A New Trinuclear Linear Copper(II) Complex: Unusual Crystal Structure with Semi-Coordinated Thiophene Moieties and Weak Antiferromagnetic Coupling Through the Bridging Imidazolate Rings

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A trinuclear copper(II) complex, $[Cu_3(imthio)_2(NO_3)_4(MeOH)_2]$ [where Himthio is 1,1-bis(imidazol-2-yl)-3-(thiophen-2-yl)-2-azapropane], has been synthesized by the reaction of Himthio with $Cu(NO_3)_2\cdot 3H_2O$ in MeOH. The structure of the copper complex is centrosymmetric and contains a linear trinuclear array of copper atoms. The central copper(II) ion, Cu1, which lies on an inversion centre, is equatorially coordinated by four nitrogen atoms from two anionic imthio ligands and axially by two semicoordinated thiophene sulfur atoms to give an octahedral environment (Cu1–S1 3.136 Å). The Himthio ligand bridges Cu1 and the terminal copper(II) ions through imidazole nitrogen atoms. The coordination around the external ions is completed by the oxygen atoms from two nitrate groups and by a methanol molecule in a distorted square-pyramidal geometry. The two terminal copper(II) complexes can be considered to be chelating ligands for the central Cu^{II} ion. The EPR spectrum of the complex in MeOH at 77 K shows two mononuclear species, as is fully confirmed by EPR simulation. Magnetic susceptibility of the complex shows weak antiferromagnetic behaviour (J = –71.37 cm^{-1}) caused by the overlapping of the magnetic orbitals of the copper atoms and the bridging imidazolate rings. (© Wiley-VCH Verlag GmbH & Co.. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Copper complexes are widely known in nature and play an essential part as biological redox catalysts in most life forms. Current interest in copper complexes focuses on the design and synthesis of mimics of active sites for their potential use in catalysis and molecular-based magnets.[1] Models of the active sites of multicopper proteins such as ascorbate oxidase,[2] cerpulasmin[3] and laccase[4] have been studied extensively, and many efforts have been made to synthesize and investigate multinuclear copper complexes with various bridges between the metal centres.[5] The commonly used ligands are based on pyrazole, benzimidazole, and pyridine moieties.[6] Due to the presence of histidine as a ligand to copper ions in most copper proteins, copper complexes with the biologically more relevant imidazolyl donors are increasingly being studied as model compounds of copper proteins' active sites.[7,8]

Sulfur-donor compounds are known to be good ligands for low-oxidation-state copper atoms. It is well known that sulfur coordination to copper plays a very important role in metalloenzyme chemistry,[9] especially in the control of the redox potentials. In copper proteins such as azurin[10] or plastocyanin,[11] thioether sulfur, thiolate and heterocyclic nitrogen atoms are coordinated to the copper atoms at the active site, and the redox reaction occurs by outer-sphere electron-transfer processes requiring a coordination-sphere reorganisation around the copper atom.[12] Long Cu−S (methionine) contacts in the range 2.7−3.2 Å, considered to be semicoordination, are of particular current interest, as protein engineering studies suggest that, notwithstanding an appreciable effect on the redox and spectroscopic properties of the active site,[13] in most cases no coordination of the S atom to the Cu^{II} ion appears to be involved.[14,15]

In the course of our research on developing relatively simple copper compounds as mimics of copper metalloenzymes, we synthesized the asymmetric tripodal ligand 1,1-bis(imidazol-2-yl)-3-(thiophen-2-yl)-2-aza-propane (Himthio) with S and N donor atoms (Figure 1).

The weak thiophene donor appears to be a good candidate for examining the semicoordination of the sulfur atom.[15] Surprisingly, the reaction of Himthio with $Cu(NO_3)_2$ in methanol results in a trinuclear copper(II) complex in which three copper ions are linearly bridged by two ligands. The crystal structure shows that the thiophene sulfur atoms are semicoordinated to the central Cu^{II} atom,

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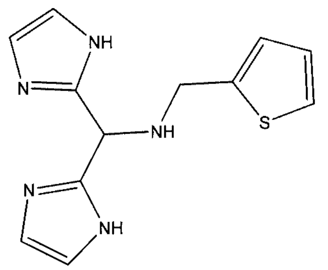

Figure 1. Molecular structure of the Himthio ligand

and such S−Cu^{II} interactions are quite rare, as analysis of the Cambridge Structural database shows. No other examples of trinuclear copper(II) complex in which the central Cu^{II} atom is coordinated by sulfur atoms have been found in the literature, it therefore represents the first example of a trinuclear linear copper(II) complex with semicoordination of thiophene moieties. The complex has been fully characterized by XRD, UV/Vis, EPR, and magnetic susceptibility measurement.

Results and Discussion

Synthesis of the Ligand and the Coordination Complex

The bis(imidazol-2-yl)amine unit[16] is a very interesting synthetic building block and can be prepared in five steps by a ring-opening and double ring-closure reaction. The Himthio ligand was synthesized by incorporating the thiophene group by nucleophilic substitution of a nitro group (see Exp. Sect.). The trinuclear copper complex, with the formula $[Cu_3(imthio)_2(NO_3)_4(MeOH)_2]$, was obtained by the reaction of 1 equiv. of imthio with 1 equiv. of copper(II) nitrate in methanol. Slow concentration of the solution at room temperature led to the formation of green, square crystals suitable for X-ray analysis. An ORTEP view of the complex, together with the atomic labelling scheme, is shown in Figure 2.

Crystal Structure of the Complex $[Cu_3(Imthio)_2(NO_3)_4(MeOH)_2]$

The structure consists of a centrosymmetric trinuclear linear molecular complex in which the central copper(II) atom occupies the inversion centre. In the $[Cu_3(imthio)_2]^{4+}$ moiety, each ligand is coordinated by four nitrogen atoms to two different copper ions. One of the two imidazolyl groups of Himthio is deprotonated and bridges the central and terminal ions through the N2 and N3 atoms.

Each of the two terminal copper atoms, Cu2 and Cu2′, is coordinated by two imidazole nitrogen atoms (N3 and N4), by two oxygen atoms from the NO_3^- anions (O1 and O4) and by the oxygen atom of the methanol (O1s); Cu2−O1 is the longest of these bonds [2.309(4) Å], so that the coordination around the metal atom can be described as a slightly distorted square pyramid, elongated towards the apex (N_2O_3 donor set, $\tau = 0.052$, where $\tau = 0$ and 1 are for perfect square-pyramidal and trigonal-bipyramidal geometries, respectively[17]).

The central Cu1 ion is coordinated by four nitrogen atoms (two amine nitrogen atoms, N1 and N1′; two imidazole nitrogen atoms, N2 and N2′) belonging to two centrosymmetric imthio ligands, thus giving origin to a CuN_4 chromophore in the equatorial plane [Cu1−N1 and Cu1−N2 distances are 2.064(3) and 1.933(3) Å, respectively].

The interatomic contact distance between Cu1 and the thiophene sulfur atoms is 3.136(2) Å. Other S−Cu distances reported in the literature range from 3.012 Å for a Cu^{II}−S containing system[18] to 2.90 Å and 3.16 Å for Cu^{I}−S,[19] which is believed to contain thiophene-*S* coordination to the Cu atom. Some Cu−O distances reported by Yates et al.[20] fall into the same range. The distance from Cu1 to the gravity centre of the thiophene ring (S1−C3−C4−C5−C6) is 3.620 Å. The angle between the Cu−S bond and the least-squares plane passing through

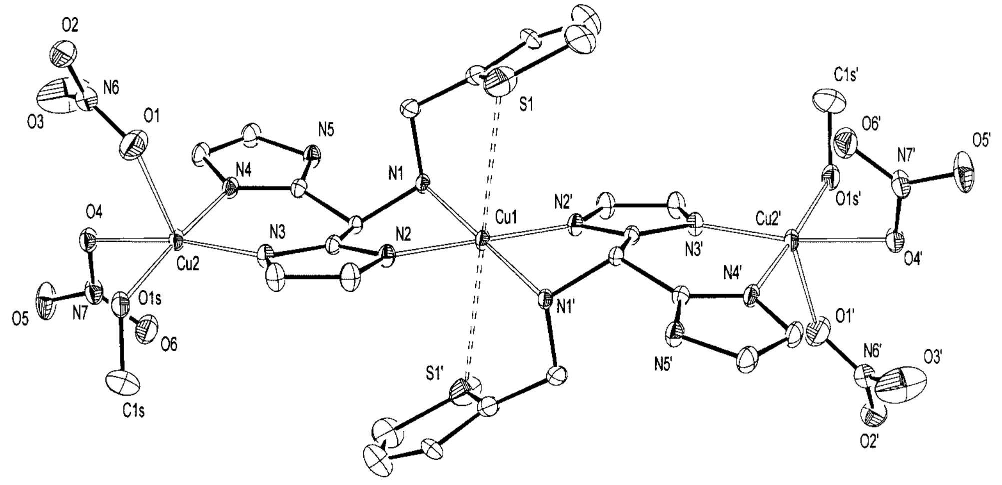

Figure 2. Thermal ellipsoid plot (20% probability level) of the trinuclear copper complex $[Cu_3(imthio)_2(NO_3)_4(MeOH)_2]$; hydrogen atoms have been omitted for clarity; selected bond lengths and angles: Cu1−N1 2.064(3), Cu1−N2 1.933(3), Cu1−S1 3.136 Å, Cu2−O1 2.309(4), Cu2−O1s 2.002(4), Cu2−O4 2.013(3), Cu2−N3 1.939(3), Cu2−N4 1.973(3) Å; N1−Cu1−N2 81.29(11), N1−Cu1−N2′ 98.71(11), S1−Cu−N1 81.3, S1−Cu1−N2 93.98, S1−Cu1−N1a 98.7, S1−Cu1−N2a 86.02, O1−Cu2−O1s 84.52(15), O1−Cu2−O4 93.53(13), O1−Cu2−N3 94.67(13), O1−Cu2−N4 101.57(13), O1s−Cu2−O4 87.05(13), O1s−Cu2−N3 89.25(15), O1s−Cu2−N4 173.77(14), O4−Cu2−N3 170.64(12), O4−Cu2−N4 91.24(11), N3−Cu2−N4 91.53(13)°

the thiophene ring is 123.38(17)° (the angle between the vector of Cu1 to the centre of gravity of the thiophene ring and the normal to the ring plane is 43.76°). The geometry around the central Cu^{2+} ion can be described as a tetragonally distorted octahedral environment, resulting from the long axial Cu1−S1 (and consequently Cu1−S1′) bond (S1−Cu1−N1: 81.3°; S1−Cu1−N2: 93.98°; S1−Cu1−N1′: 98.7°; S1−Cu1−N2′: 86.02°).

The crystal packing exhibits some π-stacking and face-to-face interactions with the shortest intramolecular ring−ring distances of 3.807(4) Å between the thiophene ring (S1−C3−C4−C5−C6) and one of the imidazole rings (N2−N3−C7−C8−C9). The dihedral angle between them is 23.97°. In the crystal the different units interact with each other through the imidazole and amine nitrogen atoms, which form intermolecular N−H···O hydrogen bonds involving the oxygens of the nitrate groups and of the methanol molecule (Figure 3). Very weak intermolecular C−H···O interactions [C1···O5 = 3.216(6) Å; C11···O3 = 3.237(6) Å] between −CH groups and nitrate oxygen atoms also contribute to the crystal packing.

Crystal structures of copper complexes with related ligands reported previously, for example 1,1-bis(imidazol-2-yl)-3-(pyridin-2-yl)-2-azapropane (Im-2Py), consist of two copper ions in distorted square-pyramidal environments.[8,21] Compared with those systems, the significant structural alteration induced by the substitution of pyridine rings by thiophene moieties and the semicoordination of thiophene sulfur atoms in the complex can be considered to have thermodynamic and/or kinetic consequences for redox reactivity.[20] It should be noted that, to the best of our knowledge, the title compound represents the first example to date of a linear trinuclear copper(II) complex in which the central Cu^{II} atom is semicoordinated with the thiophene sulfur atoms. Moreover, two lateral copper complexes can be considered as chelating ligands on the central Cu^{II} atom in the crystal structure.

Ligand-Field and UV/Vis Measurement

The ligand-field diffuse-reflectance spectrum of the crystalline powder of the complex shows a peak at $17.1 \cdot 10^3$ cm^{-1}, which is due to a d-d transition and is a normal ligand-field transition for a $CuN_2O_2(x)$ chromophore.[22,23] A strong absorption band at $28.3 \cdot 10^3$ cm^{-1} and a shoulder peak at $32.8 \cdot 10^3$ cm^{-1} can be attributed to the charge transfer from the N, O, or S to Cu^{II}. An absorption band at $37.3 \cdot 10^3$ cm^{-1} is associated with ligand π-π* transition.[24] The UV/Vis spectrum recorded in MeOH shows absorption bands as shoulder peaks at approximately 281 nm (ε = 2 054 $M^{-1}cm^{-1}$) and 372 nm (ε = 1 240 M^{-1} cm^{-1}), due to the LMCT transition from N and O to Cu^{II}.[25] The transition in the visible region of the electronic spectra is a much less intense absorption at 636 nm, which is assigned to d-d transitions.[23] The difference between the solid-state spectrum and the solution measurement suggests a change in geometry upon dissolution. The complex may therefore partially dissociate in solution.

EPR Measurements

The EPR spectra of the polycrystalline powder of the complex were recorded at room temperature and at 77 K. The complex shows axial spectra with $g_{//} = 2.28$, $g_{\perp} = 2.07$ and $A_{//} = 165$ G at room temperature. When the solid sample is measured at 77 K (liquid nitrogen), the signals become sharper with the same g and A values.

The EPR spectrum of the complex recorded in frozen solution at 77 K in MeOH shows an overlapping of two well-resolved axial signals with superhyperfine splitting superimposed on the axial and equatorial absorptions. The

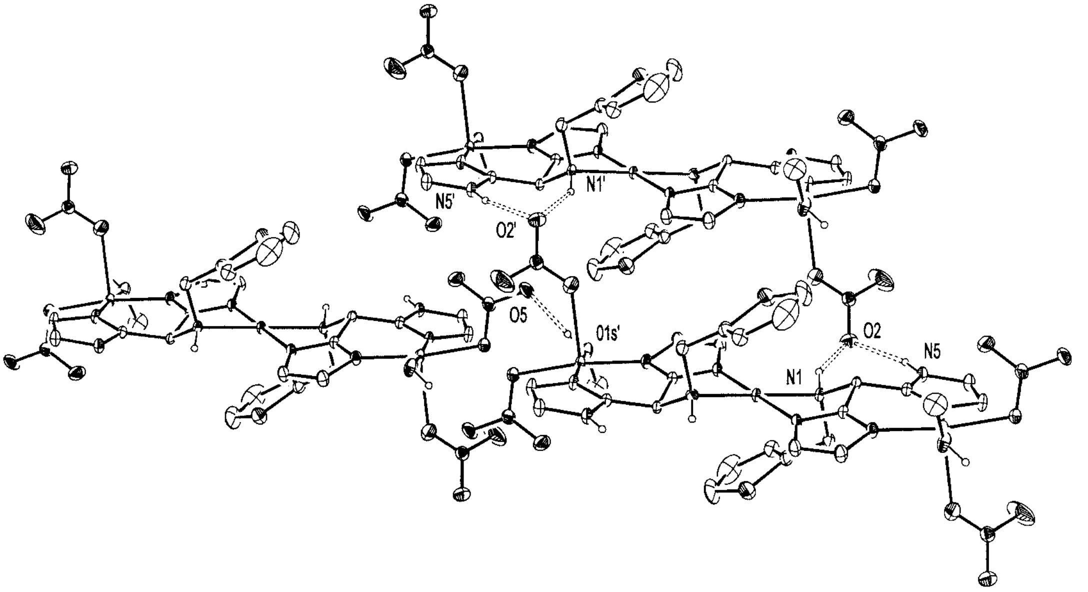

Figure 3. Perspective view showing the relevant hydrogen bonds connecting three different molecular complexes; intermolecular (D−H···A [Å]): N1−H1···O2 2.885(4), N5−H5···O2 2.848(5), O1s−H1s···O5 2.708(6)

spectrum clearly indicates the presence of two mononuclear species in solution, suggesting the dissociation of the trinuclear core. No half-field splitting signals, usually observed in the case of dinuclear species, are found. The equatorial coordination by four nitrogen donors around Cu1 in the complex results in the expected nine superhyperfine lines ($A_{N\perp}$ = 12.0 G). The spectrum was simulated satisfactorily[26] (see Figure 4) by using two noninteracting mononuclear Cu^{II} species in a ratio of 2.1:1.1. The reliability factor, defined as $R = n^{-1}[\Sigma(\chi_{obs} - \chi_{cal})^2/(\chi_{cal})^2]$ (n = number of data points), was $8.58{\cdot}10^{-4}$. The best simulating parameters for the species 1 were $g_x = 2.02$, $g_y = 2.05$ and $g_z = 2.25$, with A_z = 198 G (other A values set at 0). These values are reasonably close to those reported in the literature for CuN_4 chromophores. For species 2, the following values were obtained: $g_x \approx g_y = 2.06$ and $g_z = 2.33$, with $A_{//}$ = 175 G (other A value set at 0).

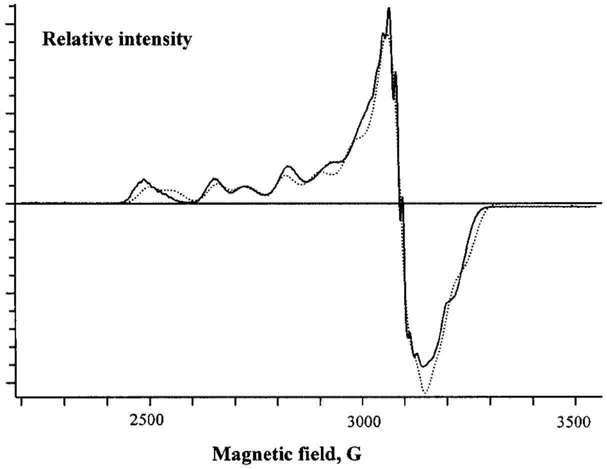

Figure 4. X-band EPR spectrum of the complex recorded at 77 K in MeOH; experimental curve (solid line) and simulated curve (dashed line) spectra of the complex (see text for further details)

Magnetic Susceptibility Measurement

The temperature-dependent magnetic susceptibility of the imidazolato-bridged trinuclear copper complex shows weak antiferromagnetic behaviour through the whole range of temperature (5−300 K). At 300 K the magnetic susceptibility has a value of 0.9725 cm^3mol^{-1}, a little bit lower than expected for three independent copper atoms (1.125 cm^3mol^{-1}). The decrease of the value of χT upon cooling is gradual and becomes slightly steeper at around 100 K, finally reaching a value of 0.2505 cm^3mol^{-1} at 5 K (Figure 5). This behaviour is typical for compounds with weak antiferromagnetism and was modelled using the spin Hamiltonian presented below:

$$H = g\beta S_zH - J_1(S_1{\cdot}S_2 + S_{1a}{\cdot}S_2) - J_2(S_1{\cdot}S_{1a}) - zJ'\langle S_z\rangle S_z$$

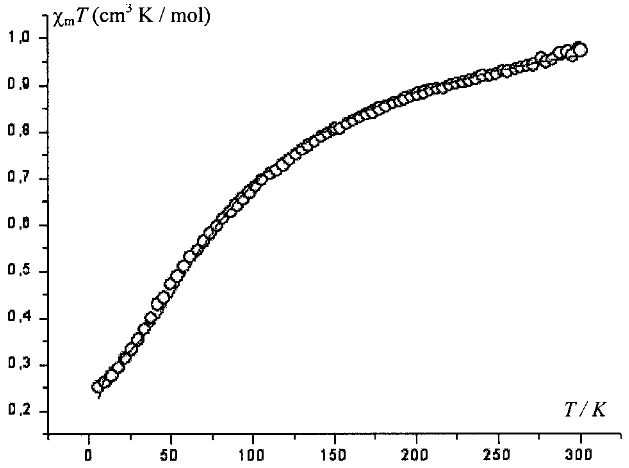

Figure 5. χ_mT vs. T plot for $[Cu_3(imthio)_2(NO_3)_4(MeOH)_2]$; the solid line is the best fit obtained with a nearest-neighbour interaction of −71.37 cm^{-1} (see text)

The first term of this Hamiltonian corresponds to the Zeeman term, for which only one isotropic g tensor has been considered for the two different Cu^{II} ions. The second and third terms are the isotropic nearest-neighbour and next-nearest-neighbour interactions, respectively; J_1 represents the exchange parameter between neighbouring Cu^{II} ions and J_2 the exchange parameter between terminal Cu^{II} ions. The latter has been neglected ($J_2 = 0$), as can be done when the compound is completely linear and the main interaction is antiferromagnetic. The last term takes into account the intermolecular interactions between the trinuclear arrays in the mean field approximation, in which J' is the intermolecular exchange interaction and z the number of trimeric neighbours (in this case 4). Considering the TIP (temperature-independent paramagnetism) and p as paramagnetic impurities, the resulting expression is:

$$\chi_mT = \{(N_ag^2\beta^2F(T)/4k_B[T - zJ'F(T)]\}(1 - p) + (N_ag^2\beta^2/2kT)p + TIP$$

$$F(T) = [1 + \exp(J_1/k_BT) + 10\exp(3J_1/2k_BT)]/[1 + \exp(J_1/k_BT) + 2\exp(3J_1/2K_BT)]$$

The best-fit parameters were $g = 2$, $J_1 = -71.37$, $zJ' = -4.03$ and $p = 0$ and the TIP is $60{\cdot}10^{-3}$ cm^3mol^{-1}, with an R value of $1.2{\cdot}10^{-4}$. The J_1 value is in good agreement with the expected value for imidazolato-bridged copper complexes reported previously.[27] Indeed, the Cu−Cu separation is large (Cu−Cu = 5.676 Å), obviously indicating that no direct exchange mechanism is likely to contribute to the magnetic coupling. Therefore, the antiferromagnetic coupling in the compound is ascribed solely to superexchange mechanisms between the magnetic orbitals of copper(II) ions ($d_{x^2-y^2}$) through the bridging imidazolate rings. The quite high value of the intertrinuclear superexchange interaction can be explained by the hydrogen-bonding network and π-π interactions between the trinuclear units in the lattice.

Conclusions

In summary, the Himthio ligand allows the preparation of a homometallic, trinuclear complex, $[Cu_3(imthio)_2(NO_3)_4$-

(MeOH)$_2$]. As Cu1 occupies an inversion centre, the resulting Cu2−Cu1−Cu2′ array is linear by symmetry. The molecular structure results in two different coordination sites within the same molecular complex, i.e. an N_4S_2 octahedral site and two N_2O_3 distorted square-pyramidal sites. The Cu−S distance is around 3.136 Å, which indicates moderate interactions between sulfur atoms and Cu^{II} atoms and results in the distortion of the ligand in the complex. Since only a limited number of linear trinuclear compounds have been reported as yet,[25,28] this trinuclear complex, with semicoordination of the thiophene sulfur atoms with Cu^{II} atoms, is unique. The crystal packing of the complex is stabilized by several hydrogen bonds and the interactions between aromatic rings. The EPR spectrum at 77 K in MeOH shows well-resolved superfine splitting signals, which are satisfactorily simulated with two mononuclear species. The magnetic susceptibility measurement of the complex indicates weak antiferromagnetic behaviour between copper(II) ions by a superexchange mechanism through the bridging imidazolate moieties. The studies not only present an unusual trinuclear copper(II) complex with semicoordinated thiophene moieties, but also provide more information about the magnetic and structural data for imidazolato-bridged complexes.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. Elemental analyses (C, H N, S) were carried out with a Perkin−Elmer 2400 series II analyser. Infrared spectra were recorded with a Perkin−Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR device, using the diffuse reflectance technique. X-band EPR spectra were recorded at room temperature and at 77 K with a Jeol RE2X electron spin resonance spectrometer using diphenylpicrylhydrazyl (DPPH) (g = 2.0036) as a standard. The UV/Vis spectra of the compound were recorded in the 250−800 nm range with a Cary 50 Varian UV/Vis/NIR spectrometer. The cyclic voltammetry measurements were performed with an Autolab PGstat10 potentiostat controlled by GPES4 software. A three-electrode system was used, consisting of a glassy carbon (GC) working electrode, a platinum (Pt) auxiliary electrode and an Ag/AgCl reference electrode. All potentials are given versus Ag/AgCl. The experiments were carried out in MeOH solution at room temperature under argon. Magnetic susceptibility measurements (5−300 K) were carried out using a Quantum Design MPMS-5S SQUID magnetometer, in a 1 kG applied field. Data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic responses of the complex, as estimated from Pascal's constants, were applied.[29]

Preparation of the 1,1-Bis(imidazol-2-yl)-3-(thiophen-2-yl)-2-azapropane (Himthio) Ligand: 2-(Aminomethyl)thiophene (0.50 g, 4.37 mmol) in water (10 mL) was added to a solution of the hydrochloride salt of bis(imidazol-2-yl)nitromethane[16] (1.0 g, 4.37 mmol) in sodium hydroxide solution (2.0 M, 5 mL) . The solution was stirred at 80 °C for 2 h, during which the product crystallised from the reaction mixture (if not, the solution was left at room temperature, until precipitation of the compound occurred). After cooling to room temperature, the reaction mixture was filtered and washed with water, ethanol and diethyl ether in air. Yield: 0.74 g, 65%. ^{1}H NMR (200 MHz, CD$_3$OD, 25 °C, 0−10 ppm): δ = 7.30 (t, 1 H, Thio-*H*), 7.02 (s, 4 H, Im-*H*), 6.92 (d, 2 H, Thio-*H*), 5.18 (s, 1 H, C*H*), 3.87 (s, 2 H, C*H*$_2$) ppm. MS: m/z = 259.9 [M + H]$^+$.

Preparation of the Copper Complex [Cu$_3$(imthio)$_2$(NO$_3$)$_4$(MeOH)$_2$]: A solution of the Himthio ligand (20.72 mg, 0.08 mmol) in methanol (10 mL) was added to a solution of Cu(NO$_3$)$_2$·3H$_2$O (19.3 mg, 0.08 mmol) in methanol (5 mL). The reaction mixture was stirred at room temperature for 30 min and filtered. The solution was left alone at room temperature for several weeks, and green crystals suitable for X-ray analysis were produced. Yield: 9.5 mg, 35%. $C_{26}H_{32}Cu_3N_{14}O_{14}S_2$ (1019.40): calcd. C 30.6, H 3.2, N 19.2, S 6.3; found C 30.9, H 2.7, N 18.7, S 6.8. IR (solid): $\tilde{\nu}$ = 1564.9, 1484.6, 1373.3, 1329.2, 1300.2, 1140.2, 1030.5, 926.1, 825.7, 750.0, 724.1, 651.2, 431.8 cm^{-1}.

X-ray Crystallographic Study: The molecular structure of [Cu$_3$(imthio)$_2$(NO$_3$)$_4$(MeOH)$_2$] was determined by single-crystal X-ray diffraction methods. Crystallographic and experimental details for the structure are summarized in Table 1. Intensity data and cell parameters were recorded at room temperature (25 °C) with a Bruker AXS Smart 1000 single-crystal diffractometer (Mo-K_α radiation) equipped with a CCD area detector. The data reduction was performed using the SAINT and SADABS programs.[30] The structure was solved by Direct Methods using the SIR97 program[31] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program.[32] All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealised geometry (C−H 0.95 Å) and refined "riding" on the corresponding parent atoms, with the exception of H1S4, which was located in the difference Fourier map. The weighting scheme used in the last cycle of refinement was

Table 1. Crystallographic data for Cu$_3$(imthio)$_2$(NO$_3$)$_4$(MeOH)$_2$

Empirical formula	$C_{26}H_{32}Cu_3N_{14}O_{14}S_2$
Formula mass	1019.40
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	9.176(5)
b [Å]	9.180(5)
c [Å]	12.804(5)
α [°]	89.718(5)
β [°]	76.847(5)
γ [°]	69.140(5)
V [Å^3]	978.0(8)
Z	1
$D_{calcd.}$ [g cm^{-3}]	1.731
Linear absorption coeff. [mm^{-1}]	1.805
F(000)	517
Crystal size [mm]	0.11 × 0..14 × 0.23
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-16 \le l \le 16$
θ range for data collection [°]	1.64−27.01
Reflections collected	10634
Independent reflections	4173 (R_{int} =0.0345)
Observed reflections [$I > 2\sigma(I)$]	2714
Data/restraints/parameters	4173/1/277
Goodness-of-fit on F^2 [a]	0.889
Final R indices (obsd. data)[b]	R_1 = 0.0407, wR_2=0.0920
R indices (all data)[b]	R_1 = 0.0735, wR_2=0.0992
Largest diff. peak /hole [e/Å^{-3}]	0.631/−0.532

[a] Goodness-of-fit $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters. [b] $R_1 = \Sigma F_o - F_c/\Sigma F_o$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$.

$w = 1/[\sigma^2 F_o^2 + (0.0544P)^2]$ [where $P = (F_o^2 + 2F_c^2)/3$]. Molecular geometry calculations were carried out using the PARST97 program[33]. Drawings were obtained by ORTEP3 in the WinGX suite.[34] All calculations were carried out with a DIGITAL Alpha Station 255 computer. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-233200 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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