Inorg. Chem. **2003**, *42*, 2109–2114

Inorganic Chemistry
Article

Versatile Ligand Behavior of Hydrotris(4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl)borate. Syntheses and Crystal Structures of Cu(I) and Bi(III) Complexes

Maria Careri, Lisa Elviri, Maurizio Lanfranchi, Luciano Marchiò,* Clara Mora, and Maria Angela Pellinghelli

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Parco Area delle Scienze 17a, I 43100 Parma, Italy

Received August 9, 2002

Preparations of copper(I) and bismuth(III) complexes of hydrotris(4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl)borate ($Tr^{Et,Me}$) are described. These complexes have been characterized by means of spectroscopy and microanalysis. Molecular structures of $[Cu(Tr^{Et,Me})]_2 \cdot 2.5CH_3CN \cdot 0.5H_2O$ (**3a**) and $[Bi(Tr^{Et,Me})_2]NO_3 \cdot 2CHCl_3$ (**4a**) have been determined by single-crystal X-ray diffraction. In the centrosymmetric dimeric copper(I) complex, $Tr^{Et,Me}$ acts in the k^3*S*,*S*′,*H*:k*S*″ coordination mode. The metal is found in a distorted trigonal geometry as the ligand exhibits an "S_3-inverted" conformation at the boron center so that a weak [B–H•••Cu] agostic interaction renders the overall coordination of the (3 + 1) type. On the other hand, in the bismuth complex, $Tr^{Et,Me}$ presents the k^3*S*,*S*′,*S*″ coordination mode and the "S_3-normal" conformation. The metal is found in a regular octahedral geometry bound by six thioxo groups of two ligands. Species distributions in solution have been studied using electrospray ionization mass spectrometry upon dissolution of **3a** and **4a** crystals in acetonitrile. Monomeric and polynuclear copper(I) complexes with different M:L ratios are present in solution, while for **4a** only the monomeric species is present.

1. Introduction

Boron-centered tripodal ligands represent a wide class of compounds that have been extensively studied for their coordination properties with transition-metal and s−p block metal ions. Since the introduction of the hydrotris(pyrazolyl)borates (Tp's) in the 1960s by Trofimenko,[1] various tripodal ligands have been prepared following the same synthetic method.[2] Hydrotris(methimazolyl)borate (Tm) was prepared a few years ago by Reglinski and co-workers, and its donor capabilities rely on the *soft* environment of three thioxo groups if compared to the *hard* donor set of the Tp ligand class (three pyrazole nitrogen atoms).[3] Particularly relevant for biomimetic aspects are the hybrid ligands hydro[bis(thioxoimidazolyl)(pyrazoly)]borates in which pyrazolyl and thioxoimidazolyl groups are present all together, providing the [S_2N] donor set as good models for diverse zinc-containing enzyme active sites.[4,5]

We have recently synthesized a new boron-centered tripodal ligand, hydrotris(thioxotriazolinyl)borato (Tt), virtually incorporating the Tp and Tm donor properties as it behaves in the [S_3] and [N_3] modes with different metals since heterocyclic nitrogen atoms and thioxo groups are

---

* Author to whom correspondence should be addressed. E-mail: marchio@unipr.it.

(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Shaver, A. Polypyrazolylborates and related Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A. Eds.; Pergamon Press: Oxford, 1987; Vol. 2; pp 245−259. (c) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *Adv. Organomet. Chem.* **1992**, *34*, 1. (d) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (e) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (f) Reger, D. L. *Coord. Chem. Rev.* **1996**, *147*, 571. (g) Etienne, M. *Coord. Chem. Rev.* **1997**, *156*, 201. (h) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107. (i) Janiak, C. *Main Group Met. Chem.* **1998**, *21*, 33.

(2) (a) Janiak, C.; Hemling, H. *J. Chem. Soc., Dalton Trans.* **1994**, 2947−2952 and references therein. (b) Shiu, K.; Lee, J. Y. *Inorg. Chem.* **1993**, *32*, 3565−3567.

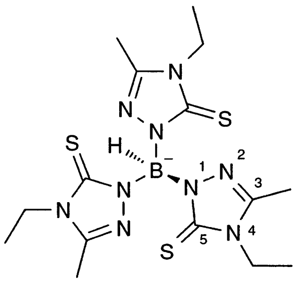
(3) (a) Reglinski, J.; Garner, M.; Cassidy, I.; Slavin, P. A.; Spicer, M. D.; Armstrong, D. *J. Chem. Soc., Dalton Trans.* **1999**, 2119−2126. (b) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. *J. Chem. Soc., Chem. Commun.* **1996**, 1975−1976.

(4) (a) Parkin, G. *J. Chem. Soc., Chem. Commun.* **2000**, *20*, 1971−1985. (b) Kimblin, C.; Bridgewater, B.; Hascall T.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 1267−1274. (c) Kimblin, C.; Bridgewater, B.; Churchill, B. M.; Hascall, T.; Parkin, G. *Inorg. Chem.* **2000**, *39*, 4240−4243. (d) Seebacher J.; Shu, M.; Vahrenkamp, H. *J. Chem. Soc., Chem. Commun.* **2001**, *11*, 1026−1027. (e) Bergquist, C.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 422−423.

(5) (a) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1999**, 2301. (b) Tesmer, M.; Shu, M.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 4022−4029.

10.1021/ic025939v CCC: $25.00

Chart 1



present on the same triazoline ring.[6] Here we report the synthesis and solid-state structures of copper(I) and bismuth(III) complexes of the hydrotris(4-ethyl-3-methylthioxotriazolinyl)borato ligand ($Tr^{Et,Me}$)[7] (Chart 1) together with electrospray ionization mass spectroscopy (ESI-MS) studies to gain insight into the speciation of the complexes in solution. Even though various Cu(I)/Tp complexes have been prepared and their crystal structures have been reported,[8] to our knowledge there is only one example of structural evidence of a copper(I) complex with a boron-centered tripodal ligand with a sulfur-rich donor set.[9] The high flexibility/versatility of $Tr^{Et,Me}$ makes it liable to adopt different conformations in the copper and bismuth complexes, and in the former the Cu(I) trigonal planar coordination is deformed by an agostic [B−H···Cu] interaction.

2. Experimental Section

2.1. General Procedures. All solvents and reagents are commercially available (Sigma-Aldrich) and were used as received except acetonitrile, which was distilled from 4 Å (1−2 mm) molecular sieves. The ^1H spectra were recorded on a Bruker 300 spectrometer at variable temperatures (220−340 K). Chemical shifts are reported in parts per million referenced to that of residual solvent protons. Infrared spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Perkin-Elmer FT-IR Nexus spectrometer. Elemental analyses (C, H, N) were performed with a Carlo Erba EA 1108 automated analyzer.

Cuprous chloride has been prepared according to published procedures and stored under nitrogen.[10]

2.2. ESI-MS. A Quattro LC (Micromass, Manchester, U.K.) triple quadrupole instrument equipped with a pneumatically assisted electrospray ionization (ESI) interface was used. An NT workstation with MassLynx v3.4 software was used for data acquisition and processing. In the ESI experiments the nebulizer gas (nitrogen, 99.999% purity) and the desolvation gas were delivered at flow rates of 55 and 550 L/h, respectively. The direct infusion mode operating with a Harvard syringe pump (Quebec, Canada) at a flow rate of 7 μL/min was used to optimize the ESI interface parameters on the MS response of the compounds. ESI-MS measurements were performed in negative ion (NI) and positive ion (PI) modes. Interface parameters were set as follows: (NI mode) capillary voltage −2.5 kV, cone voltage 40 V, extractor lens −6 V, source temperature 90 °C, desolvation temperature 90 °C, RF lens 0.3 V; (PI mode) capillary voltage 3 kV, cone voltage 40 V, extractor lens 7 V, source temperature 70 °C, desolvation temperature 70 °C, RF lens 0.7 V. Quadrupoles were tuned to unit resolution. Full-scan mass spectra were acquired over the *m*/*z* 50−1800 scan range using a step size of *m*/*z* 0.1 and a scan time of 1.5 ms with an interscan delay of 10 s.

2.3. Synthesis. Preparation of 4-Ethyl-1,4-dihydro-3-methyl-5-thioxo-1,2,4-triazole (1). In a 100 mL round-bottomed flask, 4-ethylthiosemicarbazide (10.90 g, 91.5 mmol) was heated to reflux for 3 days in glacial acetic acid (45 mL). The solution was then concentrated to half the original volume by vacuum distillation. Upon cooling, a white solid separated which was then filtered and washed with cold water (20 mL). Afterward the white product was dissolved in hot water (ca. 75 mL) and extracted into chloroform (8 × 50 mL) in a separating funnel. The organic solution was concentrated under reduced pressure, and the resulting white product was collected (4.1 g, 31%). Mp: 115.8−116.3 °C. ESI-MS (*m*/*z*, rel intens): 143, 100 ($[M + 1]^+$). ^1H NMR ($CDCl_3$): δ 1.31 (t, CH_3), 2.30 (s, CH_3), 4.02 (q, CH_2), 9.54 (s, N−H). IR (KBr pellets, cm^{-1}): 3111, 3060, 2954, 2856, 1575, 1499, 1364, 1285, 797, 694. Anal. Calcd for $C_5H_9N_3S$: C, 41.96; H, 6.29; N, 29.37. Found: C, 41.34; H, 6.40; N, 28.66.

Preparation of Sodium Hydrotris(thioxotriazolinyl)borate, $Na(Tr^{Et,Me})$ (2). 4-Ethyl-1,4-dihydro-3-methyl-5-thioxo-1,2,4-triazole (5.78 g, 40 mmol) and sodium tetrahydroborate (0.350 g, 9.1 mmol) were mixed together in a 100 mL round-bottomed flask fitted to a volumetric device for measuring hydrogen evolution. Upon stirring, the temperature was raised gradually to 120 °C, whereupon evolution of hydrogen gas began. The mixture melted at 125 °C, and the temperature was then raised to 150 °C and maintained for 4 h. The reaction mixture was allowed to cool to room temperature, and the resulting yellow glassy solid was inserted into the thimble of a Soxhlet apparatus and washed with chloroform for 6 h. From the thimble, a powdery white product was collected (4.19 g, 6.37 mmol, 70%). ^1H NMR (DMSO-d_6): δ 1.14 (t, CH_3), 2.20 (s, CH_3), 3.92 (q, CH_2). IR (KBr pellets, cm^{-1}): 2984, 2945, 2937, 2397, 1576, 1440, 1423, 1394, 1348, 1275, 990, 778. Anal. Calcd for $C_{15}H_{25}BNaN_9S_3$: C, 39.05; H, 5.42; N, 27.33. Found: C, 39.68; H, 5.19; N, 27.15.

Preparation of Bis{[hydrotris(thioxotriazolinyl)borato]copper(I)}, $[Cu(Tr^{Et,Me})]_2$ (3). Under a nitrogen atmosphere CuCl (0.070 g, 0.708 mmol) and **2** were mixed in accurately degassed methanol (40 mL) and stirred at room temperature for 4 h. The white product was filtered, washed with water, vacuum-dried, and collected (0.185 g, 54%). ESI-MS (*m*/*z*, rel intens): 1569, 10, $[Cu_4(L)_3]^+$; 1067, 54, $[Cu_3(L)_2]^+$; 1027, 40, $[Cu_2(L)_2Na]^+$; 1005, 23, $[Cu_2(L)(LH)]^+$; 796, 12, $[Cu_4(L)_3Na]^{2+}$; 1005, 23, $[Cu_2(L)(LH)]^+$; 524, 33, $[Cu(L)Na]^+$; 502, 42, $[Cu(LH)]^+$; 438, 100, $(L)^+$. IR (KBr pellets, cm^{-1}): 2974, 2932, 2442, 1576, 1468, 1443, 1376, 1275, 1103, 846, 778. ^1H NMR (25 °C, CD_3CN): δ 1.26 (t, CH_3); 2.31 (s, CH_3); 4.01(q, CH_2). Anal. Calcd for $C_{30}H_{50}B_2N_{18}S_6Cu_2$: C, 35.93; H, 4.99; N, 25.15. Found: C, 35.43; H, 4.47; N, 24.78. Crystals of X-ray quality were grown from a water/acetonitrile (1:2) solution which corresponded to $[Cu(Tr^{Et,Me})]_2 \cdot 2.5CH_3CN \cdot 0.5H_2O$ (**3a**).

---

[6] Bailey, P. J.; Lanfranchi, M.; Marchiò, L.; Parsons, S. *Inorg. Chem.* **2001**, *19*, 5030−5035.

[7] The apex indicates the substituents on the 5-thioxo-1,2,4-triazolinyl rings. The first fragment is relative to the substituent on the N^4 nitrogen atom, whereas the second is for the substituent on the C^3 carbon atom.

[8] (a) Jones, P. L.; Jeffery, J. C.; Maher, J. P.; McCleverty, J. A.; Rieger, P. H.; Ward, M. D. *Inorg. Chem.* **1997**, *36*, 3088−3095. (b) Yoon, K.; Parkin, G. *Polyhedron* **1995**, *14*, 811−821. (c) Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whittaker, J. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 11285−11298. (d) Carrier, S. M.; Ruggiero, C. E.; Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1993**, *32*, 4889−4899. (e) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711−718.

[9] Gioia Lobbia, G.; Pettinari, C.; Santini, C.; Somers, N.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2001**, *319*, 15−22.

[10] Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1−4.

Table 1. Summary of X-ray Crystallographic Data for **3a** and **4a**

	3a	**4a**
empirical formula	$C_{35}H_{58.50}B_2Cu_2N_{20.50}O_{0.50}S_6$	$C_{32}H_{52}B_2BiCl_6N_{19}O_3S_6$
fw	1115.58	1386.59
color, habit	colorless, block	red, block
cryst size, mm	0.30 × 0.30 × 0.20	0.27 × 0.25 × 0.22
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	11.983(1)	11.382(2)
b, Å	22.113(2)	13.365(2)
c, Å	20.134(2)	19.298(3)
α, deg	90	86.003(3)
β, deg	97.324(2)	73.505(3)
γ, deg	90	88.433(2)
V, Å^3	5291.6(8)	2807.9(7)
Z	4	2
T, K	293(2)	293(2)
ρ(calcd), Mg/m^3	1.400	1.640
μ, mm^{-1}	1.090	3.700
θ range, deg	1.37−26.01	1.83−26.00
total no. of reflns/no. of obsd reflns, $F > 4\sigma(F)$	20182/5721	15884/3909
R1^a	0.0417	0.0527
wR2^a	0.0992	0.0764

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Preparation of Bis[hydrotris(thioxotriazolinyl)borato]bismuth(III) nitrate, $[Bi(Tr^{Et,Me})_2]NO_3$ (4). $Bi(NO_3)\cdot 5H_2O$ (0.16 g, 0.325 mmol) was dissolved in methanol (15 mL) and the solution added to a methanolic (20 mL) solution of **2** (0.3 g, 0.650 mmol). A red precipitate instantly formed. The mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum, and the red powder was dissolved in water (30 mL) and extracted into chloroform (8 × 30 mL) in a separating funnel. The solvent was removed under vacuum from the resulting purple solution, and a red powder corresponding to $[Bi(Tr^{Et,Me})_2]NO_3$ was collected (0.138 g, 0.120 mmol, 37%). ESI-MS (*m/z*, rel intens): 1086, 100 $[Bi(L)_2 - (NO_3^-)]^+$. ^1H NMR (25 °C, $CDCl_2CDCl_2$): δ 1.27 (t, CH_3), 2.30 (s, CH_3), 3.97 (q, CH_2). IR (KBr pellets, cm^{-1}): 2976, 2853, 2501, 1567, 1429, 1383, 1270, 1173, 781. Anal. Calcd for $C_{30}H_{50}N_{19}O_3S_6B_2Bi$: C, 31.39; H, 4.36; N, 23.19. Found: C, 31.92; H, 4.56; N, 21.55. Recrystallization of the red powder from a chloroform solution gave red crystals structurally characterized by X-ray crystallography as $[Bi(Tr^{Et,Me})_2]NO_3\cdot 2CHCl_3$ (**4a**).

2.4. X-ray Crystallography. A summary of data collection and structure refinement is reported in Table 1. Single-crystal data collection was performed with a Bruker AXS Smart 1000 area detector diffractometer (Mo Kα, $\lambda = 0.71073$ Å) for **3a** and **4a**. Empirical absorption correction was applied using the program SADABS[11] (max and min absorption correction coefficient: 1.000, 0.590 (**3a**); 1.000, 0.884 (**4a**)). The structures were solved by direct methods (SIR97)[12] and refined with full-matrix least squares (SHELXL-97),[13] using the Wingx software package.[14] Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of the B−H group were found and refined for **3a,** whereas the remaining H atoms were placed at their calculated positions for both compounds. The programs Parst[15] and ORTEP[16] were also used. Full tables of bond lengths and angles, atomic positional parameters, and anisotropic displacement parameters are given in the Supporting Information.

3. Results

$[Na(Tr^{Et,Me})]$ (**2**) was prepared following the Trofimenko synthetic method employed for the synthesis of the hydrotris(pyrazolyl)borates, reacting sodium tetrahydroborate and **1** in the melt. After purification, the white solid obtained is air-stable, moderately soluble in water and methanol, and insoluble in chloroform. Complex **3** is scarcely soluble in water and in the common organic solvents and only moderately soluble in DMSO and acetonitrile. These solutions remain colorless even after prolonged exposure to air, suggesting the air stability of copper(I) in a sulfur-rich environment. On the other hand, **4** can be dissolved in water, acetonitrile, and chloroform, giving rise to bright red solutions.

3.1. Molecular Structures. 3.1.1. $[Cu(Tr^{Et,Me})]_2\cdot 2.5CH_3CN\cdot 0.5H_2O$. A molecular drawing of complex **3a** is depicted in Figure 1, and selected bond lengths and angles are reported in Table 2. In the unit cell two independent complexes are present, but the structures are substantially equivalent consisting of centrosymmetric dimeric units Cu_2L_2 with the metal ions in a distorted trigonal geometry bound by three sulfur atoms from two centrosymmetric ligands. The ligand is in fact chelating the first copper ion through sulfur atoms and bridges the second with the third thioxo group. The distortion from the ideal trigonal geometry can be explained taking into account an agostic interaction involving the borohydro moiety and the copper atom. The H−Cu distances of 2.22(3) Å for the first complex and 2.29(3) Å for the second one are slightly longer if compared to those found in the Cambridge Structural Database (1.406−2.202 Å); nevertheless, they are indicative of a metal−hydrido interaction. In fact, the sum of the coordination bond angles for both molecules is 356.13(4)° (molecule 1) and 356.09(4)° (molecule 2), and the copper atoms lie out of the plane defined by the three sulfur atoms by 0.2516(5) Å (molecule 1) and 0.2533(5) Å (molecule 2), and are directed toward the hydrido groups. The overall coordination around the metals can thus be considered of the (3 + 1) type with each ligand behaving in the unusual $k^3S,S',H{:}kS''$ coordination mode. The Cu−S bond lengths range from 2.242(1) to 2.271(1) Å for molecule 1 and from 2.244(1) to 2.296(1) Å for molecule 2 (Table 2). The bond angles S−Cu−S are not symmetric; in fact for the chelating thioxo groups the values of 134.98(4)° (molecule 1) and 135.14(4)° (molecule 2) are significantly greater with respect to the two remaining angles (115.95(4)° and 105.20(4)°, molecule 1; 117.70(4)° and 103.25(4)°, molecule 2). As a consequence of the k^3S,S',H coordination (each ligand behaves as a “scorpionate”), the chelating triazole rings and the B−H−Cu plane form dihedral angles close to 120°, Figure 1b. The distances between the two copper centers for the first and second independent units

---

(11) *Area-Detector Absorption Correction*; Siemens Industrial Automation, Inc.: Madison, WI, 1996.

(12) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(13) Sheldrick, G. M. *SHELX97. Programs for Crystal Structure Analysis*, Release 97-2; University of Göttingen: Göttingen, Germany, 1997.

(14) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837

(15) (a) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95. (b) Nardelli, M. *J. Appl. Crystallogr.* **1995**, *28*, 659

(16) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

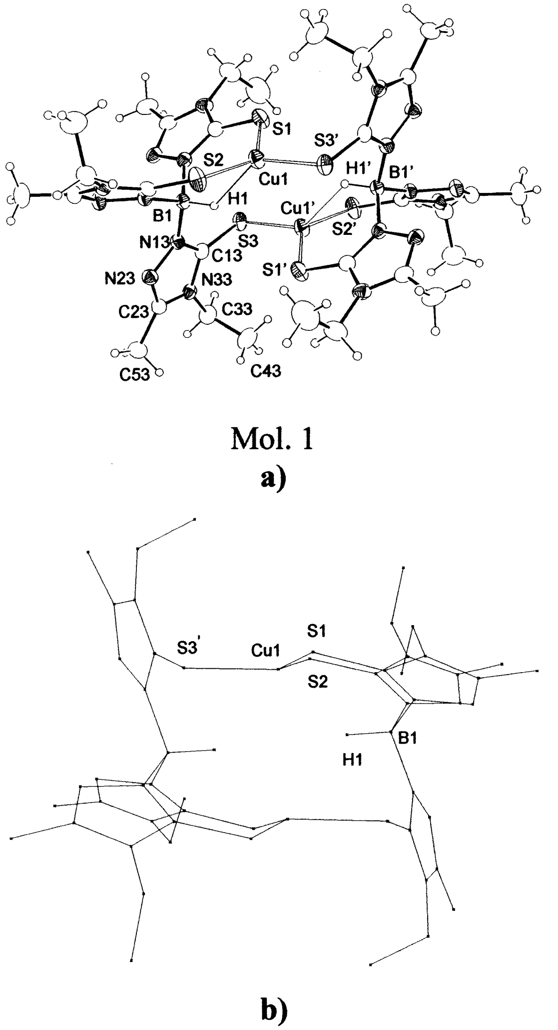


Figure 1. (a) ORTEP drawing of **3a** at the 30% thermal ellipsoid level (crystallization solvent molecules omitted). (b) Stick representation of molecule 1 of **3a**.

(4.2371(6) and 4.2767(6) Å, respectively) are too large for a possible metal−metal interaction.

3.1.2. $[\mathrm{Bi}(\mathrm{Tr}^{\mathrm{Et,Me}})_2]\cdot\mathrm{NO_3}\cdot 2\mathrm{CHCl_3}$. Recrystallization of **4** from a chloroform solution gave red crystals which X-ray crystallography proved to be $[\mathrm{Bi}(\mathrm{Tr}^{\mathrm{Et,Me}})_2]\mathrm{NO_3}\cdot 2\mathrm{CHCl_3}$ (**4a**), Figure 3. The bismuth atom presents an octahedral coordination, bound by the six thioxo groups from two ligands. The Bi−S bond lengths range from 2.744(3) to 2.836(3) Å, and the ligand bite angles and intraligand angles are close to 90°, suggesting a high coordination symmetry around the metal despite the absence of any crystallographic symmetry. The angles between the line passing through B(1)−Bi−B(2) and the triazoline planes vary from 33.8(6)° to 39.2(6)°, indicating a considerable twist of the ligand upon coordination (cf. 0° for a C_{3v} ligand symmetry).

3.2. ESI-MS Spectra. ESI-MS has proved to be a powerful tool for the analysis of ionic species in solution,[17] and several classes of chemical compounds have been characterized since its introduction.[18] Useful information regarding stoichiometry and the metal oxidation state has also been achieved for the solution speciation of coordination compounds when spectroscopic techniques proved to be insufficient or inadequate.[19] In this context, ESI-MS spectra were recorded for **3a** and **4a** by dissolving a small amount of crystals in acetonitrile to assess the nature of the complexes in solution. The mass spectrum of **3a** (PI) reveals the presence of different species corresponding to the following ion peaks: *m*/*z* 438 $[\mathrm{Tr}^{\mathrm{Et,Me}}]^+$ (100) (free ligand); *m*/*z* 502 $[\mathrm{Cu(LH)}]^+$ (L = $\mathrm{Tr}^{\mathrm{Et,Me}}$) (42); *m*/*z* 524 $[\mathrm{Cu(L)Na}]^+$ (33); *m*/*z* 566 $[\mathrm{Cu_2(L)}]^+$ (14); the dimeric complex $[\mathrm{Cu_2(L)}$-

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3a** and **4a**

3a			
molecule 1		molecule 2	
Cu(1)−S(1)	2.242(1)	Cu(2)−S(4)	2.296(1)
Cu(1)−S(2)	2.267(1)	Cu(2)−S(6)	2.244(1)
Cu(1)−S(3)^a	2.271(1)	Cu(2)−S(5)^b	2.258(1)
Cu(1)−H(1)	2.29(3)	Cu(2)−H(2)	2.22(3)
B(1)−H(1)	1.05(3)	B(2)−H(2)	1.18(3)
S(1)−Cu(1)−S(2)	134.98(4)	S(4)−Cu(2)−S(6)	135.14(4)
S(1)−Cu(1)−S(3)^a	115.95(4)	S(4)−Cu(2)−S(5)^b	103.25(4)
S(2)−Cu(1)−S(3)^a	105.20(4)	S(6)−Cu(2)−S(5)^b	117.69(4)
S(1)−Cu(1)−H(1)	82.7(7)	S(4)−Cu(2)−H(2)	78.9(8)
S(2)−Cu(1)−H(1)	79.4(7)	S(6)−Cu(2)−H(2)	83.4(7)
S(3)−Cu(1)−H(1)	136.8(7)	S(5)−Cu(2)−H(2)	136.3(8)
B(1)−H(1)−Cu(1)	133(2)	B(2)−H(2)−Cu(2)	131(2)
4a			
Bi−S(1)	2.744(3)	Bi−S(4)	2.831(2)
Bi−S(2)	2.804(3)	Bi−S(5)	2.816(3)
Bi−S(3)	2.836(3)	Bi−S(6)	2.793(3)
B(1)−H(1)	0.98	B(2)−H(2)	0.98
S(1)−Bi−S(2)	91.24(7)	S(3)−Bi−S(4)	87.25(8)
S(1)−Bi−S(3)	88.63(8)	S(3)−Bi−S(5)	94.99(7)
S(1)−Bi−S(5)	81.21(7)	S(4)−Bi−S(5)	91.10(7)
S(1)−Bi−S(6)	91.93(8)	S(4)−Bi−S(6)	92.83(8)
S(2)−Bi−S(3)	91.22(8)	S(5)−Bi−S(6)	89.61(7)
S(2)−Bi−S(4)	96.92(7)		
S(2)−Bi−S(6)	84.20(8)		

$^a -x+1, -y-1, -z+1$. $^b -x+1, -y, -z+1$.

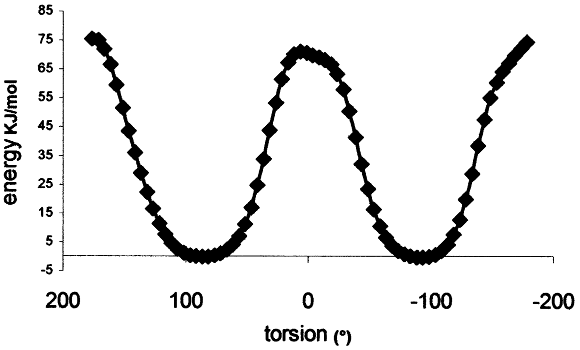


Figure 2. Nonbonded potential energies obtained by ROTENERN as a function of the representative torsion τ[C(11)−N(31)−C(31)−C(41)] (deg) in the isolated molecule of **3a**. The other ethyl groups of **3a** and **4a** showed very similar potential energy barriers.

---

(17) Agnes, G. R.; Stewart, I. I.; Horlick, G. *Appl. Spectrosc.* **1994**, *48*, 1347−1359 and references therein.

(18) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4451.

(19) (a) Ross, A. R. S.; Ikonomou, M. G.; Thompson, J. A. J.; Orians, K. J. *Anal. Chem.* **1998**, *70*, 2225−2235. (b) Spasojevic, I.; Boukhalfa, H.; Stevens, R. D.; Crumbliss, A. L. *Inorg. Chem.* **2001**, *40*, 49−58. (c) Woodcock, J. C.; Henderson, W.; Miles, C. O. *J. Inorg. Biochem.* **2001**, *85*, 187−199. (d) Walanda, D. K.; Burns, R. C.; Lawrance, G. A.; Nagy-Felsobuki, E. I. *J. Chem. Soc., Dalton Trans.* **1999**, 311−321. (e) Zhang, C., Rheinvald, V.; Lozan, V.; Wu, B.; Lassahn, P.-G.; Lang, H.; Janiak, C. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1259−1268.

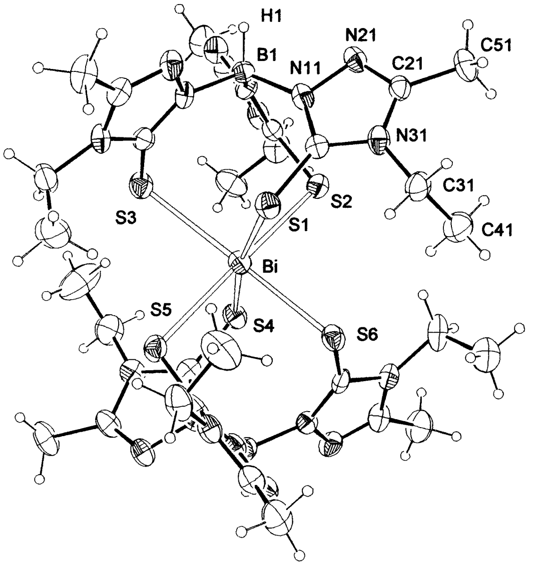


Figure 3. ORTEP drawing of **4a** at the 30% thermal ellipsoid level. The nitrate counterion and crystallization solvent molecules are omitted.

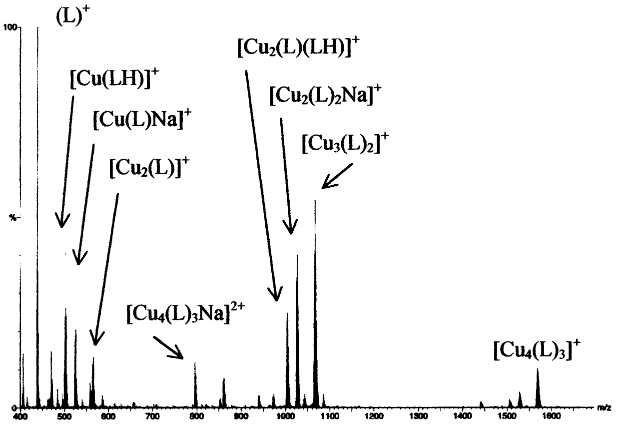


Figure 4. ESI-MS spectrum of **3a** dissolved in acetonitrile. A relative abundance of 100% corresponds to 4.71 × 10^6 counts (PI mode).

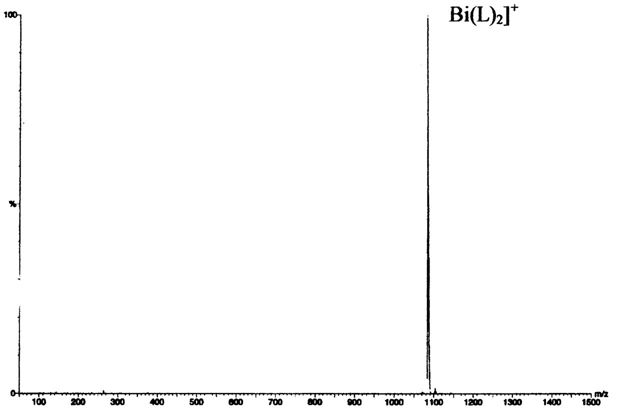


Figure 5. ESI-MS spectrum of **4a** dissolved in acetonitrile. A relative abundance of 100% corresponds to 1.02 × 10^9 counts (PI mode).

(LH)]$^+$ at *m*/*z* 1005 (23) and *m*/*z* 1027 ([Cu$_2$(L)$_2$Na)]$^+$) (40); the trinuclear complex [Cu$_3$(L)$_2$]$^+$ at *m*/*z* 1067 (54); the tetranuclear complex at *m*/*z* 1569 [Cu$_4$(L)$_3$]$^+$ (10) and *m*/*z* 796 [Cu$_4$(L)$_3$Na]$^{2+}$ (12) (Figure 4).

As illustrated in Figure 5, the ESI-MS spectra of **4a** show only one peak at *m*/*z* 1086 ([BiL$_2$]$^+$ (100), PI mode) and one peak at *m*/*z* 62 (NO$_3^-$ (100), NI mode), indicating the presence of only one species in solution, the molecular weight of which corresponds to that of the solid-state molecular structure.

4. Discussion

As the ligand Tr^{Et,Me} may present different coordination modes, due to the presence of nitrogen and thione donor groups, we are currently exploring its coordination capabilities toward transition metals and s−p block metals. In fact, it has already been shown for Tt that with its sodium salt and in the Mn(I) complex the coordination occurs through the triazoline nitrogen atoms whereas for *softer* cations such as Bi(III) and Sn(IV) the ligand adopts the S$_3$ coordination mode.[6] We are also interested in the modification of the steric hindrance around each donor group (N and S) of the triazoline rings and how this might affect the coordination ability of these ligands. The first step of this modification involves replacing the methyl groups of Tt with an ethyl group close to the C=S in each triazoline ring of Tr^{Et,Me}.

The mole ratio of 1:1 (M:L) has been chosen for the synthesis of the copper complex to favor the trigonal k^3*S*,*S*′,*S*″ coordination as was suggested for the compound [Cu(Tm)],[3b] and as was found in [(*m*-tolyl$_3$P)Cu(Tm)] and [(*p*-tolyl$_3$P)Cu(Tm)].[9] The mole ratio of 1:2 (M:L) has been preferred for the synthesis of the bismuth complex to facilitate octahedral coordination around the metal and to compare the coordination ability of Tr^{Et,Me} with respect to the less encumbered Tt ligand in [Bi(Tt)$_2$]Cl.[6]

The unexpected geometry of the copper(I) complex, as revealed by its crystal structure, can be explained considering the high flexibility of Tr^{Et,Me} as it appears that the triazoline rings are free to rotate around the B−N bond to better accommodate the two metals. Even though it was not surprising that this ligand was coordinated to Cu(I) through the sulfur atoms, a more interesting feature is the [B−H···Cu] agostic interaction and the k^3*S*,*S*′,*H*:k*S*″ coordination mode. The agostic interaction [B−H···Cu] and the sulfur-rich environment may play an important role in stabilizing the low oxidation state of the copper atom.

Also with Tp ligands dimeric copper(I) complexes were structurally characterized, but in these cases the metal is trigonally coordinated in the k^2*N*,*N*′:k*N*″ mode by pyrazolyl nitrogen atoms and the borohydrido groups point away from the metal centers.[20,21]

As regards the bismuth complex, the same coordinative situation was found for the related compound [Bi(Tt)$_2$]Cl in which the ligand is sterically less hindered in comparison to Tr^{Et,Me} as only two methyl groups surround the triazoline rings. It can be argued that the presence of the ethyl groups attached to the N^3 nitrogen atoms does not cause any steric hindrance as a consequence of the propeller-like conformation adopted by these ligands when they are S$_3$ tridentate.

A comparison of the **3a** and **4a** molecular structures reveals the coordinative flexibility of Tr^{Et,Me}. In both cases, the ligand

---

(20) Hu, Z.; Williams, R. D.; Tran, D.; Spiro, T. G.; Gorun, S. *J. Am. Chem. Soc.* **2000**, *122*, 3556−3557.

(21) Carrier, S. M.; Ruggiero, C. E.; Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1993**, *32*, 4889−4899.

Scheme 1

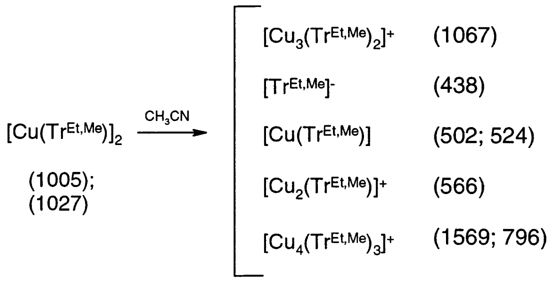
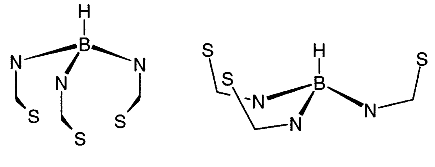


Chart 2



S_3-normal S_3-inverted

is sulfur coordinated but the conformation around the boron atom can be considered of the "S_3-normal" type for the bismuth complex whereas an "S_3-inverted" conformation is observed for the copper one, Chart 2. The S_3-inverted conformation was found for $[Na(H_2O)_6][Na(Tt)_2]$ and $[Na(Tt)(DMF)_3]$ in which the cation is bound by triazoline nitrogen atoms[9] and in the molecular structure of NaTm·4.5H_2O with the sulfur atoms surrounding the B−H bond even though the ligand does not interact with the metal ion.[3a] The inverted conformation was reported for the dimeric complexes $[Tp^{t-Bu}Cu]_2$[8d] and $[Tp^{t-Bu,Me}Cu]_2$[22] in which the copper(I) ions are digonally bound by two pyrazolyl nitrogen atoms of two ligands, but the agostic interaction has only been observed for the latter.

The presence of two independent molecules in the unit cell of **3a** can be justified by the different dispositions of the ethyl groups attached to the N3 nitrogen atoms of the triazoline rings. To have a better understanding of the coexistence of these two different conformations, nonbonded potential energy calculations were performed as a function of the torsion angle τ[C(1)−N(3)−C(3)−C(4)].[23] As can be seen from Figure 2 there are two minima when τ is ca. 90° and −90° corresponding to the two different situations encountered in the structure. This is in accordance with structural data as all the torsion angles previously defined are approximately ±90° for both molecules (range 85.5(4)−95.5(4)°). The differences between the two independent molecules can therefore be evaluated according to the sign of these torsion angles. In fact, molecules 1 and 2 present the $+ + +$ and $- + +$ conformations for each asymmetric unit, respectively. As the energy rotational barrier is low but not negligible (ca. 70 kJ/mol), crystal packing forces may account for the two molecular conformations found in the solid state. For **4a**, these torsions range from 85(1)° to 104(1)° and their signs are in the following order: $+ - - + + +$.

^{1}H NMR spectra have been recorded at variable temperatures from 263 to 340 K for **3a** (CDCN) and from 220 to 340 K for **4a** ($CDCl_2CDCl_2$) to further investigate the ethyl conformations in solution for the two complexes. The two spectra are substantially equivalent, and when the temperature in **3a** is decreased to 263 K, only a slight enlargement of the peaks of the ethyl protons is observed but no additional peaks appear; the same situation is found for **4a** when the temperature is lowered to 220 K, and no information could be obtained about the ethyl conformations even though the calculated rotational barrier appears to be quite high.

Information about speciation in solution is obtained by the ESI-MS technique that shows the presence of only one species for the bismuth complex, while for the copper one the situation is more complicated. In fact various species with different M:L ratios are present despite the fact that in the crystal the M:L ratio is 1:1. This would suggest the existence of multiple equilibria, generating mononuclear and polynuclear species due to the lability of Cu(I), Scheme 1. An analogous $[Cu_3(L)_2]^+$ species at *m*/*z* 1067 has already been proposed for the complex $[Cu_3(Tp^{Me,Me})_2]Cl$ from the analysis of its FABMS spectrum in which the metals would be digonally coordinated by two nitrogen atoms of two Tp ligands.[24] The occurrence of the ion peak corresponding to the free ligand was detected in PI mode despite the fact that $Tr^{Et,Me}$ is negatively charged. The formation of this ion may be due to the oxidation of two of the thioxo groups during the electrospray process, giving rise to the species $[Tr^{Et,Me}]^{2\bullet+}$. Similar behavior has been proposed for *N*,*N*-diethyldithiocarbamate complexes whereby the detected species were represented as radical cations in which the sulfur-rich ligand rather than the metals was considered oxidized.[25]

The IR spectra of **2**, **3a**, and **4a** exhibit weak ν(B−H) bands: 2397 cm^{-1} for **2**, 2501 cm^{-1} for **4a**, and 2442 cm^{-1} for **3a**. For the copper complex the ν(B−H) band is found at intermediate values of the corresponding bands of **2** and **4a**, indicating the weak nature of the agostic interaction in accordance with the long H···Cu bond lengths found in the solid-state structure. Even though the copper−hydride distances are not significantly different from the ones reported for the complex $[Tp^{t-Bu,Me}Cu]_2$,[22] a more simplified IR spectrum is observed for **3a**.

Acknowledgment. This work was supported by the Ministero dell'Istruzione, dell'Università e Ricerca (Rome, Italy). Thanks are also due to Daniele Belletti, Andrea Cantoni, and Gianfranco Pasquinelli for technical assistance during X-ray data collection.

Supporting Information Available: Listings of atomic coordinates of the non-hydrogen and hydrogen atoms, anisotropic displacement parameters, and bond lengths and angles for **3a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025939V

---

(22) Kiani, S.; Long, J. R.; Stavropolous, P. *Inorg. Chim. Acta* **1997**, *263*, 357−366.

(23) Nardelli, M. *ROTENER, A Fortran Routine for Calculating Non-Bonded Potential Energy*; University of Parma: Parma, Italy, 1996.

(24) Lam, M. H. W.; Tang, Y.; Fung, K.; You, X.; Wong, W. *Chem. Commun.* **1997**, 957−958.

(25) Ross, A. R. S.; Ikonomou, M. G.; Thompson, J. A.; Orians, K. J. *Anal. Chem.* **1998**, *70*, 2225−2235.