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Article

Crystal Structures of Triazine-3-thione Derivatives by Reaction with Copper and Cobalt Salts

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The reaction of 5-methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thione **L¹H₂OCH₃** with copper(II) chloride leads to the formation of an organic molecule **L²** containing two triazine rings linked by a new S–S bond. A binuclear copper(II) complex, **1**, containing **L¹** is also isolated. The reaction of **L¹H₂OCH₃** with copper(I) chloride yields a hexanuclear cluster of copper(I), **2**, in which the copper atoms form a distorted octahedron with the ligand **L¹** acting as an NS chelate and sulfur bridge, giving to the copper ion a trigonal geometry by one N and two S atoms. In any reaction of the disulfide **L²** with metal salts, complexes containing this molecule are isolated. Reactions with copper(I) and copper(II) chloride and nickel(II) and cadmium(II) nitrate produce the S–S bond cleavage, giving complexes containing the triazine **L¹** behaving as the NS anion, which show spectroscopic characteristics identical with those formed by reaction with **L¹H₂OCH₃**. However, the reaction with cobalt(II) nitrate gives a low-spin octahedral cobalt(III) complex, in which an asymmetric rupture of the disulfide **L²** has been produced, giving an unexpected complex with a new ligand and keeping the S–S bond.

Introduction

A great deal of the chemistry of metal thiolates involves thiolate as the terminal or bridging ligand. Thiolates can bond to only one metal,[1] bridging between two or three metals, to give binuclear, linear, or three-dimensional cluster compounds or high polymers, and the bridges can consist of one, three, or four thiolate S atoms.[2–6] S–S bond formation may occur in thiolate complexes with the reduction of some external oxidant or the metal, which hampers the synthesis of complexes with metals in their higher oxidation states.[7] Reactions of copper(II) with thiolates usually lead to reduction with the formation of RSSR and copper(I) species.[8] On the other hand, in some cases reactions with disulfides induce the reductive disulfide bond cleavage to give thiolate complexes.[9] Interconversion between disulfides RSSR and the corresponding 2RS⁻ is a very important redox process, involved in a wide variety of manmade functional materials and many biological systems,[10,11] although factors that control the biological RSSR/2RS⁻ interconversion are not well understood.

Current interest in developing the chemistry of multinuclear transition-metal complexes draws inspiration from two different fields such as chemistry of materials and bioinorganic chemistry. In several cases, nature has selected a mixed N/S coordination environment for the metal cofactor, including blue copper proteins, iron and cobalt nitrile hydratases, cytidine deaminase, bacteriophage T7 lysozyme, spinach carbonic anhydrase, alcohol dehydrogenase, and peptide deformylase,[12] so synthetic efforts have been applied

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(1) López-Torres, E.; Mendiola, M. A.; Rodríguez-Procopio, J.; Sevilla, M. T.; Colacio, E.; Moreno, J. M.; Sobrados, I. *Inorg. Chim. Acta* **2001**, *323*, 130–138.
(2) Golden, M. L.; Rampersad, M. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Chem. Soc., Chem. Commun.* **2003**, 1824–1825.
(3) Stange, A. F.; Klein, A.; Klinkhammer, K.-W.; Kaim, W. *Inorg. Chim. Acta* **2001**, *324*, 336–341.
(4) López-Torres, E.; Mendiola, M. A.; Pastor, C. J.; Pérez, B. S. *Inorg. Chem.* **2004**, *43*, 5222–5230.
(5) Gómez-Saiz, P.; García-Tojal, J.; Maestro, M. A.; Mahía, J.; Arnaiz, F. J.; Lezama, L.; Rojo, T. *Eur. J. Inorg. Chem.* **2003**, 2639–2650.
(6) Admas, R.; Miao, S. *Inorg. Chim. Acta* **2005**, *358*, 1401–1406.
(7) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121–185.
(8) McCleverty, J. A., Meyer, T. J., Eds. *Comprehensive Coordination Chemistry II*; Elsevier: Amsterdam, The Netherlands, 2004.
(9) Osako, T.; Ueno, Y.; Tachi, Y.; Itoh, S. *Inorg. Chem.* **2004**, *42*, 8087–8097.
(10) Patai, S., Ed. *The chemistry of thiol group*; John Wiley & Sons: London, 1984; Parts 1 and 2.
(11) Stiefel, E. I., Matsumoto, K., Eds. *Transition Metal Sulfur Chemistry*; American Chemical Society, Washington, DC, 1996.
(12) Chang, S.; Karambelkar, V. V.; Sommer, R. G.; Rheingold, A.; Goldberg, D. P. *Inorg. Chem.* **2002**, *41*, 239–248.

toward modeling of the active site of N,S-containing metalloproteins. One difficulty in handling alkylthiolate ligands includes their facile oxidation to disulfide products as well as their inherent propensity toward forming bridged polynuclear species. The only relatively easy syntheses are those of the neutral $[M^{II}N_2S_2]$ complexes, of which there are several examples, some of them published by us.[1,4,13]

In particular, multinuclear Cu^{II} complexes have been receiving considerable attention, and some recent successes include the synthesis of mixed N,S(alkylthiolate)−Cu^{II} complexes as the first models for blue copper proteins.[14,15] The flexibility of the coordination sphere around Cu^{II}, in combination with steric requirements and crystal packing forces, leads to structural diversity. The growing awareness of the involvement of cluster compounds at the active sites of biomolecules such as enzymes is another point of interest in multinuclear Cu^{II} complexes.[16,17] The chemistry of the cluster of Cu^{I} with S ligands is extremely important in life systems, and many technologies also utilize Cu^{I}−S clusters. Yet, the structure types, the bonding, and the cluster redox properties of Cu^{I}−S clusters are rather incompletely understood. It has been determined that yeast and mammalian metalloproteins (MT), proteins that contain a Cu^{I}−S cluster, function as antioxidants.[18] They can also be used as precursors for new functional materials[19] and heterogeneous catalysts.[20] There are few copper(I) thiosemicarbazone complexes structurally characterized, but different structures have been observed: monomeric, binuclear, tetranuclear, or hexanuclear clusters.[21−23]

Cu^{I}−Cu^{I} bonding interactions have widely been invoked to be a driving force for the self-assembly of Cu^{I} arrangements and to play an important role with regard to the photoluminescence of polynuclear Cu^{I} complexes containing phosphine or pyridine ligands. Weak but real d^{10}−d^{10} metal bonding is well established for second and third transition series metal complexes but, in the case of Cu^{I}, is unresolved.[24] Although an electron diffraction study on CuO_2 found evidence of Cu−Cu bonding,[25] several studies on

Chart 1. Drawing of **LH₂OCH₃**
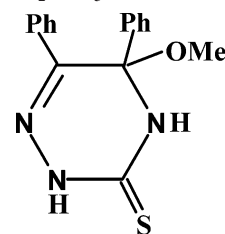
binuclear Cu^{I} complexes have denied the existence of Cu−Cu bonds.[26−28]

Reactions of 5-methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thione **L¹H₂OCH₃** (Chart 1) with divalent metal nitrates such as Co, Ni, Zn, Cd, Pb and some organotin(IV) compounds afforded complexes in which the ligand has lost the inserted OCH_3 group acting as a monoanion **L¹**.[29,30] Those complexes are NS chelates, besides in Zn, Cd, and Pb derivatives the S atom acts as a bridge, giving binuclear structures. Recently, we have observed different behavior in reactions with mercury nitrate and methylmercury chloride.[31] In both complexes, **L¹** acts as monodentate ligand by the S atom, giving a linear disposition for the Hg atom.

Following our interest in the reactivity of cyclic derivatives from benzil and thiosemicarbazide with transition-metal salts, which show variable oxidation states as well as a wide geometry and coordinative preferences, in this paper we report the structural characterization of compounds formed by the reaction of **L¹H₂OCH₃** with copper(II) and copper(I) chlorides and the reactivity of the new organic derivative **L²** with copper chlorides and cobalt(II), nickel(II), and cadmium(II) nitrates.

Experimental Section

Physical Measurements. Microanalyses were carried out using a Perkin-Elmer 2400 II CHNS/O elemental analyzer. IR spectra in the 4000−400-cm⁻¹ range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on Bruker AMX-300 and AMX-500 spectrophotometers using CDCl₃ and DMSO-d_6 as solvents and tetramethylsilane as the reference. Fast atom bombardment (FAB) mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzyl alcohol (*m*-NBA) as the matrix. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Bruker Reflex III mass spectrometer equipped with a nitrogen laser emitting at 337 nm, using ditranol as the matrix. Conductivity data were measured using freshly prepared *N,N*-dimethylformamide (DMF) solutions (ca. 10⁻³ M) at 25 °C with a Metrohm Herisau model E-518 instrument. Magnetic susceptibilities of powder samples were measured in the

(13) Calatayud, D. G.; López-Torres, E.; Mendiola, M. A.; Pastor, C. J.; Procopio, J. R. *Eur. J. Inorg. Chem.* **2005**, *21*, 4401−4409.
(14) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270−7271.
(15) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2000**, *122*, 6331−6332.
(16) Karlin, K.-D., Tyeklor, Z., Eds. *Bioinorganic Chemistry of Copper*; Chapman and Hall: New York, 1993.
(17) Pal, S.; Barik, A. K.; Gupta, S.; Hazra, A.; Kar, S. K.; Peng, S.-M.; Lee, G.-H.; Butcher, R. J.; El Fallah, M. S.; Ribas, J. *Inorg. Chem.* **2005**, *44*, 3880−3889.
(18) Liu, C. W.; Staples, R. J.; Fackler, J. P. *Coord. Chem. Rev.* **1998**, *174*, 147−177.
(19) Arnold, J. *Prog. Inorg. Chem.* **1995**, *43*, 353−418.
(20) Chiavelli, R. R.; Pecoraro, T. A.; Halbert, T. R.; Pan, W. H.; Stiefel, E. J. *J. Catal.* **1984**, *86*, 226−230.
(21) Lhuachan, S.; Siripaisarnpupat, S.; Chaichit, N. *Eur. J. Inorg. Chem.* **2003**, 263−267.
(22) Cowley, A. R.; Dilworth, J. R.; Donnelly, P. S.; Labisbal, E.; Sousa, A. *J. Am. Chem. Soc.* **2002**, *124*, 5270−5271.
(23) Asfield, L. J; Cowley, A. R.; Dilworth, J. R.; Donnelly, P. S. *Inorg. Chem.* **2004**, *43*, 4121−4123.
(24) Che, C.-M.; Mao, Z.; Miskowsky, V. M.; Tse, M.-C.; Chan, C.-K.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4084−4088.
(25) Zuo, J. M.; Kim, M.; O'Keefe, M.; Spence, J. C. H. *Nature* **1999**, *401*, 49−52.
(26) Cotton, F. A.; Feng, X.; Matusz, M.; Poli, R. *J. Am. Chem. Soc.* **1998**, *110*, 7077−7083.
(27) Poblet, J. M.; Bénard, M. *Chem. Commun.* **1998**, 1179−1180.
(28) Liu, C. W.; Irwin, M. D.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2004**, *357*, 3950−3956 and references cited therein.
(29) López-Torres, E.; Mendiola, M. A. *Polyhedron* **2005**, *24*, 1435−1444.
(30) López-Torres, E.; Mendiola, M. A.; Pastor, C. J.; Procopio, J. R. *Eur. J. Inorg. Chem.* **2003**, 2711−2717.
(31) López-Torres, E.; Mendiola, M. A.; Pastor, C. J. *Polyhedron* **2006**, in press.

range 2−293 K with a SQUID magnetometer (MPMS, Quantum Design) in a 1-T external magnetic field.

All reagents and other solvents were obtained from standard commercial sources and were used as received. CuCl was synthesized from copper sulfate pentahydrate and sulfur dioxide.

Preparation of 5-Methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, $L^1H_2OCH_3$.[32] Selected spectroscopic data: ^1H NMR (CDCl₃, 300 MHz, 25 °C) δ 9.5 (1H, NH, s), 7.6 (2H, Ph, m), 7.4 (2H, Ph, m), 7.3−7.1 (6H, Ph, m), 6.9 (1H, NH, s), 3.4 (3H, OCH₃, s); ^{13}C NMR (CDCl₃, 300 MHz, 25 °C) δ 169.7 (CS), 142.4 (CN), 141.7, 129.3, 133.7, 126.5 (Ph), 83.2 (CR₄), 50.7 (CH₃O); IR (KBr, cm⁻¹) 3184 (s) and 3131 (s) [ν(NH)], 1608 (w) [ν(C=N)], 1550 (s) [δ(NCS)], 846 (w) [ν(CS)].

Preparation of Bis[5,6-diphenyl-1,2,4-triazine]-3,3′-disulfide, L^2.[33] A solution of copper(II) chloride dihydrate (0.23 g, 0.70 mmol) in methanol (50 mL) was added to a solution of $L^1H_2OCH_3$ (0.41 g, 1.40 mmol) in methanol (50 mL). The mixture was stirred for 6 h at room temperature. The beige solid formed was filtered off, washed several times with methanol, and dried in vacuo; yield 45%; mp 205 °C; FAB⁺ (m/z) 529 ([C₃₀H₂₀N₆S₂ + 1]⁺, 100%); ^1H NMR (300 MHz, CDCl₃, 25 °C) δ 7.6−7.2 (Ph, m); ^{13}C NMR (300 MHz, CDCl₃, 25 °C) δ 167.8 (CS), 156.0, 155.3 (CN), 134.9, 134.8, 131.2, 129.9, 129.7, 128.7, 128.5 (Ph); IR (KBr, cm⁻¹) 1599 (w) and 1581 (w) [ν(C=N)], 1480 (s) [δ(NCS)], 866 (w) [ν(CS)]. Anal. Calcd for C₃₀H₂₀N₆S₂: C, 68.18; H, 3.79; N, 15.91; S, 12.12. Found: C, 67.82; H, 4.15; N, 15.85; S, 12.07.

Slow evaporation of the solid dissolved in toluene gave single crystals suitable for X-ray diffraction.

Preparation of $[Cu(L^1)_2]_2$, 1. The red solution obtained after discarding the disulfide was concentrated until a red solid appeared: yield 40%; mp 215 °C; Λ_M (DMF, Ω⁻¹ cm² mL⁻¹) 11; MALDI-TOF (m/z) 593.0 ([Cu(L¹)₂ + 1]⁺, a.i. 400), 919.0 ([Cu₂-(L¹)₃]⁺, a.i. 800); ^1H NMR (300 MHz, CDCl₃, 25 °C) δ 7.7−7.2 (Ph, m); IR (KBr, cm⁻¹) 1599 (w) and 1578 (w) [ν(C=N)], 1484 (s) [δ(NCS)], 819 [ν(CS)]. Anal. Calcd for Cu₂C₆₀H₄₀N₁₂S₄: C, 60.86; H, 3.38; N, 14.20; S, 10.82. Found: C, 60.82; H, 3.63; N, 14.65; S, 11.07.

A total of 0.052 g (0.1 mmol) of L^2 dissolved in methanol (20 mL) was treated with 0.034 g (0.20 mmol) of CuCl₂·2H₂O under several conditions: at room temperature, at room temperature with lithium hydroxide, under reflux, and under reflux in the presence of LiOH·H₂O. In all of the reactions, complex **1** was isolated, although with impurities of L^2 and other copper compounds.

Preparation of $[Cu(L^1)]_6$, 2. A total of 0.200 g (0.67 mmol) of $L^1H_2OCH_3$ was dissolved in methanol (30 mL), and 0.066 g (0.67 mmol) of CuCl was added under an argon atmosphere. The yellow mixture turned to red about 10 min later and was stirred at room temperature for 12 h. After that, the reddish solid was filtered off, washed with methanol, and vacuum-dried. The red solution was concentrated until more red solid was obtained: yield 70%; mp 250 °C (dec); Λ_M (DMF, Ω⁻¹ cm² mL⁻¹) 7; MALDI-TOF (m/z) 657.4 ([Cu₂(L¹)₂ + 1]⁺, a.i. 1450), 719.2 ([Cu₃(L¹)₂]⁺, a.i. 1200), 948.1 ([Cu₃(L¹)₃ + 1]⁺, a.i. 200), 1046.0 ([Cu₄(L¹)₃]⁺, a.i. 3400), 1375.0 ([Cu₅(L¹)₄]⁺, a.i. 2600), 1704.1 ([Cu₆(L¹)₅]⁺, a.i. 150); ^1H NMR (DMSO-d_6, 500 MHz, 25 °C) δ 7.3−7.5 (Ph, m); ^{13}C NMR (DMSO-d_6, 500 MHz, 25 °C) δ 164.6 (CS), 158.5, 153.8 (CN), 135.9, 135.6, 131.2, 130.1, 129.7, 129.4, 128.9, 128.8 (Ph); IR (KBr, cm⁻¹) 1599 (w) and 1578 (w) [ν(C=N)], 1487 (s) [δ(NCS)], and

(32) Franco, E.; López-Torres, E.; Mendiola, M. A.; Sevilla, M. T. *Polyhedron* **2000**, *19*, 441−451.

(33) Blanco, M. A.; López-Torres, E.; Mendiola, M. A.; Brunet, E.; Sevilla, M. T. *Tetrahedron* **2002**, *58*, 1525−1531.

808 [ν(CS)]. Anal. Calcd for Cu₆C₉₀H₆₀N₁₈S₆: C, 54.95; H, 3.43; N, 12.82; S, 9.77. Found: C, 54.63; H, 3.56; N, 13.02; S, 9.81.

Slow evaporation of a chloroform solution gave single crystals suitable for X-ray analysis.

The same complex was obtained from the disulfide L^2 under several conditions:

To a suspension of 0.052 g (0.10 mmol) of L^2 in methanol (20 mL) was added 0.020 g (0.20 mmol) of CuCl under an argon atmosphere. The mixture was stirred under reflux for 48 h. The red solution is concentrated until a red solid appears (yield 60%). For the same conditions but in the presence of 0.004 g (0.10 mmol) of LiOH·H₂O, the yield was 65%.

Preparation of $[Co(L^1S)_3]$, 3. A total of 0.020 g (0.064 mmol) of Co(NO₃)₂·6H₂O dissolved in ethanol (2 mL) was added over a suspension of 0.100 g (0.19 mmol) of L^2 and 0.010 g (0.19 mmol) of LiOH·H₂O in the same solvent (10 mL). The mixture was stirred under reflux for 7 days. Then the dark-green solid was filtered off, washed with methanol, and vacuum-dried: yield 68%; mp 198 °C; Λ_M (DMF, Ω⁻¹ cm² mL⁻¹) 4; FAB⁺ (m/z) 588 ([Co(L¹)₂ + 1]⁺, 20%), 620.0 ([Co(L¹)(L¹S) + 1]⁺, 25%), 650.9 ([Co(L¹S)₂]⁺, 30%), 851.0 ([Co(L¹)₃ + 1]⁺, 10%), 883.0 (Co(L¹)₂(L¹S) + 1]⁺, 29%), 914.9 ([Co(L¹)(L¹S)₂ + 1]⁺, 24%), 946.9 (Co(L¹S)₃ + 1]⁺, 5%); ^{13}C NMR (DMSO-d_6, 500 MHz, 25 °C) δ 184.2 (CS), 152.2, 153.2, 154.5 (CN), 135.0, 134.0, 133.6, 132.3, 130.1, 129.8, 128.8 (Ph); IR (KBr, cm⁻¹) 1598 (w) and 1577 (w) [ν(C=N)], 1508 (s) [δ(NCS)], 804 [ν(CS)]. μ_{eff} = 0 μ_B. Anal. Calcd for CoC₄₅H₃₀N₉S₆: C, 57.03; H, 3.17; N, 13.74; S, 20.28. Found: C, 57.25; H, 3.05; N, 13.54; S, 20.49.

Slow evaporation of a solution of the complex in DMF gave single crystals suitable for X-ray analysis.

Preparation of $[Ni(L^1)_2]$. A total of 0.055 g (0.19 mmol) of Ni(NO₃)₂·6H₂O dissolved in methanol (10 mL) was added over a suspension of 0.10 g (0.19 mmol) of L^2 and 0.008 g (0.19 mmol) of LiOH·H₂O in methanol (25 mL). The mixture was stirred under reflux for 12 h. Then the brown solid was filtered off, washed with methanol, and vacuum-dried: yield 32%; Λ_M (DMF, Ω⁻¹ cm² mL⁻¹) 11; MALDI-TOF (m/z) 587.0 ([NiL₂ + 1]⁺, a.i. 1900); IR (KBr, cm⁻¹) 1600 (w) and 1579 (w) [ν(C=N)], 1485 (s) [δ(NCS)], and 817 (w) [ν(CS)]. Anal. Calcd for NiC₃₀H₂₀N₆S₂: C, 61.36; H, 3.41; N, 14.32; S, 10.91. Found: C, 61.03; H, 3.52; N, 14.16; S, 10.87.

Preparation of $[Cd(L^1)_2H_2O]_2$. The synthesis was carried out following the same procedure as described that above but with 0.058 g (0.19 mmol) of Cd(NO₃)₂·4H₂O. The yellow solid was filtered off, washed with methanol, and vacuum-dried: yield 53%; Λ_M (DMF, Ω⁻¹ cm² mL⁻¹) 5; FAB⁺ (m/z) 643.0 ([CdL₂ + 1]⁺, 7%), 752.9 ([Cd₂L₂ − 1]⁺, 3%), 1017.9 ([Cd₂L₃]⁺, 15%); IR (KBr, cm⁻¹) 1600 (w) and 1573 (w) [ν(C=N)], 1490 (s) [δ(NCS)], 812 (w) [ν(CS)]; ^1H NMR (300 MHz, DMSO-d_6, 25 °C) δ 7.3−7.5 (Ph, m); ^{13}C NMR (300 MHz, DMSO-d_6, 25 °C) δ 128.3, 128.5, 128.8, 129.0, 129.6, 130.4, 135.6, 135.8 (Ph), 150.8, 155.1 (CN), 180.7 (CS). Anal. Calcd for C₃₀H₂₂N₆S₂OCd: C, 54.68; H, 3.34; N, 12.76; S, 9.72. Found: C, 54.92; H, 3.32; N, 13.05; S, 9.53.

X-ray Crystallography. Crystals of compounds were mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd., rotating-anode (Cu Kα radiation, λ = 1.541 78 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data of L^2 and complex **2** were collected at 100 K and those of complex **3** at 298 K, with a combination of six runs at different φ and 2θ angles, 3600 frames. The data were collected using 0.3° wide ω scans and a crystal-to-detector distance of 4.0 cm.

The substantial redundancy in data allows empirical absorption corrections (*SADABS*)[34] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum-to-maximum apparent transmission: 0.798 554 for the disulfide ligand **L²**, 0.837 882 for complex **2**, and 0.753 359 for complex **3**). The unit cell parameters were obtained by full-matrix least-squares refinements of 4286 reflections for the disulfide ligand, 6977 for complex **2**, and 28 079 for complex **3**.

The raw intensity data frames were integrated with the *SAINT*[35] program, which also applied corrections for Lorentz and polarization effects.

The software package *SHELXTL/PC*, version 6.14, package[36] was used for space group determination, structure solution, and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods (*SHELXS-97*),[37] completed with difference Fourier syntheses, and refined with full-matrix least squares using *SHELXL-97*,[38] minimizing $\omega(F_o{}^2 - F_c{}^2)^2$. Weighted R factors (R_w) and all goodness of fit values (S) are based on F^2; conventional R factors (R) are based on F. All non-H atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the *SHELXTL/PC*, version 6.14, program library. All of the H atoms were localized by electron densities, but only the H atoms bonded to chloroform in complex **2** were refined. All of the other H-atom parameters were calculated, and atoms were constrained as riding atoms, with U isotropic 20% larger than the corresponding C atoms for the phenyl H atoms. Anisotropic thermal parameters, H-atom parameters, and structure amplitudes are available as Supporting Information.
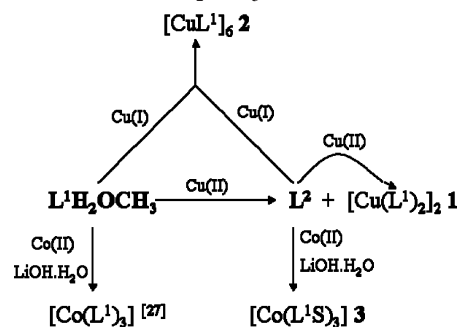
CCDC 279180 for **L²**, 279182 for complex **2**, and 279181 for complex **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (international) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

Results and Discussion

A summary of the studied reactions and the isolated compounds is presented in Scheme 1.

The reaction of the ligand **L¹H₂OCH₃** with CuCl₂·2H₂O leads to the formation of the organic molecule **L²**, whose analytical data indicate an empirical formula C₁₅H₁₀N₃S. From these data, it can be deduced that the molecule has lost the OCH₃ group, according to a mechanism previously published.[30] The FAB⁺ spectrum only shows a peak at 529.1 amu, the double of the empirical formula, corresponding to the molecular ion [**L²** + 1]⁺. For this molecular mass and from **L¹H₂OCH₃**, there are two possibilities: the opening and subsequent combination of two triazine rings forming a macrocycle or the formation of two triazines joined by a

(34) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction*, version 2.03; Universität Göttingen: Göttingen, Germany, 1997−2001.
(35) Sheldrick, G. M. *SAINT+NT, SAX Area-Detector Integration Program*; version 6.04; Bruker AXS: Madison, WI, 1997−2001.
(36) Sheldrick, G. M. *SHELXTL/PC*, version 6.14; Bruker Analytical X-ray Systems: Madison, WI, 2000.
(37) Sheldrick, G. M. SHELXS-97, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(38) *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.

Scheme 1. Reactions of **L¹H₂OCH₃** and **L²** with Cu and Co Salts

Chart 2. Proposed Structure for Complex **1**
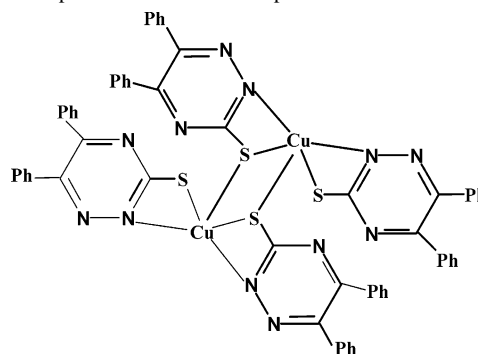
new S−S bond. The formation of disulfides by thiol oxidation is well documented, so the formation of this species is more probable than the macrocyclic one, as X-ray diffraction establishes.

In this reaction, the Cu^II complex **1** can also be isolated. Its analytical data correspond to the empirical formula C₃₀H₂₀N₆S₂Cu, so the OCH₃ group has also been lost. The MALDI-TOF spectrum shows a peak at *m/z* 593.0 corresponding to [Cu(**L¹**)₂ + 1]⁺ and a peak at *m/z* 919.0 corresponding to [Cu₂(**L¹**)₃]⁺, which indicates the presence of a dinuclear species. Experimental isotropic distribution shows the same pattern as the theoretical one for both peaks. Because of the fact that analytical data indicate the absence of chloride groups, if the complex contains two metal ions, it must contain four ligands to get the neutrality and one of them is lost to form a monopositive ion. The way to get a dinuclear species could be due to the formation of S bridges. The ligands would act as a bidentate NS and a bidentate NS and bridge via a S atom, as occurs in the complexes with other metals, such as Cd, Ni, and Pb,[29] giving a penta-coordinate geometry for the Cu ion (see Chart 2). The redox reaction in which the disulfide is obtained causes the formation of Cu^I, but in the presence of O₂, it is again oxidized to Cu^II, which forms complex **1**, as occurs in other cases described in the literature.[39,40]

On the other hand, the reaction of **L¹H₂OCH₃** with CuCl permits the synthesis of complex **2**, with ligand/metal ratio 1:1, where the ligand has lost the OCH₃ group and acts as a monoanion. The MALDI-TOF spectrum of complex **2**

(39) Ferrer, P. E. G.; Williams, A. M.; Castellano, E. C.; Piro, O. E. Z. *Anorg. Allg. Chem.* **2002**, *628*, 1979−1984.
(40) Itoh, S.; Nagagawa, M.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 4087−4088.

Figure 1. MALDI-TOF spectrum of complex **2**. Inset: isotopic pattern of the peak at 1375.0 amu.

(Figure 1) shows several peaks corresponding to different fragmentations of the cluster, because of the loss of Cu or **L¹**, although the peak corresponding to the molecular ion cannot be observed. Experimental isotropic distribution shows the same pattern as the theoretical one in every peak.

As the mass spectra have established, reactions between ligand **L¹** and CuCl₂·2H₂O lead to the formation of the Cuᴵᴵ complex **1**, as well as those with **L²**, although with impurities of other compounds. Thus, the S−S bond of ligand **L²** is reductively cleaved by the reaction with Cuᴵᴵ ions to generate the bis(thiolate)dicopper(II) complex. This reaction is favored by the strong Cuᴵᴵ−S bond and the disposition of the triazine rings and phenyl groups in the disulfide, which hinder the chelate behavior of the ligand, leading to the rupture of the S−S bond.

In the reaction of **L²** with CuCl, the Cuᴵ complex **2** is isolated as the sole reaction product. The rupture of the ligand can be explained in the same way as that for Cuᴵᴵ. In both reactions, a symmetric rupture of the disulfide ligand along the S−S bond has happened.

With cobalt(II) nitrate, the disulfide ligand **L²** yields complex **3**, with an empirical formula C₄₅H₃₀N₉S₆Co. This formula indicates an important change in the ligand composition (C₃₀H₂₀N₆S₂) and suggests that the Coᴵᴵ ion has been oxidized to Coᴵᴵᴵ. Oxidation of Coᴵᴵ salts in the presence of thiosemicarbazone ligands in ethanol, methanol, and chloroform is documented.[41−43] The possibility of oxidation increases with the presence of a basic medium. In fact, this reaction only takes place in the presence of LiOH·H₂O, which is not necessary in the reactions with Cu salts. From

the mother liqueur, an organic product was obtained and its spectroscopic data suggest that the triazine ring remains, but a OCH₃ group is bonded to the C initially joined to the S atom in **L²**. Measurements of magnetic susceptibility indicate that the complex is diamagnetic, which confirms the oxidation of the metal and the existence of a low-spin octahedral complex. In the FAB⁺ spectrum of complex **3** (Figure 2), a great number of peaks, corresponding to the loss of **L¹**, **L¹S**, S, and/or Co, can be observed. These fragments agree with a complex formed by three **L¹S** ligands bonded to one Coᴵᴵᴵ atom, with the peak at 946.9 amu being the molecular ion [Co(**L¹S**)₃ + 1]⁺. Experimental isotropic distribution shows the same pattern as the theoretical one in all of the peaks. In this case, the rupture of the disulfide **L²** is asymmetric, keeping the S−S bond, which is an unusual behavior for a disulfide molecule. To the best of our knowledge, this is the first time that this type of reaction is described. Therefore, the ligand bonded to the Co ion is **L¹S**. So, with cobalt nitrate, the complexes obtained from the ligands **L¹H₂OCH₃** and **L²** are different: with **L¹H₂OCH₃**, an octahedral complex of Coᴵᴵᴵ with the ligand **L¹** acting as a bidentate NS is obtained.[29]

This behavior differs with Cu salts, perhaps caused by a less stable Co−S bond together with the favorable octahedral arrangement for the Coᴵᴵᴵ complexes. This cleavage leads to a complex with greater stability, containing five-membered chelate rings, compared to four-membered ones.

With nickel and cadmium nitrates, two complexes with formulae [Ni(**L¹**)₂] and [Cd(**L¹**)₂H₂O]₂ are isolated. The formulae and spectroscopic data correspond to those complexes previously isolated from the ligand **L¹H₂OCH₃**,[29] so a symmetric rupture of the disulfide **L²** has occurred, as seen with Cu salts.

Crystallography. Crystallographic data of the compounds are summarized in Table 1.

(41) John, R. P.; Sreekanth, A.; Prathapachandra Kurup, M. R.; Mobin, S. M. *Polyhedron* **2002**, *21*, 2515−2521.
(42) Sau, D. K.; Butcher, R. J.; Chaudhuri, S.; Saha, N. *Polyhedron* **2004**, *23*, 5−14.
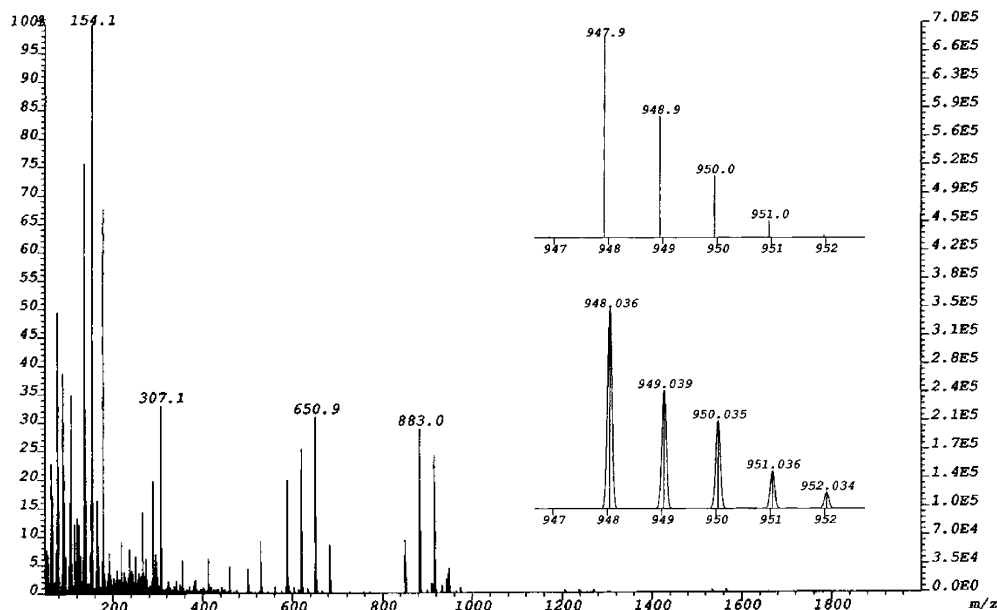(43) Saha, N. C.; Butcher, R. J.; Chaudhuri, S. *Polyhedron* **2003**, *22*, 383−390.

Figure 2. FAB$^+$ spectrum of complex **3**. Inset: isotopic pattern of the molecular ion.

Table 1. Crystal Data and Structure Refinement for **L**^{2} and Complexes **2** and **3**

	L^2	**2**	**3**
formula	$C_{30}H_{20}N_6S_2$	$C_{92}H_{62}N_{18}S_6Cl_6Cu_6$	$C_{45}H_{30}N_9S_6Co$
fw	528.64	2205.90	948.07
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Pbca$
a/Å	5.85400(10)	12.8145(3)	18.4406(3)
b/Å	11.5205(3)	14.1021(4)	20.4177(3)
c/Å	19.5150(4)	15.8709(4)	23.5628(3)
α/deg	95.7120(10)	115.896(2)	90
β/deg	93.817(2)	104.918(2)	90
γ/deg	101.781(2)	95.854(2)	90
V/Å^3	1276.88(5)	2416.06(11)	8871.7(2)
Z	2	1	8
D_c/Mg m^{-3}	1.375	1.516	1.420
abs coeff/mm^{-1}	2.144	4.615	6027
$F(000)$	548	112	3888
GOF on F^2	1.042	0.935	1.028
reflns collected	8040	17934	54959
independent reflns	4213 [R(int) = 0.0359]	8280 [R(int) = 0.0476]	8370 [R(int) = 0.0451]
final R1, wR2 [$I > 2\sigma(I)$]	0.0626, 0.1716	0.0464, 0.1080	0.0455, 0.1206
R indices (all data)	0.0748, 0.1840	0.0668, 0.1167	0.0584, 0.1297

The crystal structure of **L**^{2} consists of discrete molecules of $C_{30}H_{20}N_6S_2$. Each unit is formed by two rings of 5,6-diphenyl-3-thione-1,2,4-triazine linked by a S−S bond (Figure 3), which agrees with the spectroscopic data but rules out the structure previously proposed for this ligand.[33] The molecule has a syn conformation with respect to the S−S bond. The S−S bond distance is 2.043 Å, and the C−S−S−C torsion angle has a value of 73.58°, which are within the range expected for this type of compound.[44] Bond distances and angles in both triazine rings are almost identical (Table 2).

After loss of a methanol molecule, all C−N bond distances are very similar, which did not occur in the precursor molecule **L**^{1}**H$_2$OCH$_3$**, and have values between single and double bonds; as occurs with the N−N bond distances,[45] the C−C bond distance is much shorter than that in **L**^{1}**H$_2$OCH$_3$**.

These data indicate a strong electronic delocalization in the triazine rings. The C−S bond distances are closer to the value accepted for a single bond, as should be expected after the formation of the S−S bond. The strong electronic delocalization in both triazine rings gives them an aromatic character so that stabilizes the new disulfide molecule.

Both triazine ligands can be considered planar, with a maximum deviation of 0.044 Å for C3 and 0.038 Å for C17. S1 is 0.0084 Å above and S2 0.038 Å below these planes. The phenyl rings form, with respect to the triazine ligands, dihedral angles of 60.20° for C4−C9, 30.75° for C10−C15, 35.98° for C19−C24, and 55.88° for C25−C30.

In the triazines, bond distances and angles are close to 120°, which indicates sp^2 hybridization. In the ligand **L**^{1}**H$_2$OCH$_3$**, the angle of the C atom with the OCH$_3$ group has a value of 108.5°, corresponding to sp^3 hybridization.

(44) Delgado, E.; Hernández, E.; Mansilla, N.; Zamora, F.; Martínez-Cruz, L. F. *Inorg. Chim. Acta* **1999**, *284*, 14−19 and references cited therein.

(45) Sutton, E. *Tables of Interatomic Distances, Configuration in Molecules and Ions (Supplement)*; The Chemical Society: London, 1965.
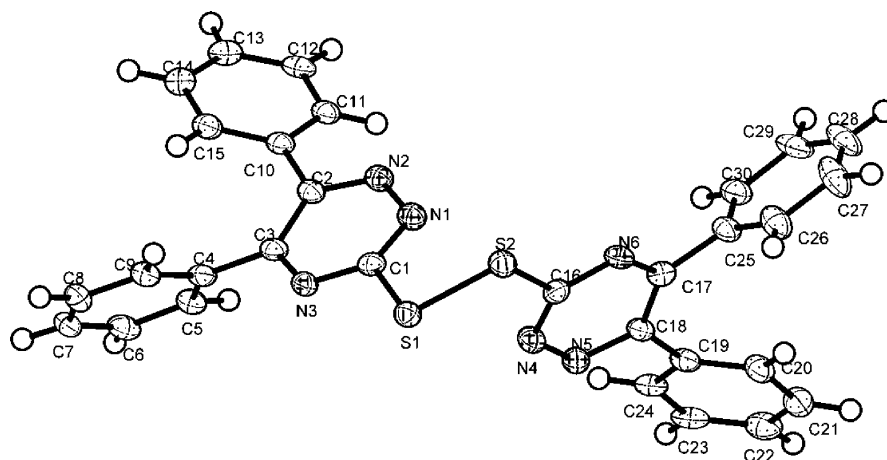
Figure 3. Molecular structure of **L²**. Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Distances and Angles for **L²**

C1−N1	1.326(4)	C16−N6	1.340(4)
C1−N3	1.335(4)	C16−S2	1.781(3)
C1−S1	1.776(3)	C17−N6	1.331(4)
C2−N2	1.331(4)	C17−C18	1.419(5)
C2−C3	1.427(4)	C18−N5	1.345(4)
C2−C10	1.486(4)	N1−N2	1.345(4)
C3−N3	1.328(4)	N4−N5	1.336(4)
C3−C4	1.487(4)	S1−S2	2.0335(11)
C16−N4	1.322(4)		
N1−C1−N3	127.5(3)	N6−C17−C25	116.5(3)
N1−C1−S1	120.3(2)	C18−C17−C25	123.7(3)
N3−C1−S1	112.0(2)	N5−C18−C17	119.6(3)
N2−C2−C3	119.8(3)	N5−C18−C19	114.5(3)
N2−C2−C10	115.2(3)	C17−C18−C19	125.9(3)
C3−C2−C10	124.9(3)	C1−N1−N2	116.3(3)
N3−C3−C2	119.3(3)	C2−N2−N1	120.5(3)
N3−C3−C4	116.3(3)	C3−N3−C1	115.9(3)
C2−C3−C4	124.5(3)	C16−N4−N5	116.8(3)
N4−C16−N6	127.5(3)	N4−N5−C18	120.4(3)
N4−C16−S2	119.9(2)	C17−N6−C16	115.6(3)
N6−C16−S2	112.6(2)	C1−S1−S2	102.66(11)
N6−C17−C18	119.7(3)	C16−S2−S1	102.69(11)

The molecules are linked together by $\pi-\pi$ interactions between the phenyl rings, with a distance of 3.613 Å.

The structure of complex **2** contains two molecules of chloroform. One of them is included in the model, and the other one is grossly disordered, which could not be modeled satisfactorily. The contribution from this solvent molecule was removed from the observed data using SQUEEZE in the software program *PLATON*,[46] and the atom count from this CHCl₃ is included in the empirical formula. This procedure has been previously reported for other inorganic neutral complexes.[47]

The molecular structure is shown in Figure 4, and selected bond distances and angles are summarized in Table 3. The crystal structure consists of hexanuclear units of [CuL¹]₆, where the six Cuᴵ atoms form a distorted octahedron (Figure 5). The complex is centrosymmetric, with the inversion point located at the center of the Cu₆ octahedron. In the complex, the Cuᴵ ions are three-coordinate by one N and two S atoms

(46) Spek, A. L. *PLATON*; The University of Utrecht: Utrecht, The Netherlands, 2004.
(47) Arnanz, A.; Marcos, M.-L.; Moreno, C.; Farrar, F. H.; Lough, A. J.; Yu, J. O.; Delgado, S.; González-Velasco, J. *J. Organomet. Chem.* **2004**, *689*, 3218−3231.

Table 3. Selected Bond Distances and Angles for Complex **2**[a]

Cu1−N4	1.994(3)	C2−C3	1.496(6)
Cu1−S1	2.2360(12)	C9−C10	1.478(6)
Cu1−S3	2.2735(11)	C16−N4	1.340(5)
Cu2−N1	1.977(4)	C16−N6	1.343(5)
Cu2−S2	2.2456(13)	C17−N5	1.342(6)
Cu2−S3#1	2.2555(11)	C17−C24	1.425(6)
Cu3−N7	1.996(3)	C17−C18	1.481(6)
Cu3−S1#1	2.2161(11)	C24−C25	1.482(6)
Cu3−S2	2.2487(11)	C31−N7	1.340(5)
S1−C1	1.761(4)	C31−N9	1.343(5)
S1−Cu3#1	2.2161(11)	C32−N9	1.332(6)
S2−C16	1.760(4)	C32−C39	1.433(6)
S3−C31	1.751(4)	C32−C33	1.479(6)
S3−Cu2#1	2.2555(11)	C39−N8	1.324(5)
C1−N3	1.333(6)	C39−C40	1.487(6)
C1−N1	1.341(5)	N1−N2	1.340(5)
C2−N2	1.328(6)	N4−N5	1.345(5)
C2−C9	1.421(6)	N7−N8	1.336(5)
N4−Cu1−S1	129.45(11)	N5−C17−C24	119.6(4)
N4−Cu1−S3	114.41(11)	N5−C17−C18	114.4(4)
S1−Cu1−S3	111.79(4)	C24−C17−C18	126.0(4)
N1−Cu2−S2	125.63(10)	N6−C24−C17	119.8(4)
N1−Cu2−S3#1	124.15(11)	N6−C24−C25	116.0(4)
S2−Cu2−S3#1	106.70(4)	C17−C24−C25	124.2(4)
N7−Cu3−S1#1	125.53(10)	N7−C31−N9	122.5(4)
N7−Cu3−S2	110.94(10)	N7−C31−S3	117.3(3)
S1#1−Cu3−S2	117.45(4)	N9−C31−S3	120.2(3)
C1−S1−Cu3#1	104.54(13)	N9−C32−C39	118.2(4)
C1−S1−Cu1	106.23(15)	N9−C32−C33	117.0(4)
Cu3#1−S1−Cu1	88.64(4)	C39−C32−C33	124.7(4)
C16−S2−Cu2	107.31(15)	N8−C39−C32	119.2(4)
C16−S2−Cu3	99.01(13)	N8−C39−C40	114.7(3)
Cu2−S2−Cu3	93.24(4)	C32−C39−C40	126.1(4)
C31−S3−Cu2#1	106.97(14)	N2−N1−C1	117.5(3)
C31−S3−Cu1	101.98(13)	N2−N1−Cu2	122.3(3)
Cu2#1−S3−Cu1	100.08(4)	C1−N1−Cu2	120.1(3)
N3−C1−N1	123.9(4)	C2−N2−N1	119.9(4)
N3−C1−S1	117.7(3)	C1−N3−C9	117.4(4)
N1−C1−S1	118.4(3)	C16−N4−N5	119.1(3)
N2−C2−C9	119.7(4)	C16−N4−Cu1	121.5(3)
N2−C2−C3	115.1(4)	N5−N4−Cu1	118.9(3)
C9−C2−C3	125.1(4)	C17−N5−N4	119.6(4)
N3−C9−C2	117.8(4)	C24−N6−C16	117.4(4)
N3−C9−C10	115.5(4)	N8−N7−C31	119.0(3)
C2−C9−C10	126.6(4)	N8−N7−Cu3	120.5(3)
N4−C16−N6	124.3(4)	C31−N7−Cu3	120.2(3)
N4−C16−S2	118.1(3)	C39−N8−N7	119.5(3)
N6−C16−S2	117.6(3)	C32−N9−C31	117.8(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, −x + 2, −y, −z + 1.

in a trigonal arrangement. There is no formal Cu−Cu bonding, although metal−metal interactions are clearly
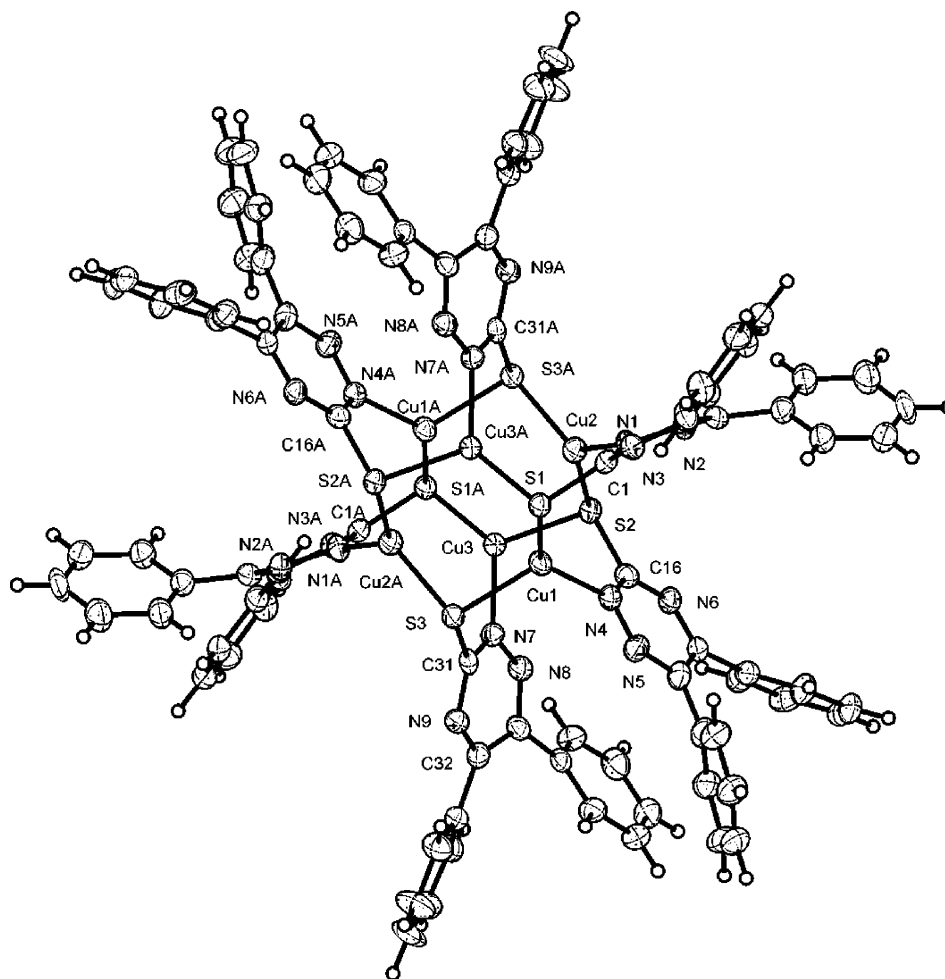
Figure 4. Molecular structure of complex **2**. Thermal ellipsoids are shown at 50% probability. CHCl₃ molecules are omitted for clarity.
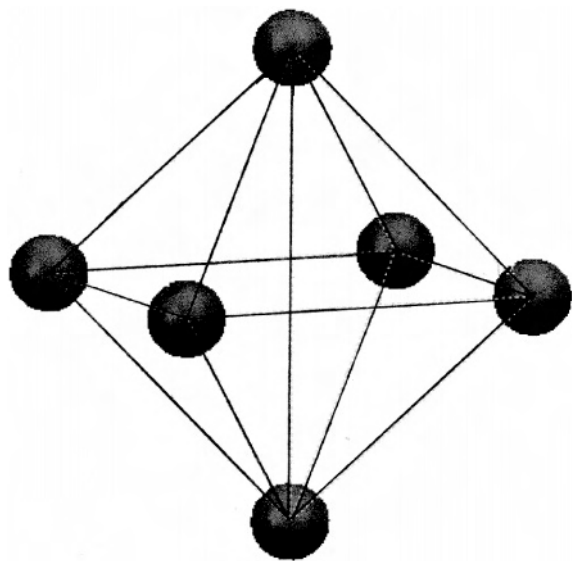
Figure 5. Cu atom arrangement in complex **2** generated with Mercury 1.4 from the crystal structure.

present, with Cu···Cu distances of 2.8125, 2.9777, and 3.0056 Å. The S atoms are also in an octahedral arrangement, although it is more distorted than the one of the Cu atoms.

The NS bidentate ligand forms S atom bridges between two Cu atoms. The ligand upon coordination is evident in the observed bond lengths in the cluster. The C—S bond

distances increase from 1.628 Å in **L¹H₂OCH₃** to 1.751, 1.760, and 1.761 Å in complex **2**, and there is also a decrease in the C—N bond lengths. The coordination mode of the ligand affords six four-membered chelate rings, and the triazine rings are almost planar. In the complex, owing to the deprotonation, there is a considerable electronic delocalization through the thiosemicarbazone backbone. As a consequence, all of the C—N bonds have almost the same length (Table 3), which does not occur in **L¹H₂OCH₃** (1.28–1.459 Å). In the complex, N—N bond distances are intermediate between the theoretical single and double bonds.[45] In addition, the N—C—C angles are close to 120°, as would be expected for sp² hybridization, while in **L¹H₂OCH₃**, they are 108°, corresponding to sp³ hybridization.

There are three types of π–π interactions between the phenyl rings, with values of 3.445, 3.483, and 3.483 Å. The Cu···Cu distance of 10.038 Å between two adjacent molecules indicates that there is no intermolecular Cu···Cu interaction.

Selected bond distances and angles of complex **3** are listed in Table 4. The complex is formed by discrete units of [Co(**L¹S**)₃], where the Co^{III} ion is hexacoordinate with a N₃S₃ environment, in a not very distorted octahedral arrangement (Figure 6), as can be observed in the bond distances and angles.

Table 4. Selected Bond Distances and Angles for Complex **3**

Co1−N7	1.946(2)	S6−C31	1.721(3)
Co1−N4	1.956(2)	C1−N3	1.331(3)
Co1−N1	1.973(2)	C1−N1	1.340(4)
Co1−S5	2.2098(8)	C2−N3	1.320(4)
Co1−S1	2.2277(9)	C2−C9	1.424(4)
Co1−S3	2.2327(9)	C9−N2	1.317(3)
S1−S2	2.0665(11)	C16−N4	1.330(4)
S2−C1	1.732(3)	C16−N6	1.343(4)
S3−S4	2.0544(13)	C17−N6	1.329(4)
S4−C16	1.731(3)	C17−C24	1.426(4)
S5−S6	2.0611(13)	C24−N5	1.324(3)
C31−N9	1.339(4)	C39−N9	1.312(4)
C31−N7	1.342(4)	N1−N2	1.336(3)
C32−N8	1.315(4)	N4−N5	1.338(3)
C32−C39	1.429(4)	N7−N8	1.338(3)
N7−Co1−N4	91.41(10)	N6−C16−S4	114.5(2)
N7−Co1−N1	90.95(9)	N6−C17−C24	118.9(3)
N4−Co1−N1	91.10(9)	N6−C17−C18	115.3(3)
N7−Co1−S5	91.68(7)	C24−C17−C18	125.8(3)
N4−Co1−S5	91.89(7)	N5−C24−C17	119.8(3)
N1−Co1−S5	175.97(7)	N5−C24−C25	114.2(3)
N7−Co1−S1	93.64(7)	C17−C24−C25	125.9(2)
N4−Co1−S1	174.59(7)	N9−C31−N7	123.9(3)
N1−Co1−S1	90.75(7)	N9−C31−S6	115.1(2)
S5−Co1−S1	86.04(3)	N7−C31−S6	121.0(2)
N7−Co1−S3	174.91(7)	N8−C32−C39	120.0(3)
N4−Co1−S3	91.40(7)	N8−C32−C33	114.1(3)
N1−Co1−S3	93.24(7)	C39−C32−C33	125.9(3)
S5−Co1−S3	83.99(3)	N9−C39−C32	119.6(3)
S1−Co1−S3	83.42(4)	N9−C39−C40	117.7(3)
S2−S1−Co1	100.49(4)	C32−C39−C40	122.7(3)
C1−S2−S1	102.34(10)	N2−N1−C1	118.2(2)
S4−S3−Co1	100.84(4)	N2−N1−Co1	119.18(17)
C16−S4−S3	102.71(12)	C1−N1−Co1	122.34(18)
S6−S5−Co1	101.26(4)	C9−N2−N1	119.7(2)
C31−S6−S5	102.50(11)	C2−N3−C1	117.4(2)
N3−C1−N1	124.5(2)	C16−N4−N5	118.7(2)
N3−C1−S2	114.4(2)	C16−N4−Co1	122.85(19)
N1−C1−S2	121.0(2)	N5−N4−Co1	118.29(18)
N3−C2−C9	118.9(2)	C24−N5−N4	120.4(2)
N3−C2−C3	115.9(3)	C17−N6−C16	117.9(3)
C9−C2−C3	125.1(3)	N8−N7−C31	118.8(2)
N2−C9−C2	120.2(2)	N8−N7−Co1	117.55(17)
N2−C9−C10	115.0(2)	C31−N7−Co1	123.1(2)
C2−C9−C10	124.8(2)	C32−N8−N7	120.0(2)
N4−C16−N6	124.1(3)	C39−N9−C31	117.8(3)
N4−C16−S4	121.4(2)		

Of the two possible isomers, the complex shows a *fac* disposition, with the N atoms in front of the S atoms. The aromatic rings are placed toward the same place, as occurs with the S atoms. The S atoms bonded to the Co ion are in the corners of a 3-Å-sided triangle. The complex presents a basket-type shape.

In the ligand, there is a S−S bond, as occurs in the free ligand **L²**, although in the complex, these distances are slightly longer than those in **L²**. The coordination mode of the ligand affords three five-membered chelate rings. Bond distances and angles in the triazine rings are very similar and indicate a great electronic delocalization, which is reflected in the similar values found in the C−N bond distances. Moreover, they can be considered planar with maximum deviations of 0.055 Å for C2, 0.022 Å for N4, and 0.002 Å for N8.

The C−S bond distances are closer to the value expected for a single bond and are shorter than those in **L²**, and the S−S ones are similar to those found in other compounds described in the literature.[9,39]

The aromatic rings form, with respect to the triazine rings, dihedral angles of 34.32° for C3−C8, 54.67° for C10−C15, 138.21° for C18−C23, 128.69° for C25−C30, 134.61° for C33−C38, and 131.60° for C40−C45.

There are two types of $\pi-\pi$ interactions between the phenyl rings with distances of 3.541 and 3.880 Å.

IR Spectroscopy. The IR spectrum of **L¹H₂OCH₃** is reported in the Experimental Section. The absence of any band in the 2600-cm⁻¹ region in any complex suggests the absence of any thiol tautomer.[48] In the spectra of the disulfide **L²** and all of the complexes, there are no bands in the 3000−3300-cm⁻¹ region, which indicates the absence of N−H bonds. Moreover, bands attributable to the nitrate group in complex **3** are not observed.[49] The absence of these bands confirms that the ligand acts as a monoanion in all of the complexes. The band corresponding to the CS moiety is shifted to lower frequencies, indicating coordination of the S atom to the metal ion. The presence of two bands attributable to C=N bonds could indicate the formation of a new imine group, due to the loss of the OCH₃ group of the ligand **L¹H₂OCH₃**, although the great electronic delocalization in the ring probably leads to there being only one C=N band and the new band could be due to the hydrazinic CN. These imine N atoms are noncoordinate to the metal ion.

NMR Spectroscopy. The NMR assignments for **L¹H₂-OCH₃** and its derivatives are listed in the Experimental Section. The ¹H NMR spectra of the ligand **L²** and all of the complexes only show a multiplet in the aromatic region, corresponding to the phenyl rings of the ligand. The absence of any signal corresponding to amine protons supports the ligand deprotonation. The absence of the singlet attributable to the OCH₃ group at 3.4 ppm confirms the loss of the inserted OCH₃ group and the formation of a new C=N bond.

In all of the ¹³C NMR spectra, the signals corresponding to the OCH₃ group and the tetrasubstituted C atom have disappeared and a new signal corresponding to an imine group is observed. In the spectra of all of these complexes, it can be observed that the imine groups are not bonded to the metal ion, as the X-ray diffraction has established, and that the signal corresponding to the thione group is deshielded, suggesting the presence of metal−S bonds.

The ¹³C NMR spectrum of complex **3** shows one signal corresponding to CS groups, three to CN, and seven to aromatic C atoms. Two isomers of octahedral complexes with asymmetric chelating ligands are possible. In the *fac* isomer, the A end of each ligand is trans to a B end, and the three ligands are equivalent. In the *mer* form, which has a triple statistical probability, two of the A ends are trans to each other, and all three ligands are chemically distinct.[50] Thus, if there is an isomer mixture, four sets of C resonances must be observed, while if only the *fac* isomer is present, we would

(48) Fenton, D. E.; Cook, D. H.; Nowell, I. W. *J. Chem. Soc., Chem. Commun.* **1977**, 274−275.
(49) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997.
(50) Ebsworth, E. A. V., Rankin, D. W. H., Cradock, S., Eds. *Structural Methods in Inorganic Chemistry*; Blackwell Scientific Publications: Oxford, U.K., 1987.
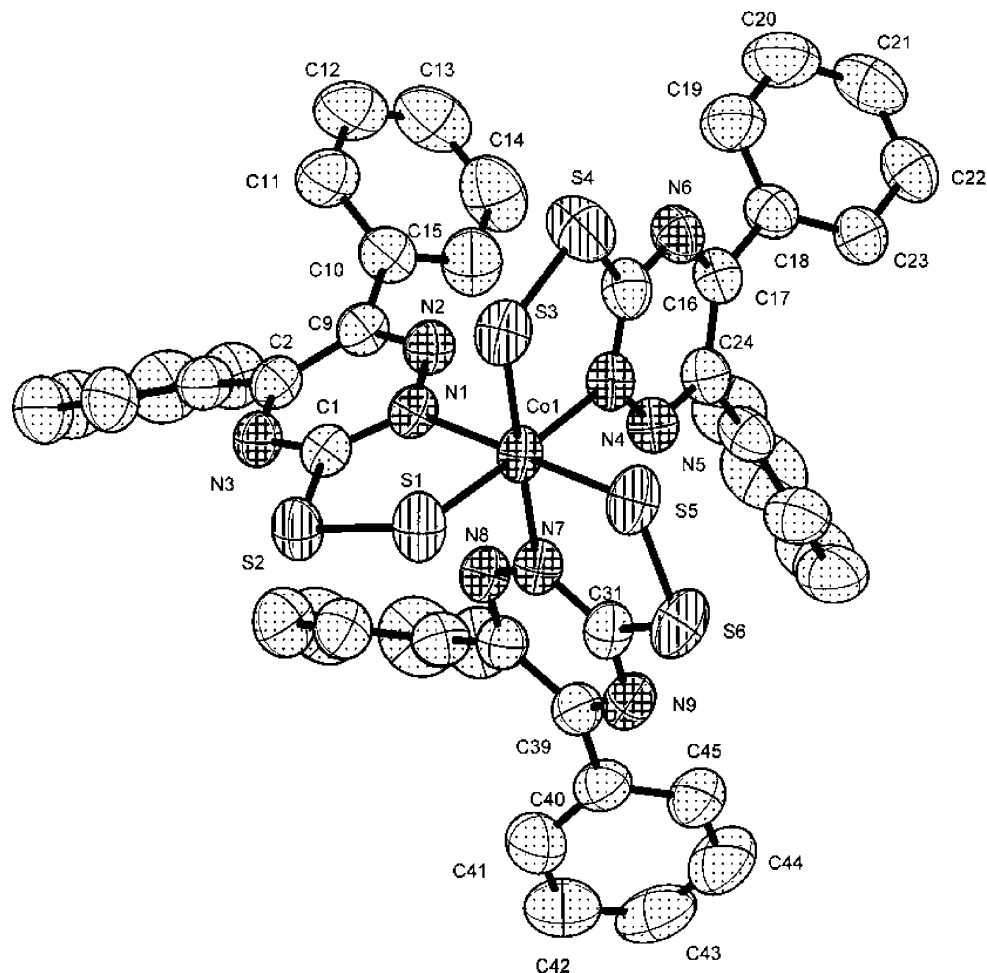
Figure 6. Molecular structure of complex **3**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity.

only see one set, as is observed, so we can establish that we have the *fac* isomer.

Conclusions

The reaction of **L¹H₂OCH₃** with copper(II) chloride leads to the formation of the organic molecule **L²** containing a S−S bond linking two triazine units, as well as a Cu^II complex containing **L¹** acting as an anion. However, in the reaction with copper(I) chloride, a hexanuclear Cu^I complex is obtained. The different results are related to the facile oxidation of **L¹H₂OCH₃** in the presence of Cu^II, whereas this reaction is not possible with Cu^I.

We have studied the reactivity of the new disulfide with copper chlorides and some nitrates such as cobalt(II), nickel-(II), and cadmium(II). In any reaction, complexes containing **L²** are obtained, probably because of the important steric requirements of the two triazine and four phenyl rings acting as chelate ligands. Reactions with Cu^I, Cu^II, Ni^II, and Cd^II give complexes in which the S−S bond has disappeared and where the ligand is **L¹** acting as in those complexes prepared from **L¹H₂OCH₃**. The reaction with Co^II leads to a Co^III complex in which the disulfide has suffered an asymmetric rupture along a C−S bond while keeping the S−S bond, with this being the first time that this behavior is described; therefore, **L¹S** is the ligand coordinated to the Co atom.

In every complex, **L¹** and **L¹S** act as NS bidentate ligands, giving four- and five-membered chelate rings, respectively. The structure of the complexes is determined by the structural preferences of the metal ions, as well as by the ligand configuration. Complex **1** consists of binuclear species, in which the S atom of two thiosemicarbazone ligands acts as a bridge between the Cu ions. Complex **2** is a hexanuclear cluster where each Cu^I ion is bonded to one N and two S atoms in trigonal geometry. Complex **3** is a monomeric structure where the Co^II ion has been oxidized to Co^III. The metal octahedral N_3S_3 arrangement is formed by three unexpected **L¹S** ligands. In this case, the complexes obtained from **L¹H₂OCH₃** and **L²** are different.