Inorg. Chem. **2001,** *40,* 6684−6693

Crystal and Solution Structures of *N,N*-Dimethylthioformamide-Solvated Copper(I), Silver(I), and Gold(I) Ions Studied by X-ray Diffraction, X-ray Absorption, and Vibrational Spectroscopy

Christina M. V. Stålhandske,[†] Claes I. Stålhandske,[‡] Ingmar Persson,*[,†] Magnus Sandström,*[,§] and Farideh Jalilehvand[||]

Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015,
SE-750 07 Uppsala, Sweden, Inorganic Chemistry 2, Chemical Center, Lund University,
P.O. Box 124, SE-221 00 Lund, Sweden, Department of Structural Chemistry,
University of Stockholm, SE-106 91 Stockholm, Sweden, and Department of Chemistry,
Stanford University, Stanford, California 94305-5080

Received February 27, 2001

Crystal structures of the solvated copper(I) and silver(I) perchlorate salts crystallizing from *N,N*-dimethylthioformamide solution have been determined by single-crystal X-ray diffraction at 295 K. Tetrakis(*N,N*-dimethylthioformamide)copper(I) perchlorate, $[\mathrm{Cu(SCHN(CH_3)_2)_4}]\mathrm{ClO_4}$, crystallizes in the monoclinic space group $P2/n$ (No. 13) with $a = 8.428(2)$, $b = 9.605(2)$, and $c = 15.096(3)$ Å, $\beta = 104.35(2)°$, and $Z = 2$. The copper(I) ion in a site of C_2 symmetry coordinates four *N,N*-dimethylthioformamide ligands in a slightly distorted tetrahedral coordination with Cu−S bond distances of 2.3249(8) and 2.3494(8) Å. The triclinic ($P\bar{1}$, No. 2) tris(*N,N*-dimethylthioformamide)silver(I) perchlorate, $\mathrm{Ag(SCHN(CH_3)_2)_3ClO_4}$, with $a = 7.4149(5)$, $b = 7.7953(5)$, and $c = 17.1482(1)$ Å, $\alpha = 98.341(5)$, $\beta = 93.910(5)$, and $\gamma = 107.084(5)°$, and $Z = 2$, contains centrosymmetric $\mathrm{Ag_2(SCHN(CH_3)_2)_6}^{2+}$ dimers in which two almost planar $\mathrm{AgS_3}$ units are held together by an asymmetric double sulfur bridge with one short and one long Ag−S bond, 2.529(1) and 2.930(1) Å, respectively. The Ag−S bond distances to the two terminal *N,N*-dimethylthioformamide ligands are 2.469(1) and 2.543(1) Å. The solvated copper(I) and silver(I) ions in solution were found by means of large-angle X-ray scattering (LAXS) to coordinate four *N,N*-dimethylthioformamide molecules with the mean Cu−S and Ag−S bond distances 2.36(1) and 2.58(1) Å, respectively, probably with distorted tetrahedral coordination geometry, while an EXAFS study gave the Cu−S bond distance 2.34(1) Å. EXAFS studies showed a linear S−Au−S entity with an Au−S bond distance of 2.290(5) Å in the structure of the solid bis(*N,N*-dimethylthioformamide)gold(I) tetrafluoroborate, $\mathrm{Au(SCHN(CH_3)_2)_2BF_4}$. The structure in solution is similar with a mean Au−S bond distance of 2.283(4) Å. Raman and infrared vibrational spectra of the solvated copper(I), silver(I), and gold(I) ions in the solid state and *N,N*-dimethylthioformamide solution have been recorded and assigned.

Introduction

Coordination compounds of the d^{10} ions copper(I), silver(I), and gold(I) of group 11 are strongly dominated by two- (linear), three- (trigonal), and four-coordination (tetrahedral), and higher coordination numbers occur only rarely.[1,2] In many cases, the primary coordination number is lower than that sterically possible, indicating a strongly covalent bonding character. The copper(I),[3] silver(I),[4−8] and gold(I) ions[9] are four-coordinated in oxygen and nitrogen donor solvents, as well as the copper(I) and silver(I) ions in the sulfur donor solvent tetrahydrothiophene.[3,10] However, their solid solvates crystallizing from saturated solutions sometimes display lower coordination numbers.[11−13]

A limited number of two-coordinated linear copper(I) complexes has been reported,[14−19] with mean Cu−S bond distances

---

[†] Swedish University of Agricultural Sciences.

[‡] Lund University.

[§] University of Stockholm.

[||] Stanford University.

(1) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday: A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, G. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. The Cambridge Crystallographic Data Centre: computer-based search, retrieval, analysis and display of information. *Acta Crystallogr., Sect. B* **1979**, *35*, 2331 and references therein.

(2) *Inorganic Crystal Structure Database*, release 98/1; Gmelin Institut, Fachinformationzentrum: Karlsruhe, Germany, 1998.

(3) Persson, I.; Penner-Hahn, J. E.; Hodgson, K. O. *Inorg. Chem.* **1993**, *32*, 2, 2497.

(4) Yamaguchi, T.; Johansson, G.; Holmberg, B.; Maeda, M.; Ohtaki, H. *Acta Chem. Scand., Ser. A* **1984**, *38*, 437.

(5) Sandström, M.; Neilson, G. W.; Johansson, G.; Yamaguchi, T. *J. Phys. C* **1985**, *18*, L1115.

(6) Gaizer, F.; Johansson, G. *Acta Chem. Scand., Ser. A* **1988**, *42*, 259.

(7) Hultén, F.; Persson, I. *Acta Chem. Scand., Ser. A* **1987**, *41*, 87.

(8) Nilsson, K.; Persson, I. *Acta Chem. Scand., Ser. A* **1987**, *41*, 139.

(9) Ahrland, S.; Persson, I.; Yuchi, A.; Penner-Hahn, J. E. *Inog. Chem.* **1989**, *28*, 1833.

(10) Johnsson, M.; Persson, I. *Inorg. Chim. Acta* **1987**, *130*, 215.

(11) Norén, B.; Oskarsson, Å. *Acta Chem. Scand., Ser. A* **1984**, *38*, 479.

(12) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 8972.

(13) Nilsson, K. Thesis, Lund University, Lund, Sweden, 1986.

(14) Burschka, C. *Z. Anorg. Allg. Chem.* **1980**, *463*, 65.

(15) Savelsberg, G.; Schäfer, H. *Z. Naturforsch.* **1978**, *33b*, 711.

(16) Sampanthar, J. T.; Vittal, J. J.; Dean, P. A. W. *J. Chem. Soc., Dalton Trans.* **1999**, 3153.

(17) Becker, B.; Wojnowski, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Polyhedron* **1990**, *9*, 1659.

(18) Fujisawa, K.; Imai, S.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 168.

10.1021/ic010226i CCC: $20.00

in the range 2.14−2.17 Å, while numerous copper(I) complexes with planar trigonal coordination of sulfur donor ligands are known.[1,2,19,20] The Cu−S bond distances are in the range 2.24−2.26 Å, as e.g. for the $[Cu(SP(CH_3)_3)_3]ClO_4$,[22] $[Cu(SC(N(CH_2))_2)_3]BF_4$,[23] and $[(C_6H_5)_4)P]_2[Cu(SC_6H_5)_3]$ compounds.[24] However, the most common coordination geometry is tetrahedral, which often is distorted as in the crystal structures of $[Cu(SCH(NH_2)_2)_3]Cl$ and $[Cu_2(SCH(NH_2)_2)_6]BF_4$,[25,26] with Cu−S bond distances in the range 2.27−2.5 Å. Regular CuS_4 tetrahedra are found in the compounds $[Cu(SCCH_3NH_2)_4]Cl$ and $Na_{4n}[Cu^{II}(NH_3)_4]_n[Cu^{I}(S_2O_3)_2]_{2n}$ with Cu^{I}−S bond distances of 2.34 and 2.36 Å,[27,28] respectively.

The silver ion displays a wide range of coordination numbers (from 2 to 6) in coordination compounds with sulfur donor ligands.[20,21] The two-coordinated silver(I) complexes are linear with Ag−S bond distances in the range 2.35−2.40 Å; examples of such complexes are $(C_{10}H_{25}As_5O_5)_2NH_4[Ag(SCN)_2]$,[29] $(C_6H_5)_4P[Ag(SCOCH_3)_2]$,[16] and $(C_2H_5)_3NH[Ag(SCOC_6H_5)_2]$.[16] The three-coordinated silver(I) complexes with sulfur donor ligands are trigonal with mean Ag−S bond distances close to 2.50 Å in the most regular complexes, as in $[Ag(SC_4H_8)_2]BF_4$,[11] $[Ag(SS_2CS_2C_2(CH_3)_2)_3]PF_6$,[30] and $[Ag(SC_3H_6N_2)_3]NO_3$.[31] A regular tetrahedral AgS_4 geometry is found in $(NH_4)_5Cl_2[Ag(S_2O_3)_4]$ with a Ag−S bond distance of 2.58 Å,[32] and a slightly distorted AgS_4 tetrahedron in $[Ag(SC_6H_7N)_4]BF_4$, mean Ag−S = 2.57 Å.[33] A large number of complexes with markedly distorted tetrahedral AgS_4 geometry is reported with mean Ag−S bond distances in the range 2.55−2.60 Å.[27] A few complexes with silver coordinating five sulfur atoms are described, but they are highly distorted.[34,35] A fairly large number of octahedrally six-coordinated silver(I) complexes with tri- and hexathio ligands is reported; the mean Ag−S bond distances are in the range 2.72−2.75 Å as for bis(1,4,7-trithiacyclononane-*S*,*S*′,*S*′′)-silver(I) trifluoromethanesulfonate and pentaiodide[36−38] and (1,4,7,10,13,16-hexathiacyclooctadecane)silver(I) hexafluorophosphate and iodide tris(diiodine).[39−41]

Gold(I) complexes with sulfur donor ligands are almost always linear with short Au−S bond distances, 2.27−2.31 Å.[27,28] With monodentate sulfur donor ligands as in $C_{36}H_{30}NP_2[Au(SH)_2]$,[42] $(C_6H_5)_4As[Au(SCN)_2]$,[43] $[Au(SC(NH_2)_2)_2]Br$,[44] $[Au(SC(NH_2)_2)_2]ClO_4$,[45] and $(C_6H_5)_4As[Au(SC_6H_5)_2]$,[46] monomeric complexes are always formed. The reason the Au−S bonds are shorter than Ag−S in two-coordinated complexes is certainly a relativistic effect, contracting the s and p orbitals and allowing the more exposed 5d orbitals of the gold atom a greater involvement in the bonding. Dimeric complexes are often formed with bidentate ligands, Au_2L_2, where two gold(I) ions linearly coordinate one sulfur in each ligand as in bis(dialkyldithiocarbamato)digold(I).[47−49]

Previous structural studies of the solvated isoelectronic (d^{10}) group 12 ions, zinc(II), cadmium(II), and mercury(II), showed octahedral six-coordination to be prevalent in a range of solvents.[50,51] However, the zinc(II) and mercury(II) ions are tetrahedrally solvated in solvents with particularly strong electron-pair donor ability, as e.g. liquid ammonia[52,53] and *N*,*N*-dimethylthioformamide,[54] while mercury(II) forms a linear disolvate with *N*,*N*-dimethylthioformamide in the perchlorate salt.[54] The cadmium ion remains octahedrally six-coordinated also in these solvents.[52−54] The reason zinc(II) tends to have a lower coordination number than 6 for stronger field ligands probably originates from the interaction with the atomic d orbitals.[54] In octahedral coordination geometry, the increasing energy gap Δ_{oct} between nonbonding and antibonding molecular orbitals makes it more costly to exceed the 18-electron rule by filling the antibonding orbitals with electron pairs from more than four ligands.

In the present work, the coordination of the strong electron-pair donor solvent *N*,*N*-dimethylthioformamide has been investigated for the monovalent group 11 ions, copper(I), silver(I), and gold(I), both in solution and the solid state, for a better understanding of this variety of coordination geometries. The only copper(I) complexes with *N*,*N*-dimethylthioformamide that

---

(19) Pilloni, G.; Longato, B.; Bandoli, G.; Corain, B. *J. Chem. Soc., Dalton Trans.* **1997**, 819.

(20) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, G. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. The Cambridge Crystallographic Data Centre: computer-based search, retrieval, analysis and display of information. *Acta Crystallogr., Sect. B* **1979**, *35*, 2331 and references therein.

(21) *Inorganic Crystal Structure Database*; Gmelin Institut, Fachinformationzentrum: Karlsruhe, Germany, 1998; and references therein.

(22) Eller, P. G.; Corfield, P. W. R. *J. Chem. Soc., Chem. Commun.* **1971**, 105.

(23) Weiniger, M. S.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1140.

(24) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993.

(25) Truter, M. R.; Rutherford, K. W. *J. Chem. Soc.* **1962**, 1748.

(26) Ferrari, A.; Braibanti, A.; Tiripicchio, A. *Acta Crystallogr.* **1966**, *21*, 605.

(27) Okaya, Y.; Knobler, C. B. *Acta Crystallogr.* **1964**, *17*, 928.

(28) Taylor, I. F.; Weiniger, M. S.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2835.

(29) Hausler, T.; Sheldrick, W. S. *Chem. Ber.* **1997**, *130*, 371.

(30) Olk, R. M.; Hoyer, E.; Faure, R.; Loiseleur, H.; Thomas-David, G. *Cryst. Struct. Commun.* **1982**, *11*, 585.

(31) Casas, J. S.; Martinez, E. G.; Sanchez, A.; Gonzalez, A. S.; Sordo, J.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1996**, *241*, 117.

(32) Bigolo, F.; Tiripicchio, A.; Tiripicchio Camellini, M. *Acta Crystallogr., Sect. B* **1972**, *28*, 2079.

(33) Giusti, G.; Geier, G.; Currao, A.; Nesper, R. *Acta Crystallogr., Sect. C* **1996**, *52*, 1914.

(34) Roesky, H. W.; Gries, T.; Jones, P. G.; Weber, K.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1781.

(35) Roesky, H. W.; Hofmann, H.; Jones, P. G.; Pinkert, W.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1215.

(36) Clarkson, J. A.; Yagbasan, R.; Blower, P. J.; Rawle, S. C.; Cooper, S. R. *Chem. Commun.* **1987**, 950.

(37) Blower, P. J.; Clarkson, J. A.; Rawle, S. C.; Hartman, J. A. R.; Wolf, R. E., Jr.; Yagbasan, R.; Bott, S. G.; Cooper, S. R. *Inorg. Chem.* **1989**, *28*, 4040.

(38) Blake, A. J.; Gould, R. O.; Li, W.-S.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *Inorg. Chem.* **1998**, *37*, 5070.

(39) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M. *Polyhedron* **1989**, *8*, 513.

(40) Blake, A. J.; Gould, R. O.; Parsons, S.; Radek, C.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2374.

(41) Blake, A. J.; Gould, R. O.; Li, W.-S.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *Inorg. Chem.* **1998**, *37*, 5070.

(42) Vicente, J.; Chicote, M.-T.; Gonzalez-Herrero, P.; Jones, P. G.; Ahrens, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1852.

(43) Schwerdtfeger, P.; Boyd, P. D. W.; Burrell, A. K.; Robinson, W. T.; Taylor, M. J. *Inorg. Chem.* **1990**, *29*, 3593.

(44) Porter, L. C.; Fackler, J. P., Jr.; Costamagna, J.; Schmidt, R. *Acta Crystallogr., Sect. C* **1992**, *48*, 1751.

(45) Lin, C.-C.; Liu, S.-X.; Yong, R.-S. *Chin. J. Struct. Chem.* **1990**, *9*, 42.

(46) Bates, P. A.; Waters, J. M. *Acta Crystallogr., Sect. C* **1985**, *41*, 862.

(47) Heinrich, D. D.; Wang, J.-C.; Fackler, J. P., Jr. *Acta Crystallogr., Sect. C* **1990**, *46*, 1444.

(48) Jennische, P.; Olin, Å.; Hesse, R. *Acta Chem. Scand.* **1972**, *26*, 2799.

(49) Jennische, P.; Anacker-Eickhoff, H.; Wahlberg, A. *Acta Crystallogr. Sect. A* **1975**, *31*, 5143.

(50) Sandström, M.; Persson, I.; Ahrland, S. *Acta Chem. Scand., Ser. A* **1978**, *32*, 607.

(51) Åkesson, R.; Sandström, M.; Stålhandske, C.; Persson, I. *Acta Chem. Scand.* **1991**, *45*, 165.

(52) Gans, P.; Gill, B. *J. Chem. Soc., Dalton Trans.* **1976**, 779.

(53) Chingakule, D. D. K.; Gans, P.; Gill, B. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1329.

(54) Stålhandske, C. M. V.; Stålhandske, C. I.; Persson, I.; Sandström, M. *Inorg. Chem.* **1997**, *36*, 3167.

previously have been structurally characterized are the copper(I) chloride and cyanide solvates. *N*,*N*-dimethylthioformamide copper(I) chloride has a trigonal, almost planar, coordination with a short Cu−S bond distance of 2.23 Å and Cu−Cl bond distances of 2.26 Å.[55] In the corresponding (*N*,*N*-dimethylthioformamide)copper(I) cyanide compound a network of distorted copper(I) coordination tetrahedra is formed, consisting of two sulfur atoms from *N*,*N*-dimethylthioformamide ligands and one carbon and one nitrogen atom from bridging cyano ligands. The Cu−S bond distances are 2.32 and 2.71 Å and 2.30 and 2.97 Å, in two sets of tetrahedra, respectively.[56] No silver(I) and gold(I) compounds with *N*,*N*-dimethylthioformamide as ligand have been reported.

Experimental Section

Preparations. *N*,*N*-Dimethylthioformamide was prepared from *N*,*N*-dimethylformamide (Merck) and phosphorus pentasulfide (Merck) according to the procedure described by Gutmann et al.[57] Tetrakis(*N*,*N*-dimethylthioformamide)copper(I) perchlorate, $[Cu(SCHN(CH_3)_2)_4]ClO_4$, was synthesized as described by Gritzner et al.[58] by mixing solid $Cu(ClO_4)_2{\cdot}6H_2O$ (G.F. Smith) and *N*,*N*-dimethylthioformamide, filtering off the elemental sulfur formed, and heating the solution to 70 °C for 3 h. After addition of diethyl ether and cooling the mixture, bright yellow crystals formed, which were recrystallized from *N*,*N*-dimethylthioformamide. Silver trifluoromethanesulfonate, $AgCF_3SO_3$, was prepared from silver(I) oxide as described by Hedwig et al.[59] The dry salt was kept at 150 °C until used. Concentrated *N*,*N*-dimethylthioformamide solution of silver trifluoromethanesulfonate decomposes by forming a black precipitate, which prevented crystallization of solid silver trifluoromethanesulfonate solvates. Solid tris(*N*,*N*-dimethylthioformamide)silver(I) perchlorate, $[Ag(SCHN(CH_3)_2)_3]ClO_4$, was prepared by dissolving anhydrous $AgClO_4$ (G.F. Smith, dried under vacuum at 100 °C) to saturation at 35 °C in *N*,*N*-dimethylthioformamide, followed by cooling in refrigerator.

Warning! *Addition of N,N-dimethylthioformamide to anhydrous* $AgClO_4$ *causes a violent explosion. Thus,* $AgClO_4$ *must be added to N,N-dimethylthioformamide,* to ensure that an excess of *N*,*N*-dimethylthioformamide is present. However, it was found that *N*,*N*-dimethylthioformamide could be added to the acetonitrile solvate of silver perchlorate, $[Ag(NCCH_3)_4]ClO_4$, without violent reactions, probably because no direct coordination between the silver(I) and perchlorate ions then takes place. Perchlorates of metal complexes with organic ligands are potentially explosive and should always be handled with caution. They become, however, very unstable when the perchlorate ions are distorted by formation of direct metal−perchlorate oxygen bonds.[54,60]

An *N*,*N*-dimethylthioformamide solution of gold(I) tetrafluoroborate was prepared in the following way. A gold foil (Heraeus, 99.9%) was treated with 1.0 g nitrosyl tetrafluoroborate (Merck) dissolved in 50 mL of freshly distilled acetonitrile (Fluka), and the reaction mixture was stirred at 35 °C for 2 days. The gold foil was taken out of the reaction mixture and weighed; normally about 0.3 g of gold was dissolved by oxidation: $Au(s) + NO^+ \rightarrow Au^+ + NO(g)$. A 5 mL volume of *N*,*N*-dimethylthioformamide was added to the acetonitrile solution. Remaining nitrosyl ions then react with *N*,*N*-dimethylthioformamide to form elemental sulfur, which was filtered off. By means of a rotavapor the acetonitrile was evaporated off and the total volume reduced to about 2.5 mL. The resulting *N*,*N*-dimethylthioformamide solution of gold(I) tetrafluoroborate is dark reddish brown and was studied by EXAFS without further purification. Further evaporation, followed by cooling in refrigerator, resulted in precipitation of a small amount of yellow crystals of bis(*N*,*N*-dimethylthioformamide)gold(I) tetrafluoroborate, $Au(SCHN(CH_3)_2)_2BF_4$. The quality of these crystals did not allow a crystallographic study, and the local structure of gold(I) in the complex was therefore studied by EXAFS.

Table 1. Crystallographic Data of Tetrakis(*N*,*N*-dimethylthioformamide)copper(I) Perchlorate and Tris(*N*,*N*-dimethylthioformamide)silver(I) Perchlorate

	$Cu(SCHN(CH_3)_2)_4ClO_4$	$Ag(SCHN(CH_3)_2)_3ClO_4$
fw	519.633	474.796
space group	$P2/n$, No. 13 (monoclinic)	$P\bar{1}$, No. 2 (triclinic)
T/K	295	295
a/Å	8.428(2)	7.4149(5)
b/Å	9.605(2)	7.7953(5)
c/Å	15.096(3)	17.14819(9)
α/deg	90	98.341(5)
β/deg	104.35(2)	93.910(5)
γ/deg	90	107.084(5)
$\rho_{calcd}{}^a$/g·cm^{-3}	1.457	1.694
$\rho_{obsd}{}^b$/g·cm^{-3}	1.46(2)	1.67(2)
V/Å^3	1183.9(9)	931.0(2)
Z	2	2
R^c	0.035	0.040
$R_W{}^d$	0.045	0.051
μ(Mo Kα)/cm^{-1}	13.99	15.54

[a] Calculated density. [b] Experimental density (see text). [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|\ F_o|)^2]^{1/2}$.

Table 2. Composition of the *N*,*N*-Dimethylthioformamide (DMTF) Solutions Studied by LAXS and EXAFS[a]

	$[M^+]$	$[X^-]$	[DMTF]	ρ/g·cm^{-3}	μ/cm^{-1}
Cu^+	1.0	1.0[b]	11.3	1.17	7.59
Ag^+	0.86	0.86[c]	10.8	1.18	6.52
Au^+	0.30	0.30[d]	12.0		

[a] The concentrations in mol·dm^{-3}, the density, ρ, at 25 °C, and the linear absorption coefficient, μ, for Mo Kα radiation, are given. [b] $X = ClO_4^-$. [c] $CF_3SO_3^-$. [d] BF_4^-.

Crystallography. X-ray diffraction data were collected by means of a CAD4 four-circle single-crystal diffractometer using Mo Kα ($\lambda = 0.710\ 69$ Å) radiation at room temperature. The unit cell parameters were determined from 25 well-centered high-angle reflections, and two standard reflections were measured regularly during the data collection. Direct methods and finally full-matrix least-squares refinements were used to solve and refine the structures. For the copper(I) solvate it was possible to refine the position of the formyl hydrogen atoms, but the methyl hydrogen atoms were included in their calculated positions assuming tetrahedral geometry and the apparent (for X-ray diffraction) C−H bond distance 0.96 Å. The perchlorate ion was disordered and was described by two alternative orientations of the oxygen atoms during the refinement. For the silver(I) solvate the positions of all atoms, including the hydrogens, were found and refined. Details about the data collections and refinements are given in Table 1.

Large-Angle X-ray Scattering (LAXS). The scattering from the free surface of the *N*,*N*-dimethylthioformamide solutions of copper(I) perchlorate and silver(I) trifluoromethanesulfonate was measured with a large-angle Θ−Θ goniometer described previously.[61,62] The composition, density, and linear absorption coefficients of the solutions are given in Table 2. Intensity data were collected in the range $1 < \Theta < 65°$ using Mo Kα radiation, following the same procedure as described earlier;[62] the scattering angle is 2Θ.

The experimental intensities were corrected for polarization and normalized to a stoichiometric unit of volume corresponding to one metal atom. Corrections for absorption[63] and multiple scattering[64] were necessary due to the low absorption; see Table 2. After subtraction of

---

(55) Stålhandske, C. I. Unpublished results.

(56) Kirfel, A. *Acta Crystallogr., Sect. B* **1977**, *33*, 2788.

(57) Gutmann, V.; Danksagmüller, K.; Duschek, O. *Z. Phys Chem. Neue Folge (Frankfurt)* **1974**, *92*, 199.

(58) Gritzner, G.; Linert, W.; Gutmann, V. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1193.

(59) Hedwig, G. R.; Parker, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 6589.

(60) Ahrland, S.; Björk, N. O. *Acta Chem. Scand., Ser. A* **1974**, *28*, 823.

(61) Johansson, G. *Acta Chem. Scand.* **1966**, *20*, 553; **1971**, *25*, 2787.

(62) Stålhandske, C. M. V.; Persson, I.; Sandström, M.; Kamienska-Piotrowicz, E. *Inorg. Chem.* **1997**, *36*, 3174.

(63) Milberg, M. *J. Appl. Phys.* **1958**, *29*, 64.

(64) Johansson, G.; Sandström, M. *Chem. Scr.* **1973**, *4*, 195.

Table 3. Model Parameters for the Solvated Metal Ion Complexes $[M(SCHN(CH_3)_2)_n]^+$, M = Cu and Ag, Used in the LAXS Calculations[a]

		Cu^+	Ag^+
M−S	d	2.36(1)	2.58(1)
	σ_l	0.046(2)	0.065(3)
	n	4	4
S···S$_{comp}$	*d*	3.85(2)	4.16(6)
	σ_l	0.105(10)	0.148(14)
	n	6	6
M···C	d	3.26(2)	3.50(3)
	σ_l	0.084(12)	0.089(12)
	n	4	4
M···N	d	4.54[b]	4.76(4)
	σ_l	0.12	0.12(1)
	n	4	4
M···C′	d	5.23[b]	5.47[b]
	σ_l	0.125	0.125
	n	4	4
M···C″	d	5.58[b]	5.82[b]
	σ_l	0.13	0.13

[a] *d* denotes the distances, σ_l the mean square deviation, and *n* the number of distances. Distance *d*/Å, displacement parameter σ_l/Å, and number of distances/metal atom *n*. S···S$_{comp}$ represents the sulfur−sulfur interaction within the complex. For parameters refined by least-squares methods probable errors are given (within parentheses, ~90% confidence limit). [b] Estimated from crystal structure; C denotes the formyl carbon, and C′and C″_denote the two methyl carbons of *N,N*-dimethylthioformamide. [c]Calculated by assuming S−C 1.68 Å.[54]

the structure-independent coherent and Compton scattering, the reduced structure-dependent intensity function *i*(*s*) was extracted and transformed by Fourier methods to a modified radial distribution function, expressed as $D(r) - 4\pi r^2\rho_0$. The KURVLR program was used for the data correction and treatment procedures.[64] Minor spurious peaks below 1.2 Å in the RDFs were removed by a Fourier back-transformation procedure,[65] to obtain a better alignment of the intensity function. Model intensity contributions, $i_{calc}(s)$, were calculated for distinct interatomic interactions:

$$i_{calc}(s) = \Sigma_p\Sigma_q(f_p' f_q' + \Delta f_p''\Delta f_q'') \exp(-2\sigma_l{}^2{}_{pq}s^2) \sin(sr_{pq})/(sr_{pq}) \tag{1}$$

The parameters characterizing the interatomic interactions are r_{pq}, the mean distance separating the atoms p and q, and $\sigma_l{}^2{}_{pq}$, the mean square deviation from the mean distance (see Table 3). Anomalous dispersion corrections, $\Delta f'$ and $\Delta f_p''$, are included in the atomic scattering factor expression ($f' = f + \Delta f'$). All summations are made over a unit of volume containing one metal atom.

The STEPLR program was then used for least-squares refinements of the model parameters by comparison with the experimental reduced intensities for high *s*-values, $s > 4.5$ Å^{-1}, for which nonbonded intermolecular intensity contributions can be neglected.[66] The model used includes the intramolecular interactions between the metal ion and the solvating *N,N*-dimethylthioformamide ligands and those within the *N,N*-dimethylthioformamide molecules and the anions. The perchlorate ion was described in tetrahedral geometry with a Cl−O bond distance of 1.425 Å,[67] and for the trifluoromethanesulfonate ion C−F, S−O, and S−C bond distances of 1.336, 1.442, and 1.310 Å, respectively, were used.[68] Hydrogen-bonded intermolecular interactions between the *N,N*-dimethylthioformamide molecules were included, assuming that about 70% of the *N,N*-dimethylthioformamide molecules are hydrogen bonded to each other in the free solvent, as previously estimated for pure liquid *N,N*-dimethylthioformamide.[62,69,70]

EXAFS. Cu K- and Au L$_{III}$-edge EXAFS measurements of the *N,N*-dimethylthioformamide solutions of copper(I) perchlorate and gold(I) tetrafluoroborate were performed in transmission and fluorescence mode using the wiggler beam line 4-1 at Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA. SSRL operates at 3.0 GeV and a maximum current of 100 mA. The EXAFS station was equipped with a Si[220] double crystal monochromator. Internal calibration was made with copper and gold metal foils, respectively, and higher order harmonics were discarded by detuning the second monochromator crystal to 50% of maximum intensity at the end of the scans. The EXAFSPAK program package was used for the treatment of the EXAFS data,[71] by means of standard procedures for preedge subtraction, normalization, and spline removal. A model function for the EXAFS oscillations, $\chi(k)$, was constructed using ab initio calculated phase $\phi(k)$, amplitude $f_{eff}(k)$, and mean free path $\lambda(k)$ parameters computed by the FEFF7 program,[72] for each backscattering pathway *i* (*k* is the scattering variable):

$$\chi_i(k) = \frac{nS_0{}^2}{kd^2}|f_{eff}(k)|_i \exp(-2k^2\sigma_e{}^2) \exp[-2d/\lambda(k)] \sin[2kd + \phi_i(k) - (^4/_3)C_3k^3] \tag{2}$$

The parameters of the model function were refined by least-squares curve-fitting to the k^3-weighted EXAFS data; see Table 4. In cases when there is a *k*-dependent phase-shift of a pathway, indicating asymmetry in the distribution of the distances, the cumulant expansion method can be used. The third cumulant, C_3, accounts for this phase shift. The software WinXAS[73] was used for the evaluation of asymmetry effects.

Vibrational Spectroscopy. Far- and mid-infrared spectra of the copper(I) and silver(I) compounds in the solid state and in solution were recorded at room temperature with a Perkin-Elmer 1760X spectrometer, 50−500 cm^{-1}, and a Perkin-Elmer 1700X spectrometer, 400−4000 cm^{-1}. Both instruments were equipped with deuterated triglycine sulfate (DTGS) detectors.

Raman spectra of the copper(I) and silver(I) *N,N*-dimethylthioformamide solutions were recorded by means of a DILOR Z24 triple monochromator using photon counting. The green 514.5 nm line (about 500 mW at the sample) of a Coherent Radiation Laboratories Innova 90-5 argon ion laser was used to irradiate the samples. However, the solid *N,N*-dimethylthioformamide solvates of copper(I) and silver(I) decomposed in the green laser light; therefore, a Bruker IFS 66 Raman spectrometer equipped with a YAG laser, $\lambda = 1064.5$ nm (50 mW at the sample), was used for the solids. All spectra were recorded at room temperature. For the small amount of the solid bis(*N,N*-dimethylthioformamide)gold(I) tetrafluoroborate Raman spectra were measured by means of a Renishaw System 1000 spectrometer, equipped with a Leica DMLM microscope, a 25 mW diode laser (780 nm), and a Peltier-cooled CCD detector.

Results and Discussion

Crystallography. The atomic coordinates and the equivalent isotropic displacement coefficients of the copper(I) and silver(I) compounds are given in Tables S1 and S2 (Supporting

---

(65) Levy, H. A.; Danford, M. D.; Narten, A. H. *Data Collection and Evaluation with an X-ray Diffractometer Designed for the Study of Liquid Structure*; Technical Report ORNL-3960; Oak Ridge National Laboratory: Oak Ridge, TN, 1966.
(66) Molund, M.; Persson, I. *Chem. Scr.* **1985**, *25*, 197.
(67) Berglund, B.; Thomas. J. O.; Tellgren, R. *Acta Crystallogr., Sect. B* **1975**, *31*, 1842.
(68) Nieuwpoort, G.; Verschoor, G. C.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1983**, 531.
(69) Stålhandske, C. M. V.; Persson, I.; Sandström, M.; Åberg, M. *Inorg. Chem.* **1997**, *36*, 4945.
(70) Borrmann, H.; Persson, I.; Sandström, M.; Stålhandske, C. M. V. *J. Chem. Soc., Perkin Trans. 2* **2000**, 393.
(71) George, G. N.; Pickering, I. J. *EXAFSPAK-A Suite of Computer Programs for EXAFS Analysis*; SSRL, Stanford University: Stanford, CA, 1993.
(72) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *J. Phys. Rev. B* **1995**, *52*, 2995. Ankudinov, A. L.; Rehr, J. J. *Phys. Rev. B* **1997**, *56*, R1712. The FEFF program is available from the following: http://Feff.phys.washington.edu/feff.
(73) Ressler, T. *J. Synchrotron Radiat.* **1998**, *5*, 118.

Table 4. EXAFS Model Parameters for Solvated Copper(I) and Gold(I) Ions in *N*,*N*-dimethylthioformamide (DMTF) Solution and in the Solid State[a]

interaction	N	d/Å	σ_e^2/Å^2	C_3/Å^3	ΔE_o/eV	S_o^2
Cu^+/DMTF						
Cu−S	4	2.30(1)	0.085(2)		−14(1)	0.61(2)
Cu···C	4	3.17(3)	0.13(2)			
Cu−S−C[b]	8	3.49(5)	0.11(3)			
Cu−S−Cu−S[c]	4	4.64(4)	0.10(2)			
Cu−S[d]	4	2.34(2)	0.099(3)	0.0008(2)	−14(1)	
Au^+/DMTF						
Au−S	2.0(1)	2.283(4)	0.049(2)		−16(1)	0.83
Au···C	2	3.14(3)	0.13(2)			
Au−S−Au−S[c]	2	4.54(2)	0.11(1)			
Au(dmtf)$_2$BF$_4$						
Au−S	2	2.290(5)	0.040(2)		−16(1)	0.84(3)
Au···C	2	3.20(2)	0.074(2)			

[a] The parameters are number of interactions (*N*), M−S bond distance (*R*/Å), Debye−Waller factor (σ^2/Å^2), and threshold shift (ΔE_o/eV). For parameters refined by least-squares methods to k^3-weighted data probable errors are given (within parentheses, ∼90% confidence limit). [b,c] Multiple scattering pathways, 3 and 4 legs, respectively. [d] *R*-space refinement of Fourier-filtered Cu−S interaction including phase-shifting third anharmonic cumulant (C_3/Å^3) to account for asymmetry in the M−S distribution.

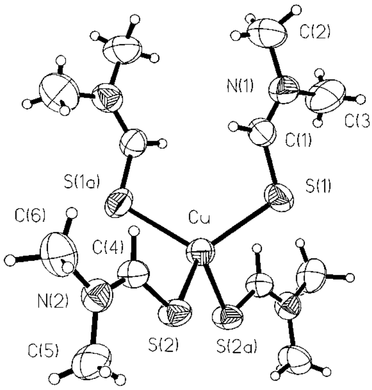

Figure 1. Tetrakis(*N*,*N*-dimethylthioformamide)copper(I) ion in C_2 symmetry with thermal ellipsoids enclosing 50% of the atomic electron density. The bond distances are Cu−S(1) 2.325(1) Å and Cu−S(2) 2.349(1) Å.

Information), respectively, and the interatomic distances and angles in Table S3.

Crystal Structure of [Cu{SCHN(CH$_3$)$_2$}$_4$]ClO$_4$. The structure is built up from discrete [Cu{SCHN(CH$_3$)$_2$}$_4$]$^+$ complexes and perchlorate ions. The copper atom, located on a 2-fold axis, coordinates the sulfur atoms of four *N*,*N*-dimethylthioformamide molecules in a distorted CuS$_4$ tetrahedron (Figure 1), with the Cu−S bond distances 2.3249(8) and 2.3494(8) Å and the S−Cu−S angles in the range 99.0−123.5° (Table S3). The Cu−S−C angles 107.1 and 109.3° are significantly larger than those found for other *N*,*N*-dimethylthioformamide solvates, i.e. of zinc(II), cadmium(II), mercury(II),[54] iron(II),[74] and silver(I) (see below). The mean Zn−S bond distance, 2.34 Å, in the tetrahedrally coordinated zinc(II) complex, [Zn{SCHN(CH$_3$)$_2$}$_4$]$^{2+}$, is similar but the mean Zn−S−C angle is significantly smaller 102.5°, and in the strongly bonded bis-solvate of mercury(II), [Hg{SCHN(CH$_3$)$_2$}$_2$]$^{2+}$, the Hg−S−C angle is only 101.3(4)°.[54]

The bond distances and angles of the planar (within 0.01 Å for non-hydrogen atoms) *N*,*N*-dimethylthioformamide ligands of the [Cu{SCHN(CH$_3$)$_2$}$_4$]ClO$_4$ compound are generally in good agreement with the values found for other *N*,*N*-dimethylthioformamide solvates (cf. Table S3 and refs 62 and 74), as well as for crystalline *N*,*N*-dimethylthioformamide.[70] However, there is a small increase in the S−C bond distances and a corresponding decrease in the formyl C−N bond distance with increasing softness of the metal ion. This is also consistent with the Raman and infrared spectra where a downward shift is observed of the bands related to the S−C bond and an upward shift of the bands related to the N−C(formyl) bond; see below. A packing view (Figure S1) shows the planar ligands to have almost parallel orientation, with the angle between the normals to the planes being only 10.9°.

The perchlorate ion shows severe rotational disorder, and the Cl−O bond distances appear much shorter than normally. The oxygen atom positions were modeled by two alternative orientations of the oxygen atoms around the 2-fold axis through the chlorine atom.

Crystal Structure of [Ag{SCHN(CH$_3$)$_2$}$_3$]ClO$_4$. The structure consists of discrete dimeric [Ag$_2${SCHN(CH$_3$)$_2$}$_6$]$^{2+}$ complexes and perchlorate ions. Each silver ion has three short Ag−S bonds to *N*,*N*-dimethylthioformamide molecules, 2.469(2), 2.529(1), and 2.543(1) Å, forming an almost planar AgS$_3$ entity with the silver atom 0.32 Å above the S_3 plane. Two such AgS$_3$ entities are held together by long bridging Ag···S interactions, 2.930(1) Å, giving rise to a centrosymmetric dimeric complex with an asymmetric double sulfur bridge (Fig. 2). The S−Ag−S angles of the AgS$_3$ unit are 104.78(4), 118.56(5), and 131.39(5)°, with the largest angle between the two shortest Ag−S bonds. The Ag−S−C angles to these *N*,*N*-dimethylthioformamide molecules, 104.5(2), 105.5(2), and 106.4(2)°, are smaller than corresponding angles in the copper complex. Similar coordination geometry of S-atoms around Ag (3 + 1) has been found previously in the structures of several minerals, e.g. marrite, PbAgAsS$_3$,[75] smithithe, AgAsS$_2$,[76] miargyrite, AgSbS$_2$,[77] hatchite, PbTlAgAs$_2$S$_5$,[78] xanthoconite, Ag$_3$AsS$_3$,[79] and aramayoite, Ag(Sb,Bi)S$_2$.[80] A unit cell view (Figure S2) shows the dimers to be stacked on top of each other perpendicular to the *a* axis.

The oxygen atoms of the perchlorate ion appear to have relatively large temperature factors and short Cl−O distances, Table S3. Such features are typical for limited disorder in a non-hydrogen-bonded structure, but there was no need to introduce alternative positions in the modeling.

---

(74) Baumgartner, O. *Acta Crystallogr., Sect. C* **1986**, *42*, 1723.

(75) Wuensch, B. J.; Nowacki, W. *Z. Kristallogr.* **1967**, *125*, 459.

(76) Hellner, E.; Burzlaff, H. *Naturwissenschaften* **1964**, *51*, 35.

(77) Knowles, C. R. *Acta Crystallogr.* **1964**, *17*, 847.

(78) Marumo, F.; Nowacki, W. *Z. Kristallogr.* **1967**, *125*, 249.

(79) Engel, P.; Nowacki, W. *Acta Crystallogr., Sect. B* **1968**, *24*, 77.

(80) Mullen, D. J. E.; Nowacki, W. *Z. Kristallogr.* **1974**, *139*, 54.

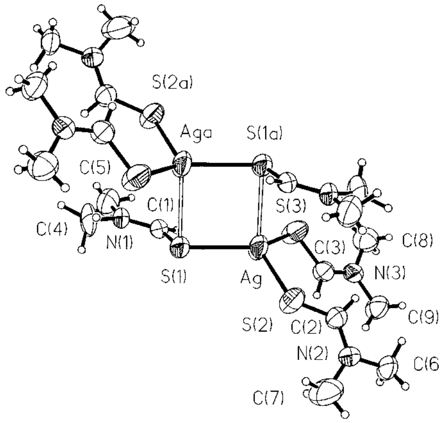

Figure 2. Centrosymmetric dimeric $[Ag_2(SCHN(CH_3)_2)_6]^{2+}$ entity with 50% probability ellipsoids. The bond distances are Ag−S(1) 2.529(1), Ag−S(2) 2.543(1), and Ag−S(3) 2.469(1) Å. The unfilled bond of the asymmetric double sulfur bridge, Ag−S(1a), is 2.930(1) Å.

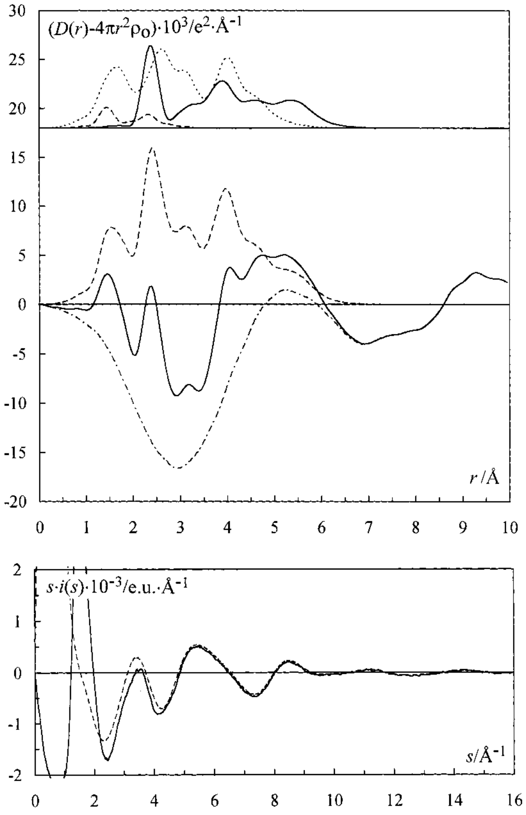

Figure 3. LAXS radial distribution curves for 1.0 M copper(I) perchlorate in *N,N*-dimethylthioformamide: (top) separate model contributions $[Cu(SCHN(CH_3)_2)_4]^+$ complex as in Table 3 (solid line), ClO_4^- (dashes), solvent molecules (dots);[70] (middle) experimental $D(r) - 4\pi r^2\rho_0$ (solid line), model (dashes), difference (dash−dots); (bottom) reduced LAXS intensity functions $s(i(s))$ (solid line), model $s(i_{calc}(s))$ (dashes).

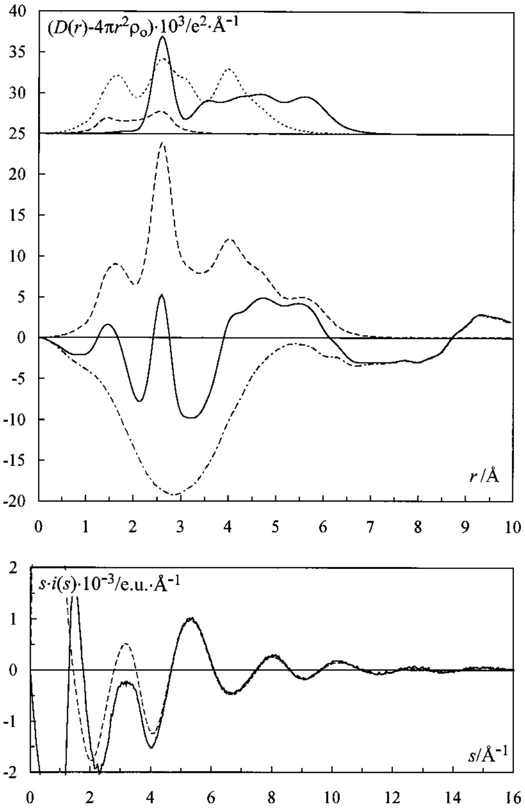

Figure 4. LAXS radial distribution curves for 0.86 M silver(I) trifluoromethanesulfonate in *N,N*-dimethylthioformamide: (top) separate model contributions $[Ag(SCHN(CH_3)_2)_4]^+$ complex as in Table 3 (solid line), $CF_3SO_3^-$ (dashes), solvent molecules (dots);[70] (middle) experimental $D(r) - 4\pi r^2\rho_0$ (solid line), model (dashes), difference (dash−dots); (bottom) reduced LAXS intensity functions $s(i(s))$ (solid line), model $s(i_{calc}(s))$ (dashes).

Large-Angle X-ray Scattering. The experimental radial distribution functions, RDFs, of the *N,N*-dimethylthioformamide solutions of copper(I) perchlorate and silver(I) trifluoromethanesulfonate and the separate contributions from the different entities in the model are shown in Figures 3 and 4, respectively. The RDF of the copper(I) solution shows six distinguishable peaks at about 1.5, 2.4, 3.2, 4.0, 4.7, and 5.3 Å, of which the first five contain contributions from distances within the *N,N*-dimethylthioformamide molecule[70] and the perchlorate ion.[67] The Cu−S and S···S distances from the solvated copper(I) ion are major contributors to the distinct peaks at 2.4 and 4.0 Å. The Cu−S contribution is sufficiently well-defined to allow least-squares refinements of model intensity values in the high-*s* region of the experimental intensity function, which resulted in a mean Cu−S bond length of 2.36(1) Å. Also, it was possible to obtain a refined value for the S···S distances, 3.85(2) Å, despite the overlap, Table 3 and Figure 3. The *d*(M−S)/*d*(S−S) ratio 0.613(5) agrees with the theoretical one for a regular tetrahedral arrangement, 0.612. The Cu−S bond distance in the $Cu\{SCHN(CH_3)_2\}_4^+$ complex is in good agreement with the mean distances of most other tetrahedral complexes with four sulfur atoms coordinated to copper(I)[27,28] but is significantly longer than that determined by EXAFS for the tetrakis(tetrahydrothiophene)copper(I) solvate, 2.30 Å,[3] and much longer than that expected for a trigonal complex.[23−25]

The RDF of the silver(I) solution shows as for the copper(I) solution two main peaks at about 1.5 and 2.6 Å and a small peak at 3.2 Å, while the peaks between 4 and 6 Å are broader. All peaks below 5 Å have contributions from distances within the solvate, the *N,N*-dimethylthioformamide molecule,[70] and/or the trifluoromethanesulfonate ion[68] (Figure 4). The Ag−S bond distances from the solvated silver(I) ion could be determined from a least-squares refinement in the same way as for the copper(I) solution, giving a mean Ag−S bond distance of 2.58(1) Å, which is close to the Ag−S bond distance in other tetrahedral silver(I) complexes with sulfur donor ligands.[27,32,33] This strongly indicates that the silver ion coordinates four *N,N*-dimethylthioformamide molecules in solution forming a $Ag\{SCHN(CH_3)_2\}_4^+$ complex. The solvated ion gives a diffuse

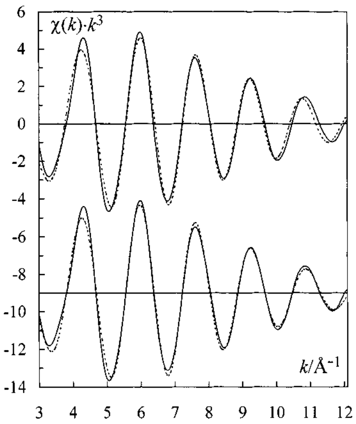

Figure 5. (Top) EXAFS $\chi(k)k^3$ function of 1.0 M copper(I) perchlorate in *N*,*N*-dimethylthioformamide (solid line) and calculated model function (Table 4) without the phase-shifting C_3 term (dashes) and (bottom) fit with the phase-shifting C_3 term included.

contribution around 4.2 Å in the RDF corresponding to S···S distances with a large spread indicating a flexible or distorted tetrahedral geometry. This is also shown by the large value of the displacement parameter, $\sigma_l = 0.065(3)$ Å, obtained as half of the root-mean-square deviation in the Ag−S distance. This value is somewhat larger than normally found for a tetrahedral configuration, e.g. $\sigma_l = 0.049(3)$, 0.048(3), and 0.050(5) Å for the $Cu(SCHN(CH_3)_2)_4^+$, $Zn(SCHN(CH_3)_2)_4^{2+}$, and $Hg(SCHN(CH_3)_2)_4^{2+}$ complexes in solution, respectively.[62] The distortion of the structure is explained as a consequence of the long S···S distances between the ligands and the plasticity of the complex due to the electronic structure of the central ion. The cadmium ion, which is isoelectronic with silver(I), forms a six-coordinated *N*,*N*-dimethylthioformamide solvate with the Cd−S distance 2.70 Å in solution.[62] Evidently, the solvation behavior of the silver ion resembles the mercury(II) more than the cadmium(II) ion. There is no indication in the RDF of an Ag···Ag distance around 3.87 Å as found for the dimer in the crystal structure.

EXAFS. When the filtered EXAFS data, corresponding to the first shell of sulfur backscatterers around the solvated copper(I) ion in *N*,*N*-dimethylthioformamide solution, is fitted with a model function for a single symmetric shell, there is a phase difference at high *k*-values showing that the distribution of the Cu−S distances is asymmetric. The cumulant expansion method can then be used, introducing the third cumulant, C_3, to account for the phase shift. When the Cu−S peak in the FT was modeled in this way, the phase difference disappears and a good fit is obtained by a single shell of scatterers increasing the mean Cu−S bond distance to 2.34(2) Å, with $\sigma_e = 0.099(3)$ Å and $C_3 = 0.0008(2)$ Å^3 (Figure 5). An acceptable fit can also be obtained by introducing two backscattering shells with two sulfur atoms in each. Such a refinement gives the Cu−S bond distances 2.27(1) and 2.39(2) Å, with corresponding σ_e values 0.07(1) and 0.09(1) Å, respectively.

The EXAFS data of the *N*,*N*-dimethylthioformamide solution of gold(I) tetrafluoroborate indicate only a single symmetric shell of backscatterers around the gold(I) ion. Curve-fitting of the experimental data using ab initio calculated EXAFS phase and amplitude parameters from the FEFF7 (version 7.01) program[72] resulted in a Au−S bond distance of 2.283(4) Å, $\sigma_e = 0.049(2)$ Å, and a coordination number of 2.0(1), when using the amplitude reduction factor, $S_o^2 = 0.83$, obtained from the refinement of the solid $[Au(SCHN(CH_3)_2)_2]BF_4$ phase. The Au−S distance is obtained with high precision in the least-squares refinements. This reflects the low noise level and does not include systematic errors in e.g. in the E_o determination and in the backscattering parameters, which have been included in the estimated probable errors in Table 4.

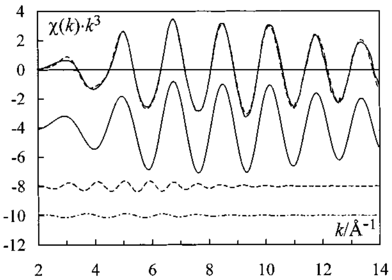

Figure 6. (Top) EXAFS $\chi(k)k^3$ function of 0.3 M $AuBF_4$ in *N*,*N*-dimethylthioformamide (solid line) and calculated model function (dashes) as in Table 4. (Bottom) Individual model contributions Au−S (solid line), Au···C (dashed line), and multiple scattering within AuS_2 (dash−dotted line).

The Au···C distance has been refined to 3.14(3) Å, which gives a Au−S−C bond angle of about 104°, and the linear three- and four-leg multiple scattering paths, refined to 4.54(2) Å, are close to the expected double Au−S bond distance. The fit of the experimental data and the corresponding Fourier transforms are shown in Figure 6. The short Au−S bond distance and also the refined coordination number show that the *N*,*N*-dimethylthioformamide-solvated gold(I) complex is two-coordinated, certainly in a linear fashion. The refinement of solid bis(*N*,*N*-dimethylthioformamide)gold(I) tetrafluoroborate resulted in the bond distances Au−S 2.290(5) Å and Au···C 3.20(2) Å, giving an Au−S−C a bond angle of about 106°, with essentially the same structure as in solution.

Comparison of M−S Bond Distances. A transfer thermodynamic study strongly indicates a higher bond strength of the solvated silver(I) ion in *N*,*N*-dimethylthioformamide than in tetrahydrothiophene solution.[81] However, a comparison of the Cu−S and Ag−S bond lengths shows that they are about 0.05 Å longer in the *N*,*N*-dimethylthioformamide (Tables 3, 4, and S2) than in the tetrahydrothiophene solvates.[3,10] This indicates that the lone pair of the sulfur atom is more available for bond formation in the *N*,*N*-dimethylthioformamide molecule than in tetrahydrothiophene. An analogous case is also the solvation of the copper(I) and silver(I) ions in the nitrogen donor solvents pyridine and acetonitrile where the metal−nitrogen bond distances are ca. 0.05 Å longer in the pyridine-solvated copper(I) and silver(I) ions in solution[3,82] than in the corresponding acetonitrile solvates,[3,83] despite stronger bonds in the pyridine solvates.[81]

However, the linear gold(I) solvates of tetrahydrothiophene[84] and *N*,*N*-dimethylthioformamide show the opposite behavior with average Au−S bond distances of 2.32(1) and 2.283(4) Å, respectively. Thus, correlating bond length and bond strength is not straightforward in cases of soft−soft interactions, in particular for this heavy d^{10} ion where vibronic coupling (or second-order Jahn Teller effects) allows participation of the exposed d_{z^2} orbital in the bonding,[85] and promotes a linear coordination geometry.[62]

---

(81) Inerowicz, H. D.; Li, W.; Persson, I. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2223.

(82) Hultén, F.; Persson, I. *Acta Chem. Scand., Ser. A* **1987**, *41*, 87.

(83) Nilsson, K.; Persson, I. *Acta Chem. Scand., Ser. A* **1987**, *41*, 139.

(84) Ahrland, S.; Norén, B.; Oskarsson, Å. *Inorg. Chem.* **1985**, *24*, 1330.

(85) Bersuker, I. B. *Electronic Structure and Properties of Transition Metal Compounds*; Wiley-Interscience: New York, 1996; Chapters 7.3 and 9.4.

Table 5. Raman and IR Frequencies, cm^{-1}, for Copper(I) Perchlorate, Silver(I) Trifluoromethanesulfonate, and Gold(I) Tetrafluoroborate in *N*,*N*-dimethylthioformamide Solution and in the Solids Tetrakis(*N*,*N*-dimethylthioformamide)copper(I) and -silver(I) Perchlorate and Bis(*N*,*N*-dimethylthioformamide)gold(I) Tetrafluoroborate

Cu$^+$				Ag$^+$				Au$^+$				
IR		Raman		IR		Raman		IR		Raman		tentative assignment^a
soln	solid	soln	solid	soln	solid	soln	solid	soln	solid	soln	solid	
							153 w		139 w		143 s	$\delta(\mathrm{MS_2})$
									191 w			$\delta(\mathrm{CS})$, $\nu_s(\mathrm{Au{-}S})$
							218 vw		219 w			$\tau((\mathrm{NCH_3})$
		231 w		220 w		230 vw	240 w		236 w			$\tau(\mathrm{CH_3})$
		275 w				273 w			272 m			$\delta(\mathrm{NCS}) + \rho(\mathrm{C'_2N})$
	299 w	300 w	302 m									$\nu(\mathrm{Cu{-}S})$
				285 w, br	297 w	296 sh, w	299 w					$\nu(\mathrm{Ag{-}S})$
				314 vw		312 vw						$\mathrm{CF_3SO_3^-}$: $\nu_s(\mathrm{CS})^b$
						347 vw						$\mathrm{CF_3SO_3^-}$: $\rho(\mathrm{SO_3})^b$
364 m		369 sh		367 m		366 w				364 m		$\gamma(\mathrm{C'N})$
382 sh	384 s	383 sh	383 m									$\nu(\mathrm{Cu{-}S})$
				382 m	391 s	384 sh, w	391 m					$\nu(\mathrm{Ag{-}S})$
406 m	405 m	407 m	408 m	407 m	407 m	406 m	410 m			405 s		$\sigma(\mathrm{C'_2N}) + \rho(\mathrm{C'_2N})$
		459 w	459 w		469 w		458 w					$\delta(\mathrm{ClO_4^-})^c$
520 m	514 m	519 m	516 s	519 m	517 m	520 m	516 m		521 m	520 s		$\sigma(\mathrm{C'_2N}) + \delta(\mathrm{CS})$
				573 vw					533 m	582 w		$\mathrm{CF_3SO_3^-}$: $\delta_{as}(\mathrm{CF_3})^b$
625 m	625 s	623 w	623 vw	627 m	627 s		623 w					$\delta(\mathrm{ClO_4^-})^c$
	630 w											
637 w	637 m			639 s	637 m							$\mathrm{CF_3SO_3^-}$: $\delta_s(\mathrm{SO_3})^b$
				651 sh, w								
				754 vw	754 w	767 vw	764 w					$\mathrm{CF_3SO_3^-}$: $\delta_s(\mathrm{CF_3})^b$
								764 vw	771 w			$\nu_s(\mathrm{BF_4^-})$
	793 vw							790 vw				
								811 w	812 w			
824 m	824 m	825 s	827 s	824 m	824 m	824 s	826 m	824 m	827 w	823 s		$\nu_s(\mathrm{C'_2N})$
			906 w				909 w					$\gamma(\mathrm{CH})^a$
917 m	921 w	912 w	919 sh w	917 m	914 sh, w	918 w		920 m		913 w		$\gamma(\mathrm{CH})$
930 w, sh	928 m	931 m	934 m		937 s		932 s					$\nu_s(\mathrm{ClO_4^-})^c$
941 w, sh	941 s			942 sh,w	941 m		944 m					$\nu(\mathrm{CS})^d$
952 m	948 m	958 s	954 s	953 m	957 m	956 sh, m						$\nu(\mathrm{CS})^d$
969 m	969 vw	970 sh		969 m	970 sh, w	968 m	968 w	968 m		970 s		$\nu(\mathrm{CS})$
				1032 m	1032 m		1031 s					$\mathrm{CF_3SO_3^-}$: $\nu_s(\mathrm{CF_3})^b$
1052 m	1048 m	1050 vw		1046 w	1047 m		1046 w	1055 s	1064 m	1052 w		$\rho(\mathrm{CH_3})$
1095 s	1083 s	1097 m	1095 w	1084 m	1088 s	1098 vw	1085 w	1097 s	1084 s	1099 m		$\rho(\mathrm{CH_3})$
	1110 s			1110 m	1111 s	1105 w		1122 s				$\nu_{as}(\mathrm{ClO_4})$ ^{c}
1135 s	1130 s	1134 m	1134 m	1134 s	1137 s	1135 m	1137 m	1135 s	1133 m	1132 m		$\rho(\mathrm{CH_3})$
										1144 m		
	1139 s			1153 m	1180 w		1147 m, sh	1174 m				
1206 w	1202 w	1205 w		1206 w	1203 w	1206 w		1207 w		1209 w		$\mathrm{n_{as}(X_2N)}$
				1224 w		1224 w						$\mathrm{CF_3SO_3^-}$: $\nu_s(\mathrm{CF_3})$
				1270		1295 w						$\mathrm{CF_3SO_3^-}$: $\nu_s(\mathrm{SO_3})$
						1300 w						
						1305 w						
1386 m	1380 m	1384 s	1384 m	1385 m	31385 m	1384 s	1385 s	1386 m	1379 m	1386 s		$\delta_s(\mathrm{CH_3})$
1400 s	1404 s		1401 m	1400 s	1405 s	1400 s, sh	1408 s	1399 s	1402 s	1413 s		$\delta_s(\mathrm{NCH})$
1414 s	1409 s	1412 s	1414 m	1415 s	1416 s	1413 s	1422 s	1415 s	1429 m			$\delta_s(\mathrm{CH_3})$
	1417 sh											
1442 m	1442 m	1441 m	1438 w	1443 m	1438 m	1444 m	1440 m	1443 m		1443 m		$\delta_{as}(\mathrm{CH_3})$
			1458 w									
1466 m	1462 m	1462 m	1468 w	1465 m	1462 m	1465 m	1463 m	1464 m		1463 m		$\delta_{as}(\mathrm{CH_3})$
							1473 m					

[a] Based on normal coordinate analysis of DMTF in ref 86 and assignments in ref 62. [b]Reference 89. [c]Reference 87. [d]Coordinated ligand.

Vibrational Spectroscopy. The bands observed in the vibrational spectra (Table 5) can be divided into three groups of origin, the internal vibrations of the *N*,*N*-dimethylthioformamide molecule, the metal–ligand bonds, and the perchlorate or trifluoromethanesulfonate anion. Previously, a full assignment based on normal coordinate analyses in combination with quantum chemical calculations has been made of the 30 normal modes of the *N*,*N*-dimethylthioformamide molecule,[86] and the spectra of the solvated zinc, cadmium, and mercury(II) ions have been analyzed.[62,86]

The metal–ligand stretching vibrations occur at similar frequencies for the copper(I) and silver(I) solvates. The metal–sulfur stretching contributes strongly to the band between 380 and 390 cm^{-1} but also to the weaker band around 300 cm^{-1}; see Table 5. Comparisons of solution and solid state spectra show that the bands from the copper(I) complexes are quite similar, although the solution spectra show some shift toward lower frequencies, while the shift is slightly larger for the silver complexes. The Ag–S stretching frequency in the *N*,*N*-dimethylthioformamide-solvated silver ion in solution is found at 384 cm^{-1} but at 391 cm^{-1} in the solid structure. This shift is consistent with the stronger Ag–S bonding to the three *N*,*N*-dimethylthioformamide molecules in the solid state than to the four in solution.

The gold(I) solution had lower concentration, approximately 0.2 mol·dm^{-3}, and the solvent dominates the spectrum. The few Raman bands possible to distinguish as belonging to the gold-

---

(86) Stålhandske, C. M. V.; Mink, J.; Sandström, M.; Papai, I.; Johansson, P. *Vib. Spectrosc.* **1997**, *14*, 207.

(I) complex are found at 139, 190, 926, and 1587 cm^{-1}. In the solid compound [Au(SCHN(CH$_3$)$_2$]BF$_4$ the corresponding bands are at 143, 189, 928, and 1599 and 1586 cm^{-1}. Assignments can be made by comparisons with the previously analyzed bis(*N*,*N*-dimethylthioformamide)mercury(II) perchlorate. The Au−S stretching frequency probably coincides with the γ(C′N) from *N*,*N*-dimethylthioformamide and the ν_2 deformation mode of the tetrafluoroborate anion, found as two overlapping bands at 359 and 360 cm^{-1}.[86,87] The low-frequency band at 143 cm^{-1} is probably the symmetric bending of Au−S−C. This vibrational mode has somewhat lower frequency in bis(*N*,*N*-dimethylthioformamide)mercury(II) perchlorate where it is found at 115 cm^{-1}.[77] The band at 189 cm^{-1}, present in bis(*N*,*N*-dimethylthioformamide)mercury(II) perchlorate, originates from a bending mode, δ_s(NCS), and a rocking mode, ρ(NC′$_2$), of the coordinated ligand.

The C−S stretching frequency of the free *N*,*N*-dimethylthioformamide solvent molecules is found at 969 cm^{-1} and shifts downward at coordination to about 955 cm^{-1} for both copper(I) and silver solvates. This shows an even weaker coordination (M−S bond) than for the weakly bonded ligands of the six-coordinated [Cd{SCHN(CH$_3$)$_2$}$_6$]ClO$_4$ solvate with a C−S band at 949 cm^{-1}.[62] For the [Zn{SCHN(CH$_3$)$_2$}$_4$]CF$_3$SO$_3$ solvate, with almost the same M−S bond length as the [Cu{SCHN(CH$_3$)$_2$}$_4$]ClO$_4$ compound, the larger shift of C−S band to 940 cm^{-1} shows a more covalent character of the M−S bond, which is even more pronounced for the [Hg{SCHN(CH$_3$)$_2$}$_4$]$^{2+}$ solvate in solution where the C−S band is observed at 931 cm^{-1}.[62]

Because of the strong π-electron charge transfer from the nitrogen to the sulfur atom in thioformamides, as shown by quantum chemical calculations,[86] also the C−N stretching mode of the formyl group is sensitive to the strength of coordination.[67,68] The band dominated by C−N stretching in the free *N*,*N*-dimethylthioformamide solvent molecules at about 1540 cm^{-1} shifts upward to about 1560 cm^{-1} both for the *N*,*N*-dimethylthioformamide-solvated copper(I) and silver ions in solution. This can be compared to 1565, 1578, and 1587 cm^{-1} for the four-, six-, and four-coordinated zinc, cadmium, and mercury(II) ions in *N*,*N*-dimethylthioformamide solution, respectively, showing the same tendency at increasing metal−sulfur coordination strength as for the shift of the C−S stretching band. The upward shift of the C−N band is consistent with an increase in its double bond character, due to π-back-bonding from the metal atom into the delocalized S−C−N system.

In the far-infrared region liquid *N*,*N*-dimethylthioformamide shows two marked bands, the out-of-plane vibration of the nitrogen atom found at 363 cm^{-1}, γ(C′−N), and a scissoring-rocking mode of the NC′ entity found at 405 cm^{-1} (Table 5).[89] At coordination, the out-of-plane mode becomes hindered because of the increasing C−N double-bond character and virtually disappears in the solid solvates, while the 405 cm^{-1} band is hardly affected.

No significant frequency shifts are found for the bands belonging to the anions as expected for noncoordinated or weakly solvated anions.

Conclusions

The copper(I) ion solvated by *N*,*N*-dimethylthioformamide has similar four-coordination in solution as in the crystalline solvate obtained from the solution. The Cu−S bond distances in solution seem to have a large and asymmetric distribution, giving a mean value that to some extent depends on the inherent weighting in the different structural methods used. The mean value, 2.35(2) Å, is close to that in the solid state, 2.336 Å (Tables 3 and S2). In the vibrational spectra of the solution, there is a slight shift of the Cu−S stretching frequency toward lower wavenumbers. The crystal structure of the solvate shows a distorted tetrahedral coordination geometry of the solvated copper(I) ion, in particular a large variation in the S−Cu−S angles, but the average structure in solution seems to be more regular. The mean Cu−S−C bond angle is somewhat larger in the solid state, ca. 108°, than found for *N*,*N*-dimethylthioformamide ligands in other solvates, and it seems that the M−S−C angle increases when the covalency of the M−S bond decreases.

The isoelectronic copper(I) and zinc(II) ions have a similar tetrahedral coordination in *N*,*N*-dimethylthioformamide solution. However, the somewhat distorted tetrahedral four-coordination of the silver(I) ion in *N*,*N*-dimethylthioformamide solution is quite different from that of the six-coordinated isoelectronic cadmium(II) ion and resembles the solution structure of the four-coordinated mercury(II) ion. In the solid solvate crystallizing from solutions of silver perchlorate in *N*,*N*-dimethylthioformamide almost trigonal planar AgS$_3$ units are found, joined by a long Ag···S interaction. This gives rise to a 3 + 1 coordination in discrete dimeric [Ag$_2$(SCH(N(CH$_3$)$_2$)$_6$]$^{2+}$ complexes, in which the silver atoms are joined by an asymmetric double sulfur bridge.

Gold(I) coordinates two *N*,*N*-dimethylthioformamide molecules in the solid state, most probably in linear fashion, with an Au−S bond distance of 2.293(2) Å. *N*,*N*-dimethylthioformamide is obviously a sufficiently strong electron-pair donor to maintain a linear coordination around gold(I) even in solution without increase in the Au−S bond distance; i.e., there are no significant equatorial Au−S interactions with the solvent molecules, while tetrahedral gold(I) solvates are formed with the less strong electron-pair donors pyridine and acetonitrile.

Thus, the monovalent d^{10} metal ions display tetrahedral coordination and the divalent ions octahedral coordination, in all oxygen and nitrogen donor solvents without steric hindrance. The higher coordination number of the solvated divalent ions is probably connected to the increased contraction of the d orbitals for the higher oxidation state. This gives a small splitting, Δ_{oct}, which also may be further reduced by the π-donor ability of the ligands.[90] The energy loss will then become less severe for the filling of two antibonding molecular orbitals that is required for six sulfur-donor ligands to a d^{10} ion in an octahedral bonding scheme.

In *N*,*N*-dimethylthioformamide solution the coordination geometry becomes linear of the gold(I) ion and tetrahedral of the zinc and mercury(II) ions, while the other d^{10} metal ions maintain their normal coordination figures. This implies a stronger interaction between the metal ions and the sulfur donor ligands, destabilizing octahedral coordination. The strong tendency toward linear coordination for the gold(I) ion, and also to a lesser extent for the mercury(II) ion, must be connected to vibronic coupling or second-order Jahn−Teller effects.[85] The relativistic effects expose the 5d$_{z^2}$ orbital, more for the monovalent gold(I) ion, and allow it to participate significantly in the bonding.

---

(87) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley-Interscience: New York, 1997; Part A, Chapter II-6.

(88) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1995**, *117*, 2201.

(89) Johnston, D. H.; Shriver, D. F. *Inorg. Chem.* **1993**, *32*, 1045.

(90) Gerloch, M.; Constable, E. C. *Transition Metal Chemistry*; VCH: Weinheim, Germany, 1994; Chapter 6.

Acknowledgment. The financial support from the Swedish Research Council is gratefully acknowledged. We wish to thank Dr. Hans Kariis for recording the Raman spectra at the Bruker IFS 66 instrument at the University of Linköping. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The SSRL Structural Molecular Biology Program is supported by the Department of Energy, Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program.

Supporting Information Available: Tables S1−S3, listing atomic coordinates, equivalent isotropic displacement coefficients, and interatomic bond distances and angles, Figures S1−S4, showing packing views and displaying fits of the EXAFS data and contributions of different scattering paths, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010226I