has been established for a long time that pseudohalide ions, N₃⁻, OCN⁻ and SCN⁻, bind metal centers in both terminal and bridging modes. As a bridging ligand these ions tend to form mainly two types of bridging: μ -1,1 (end-on) and μ -1,3 (end-end). This has been a subject of extensive research in recent years.^[1-10]

The complexes prepared in this study have been designed from the binuclear symmetrical structured [(2,2'-bipyridyl)- μ -(isocyanato)-isocyanatocopper(II)] complex found in the literature.^[11] Each Cu atom in this complex is coordinated by two nitrogens of the bipyridyl group, a cyanate ion and two end-on μ -bridged cyanate groups, leading to the formation of a distorted square-pyramidal coordination. The copper(II) ions are bonded to one another through a cyanate ion. In addition, it has been known since 1975 that ONNO type Schiff base and Cu(II) ions tend to form binuclear and halogen carrying complexes.^[12] Considering these circumstances the idea of combining binuclear Cu(II) complexes with an azide ion via μ -bridges was conceived, leading to the synthesis of linear chain tetranuclear complexes combined through μ -bridges. The general formula of the ligands H₂L and H₂LDM are given in Figure 1.

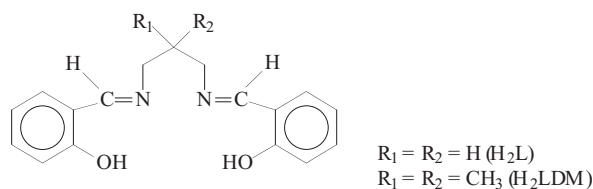


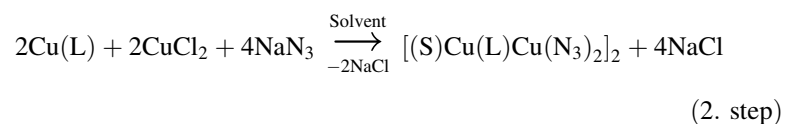
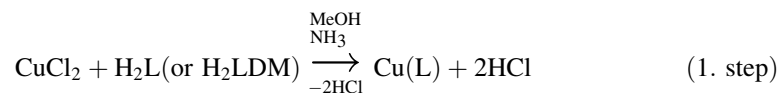
Figure 1. General formula of the ligands H₂L and H₂LDM.



RESULTS AND DISCUSSION

Analytical and Geometrical Results

The general reaction mechanism for the complexes prepared is given in the following equations.



Elemental analysis results (Table 1) cannot confirm that the complexes are tetranuclear as they are of centro symmetry. Only two prominent IR peaks at 2048 and 2063 cm^{-1} , specific for $\nu(\text{N}=\text{N})$ stretching bands of the azide group, were observed indicating the presence of two different azide groups. From the limiting resonance forms for the azide group (Figure 2), the double bond structure is considered to be the most suitable form for the formation of μ -bridges. The azide group is known to form μ -bridges in 1:1 or end-on and 1:3 end-end structures.^[4,5] The bridging modes of an azide ion are shown in Figure 3. The double bond form is more suitable for both μ -bridge structures, whereas the triple bond form are more suitable for a monodentate ligand (Figure 2). The end-on azides are located upwards and downwards from the bridge plane, respectively. The terminal azides are in a *trans* position, each being perpendicular to the end-on azide corresponding to the other symmetric unit. The bond distances obtained from x-ray diffraction studies justify this conclusion.

Some bond lengths of compound (2) are given in Table 4. The N^7-N^8 and N^6-N^7 bond distances for the azide group attached to the second Cu^2 atom are 1.24(2) and 0.756(16) Å, respectively. This indicates that one of the bonds is a single bond and the other a triple bond. On the other hand, the distance between the N atoms of the μ -bridged azide molecules are shorter than the N^7-N^8 single bond. In studies with similar complexes without μ -bridges, the stretching band for the azide group was found at 2040 and 2100 cm^{-1} .^[4]

As mentioned before, although the elemental analysis results indicate the presence of two Cu ions, it does not constitute proof of a tetranuclear

Table 1. Elemental analysis results.

| Compound | Empirical formula | Formula weight | M.p. (°C) | Yield | Elemental analyses, % | | | |
|--|---|----------------|-----------|---------------|-----------------------|-------------|-------------|---------------|
| | | | | | calc. (found) | | found | |
| | | | | | C | H | N | Cu |
| Cu(L) | C ₁₇ N ₂ H ₁₆ O ₂ Cu | 343.55 | >360 | 1.40 g (82%) | 54.61 (54.39) | 4.69 (4.76) | 8.14 (8.22) | 18.48 (18.69) |
| Cu(LDM) | C ₁₉ N ₂ H ₂₀ O ₂ Cu | 371.55 | 314 | 1.41 g (76%) | 61.36 (60.97) | 5.42 (5.20) | 7.53 (7.63) | 17.08 (17.79) |
| [(DMF)Cu(L)Cu(N ₃) ₂] ₂ | C ₄₀ N ₁₈ H ₄₆ O ₆ Cu ₄ | 1129.06 | 225 | 0.295 g (52%) | 42.55 (42.19) | 4.10 (3.97) | | 22.51 (22.69) |
| [(DMSO)Cu(L)Cu(N ₃) ₂] ₂ | C ₃₈ N ₁₆ H ₄₄ O ₈ S ₂ Cu ₄ | 1138.72 | 228 | 0.296 g (52%) | 40.07 (40.46) | 3.89 (3.91) | | 22.32 (21.77) |
| [(Dioxane)Cu(LDM)Cu(N ₃) ₂] ₂ | C ₄₆ N ₁₆ H ₅₆ O ₈ Cu ₄ | 1214.66 | 227 | 0.445 g (73%) | 45.46 (45.59) | 4.65 (4.49) | | 20.92 (21.17) |
| [(THF)Cu(LDM)Cu(N ₃) ₂] ₂ | C ₄₆ N ₁₆ H ₅₆ O ₈ Cu ₄ | 1214.20 | 230 | 0.196 g (76%) | 46.69 (47.01) | 4.77 (4.83) | | 21.48 (21.94) |
| [(DMF)Cu(LDM)Cu(N ₃) ₂] ₂ | C ₄₄ N ₁₈ H ₅₄ O ₆ Cu ₄ | 1184.20 | 239 | 0.450 g (33%) | 44.59 (44.47) | 4.59 (4.31) | | 21.44 (21.57) |

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Figure 2. The resonance boundary formula for the azide group.

complex structure. The essential proof of the tetranuclear complex structure is derived from x-ray studies. X-ray diffraction explains that two units of the complexes, [(S)Cu(L)Cu(N₃)₂] or [(S)Cu(LDM)Cu(N₃)₂], are bonded to each other to form a Cu-N₃-Cu-N₃ ring. The general formula of the complex structures synthesized is given in Figure 4.

Figure 5 shows the second and third copper(II) ions to be bonded with two μ -azido bridges in a 1:1 form, with the coordinate bond length for the Cu²⁺-N³ and Cu²⁺-N³ⁱ bond distance of 2.002 (8) and 2.012 (7) Å, respectively.

The copper(II) ion coordination can easily be understood from the x-ray studies. As shown in Figure 5, all the copper ions are seen to possess a square pyramidal coordination sphere. The terminal and other copper ions are seen to be in the center of the N₂O₃ and N₃O₂ coordination sphere, respectively, leading to a distorted square-pyramidal structure.

In the literature a τ geometric factor has been used to describe penta-coordinated structures since 1984. The τ value is calculated from the angles in the vicinity of the central atom,^[13]

$$\tau = \frac{\alpha - \beta}{60}$$

α and β are the two largest angle values in the vicinity of the central atom within a coordination sphere. If τ equals zero the coordination is said to be an ideal square-pyramid, whereas if τ equals one it is said to be an ideal triangular bipyramid.^[13]

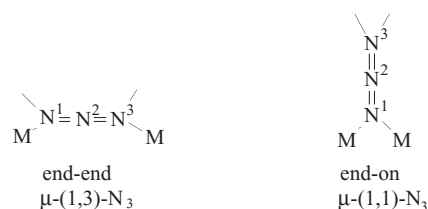


Figure 3. Bridging modes of azide ion.

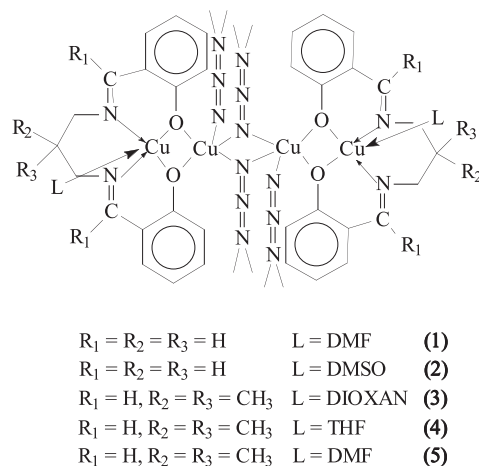


Figure 4. Molecular model of the complex structures synthesized.

In this study the τ values for the four copper ions in the complexes were calculated using the data of Table 4; for the copper atoms Cu(1) and Cu(4) the τ value equals 0.020, whereas for the copper atoms Cu(2) and Cu(3) the τ value equals 0.108. As those values are seen to be closer to zero the coordination can be described as square-pyramidal which is the most common structure for copper(II) coordination.^[14] The four copper(II) ions are located on a linear chain. These types of tetranuclear copper(II) complex coordination compounds are rarely seen in the literature.^[15]

X-Ray Crystallography

The final atomic parameters are presented in Table 2 and the crystal and experimental data are given in Table 3. Some of the important co-

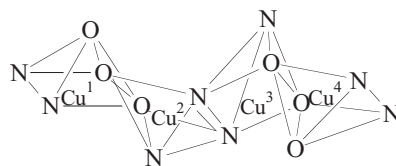


Figure 5. Schematic representation of the tetranuclear copper(II) complex coordination compounds.



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Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the [(DMSO)Cu(L)Cu(N₃)₂]₂ complex. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| Atom | X | y | z | U(eq) |
|--------|----------|----------|----------|---------|
| Cu(1) | 3482(1) | 3378(1) | 5701(1) | 48(1) |
| Cu(2) | 556(1) | 3954(1) | 5125(1) | 48(1) |
| O(1) | 1673(5) | 3412(4) | 6061(3) | 50(2) |
| O(2) | 2582(5) | 3884(5) | 4719(3) | 55(2) |
| N(1) | 4148(7) | 3063(6) | 6839(5) | 62(2) |
| N(2) | 5199(7) | 3596(5) | 5228(5) | 53(2) |
| N(3) | 656(7) | 5266(5) | 5626(4) | 57(2) |
| N(4) | 1229(7) | 5539(5) | 6252(5) | 50(2) |
| N(5) | 1756(9) | 5791(7) | 6842(6) | 87(3) |
| N(6) | -190(20) | 2737(11) | 4652(11) | 103(6) |
| N(7) | -449(14) | 2282(10) | 4838(11) | 76(4) |
| N(8) | -910(20) | 1531(16) | 5119(15) | 250(11) |
| C(1) | 1239(8) | 3339(6) | 6841(5) | 46(2) |
| C(2) | -72(9) | 3453(7) | 6959(6) | 64(3) |
| C(3) | -533(10) | 3405(7) | 7747(6) | 65(3) |
| C(4) | 247(11) | 3258(7) | 8436(6) | 67(3) |
| C(5) | 1571(11) | 3145(7) | 8329(6) | 65(3) |
| C(6) | 2065(9) | 3187(6) | 7524(5) | 49(2) |
| C(7) | 3464(10) | 3036(7) | 7488(6) | 61(3) |
| C(8) | 5640(19) | 3049(15) | 7135(12) | 52(5) |
| C(9) | 6322(9) | 2620(9) | 6307(7) | 86(4) |
| C(10) | 6440(9) | 3425(8) | 5720(7) | 75(3) |
| C(11) | 5344(9) | 3859(7) | 4476(6) | 58(3) |
| C(12) | 4334(9) | 4048(6) | 3833(5) | 53(2) |
| C(13) | 4748(11) | 4223(8) | 3024(6) | 75(3) |
| C(14) | 3894(11) | 4388(8) | 2388(6) | 79(3) |
| C(15) | 2571(10) | 4377(7) | 2517(6) | 67(3) |
| C(16) | 2169(9) | 4208(7) | 3300(5) | 56(3) |
| C(17) | 3024(8) | 4035(6) | 3967(5) | 46(2) |
| S(1) | 2505(11) | 1115(7) | 5161(6) | 120(4) |
| C(19) | 2010(40) | 810(20) | 4440(20) | 83(14) |
| C(18) | 1926(13) | 757(10) | 6118(8) | 112(5) |
| O(3) | 3615(8) | 1776(5) | 5305(5) | 89(2) |
| S(1A) | 3298(10) | 768(6) | 5546(7) | 95(5) |
| C(8A) | 5460(20) | 2594(16) | 6990(13) | 59(6) |
| C(19A) | 3150(20) | -18(17) | 4886(14) | 116(10) |

**Table 3.** Crystal and experimental data.

| |
|---|
| Formula: $C_{38}H_{20}Cu_4N_{16}O_6S_2$ |
| Formula weight = 1114.98 |
| Crystal system: Monoclinic |
| Space group: $P_{21/n}$ $Z=2$ |
| $a = 10.305(2) \text{ \AA}$ $b = 13.969(3) \text{ \AA}$ $c = 16.029(3) \text{ \AA}$ |
| $\beta = 92.76(2)^\circ$ |
| $V = 2304.7(8) \text{ \AA}^3$ |
| $D_x = 1.607 \text{ g/cm}^3$ |
| $\mu = 1.974 \text{ mm}^{-1}$ |
| $T = 293 \text{ K}$ |
| Color: Dark green |
| $F(0\ 0\ 0) = 1112$ |
| Crystal size: $0.12 \times 0.42 \times 0.18 \text{ mm}$ |
| Radiation = Mo K_α |
| $R = 0.062$ $R_w = 0.151$ |
| No. of reflections used = 3010 |
| No. of parameters = 307 |
| Goodness-of-fit = 1.043 |
| $(\Delta\rho)_{\max} = 0.53 \text{ e\AA}^{-3}$ |
| $(\Delta\rho)_{\min} = -0.45 \text{ e\AA}^{-3}$ |
| Instrumentation: Siemens P4 diffractometer |
| Program system: Siemens SHELXTL PLUS Version 5.03 |
| Structure determination and refinement: SHELXS and SHELXL-97 |
| Treatment of hydrogen atoms: Geometric calculations |

ordinative bonds and angles are given in Table 4. An ORTEP drawing of the molecule with 50% probability displacement thermal ellipsoids and the atomic numbering scheme is shown in Figure 6.

Infrared Spectra

Some of the most important IR bands for the five compounds are given in Table 5. The major interest of the IR spectra of these compounds are the bands corresponding to $\nu_{\text{asym}}(\text{N}_3)$ stretching vibrations. The $\nu_{\text{asym}}(\text{N}_3)$ mode appears as very strongly split bands at 2069 and 2042 cm^{-1} which is consistent with the structure containing two different azide groups, end-on bridging and terminal azide ligands. These data are consistent with literature values.^[17,18] A similar situation was found in the related copper-azido complex, $[\text{Cu}(4\text{-ethylpyridine})(\text{N}_3)_2]$. Its IR spectrum exhibits the azide asymmetric stretch as two very strong peaks at 2073 and 2033 cm^{-1} .^[19]

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Table 4. Selected bond lengths (Å) and bond angles (°) of [(DMSO)Cu(L)Cu(N₃)₂]₂.

| | | | | | |
|------------------------------|----------|-------------------------|-----------|-------------------------------|-----------|
| Cu(1)–O(2) | 1.922(5) | Cu(2)–O(1) | 1.996(5) | N(3)–N(4) | 1.201(9) |
| Cu(1)–N(1) | 1.968(7) | Cu(2)–N(6) | 2.000(15) | N(3)–Cu(2) ⁱ | 2.012(7) |
| Cu(1)–O(1) | 1.978(5) | Cu(2)–N(3) | 2.002(8) | N(4)–N(5) | 1.125(10) |
| Cu(1)–N(2) | 1.982(7) | Cu(2)–N(3) ⁱ | 2.012(7) | N(6)–N(7) | 0.756(16) |
| Cu(1)–O(3) | 2.332(7) | Cu(2)–O(2) | 2.219(5) | N(7)–N(8) | 1.24(2) |
| O(2)–Cu(1)–N(1) | 167.0(3) | | | N(6)–Cu(2)–O(2) | 101.6(6) |
| O(2)–Cu(1)–O(1) | 78.8(2) | | | N(3)–Cu(2)–O(2) | 97.3(3) |
| N(1)–Cu(1)–O(1) | 91.5(3) | | | N(3) ⁱ –Cu(2)–O(2) | 114.5(3) |
| O(2)–Cu(1)–N(2) | 92.0(3) | | | C(1)–O(1)–Cu(1) | 128.8(5) |
| N(1)–Cu(1)–N(2) | 96.4(3) | | | C(1)–O(1)–Cu(2) | 121.3(5) |
| O(1)–Cu(1)–N(2) | 168.2(3) | | | Cu(1)–O(1)–Cu(2) | 107.9(2) |
| O(2)–Cu(1)–O(3) | 99.4(3) | | | C(17)–O(2)–Cu(1) | 129.0(5) |
| N(1)–Cu(1)–O(3) | 90.9(3) | | | C(17)–O(2)–Cu(2) | 128.9(5) |
| O(1)–Cu(1)–O(3) | 99.9(3) | | | Cu(1)–O(2)–Cu(2) | 101.5(2) |
| N(2)–Cu(1)–O(3) | 88.7(3) | | | C(7)–N(1)–C(8A) | 112.3(10) |
| O(1)–Cu(2)–N(6) | 99.2(5) | | | C(8A)–N(1)–Cu(1) | 121.0(9) |
| O(1)–Cu(2)–N(3) | 91.6(3) | | | N(4)–N(3)–Cu(2) | 129.8(6) |
| N(6)–Cu(2)–N(3) | 160.4(6) | | | N(4)–N(3)–Cu(2) ⁱ | 126.4(6) |
| O(1)–Cu(2)–N(3) ⁱ | 166.9(3) | | | Cu(2)–N(3)–Cu(2) ⁱ | 103.7(3) |
| N(6)–Cu(2)–N(3) | 91.0(5) | | | N(5)–N(4)–N(3) | 179.3(10) |
| | | | | N(6)–N(7)–N(8) | 178(3) |

Symmetry code: (i) – x, – y + 1, – z + 1.

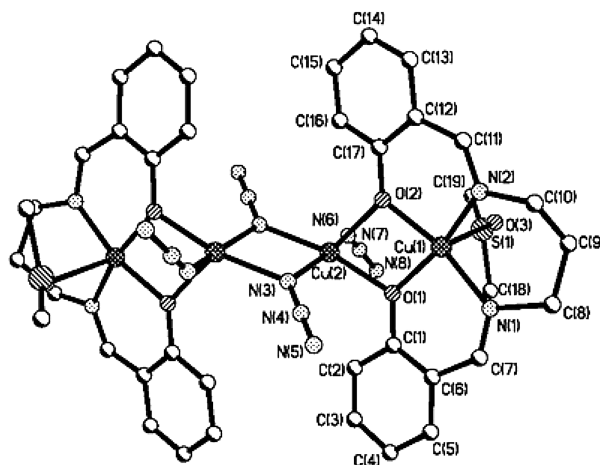


Figure 6. A perspective view of the complex $[(\text{DMSO})\text{Cu}(\text{L})\text{Cu}(\text{N}_3)_2]_2$.

EXPERIMENTAL

Chemicals and Apparatus

All reagents and solvents used in the preparations were purchased from Merck, Aldrich or Carlo Erba and used without further purification. The elemental analyses for the ligands and complexes were carried out with an Eurovector 3018 CHNS analyser. To ensure correctness, N analyses for the complexes were repeated using the Kjeldahl method. Melting points were measured using a Gallenkamp melting point apparatus. IR spectra were recorded on a Mattson FTIR 1000 spectrophotometer in KBr disks in the range $4000\text{--}250\text{ cm}^{-1}$. XRD studies were performed on a Siemens P4 diffractometer. A suitable crystal for the x-ray data collection was selected directly from the reaction media, because recrystallization of the complex was impossible due to decomposition of the complex. The dark brown crystal of compound (2) was mounted on a glass fiber with silicone cement at room temperature and no hydrocarbon oil was used. The intensity data were collected at room temperature using a Siemens P4 diffractometer with MoK_α radiation using a $w/2\theta$ scan mode. The cell parameters were determined from the least-squares of 25 centered reflections. Three standard reflections for every 120 minutes were periodically measured during data collection and showed no significant intensity variations. Cell refinement and data reduction were carried out using the SHELXL97^[16] program.

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Table 5. IR spectroscopic data^a obtained in KBr discs.

| Comp. no. | $\nu(\text{C}-\text{H}_{\text{ar}})$ | $\nu(\text{C}-\text{H}_{\text{aliph}})$ | $\nu_{\text{asym}}(\text{N}_3)$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{S}=\text{O})$ |
|-----------|--------------------------------------|---|---------------------------------|--------------------------|--------------------------|--------------------------|
| (1) | 3026 w-3044 w | 2964 w-2917 w 2860 w | 2048 s-2065 s | 1654 s | 1624 s | |
| (2) | 3028 w-3046 w | 2859 w-2912 w 2970 w | 2042 s-2069 s | | 1624 s | 1025 s |
| (3) | 3028 w-3042 w | 2870 m-2963 m | 2036 s-2074 s | | 1624 s | |
| (4) | 3026 m-3040 m | 2866 s-2922 s 2966 s | 2038 s-2076 s | | 1625 s | |
| (5) | 3019 m-3038 m | 2883 m-2930 m 2967 m | 2033 s-2078 s | 1652 s | 1629 s | |

^as: sharp, m: medium, w: weak.



The structure was solved by direct methods using the solution program SHELXS97.^[16] All non-hydrogen atoms were refined isotropically and then anisotropically by the full matrix least squares method. All the hydrogen atoms bonded to carbon atoms were placed geometrically. All hydrogen atoms were refined as riding with $U_{eq}(H) = 1.2 U_{iso}(C)$.

Preparation of Ligands

The ligands *N,N'*-bis(salicylidene)-1,3-diaminopropane (LH₂) and *N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-diaminopropane (LDMH₂) were prepared by the condensation reaction of diamine and salicylaldehyde in ethanol.^[20]

Preparation of Complexes

All the present complexes were prepared in two stages; the first stage is the preparation of the mononuclear copper complexes. In the second stage these mononuclear complexes are transformed into tetranuclear complexes with the aid of the azide ion.

First Stage. Preparation of the Mononuclear Cu(II) Complexes {Cu(L) and Cu(LDM)}

Cu(L) was prepared according to the literature procedure.^[20] *N,N'*-Bis(salicylidene)-1,3-diaminopropane (1.410 g, 0.005 mol) was dissolved in hot EtOH (50 mL). To this solution was added 10 mL of ammonia (20%) and CuCl₂·2H₂O (0.850 g, 0.005 mol) dissolved in 30 mL of hot water. The resulting solution was left to stand at atmospheric conditions for 3 hours. The green needle-like precipitate was filtered and dried at 80 °C.

The Cu(LDM) complex was prepared following the procedure described elsewhere^[21] from *N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-diaminopropane (1.550 g, 0.005 mol) and CuCl₂·2H₂O (0.850 g, 0.0005 mol).

Second Stage. Preparation of Tetranuclear Complexes

CAUTION: Azido complexes of metal ions in the presence of ligands are potentially explosive. Although we have encountered no such problems with azido complexes, only a small amount of material should be prepared and handled with care.

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Preparation of [(DMF)Cu(L)Cu(N₃)₂]₂ (1)

Bis{[N,N'-dimethylformamide- μ -N,N'-bis(salicylidene)-1,3-propanediaminocopper(II)](azido)-(μ -azido-1:1)copper(II)}. Alternative name: Bis{N,N'-dimethylformamide-1 κ N;4 κ N- μ -2,2'-(1,3-propandiyl-bis(nitrilomethylidyne)diphenolato,1 κ^4 N,N',O,O':2 κ^2 O,O',4 κ^4 N,N',O,O':3 κ^2 O,-O'-azido-2 κ N:3 κ N}tetracopper(II). The CuL complex (0.344 g, 0.001 mol) was dissolved in hot DMF (40 mL). To this solution were added solutions of CuCl₂·2H₂O (0.170 g, 0.001 mol) in 20 mL hot methanol and NaN₃ (0.130 g, 0.002 mol) in 10 mL hot water. The mixture was stirred and left to stand at atmospheric condition for 3 or 4 days. The resulting dark brown crystalline precipitate was filtered and dried in the open air.

Preparation of [(DMSO)Cu(L)Cu(N₃)₂]₂ (2)

Bis{[dimethylsulfoxide- μ -N,N'-bis(salicylidene)-1,3-propanediaminocopper(II)](azido)-(μ -azido-1:1)copper(II)}. Alternative name: Bis{N,N'-dimethylsulfoxide-1 κ O;4 κ O- μ -2,2'-(1,3-propandiyl-bis(nitrilomethylidene)diphenolato,1 κ^4 N,N',O,O':2 κ^2 O,O',4 κ^4 N,N',O,O':3 κ^2 O,O'-azido-2 κ N:3 κ N- μ -azido-2 κ N:3 κ N;3 κ N:2 κ N}tetracopper(II). The CuL complex (0.344 g, 0.001 mol) was dissolved in hot DMSO (40 mL). To this solution were added solutions of CuCl₂·2H₂O (0.170 g, 0.001 mol) in 20 mL hot methanol and NaN₃ (0.130 g, 0.002 mol) in 10 mL hot water. The mixture was stirred and left to stand in atmospheric conditions for 3 or 4 days. The resulting dark brown crystalline precipitate was filtered and dried in the open air.

Preparation of [(Dioxane)Cu(LDM)Cu(N₃)₂]₂ (3)

Bis{[(dioxane)- μ -N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminocopper(II)](azido)-(μ -azido-1:1)copper(II)}. Alternative name: Bis{dioxane-1 κ O;4 κ O- μ -[2,2'-(1,3-propandiyl-bis(nitrilomethylidene)diphenolato]-1 κ^4 N,N',O,O':2 κ^2 O,O',4 κ^4 N,N',O,O':3 κ^2 O,O'-azido-2 κ N:3 κ N- μ -azido-2 κ N:3 κ N}tetracopper(II). To a solution of Cu(LDM) (0.372 g, 0.001 mol) in 50 mL of hot dioxane was added a solution of CuCl₂·2H₂O (0.170 g, 0.001 mol) in 20 mL MeOH followed by the addition of NaN₃ (0.130 g, 0.002 mol) in 5 mL hot water. The mixture was stirred and left to stand under atmospheric conditions for 2 or 3 days. The resulting precipitate was filtered and dried in the open air.

Preparation of [(THF)Cu(LDM)Cu(N₃)₂]₂ (**4**)

Bis{[(tetrahydrofuran)-μ-N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato-copper(II)](azido)-(μ-azido-1:1)copper(II)}. Alternative name: Bis{tetrahydrofuran-1κO;4κO-μ-[2,2'-(1,3-propanediylbis(nitrilomethylidene)diphenolato]1κ⁴N,N',O,O':2κ²O,O',4κ⁴N,N',O,O':3κ²O,-O'-azido-2κN:3κN-μ-azido-2κN:3κN}tetracopper(II). To a solution of Cu(LDM) (0.372 g, 0.001 mol) in 50 mL of hot THF was added a solution of CuCl₂·2H₂O (0.170 g, 0.001 mol) in 20 mL MeOH followed by the addition of NaN₃ (0.130 g, 0.002 mol) in 5 mL hot water. The mixture was left to stand under atmospheric conditions for 2 or 3 days. The resulting precipitate was filtered and dried in open air.

Preparation of [(DMF)CuLDMCu(N₃)₂]₂ (**5**)

Bis{[(N,N'-dimethylformamide)-μ-N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propane-diaminato-copper(II)](azido)-(μ-azido-1:1)copper(II)}. Alternative name: Bis{N,N'-dimethylformamide-1κO;4κO-μ-[2,2'-(1,3-propanediyl-bis(nitrilomethylidene)diphenolato]-1κ⁴N,N',O,O':2κ²O,O',-4κ⁴N,N',O,O':3κ²O,O'-azido-2κN:3κN-μ-azido-2κN:3κN}tetracopper(II). To a solution of Cu(LDM) (0.372 g, 0.001 mol) in 50 mL of hot DMF was added a solution of CuCl₂·2H₂O (0.170 g, 0.001 mol) in 20 mL MeOH followed by the addition of NaN₃ (0.130 g, 0.002 mol) in 5 mL hot water. The mixture was left to stand under atmospheric conditions for 3 or 4 days. The resulting precipitate was filtered and dried in open air.

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Referee I: A. H. Cowley
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