Inorganic Chemistry

Communication

pubs.acs.org/IC

Synthesis, Characterization, and Reactivity of a Novel μ-η^2:η^2-Diselenidodicopper(II) Complex

Jun Matsumoto, Yuji Kajita, and Hideki Masuda*

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan

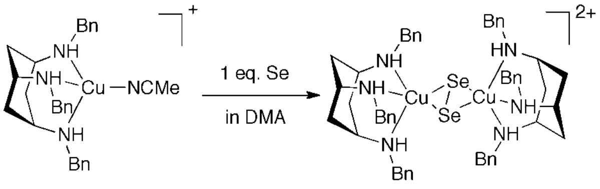
S Supporting Information

ABSTRACT: The first μ-η^2:η^2-diselenidodicopper(II) complex has been obtained in the reaction of a copper(I) complex with *N*,*N*′,*N*″-tribenzyl-*cis*,*cis*-1,3,5-triaminocyclohexane and elemental selenium. The structure and reactivity of the complex is described.

Selenium-containing proteins, selenoproteins, serve a variety of important roles in cellular activity.[1−3] The functions of a number of selenoproteins have not yet been ascertained, although it is thought that they involve substantially the chelation of heavy metals.[2] In some cases, selenium appears to provide protection against metal toxicity.[4] These findings may indicate a specificity of selenide for binding metals such as copper and iron, but the essential basis of this behavior is unknown.[5−7] On the other hand, much attention has been focused on the chemistry of transition-metal compounds containing dichalcogen ligands because of their unique structures and reactivities[8−14] and their involvement in biological systems.[15−17] For the above reasons, it is also intriguing to explain the chemical properties of the dicopper complex bridged with diselenide dianion (Se_2^{2-}). However, such a complex has not been prepared, in contrast to substantial knowledge on the systems of selenidomulticopper clusters.[18−24] This is probably due to the fact that stable selenidocopper clusters or their salts are mainly generated from the reaction of copper salts with selenium sources. Therefore, only structural information about such complexes has been reported, and their reactivity has been rarely studied.

We selected a *cis*,*cis*-1,3,5-triaminocyclohexane derivative as the supporting ligand for the purpose of eliminating the generation of selenidocopper salts. This ligand has a strong σ-donating ability and is expected to indicate a strong chelating effect in the formation of 6-6-6-membered chelate rings. Herein, we report the first X-ray structure and chemical properties of a μ-η^2:η^2-diselenidodicopper complex. Additionally, the reactivities of the complex with PPh₃, CO, MeCN, xylyl isocyanide, and dioxygen are also described and discussed.

Scheme 1. Synthesis of Complex 2



1   2

The addition of elemental selenium (1 equiv) to a pale-yellow solution of $[Cu(MeCN)(Bn_3TACH)](SbF_6)$ (**1**; Bn_3TACH = *N*,*N*′,*N*″-tribenzyl-*cis*,*cis*-1,3,5-triaminocyclohexane) in *N*,*N*-dimethylacetamide (DMA) at room temperature resulted in a sudden change to a green color. After stirring for 6 h, the color changed to dark-brown and a black precipitate was filtered off. By condensation in a vacuum and crystallization from CH_2Cl_2/Et_2O, dark-brown crystals of $[Cu_2(Se_2)(Bn_3TACH)_2](SbF_6)_2\cdot 2DMA$ (**2**·2DMA) were isolated in 23.5% yield (Scheme 1). An oily green product was obtained from the filtrate. Other redox processes may have occurred between the copper(I) ion and elemental selenium. However, other copper species were not isolated. From the treatment of **1** with excess amounts of elemental selenium (2 equiv), **2**·2DMA was obtained in 30.9% yields as crystals, whose structures were determined by X-ray analysis. The X-ray structure of **2**·2DMA revealed a unique $\{Cu^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)\}$ core structure (Figure 1). The solution and solid-state structures of **2** were also identified by mass spectrometry, elemental analysis, and IR, absorption, reflectance, and multinuclear NMR spectroscopies. The structure of **2**·2DMA includes a centrosymmetric binuclear complex pentacoordinated in a square-pyramidal geometry (τ = 0.01)[25] with two secondary amino nitrogen atoms (N1 and N2) and two selenium atoms in equatorial positions. The remaining nitrogen atom N3 is located at the apical position. The dihedral angle (ϕ) between the two planes defined by the $CuSe_2$ plane is 180.0°, and the Cu_2Se_2 core is completely planar. The copper(II) coordination geometry is structurally similar to that of the μ-η^2:η^2-disulfidodicopper complex analogues $[Cu_2(S_2)(Bn_3TACH)_2](SbF_6)_2$ (**3**; ϕ = 180.0°) reported previously, whereas the dihedral angles in $[Cu_2(S_2)(R_3TACH)_2](SbF_6)_2$ (R = Et or iBu) are smaller than 180° (ϕ < 180.0°).[26] The Cu···Cu and Se−Se distances for **2**·2DMA are 4.0636(6) and 2.3898(5) Å, respectively. The Se−Se distance of the $\{Cu^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)\}$ core is significantly longer than that of Se_2 [2.19(3) Å][27] and is similar to the Se−Se distance in the crystal of Na_2Se_2 [2.38(5) Å].[27] This clearly indicates that the diselenide molecule in the Cu_2Se_2 core is reduced by two electrons. The Se−Se bond length is similar to that of the $La_2(\eta\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)$ core [2.385(4) Å; ϕ = 180.0°],[28] while it is slightly longer than that of the $Ni_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)$ complex with

Received: December 14, 2011
Published: January 18, 2012

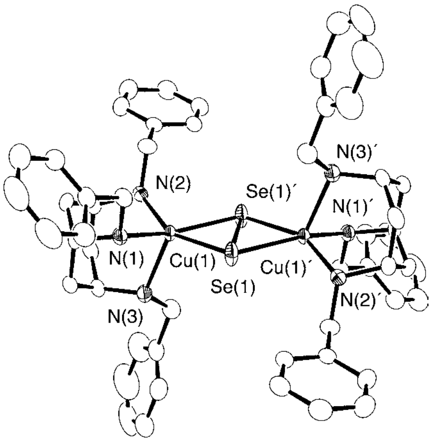


Figure 1. X-ray structure of the cationic portion of **2**·2DMA, showing 50% probability thermal ellipsoids. The hydrogen atoms and the solvent molecules have been omitted for clarity. Selected interatomic distances [Å]: Se1−Se1′ 2.3898(5), Cu1···Cu1′ 4.0636(6), Cu1−Se1 2.3521(5), Cu1−Se1′ 2.3621(4), Cu1−N1 2.0314(18), Cu1−N2 2.002(3), Cu1−N3 2.199(3).

β-diketiminate [2.3304(6) Å; ϕ = 134.35°],[29] $Ir_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ [2.3628(7) Å; ϕ = 75.77°],[30] and $MoMn(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ [2.3144(6) Å; ϕ = 80.85°] cores.[31] Interestingly, the Se−Se bond is shorter when the dihedral angle, ϕ, is smaller than 180°. Shorter Se−Se bonds appear in diselenidodimetal complexes with dihedral angles smaller than ϕ = 180.0°. This fact suggests that electron transfer by back-donation from metal ions to the antibonding orbital of the diselenide molecule causes a weakening of the bending of the M_2Se_2 plane. The $Cu{-}N_{TACH}$ bond lengths [2.0314(18), 2.002(3), and 2.199(3) Å] are very similar to those of **3** [2.024(3), 2.002(3), and 2.195(3) Å] and are shorter than those of $[Cu_2(OH)_2(Bn_3TACH)_2](ClO_4)_2$ [**4**; 2.0451(11), 2.0301(10), and 2.2495(11) Å].[32] This trend may indicate that the order of the electron-donating ability from the TACH ligand to the copper(II) ion is **2** ≈ **3** > **4**, suggesting that the electron-donating abilities of diselenide and disulfide are smaller than that of hydroxide.

It is clear from our spectroscopic results that the $Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)$ structure of complex **2** is retained in solution. Complex **2** is ESR-silent in acetone, and its ^1H NMR spectrum in acetone-d_6 exhibits peaks in the diamagnetic region. These results indicate strong antiferromagnetic coupling between the copper(II) ions. The UV−vis absorption spectrum of **2** (Figure 2) in CH_2Cl_2 at ambient temperature has multiple spectral features at λ_{max} [nm] (ε_{max}, M^{-1} cm^{-1}) = 294 (sh, 5400), 375 (16 000), 433 (11 000), 476 (sh, 7900), and 705 (510). The spectral pattern of **2** is very similar to that of **3** reported previously, although the bands are slightly red-shifted relative to those of **3**. The two bands at 375 and 476 nm are assigned to the in-plane diselenido π^*_σ-to-Cu^{II} charge-transfer (CT) transition, and the band at 433 nm is assigned to the out-of-plane diselenido π^*_v-to-Cu^{II} CT. The ^{77}Se NMR spectrum of **2** in acetone-d_6 has a resonance at 1070.6 ppm. ^{77}Se NMR spectra of $\mu\text{-}\eta^2{:}\eta^2$-diselenide species and copper-bound inorganic selenide have not been reported, although spectra of previously reported selenium-containing compounds have been recorded in the range of −800 to +2400 ppm. For the tungsten and molybdenum selenide compounds reported previously, those of the bridging selenide are observed in the range of 1100 > δ > 600 ppm and those of metal-bound selenide are detected in the range of 1100 > δ > 500 ppm.[10] So, the peak detected for complex **2** is reasonable as the diselenide ligand bridged between two copper(II) ions. The positive electrospray ionization mass spectrometry (ESI-MS) spectrum of complex **2** was also measured in acetone, and the isotope pattern was observed at m/z 1318.8, which is assignable to $[M - SbF_6]^+$. This structure has been confirmed to be retained in solution and in the gaseous phase.

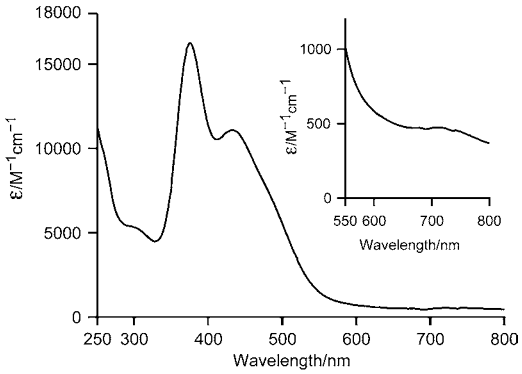


Figure 2. UV−vis spectrum of **2** (5.0×10^{-5} M) in CH_2Cl_2. Inset: UV−vis spectrum of a concentrated CH_2Cl_2 solution of **2** (2.5×10^{-4} M).

It is very important to understand the reactivity of copper−selenium complexes when we consider the biological selenium cycle, but this area has been rarely investigated. Therefore, we studied the reactivity of **2** toward exogenous substrates that were previously investigated in the copper−sulfur systems.[33−35] The results are quite interesting from the viewpoint of selenium-atom transfer. The reaction of **2** with 4 equiv of PPh_3 provides 2 equiv of $Se{=}PPh_3$, as determined by monitoring of ^{31}P NMR spectra. A single crystal of $[Cu(Bn_3TACH)(PPh_3)](SbF_6)\cdot CH_2Cl_2$ was obtained from the mixture, and a fragment of $[Cu(Bn_3TACH)(PPh_3)]^+$ was also detected in ESI-MS analysis. The reaction of **2** and 2 equiv of xylyl isocyanide (CN-xylyl) afforded the copper(I) complex $[Cu(Bn_3TACH)(CN\text{-}xylyl)](SbF_6)$ without any detection of selenium-inserted Se═C═N-xylyl species. When an acetone solution of **2** was stirred under a CO atmosphere (1 atm), the brown color disappeared and the previously reported carbonyl complex $[Cu(CO)(Bn_3TACH)](SbF_6)$ was obtained, as confirmed by the observation of ν_{CO} 2076 cm^{-1}.[32] The brown precipitate was separated and identified as elemental selenium. Additionally, when excess MeCN was added to an acetone solution of **2**, the brown color bleached and a brown precipitate was isolated. The starting material **1** was recovered from the mixture. Therefore, it has been clarified that complex **2** is easily reduced from copper(II) to copper(I) by reaction with exogenous substrates to generate elemental selenium. This indicates that the metal center is easily stabilized in a low valence.

A CH_2Cl_2 solution of **2** at room temperature reacts with dioxygen to produce a green solution with UV−vis features at λ_{max} = 359 nm (ε = 3900 M^{-1} cm^{-1}) and 636 nm (ε = 410 M^{-1} cm^{-1}). These spectral features are characteristic of the bis(μ-hydroxo)dicopper(II) complex **4** reported previously.[32] This means that a bis(μ-oxo)dicopper species would have been generated after the selenium exchange. Reaction intermediates were not detected at low temperature because of their instability. This reaction obeys pseudo-first-order kinetics, and the half-life time was estimated to be $t_{1/2}$ ~ 9.7 h, as measured by monitoring of the intensity of the peak at 375 nm. The half-life of the μ-η^2:η^2-disulfidodicopper(II) complex **3** was found to be ~5.7 h. The Cu_2Se_2 species may be more stable than the Cu_2S_2 species in reactions with dioxygen. In this reaction, the diselenidodicopper(II) complex, dioxygen, and two external hydrogen atoms have been consumed, and the bis(μ-hydroxo)-dicopper(II) complex and 2 equiv of elemental selenium have been generated. The organism *Thiobacillus ferrooxidans* is known to oxidize copper(II) selenide to generate elemental selenium, as shown in Scheme 2.[5] Thus, the reaction of **2** with dioxygen may be comparable to the reaction in *T. ferrooxidans*. Here we propose that copper selenide may serve through coordination with coligands similar to Bn_3TACH-like in the oxidation process of *T. ferrooxidans*.

Scheme 2. Oxidation Reaction Catalyzed by *T. ferrooxidans*

$$2CuSe + 4H^+ + O_2 \xrightarrow{\textit{T. ferroxidans}} 2Cu^{2+} + 2Se^0 + 2H_2O$$

In summary, we have synthesized and characterized a new TACH ligand-supported Cu_2Se_2 complex, $[Cu^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)(Bn_3TACH)_2](SbF_6)_2$ (**2**). Using UV−vis and ^{77}Se NMR spectroscopies and crystal structure analysis, we determined that the Cu_2Se_2 core has characteristics similar to those of other Se_2^{2-} compounds. We have also observed the conversion of **2** to the copper(I) adduct in a reaction of **2** with PPh_3, xylyl isocyanide, CO, and MeCN as exogenous substrates. Furthermore, in the reaction of **2** with dioxygen, diselenium is displaced by dioxygen to produce $[Cu_2(OH)_2(Bn_3TACH)_2]^{2+}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthesis, spectra, spectral data, crystallographic data, and ORTEP drawings for complex **2**·2DMA (CCDC 839737) and $[Cu(Bn_3TACH)(PPh_3)](SbF_6)\cdot CH_2Cl_2$ (CCDC 839738). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: masuda.hideki@nitech.ac.jp.

■ ACKNOWLEDGMENTS

We gratefully acknowledge support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and the Knowledge Cluster Project.

■ REFERENCES

(1) Behne, D.; Kyriakopoulos, A. *Annu. Rev. Nutr.* **2001**, *21*, 453−473.

(2) Jacob, C.; Giles, G. I.; Giles, N. M.; Sies, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4742−58.

(3) Stolz, J. F.; Basu, P.; Santini, J. M.; Oremland, R. S. *Annu. Rev. Microbiol.* **2006**, *60*, 107−130.

(4) Lenza, M.; Lens, P. N. L. *Sci. Total Environ.* **2009**, *407*, 3620−3633.

(5) Torma, A. E.; Habashi, F. *Can. J. Microbiol.* **1972**, *18*, 1780−1781.

(6) Oremland, R. S.; Herbel, M. J.; Blum, J. S.; Langley, S.; Beveridge, T. J.; Ajayan, P. M.; Sutto, T.; Ellis, A. V.; Curran, A. S. *Appl. Environ. Microbiol.* **2004**, *70*, 52−60.

(7) Bui, B. T. S.; Mattioli, T. A.; Florentin, D.; Bolbach, G. R.; Marquet, A. *Biochemistry* **2006**, *45*, 3824−3834.

(8) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245−280.

(9) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223−266.

(10) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195−219.

(11) Shibahara, T.; Cnh, H. N. H. H. C. H. *Coord. Chem. Rev.* **1993**, *123*, 73−147.

(12) Aullón, G.; Hamidi, M.; Lledós, A.; Alvarez, S. *Inorg. Chem.* **2004**, *43*, 3702−3714.

(13) Adams, R. D.; Kwon, O.-S.; Miao, S. *Acc. Chem. Res.* **2005**, *38*, 183−190.

(14) Alvarez, S.; Hoffmann, R.; Mealli, C. *Chem.—Eur. J.* **2009**, *15*, 8358−8373.

(15) York, J. T.; Bar-Nahum, I.; Tolman, W. B. *Inorg. Chim. Acta* **2008**, *361*, 885−893.

(16) Tolman, W. B. *Angew. Chem., Int. Ed.* **2010**, *49*, 1018−1024.

(17) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013−1045.

(18) Liu, C. W.; Hung, C.-M.; Chen, H.-C.; Wang, J.-C.; Keng, T.-C.; Guo, K. *Chem. Commun.* **2000**, 1897−1898.

(19) Lorenz, A.; Fenske, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 4402−4406.

(20) Strobel, S.; Schleid, T. *J. Solid State Chem.* **2003**, *171*, 424−428.

(21) Liu, C. W.; Hung, C.-M.; Santra, B. K.; Wang, J.-C.; Kao, H.-M.; Lin, Z. *Inorg. Chem.* **2003**, *42*, 8551−8556.

(22) Nitschke, C.; Fenske, D.; Corrigan, J. F. *Inorg. Chem.* **2006**, *45*, 9394−9401.

(23) Eichhöfer, A.; Olkowska-Oetzel, J.; Fenske, D.; Fink, K.; Mereacre, V.; Powell, A. K.; Buth, G. *Inorg. Chem.* **2009**, *48*, 8977−8984.

(24) Fu, M.-L.; Issac, I.; Fenske, D.; Fuhr, O. *Angew. Chem., Int. Ed.* **2010**, *49*, 6899−6903.

(25) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. V.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

(26) Kajita, Y.; Matsumoto, J.; Takahashi, I.; Hirota, S.; Funahashi, Y.; Ozawa, T.; Masuda, H. *Eur. J. Inorg. Chem.* **2008**, 3977−3986.

(27) Mazwell, L. R.; Mosley, V. M. *Phys. Rev.* **1940**, *57*, 21−23.

(28) Chen, J.-F.; Jin, Q.-Y.; Pan, Y.-L.; Zhang, Y.; Jia, D.-X. *Chem. Commun.* **2009**, 7212−7214.

(29) Yao, S.; Xiong, Y.; Zhang, X.; Schlangen, M.; Schwarz, H.; Milsmann, C.; Driess, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4551−4554.

(30) Cade, I. A.; Hill, A. F.; McQueen, C. M. A. *Organometallics* **2009**, *28*, 6639−6641.

(31) Adams, R. D.; Kwon, O.-S. *Inorg. Chem.* **2003**, *42*, 6175−6182.

(32) Kajita, Y.; Arii, H.; Saito, T.; Saito, Y.; Nagatomo, S.; Kitagawa, T.; Funahashi, Y.; Ozawa, T.; Masuda, H. *Inorg. Chem.* **2007**, *46*, 3322−3335.

(33) Helton, M. E.; Maiti, D.; Zakharov, L. N.; Rheingold, A. L.; Porco, J. A.; Karlin, K. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1138−1141.

(34) Brown, E. C.; Bar-Nahum, I.; York, J. T.; Aboelella, N. W.; Tolman, W. B. *Inorg. Chem.* **2007**, *46*, 486−496.

(35) Bar-Nahum, I.; York, J. T.; Young, J. V. G.; Tolman, W. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 533−536.