A Homoleptic Copper(II)−Thiocyanato Linear Chain

Christopher A. White,[†] Glenn P. A. Yap,[‡] N. P. Raju,[§] J. E. Greedan,[§] and Robert J. Crutchley*,[†]

Ottawa-Carleton Chemistry Institute, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario Canada K1S 5B6, University of Ottawa, Ottawa, Ontario Canada, K1N 6N5, and Brockhouse Institute for Materials Research, McMaster University, Hamilton Ontario, Canada L8S 4M1

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The use of small molecules to bridge magnetic centers has recently gained much interest because of the discovery of molecular magnetic materials based on metal-cyano bridges,[1] and this has led us to reexamine the coordination chemistry of thiocyanates. Metal−thiocyanato chemistry has had a considerable history of investigation[2] and examples of copper(II) homoleptic systems have been confined to cation salts of $[Cu(SCN)_4]^{2-}$. In this study, we show that under conditions of excess Cu(II) ions, it is possible to synthesize a novel tetraphenylarsonium copper(II) thiocyanato anion salt, having the stoichiometry $[AsPh_4][Cu(SCN)_3]$ **1**. Furthermore, the crystal structure of **1** revealed the complex salt to be a rare example of a metal−thiocyanato one-dimensional chain compound,[3] containing equatorial−equatorial copper−thiocyanato bridges.[3b]

The complex salt **1** was synthesized by combining concentrated methanolic solutions of $Cu(CF_3SO_3)_2 \cdot nH_2O$[4] with $(AsPh_4)SCN$[5] in a 1:2 molar ratio. After 4 days in the dark, evaporation of the yellow/brown solution yielded small white crystals of $(AsPh_4)(CF_3SO_3)$ and very large brown rectangular prisms of **1**.[6] The crystals of **1** were manually separated and washed with hot ethanol to remove any residual $(AsPh_4)(CF_3SO_3)$. A single crystal was selected for crystallographic analysis.[7]

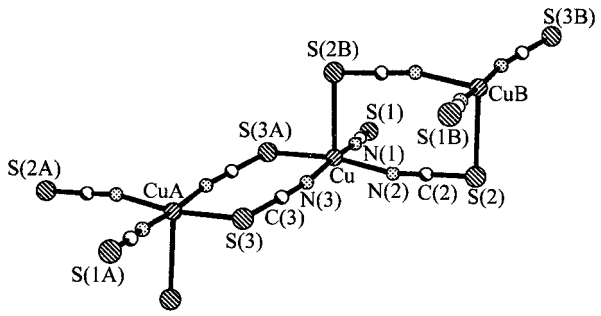

Figure 1. Ball-and-stick drawing of a fragment of the chain structure of **1**. The tetraphenylarsonium counterions have been excluded for clarity.

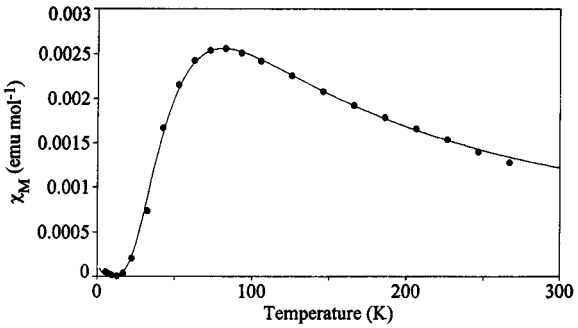

Figure 2. Temperature dependence of molar magnetic susceptibility of **1**. The solid line is the best fit of data using eq 1. See text for details.

The results of this analysis are given in Figure 1 and in the Supporting Information and show that each Cu(II) ion of **1** is in a distorted square pyramidal coordination sphere made up of two sulfur donor atoms in axial and equatorial coordination sites and three nitrogen donor atoms, all in the equatorial plane. A linear chain of Cu(II) ions is formed by alternating pairs of equatorial−axial (EA) and equatorial−equatorial (EE) copper−thiocyanato bridges. An equatorial, monodentate, thiocyanato-*N* ligand completes the coordination sphere about each Cu(II) ion. The separation between the uncoordinated sulfur atom of this monodentate thiocyanato ligand and the nearest Cu(II) ion on another chain is 5.63 Å and suggests that there will be weak if any interaction between chains.

The temperature-dependent magnetic susceptibility of **1** from 2 to 270 K in Figure 2 shows a smooth maximum at $T_N = 80$ K that is characteristic of intramolecular antiferromagnetic exchange.[8] At lower temperatures, the drop in susceptibility approaches zero and then begins to increase at around 10 K. This increase is most likely due to mononuclear impurities. The

[†] Carleton University.
[‡] University of Ottawa.
[§] McMaster University.

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(5) $AsPh_4(SCN)$ was prepared by the aqueous addition of NH_4SCN and $AsPh_4Cl \cdot H_2O$ in a 1:1 molar ratio. The white precipitate formed immediately, was filtered, and subsequently recrystallized by ether diffusion into an acetonitrile solution yielding large pale yellow needles Yield 48% after recrystallization, Anal. Calcd (found): C, 68.02 (67.98); H, 4.57 (4.37); N, 3.17 (3.20). IR ν(SCN) 2052 cm^{-1}.
(6) Anal. Calcd (found): C, 52.21 (51.47); H, 3.25 (3.01); N, 6.76 (6.48). IR ν(SCN) 2076, 2109, and 2153 cm^{-1}. The % found elemental analyses suggests the presence of an inorganic salt impurity.
(7) Crystal data (297 K) for **1**: monoclinic, $P2(1)/c$, $a = 13.838(3)$ Å, $b = 9.679(2)$ Å, $c = 21.623(5)$ Å, $V = 2797.2(11)$ Å^3, $Z = 4$, $\lambda = 0.710\,73$ Å, $\mu = 2.199$ mm^{-1}. A total of 17 682 independent reflections were collected ($1.95° \leq \theta \leq 22.50°$), of which 3661 were used in the refinement, leading to final discrepancy indices [$I > 2\sigma(I)$] of R1 = 0.0356 and wR2 = 0.0916. GOF = 1.068.
(8) Magnetic measurements were performed on fine crystalline material without pre-grinding to a powder. The diamagnetic correction used for $[AsPh_4][Cu(SCN)_3]$ was -367×10^{-6} emu/mol.

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Table 1. Geometry, Bridging Modes, and Exchange Constants for Copper(II)−Thiocyanato Bridged Systems

complex[a]	geometry[b]	bridging mode[c]	J (cm^{-1})[d]	ref
$Cu_2(\mu\text{-NCS})_2(Et_3dien)_2](ClO_4)_2$	OC	EA	+7.7	7
$[Cu_2(\mu\text{-NCS})_2(Me_5dien)_2](ClO_4)_2$	SPY	EA	+1.6	7
$[Cu_2(\mu\text{-NCS})_2(ept)_2](ClO_4)_2$	OC	EA	+1.3	7
$[Cu\{O(CH_2)_3N(methyl)_2\}(\mu\text{-NCS})]_n$	SPY	EA	neg	3m
$[Cu\{O(CH_2)_3N(ethyl)_2\}(\mu\text{-NCS})]_n$	SPY	EA	neg	3m
$[Cu\{O(CH_2)_3N(n\text{-butyl})_2\}(\mu\text{-NCS})]_n$	SPY	EA	neg	3m
$[Cu(bheg)(\mu\text{-NCS})]_n$	OC	EA	neg	3j
$[Cu(4\text{-bromopyridine})_2(\mu\text{-NCS})_2]_n$	OC	EA	*e*	3l
$[Cu(bpm)(\mu\text{-NCS})_2]_n$	OC	EA	−0.6	3g
$[Cu(bpm)(\mu\text{-NCS})_4]_n$	OC	EA	neg	3g
$[\{Cu_2(tmen)_2NCS(\mu\text{-Cu(pba)})\}(\mu\text{-NCS})]_n\cdot(3H_2O)]_n$	SPY	AA	wf	3d
$\{[Cu(NCS)(\mu\text{-NCS})(Hmtpo)(H_2O)]_2\}_n$	OC	EE/EA	−148	3b
1	SPY	EE/EA	−90	this work

[a] Ligand abreviations, Et_3dien = 1,4,7-triethyldiethylenetriamine, Me_5dien = 1,1,4,7,7-pentamethyldiethylenetriamine, ept = *N*-(2-aminoethyl)-1,3-propanediamine, bpm = 2,2′-bipyrimidine, bheg = *N*,*N*-bis(2-hydroxyethyl)glycinato, tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tren = tris(2-aminoethyl)amine, pba = 1,3-propanediyl-bis(oxamato), Hmtpo = 4*H*,7*H*,5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine. [b] OC, octahedral geometry; SPY, square pyramidal geometry. [c] EA, equatorial−axial bridge; EE, equatorial−equatorial bridge; AA, axial−axial bridge. [d] $H = -JS_A\cdot S_B$, from magnetic susceptibility measurements; neg, negligible interaction; wf, weakly ferromagnetic. [e] Not determined.

alternating exchange interactions of a linear chain of **1** are illustrated by

$$Cu \overset{J}{\text{—}} Cu \overset{J'}{\text{—}} Cu \overset{J}{\text{—}} Cu \overset{J'}{\text{—}} Cu \overset{J}{\text{—}} Cu \overset{J'}{\text{—}}$$

where J is the exchange constant mediated by an EE bridge and J' is the exchange constant mediated by an EA bridge. Table 1 summarizes the exchange constants found for the few copper−thiocyanato bridged systems in the literature.[3,9] The EA copper−thiocyanato bridge appears to promote weakly ferromagnetic or very weakly antiferromagnetic exchange whereas strong antiferromagnetic exchange was observed for the single example of a complex possessing an EE bridge. Under conditions in which the ratio J'/J is very small, it is possible to simplify treatments of alternating antiferromagnetic chains[10] or alternating antiferromagnetic−ferromagnetic chains[11] to the case of magnetically isolated Cu(II) dimers.

The solid line in Figure 2 is the best fit of data using a modified Bleaney−Bowers equation for exchange-coupled dimers,[12]

$$\chi = \frac{Ng^2\beta^2}{kT[3+\exp(-J/kT)]}(1-\rho) + \frac{Ng^2\beta^2}{2kT}(\rho) \qquad (1)$$

for a Hamiltonian of the form $H = -JS_A\cdot S_B$, where J is the singlet−triplet energy gap. The modification to this expression, seen in the second term, accounts for the presence of uncoupled species, quantified by ρ. During the modeling process, no correction for TIP was made and g, J, and ρ were all taken as adjustable parameters. The best fit gave values of $g = 2.1$, $J = -90$ cm^{-1}, and $\rho = 3.6 \times 10^{-4}$. The agreement factor[13] is quite acceptable ($r^2 = 0.998$).

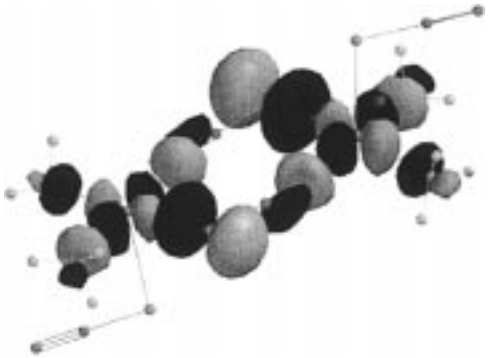

Figure 3. HOMO of the model complex $[\{Cu(NH_3)_2(NCS)\}_2(\mu\text{-NCS})_2]$ where the bridging thiocyanates are EE and the monodentate thiocyanato ligand occupies the axial coordination site. The semiempirical calculation was constrained by the bond angles and lengths derived from the X-ray structure of **1**.

The one-dimensional chain material **1**, is only the second example of a compound containing Cu−NCS−Cu equatorial−equatorial bridges[3b] and confirms the strong antiferromagnetic exchange mediated by this bridge. We performed a semiempirical calculation[14] on the model complex $[\{Cu(NH_3)_2(NCS)\}_2(\mu\text{-NCS})_2]$ where the bridging thiocyanates are EE and monodentate thiocyanato-*S* ligands occupy axial coordination sites. The calculation was constrained by the bond angles and lengths derived from the X-ray structure of **1** and gave the highest occupied molecular orbital HOMO shown in Figure 3. The HOMO illustrates the superexchange pathway for antiferromagntic coupling between the two Cu(II) $d_{x^2-y^2}$ orbitals and is consistent with EPR studies of square pyramidal Cu(II) complexes that show the odd electron to reside in a $d_{x^2-y^2}$ orbital.[15] It is also important to note that there is no contribution to the HOMO from the axial thiocyanato ligand. To emphasize this point, a semiempirical calculation of the model complex $[\{Cu(NH_3)_2(NCS)\}_2(\mu\text{-NCS})_2]$, where the thiocyanato bridges are EA and monodentate thiocyanato-*N* ligands occupy the equatorial sites trans to a bridging thiocyanate, gave two degenerate singly occupied molecular orbitals (see Supporting Information). The isolation of Cu(II) spins in $d_{x^2-y^2}$ orbitals is apparent and, as the pathway for interaction between copper ions is orthogonal, the prediction of ferromagnetic exchange via the EA thiocyanato bridge is generally consistent with the data shown in Table 1.

To conclude, the strategy used to synthesize **1** should be applicable to other metal ions and small atom bridging ligands and will hopefully lead to multidimensional materials possessing interesting magnetic and electronic properties.

Supporting Information Available: Full listings of crystal structure data, tables of atomic parameters, anisotropic thermal parameters, bond lengths, bond angles, a labeled ORTEP drawing; and a figure showing the two degenerate singly occupied molecular orbitals of the model complex $[\{Cu(NH_3)_2(NCS)\}_2(\mu\text{-NCS})_2]$, where the thiocyanato bridges are EA and monodentate thiocyanato-*N* ligands occupy the equatorial sites trans to a bridging thiocyanate. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The agreement factor was defined as

$$r^2 = 1 - (\textstyle\sum_{i=1}^{n}(\hat{y}_i - y_i)^2 \div \sum_{i=1}^{n}(y_i - \bar{y})^2).$$

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