Synthesis, X-ray Structure, and Characterization of Ag(hfa)·Tetraglyme [hfa = Hexafluoroacetylacetonate]: A Novel Adduct for the Fabrication of Metallic Silver Based Films via in Situ Self Reduction[†]

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Received August 9, 1999
Revised Manuscript Received October 25, 1999

Introduction

Silver-based films, e.g., silver metal, silver-metallized polymeric or nanocluster embedded films, are materials of great interest for potential applications as contacts in microelectronics,[1] surface conductive flexible polymeric tapes,[2] materials for the construction of adaptive[3] and elastomeric optical[4] devices and for the applications of nanomaterials in chemical catalysis[5] or as magnetic,[6] electronic[7] and photonic[8] materials related to their properties that change as a function of particles size and geometries.[9]

Moreover, silver films are also of great interest, because of their potential applications for VLSI (very large scale integrated circuits) metallization and as components for high-temperature superconducting materials.[10]

The route usually adopted for the fabrication of metallized polymeric films implies a two-step process. In the first step, the polymeric film is prepared, and successively, the metal is deposited onto the film surface by different processes such as sputtering, electrodeposition or thermal and photochemical induced chemical vapor deposition. Unfortunately, the two-step metallized polymeric films have problems associated with the adhesion of the metals to the polymers.[11−13] Therefore, a single-step route which implies thermal reduction of polymer-soluble silver(I) complexes to metallic silver is highly desirable.[14−17]

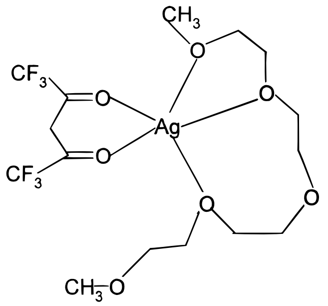
In this context, nanocomposite materials can be produced using a wide variety of chemical and physical synthetic methods. Nevertheless, only recently chemical methods employing the use of silver(I) complexes in polymers or silica xerogel matrixes[18−25] have been proposed to produce thick films or bulk materials. The procedures involved in the fabrication of such composites are governed by the solubility of the silver precursor either in the polymer solution or in the host matrix precursor and by its thermal stability. Sol gel strategies as well as supercritical infusion are often employed. For these applications, well-soluble precursors, suitable for a viable preparation of metal−matrix solutions would permit the synthesis of thin film and bulk materials whose metal contents are governed by the precursor concentration in the starting solution.

For all these processes, the nature of the silver(I) complexes is thus of crucial importance. In fact, the complex precursors must have certain prerequisites such as clean decomposition pathways to metallic silver, low decomposition temperatures, and, when used for the preparation of polymeric nanocomposites, a good solubility in the polymer−solvent mixture. Finally, they must be easily synthesized and purified to avoid long and costly synthetic procedures.

Herein, we report the synthesis of the adduct of Ag(hfa) (Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) with a polyether such as tetraglyme (tetraglyme (L) = 2,5,8,11,14-pentaoxatetradecane). Application of the new silver(I) complex to the fabrication of silver and silver-containing thin films (thickness $< 1\ \mu$m) via in situ thermal reduction is also reported.

The single-step reaction of silver oxide with hexafluoroacetylacetone and polyether in dichloromethane [eq 1] yields reproducibly an anhydrous, air stable adduct in 1 h in air.[26]

$$Ag_2O + 2\,Hhfa + 2\,L \rightarrow 2\,Ag(hfa)\bullet L + H_2O \qquad (1)$$



The adduct is soluble in dichloromethane and can be isolated as colorless crystalline powder by removal of the solvent. It has been characterized by ^{1}H and ^{13}C

[†] Communicated in part: Fragalà, M. E.; Compagnini, G.; Malandrino, G.; Puglisi, O. *Book of Abstracts*; 9th International Symposium on Small Particles and Inorganic Clusters ISSPIC 9; Lausanne, Switzerland, September 1−5, 1998.

(1) Glim. R.; Schlamp, G. *Met. Technol.* **1987**, *41*, 34.

(2) Endrey, A. L. (to Du Pont). Electrically Conductive Polymeric Compositions. U. S. Patents 3,073,784, 1963.

(3) Hubin, N.; Noethe, L. *Science* **1993**, *262*, 1390.

(4) Wilbur, J. L.; Jackman, R. J.; Whitesides, G. M.; Cheung, E. L.; Lee, L. K.; Prentiss, M. G. *Chem. Mater.* **1996**, *8*, 1380.

(5) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(6) Roost, N; Ackermann, L.; Pacchioni, G. *Chem. Phys. Lett.* **1992**, *93*, 94.

(7) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(8) Stucky, G. D.; MacDougall, J. E. *Science* **1990**, *247*, 669.

(9) Gleiter, G. *Adv. Mater.* **1992**, *4*, 474.

(10) Matsumoto, Y.; Abe, T.; Tanaka, M.; Tazawa, T.; Sato, E. *Mater. Res. Bull.* **1988**, *23*, 1241.

(11) Green, P. F.; Berger, L. L. *Thin Solid Films* **1993**, *224*, 209.

(12) Gerenser L. J.; Goppert-Berarducci, K. E.; Baetzold, R. C.; Pochan, J. M. *J. Chem. Phys.* **1991**, *95*, 4641.

(13) Mittal, K. L. *J. Vac. Sci. Technol.* **1976**, *13*, 19.

(14) Southward, R. E.; Boggs, C. M.; Thompson, D. W.; St. Clair A. K. *Chem. Mater.* **1998**, *10*, 1408.

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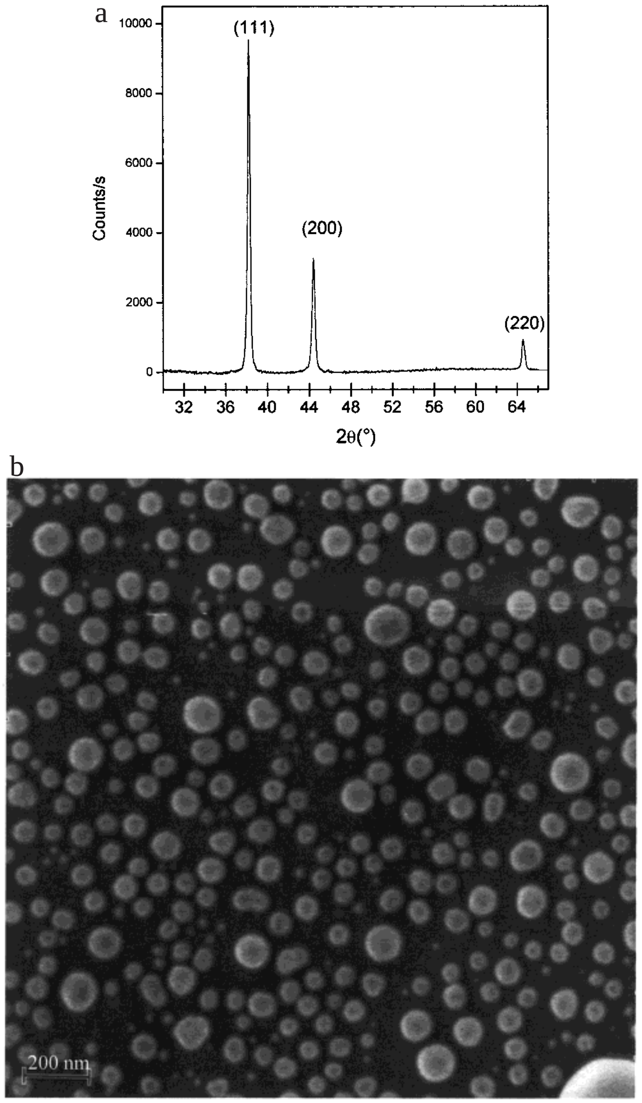

Figure 2. X-ray diffraction pattern (a) of a silver metal film deposited on Si(100) and SEM image (b) of a silver metal film deposited on Si(100).

NMR, mass spectrometry, and elemental analysis. It is nonhygroscopic, can be handled in air and melts at 41–43 °C.

One of the key properties of this adduct lies in the high solubility in organic solvents such as ethanol, chloroform, acetone, pentane, THF (tetrahydrofurane), NMP (*N*-methylpiyrrolidone), thus allowing the fabrication of thin silver films by spin coating on different substrates. In addition, the complex is highly soluble in different polymeric solutions such as polyamic acid solution or common commercial spin on glass solutions thus allowing the preparation of both silver-metallized polymer thin films and nanocomposites thin films in which silver nanoclusters are embedded in an insulating matrix (polyimide or silica) by controlling the concentration of the solution silver adduct.

With regard to the thermal behavior of the adduct, the atmospheric pressure thermal gravimetric analysis[27] indicates a single-step weight loss in the 100–255 °C temperature range with a 22% residue left. This residue consists of almost pure metallic silver whose percentage agrees well with the silver content in the compound (20%). These observations are well-tuned with the classically expected metal–ligand coordination strength of O-donor ligands vs Ag. In fact, they form weak complexes with the silver ion since the relative stability of silver–ligand bonds is in the order P > S > N > O.[28]

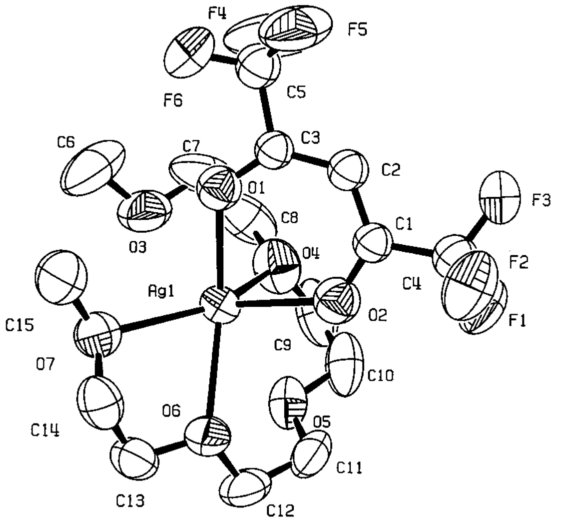

Figure 1. ORTEP drawing of the crystal structure of Ag(hfa)·tetraglyme. CF_3's have been omitted for clarity. Important bond distances (Å) are Ag1–O1 = 2.408(4), Ag1–O2 = 2.456(4), Ag1–O4 = 2.591(5), Ag1–O6 = 2.538(4), and Ag1–O7 = 2.582(4).

The crystal structure[29] (Figure 1) consists of a mononuclear complex in which the tetraglyme ligand is coordinated through three of the five oxygen atoms thus resulting in a silver coordination of 5. The Ag–O(diketone) bond distances are 2.408 and 2.456 Å. These values compare well with the distances usually observed

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(15) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1997**, *9*, 1691.

(16) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Caplan, M. L.; St. Clair, A. K. *Chem. Mater.* **1995**, *7*, 2171.

(17) Southward, R. E.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1997**, *9*, 501.

(18) Rosolovsky, J.; Boggess, R. K.; Rubira, A. F.; Taylor, L. T.; Stoakley, D. M.; St. Clair, A. K. *J. Mater. Res.* **1997**, *12*, 3127.

(19) Watkins, J. J.; MacCarty, T. J. *Chem. Mater.* **1995**, *7*, 1991.

(20) Deki, S.; Kakamatsu K.; Yano, T.; Mizuhata, M.; Kajinami, A. *J. Mater. Chem.* **1998**, 8, 1865.

(21) Carpenter, J. P.; Luckehart, C. M.; Milne, S. B.; Henderson, D. O.; Mu, R.; Stock, S. R. *Chem. Mater.* **1997**, *9*, 3164.

(22) Breitscheidel, B.; Zieder, J.; Schubert, U. *Chem. Mater.* **1991**, *3*, 559.

(23) Morke, W.; Lamber, R.; Schubert, U.; Breitscheidel, B. *Chem. Mater.* **1994**, *6*, 1659.

(24) Yanagihara, N.; Uchida, K.; Wakabayashi, M.; Hara, T. *Mater. Res. Symp. Proc.* **1991**, *501*, 227.

(25) Weiping, C.; Lide, Z. *J. Phys. Condens. Matter* **1997**, *9*, 7257.

(26) **Ag(hfa)·tetraglyme.** ^1H NMR (500 MHz, $CDCl_3$): δ 3.35 (s, 6H, OCH_3), 3.59 (m, 8H, OCH_2), 5.72 (s, H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 58.24(s, OCH_3), 70.06 (s, OCH_2), 70.12 (s, OCH_2), 70.15 (s, OCH_2), 71.61 (s, OCH_2), 86.02 (s, CH), 117.63 (q, 286 Hz, CF_3), 172.98 (q, 34 Hz, CO). Anal. Calcd for $AgC_{15}H_{23}O_7F_6$: C, 33.40; H, 4.46. Found: C, 33.37; H, 4.83. MS (FAB *m/z* (fragment); M = Ag(hfa)·tetraglyme): 331 $(M - hfa)^+$ 100%, 109 $(Ag)^+$ 11%. The given *m/z* ratios are related to the isotope ^{109}Ag.

(27) Experiments were performed with a temperature ramp up of 5 °C/min under N_2 and with a 4 mm alumina sample pan.

(28) Lancashire, R. J. In *Comprehensive Coordination Chemistry*; Wilkinson G., Gillard R. D., McCleverty J. A., Eds.; Pergamon Press: Oxford, UK, 1987; Vol. 5, pp 775–859.

(29) Crystal data for $AgC_{15}H_{23}O_7F_6$, monoclinic, $P2_1/a$, $a = 8.756(5)$ Å, $b = 17.325(5)$ Å, $c = 14.202(5)$ Å, $\beta = 106.420(5)°$, Z = 4, $\rho_{calc} = 1.727$ g/cm^3, $V = 2066(2)$ Å^3, $T = 295(2)$ K, Mo Kα $\lambda = 0.71069$ Å, 4784 unique data collected ($\theta - 2\theta$ technique, $2.69° < \theta < 24.99°$) of which 3632 have $F_o > 2\sigma(F_o)$ and were used for structure solution and refinement, $R = 0.0461$, $R_w = 0.0710$.[30,31]

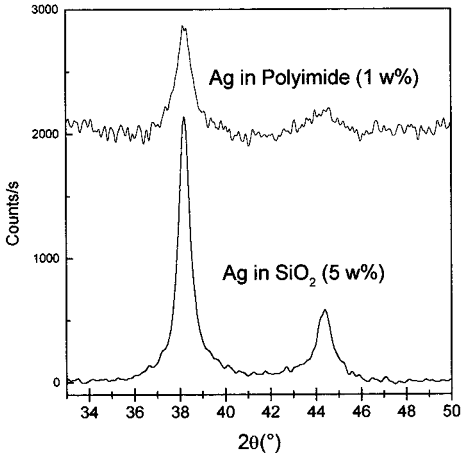

Figure 3. X-ray diffraction patterns of silver nanoclusters embedded respectively in a SiO_2 and in a polyimide thin film deposited on Si(100).

for various adducts of Ag(hfa),[32] e.g., with those observed in related complexes with polyamine ligands.[32f] The Ag–O(tetraglyme) bond distances range from 2.538 to 2.591 Å. Note, in addition, that one of the two uncoordinated oxygen atoms (O5) has only a weak contact with the Ag ion since the inferred distance (2.768 Å) represents a limit value of the Ag–O bond distances found, for example, in the dinuclear β-diketonate complex ((1,5-DMCOD)Ag(hfa))$_2$ [1,5-DMCOD = 1,5-dimethylcyclooctadiene]. The remaining tetraglyme oxygen atom (O3) lies too far (2.961 Å) to interact even weakly with the Ag ion.

The Ag(hfa)·tetraglyme adduct has been successfully applied to the deposition of both silver and silver containing nanostructured thin films.

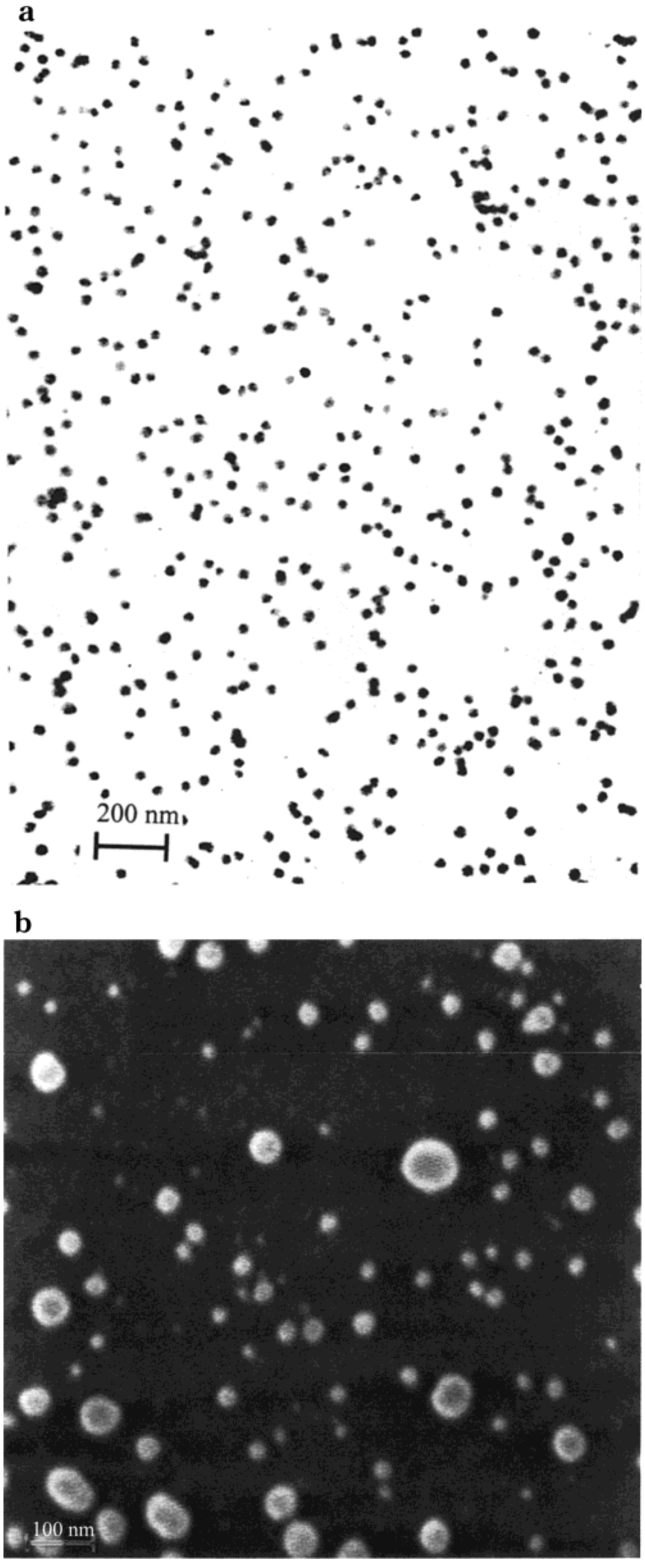

Figure 4. (a) TEM image of silver nanoclusters embedded in a polyimide film deposited on Si(100), and (b) SEM image of silver nanoclusters embedded in a SiO_2 film deposited on Si-(100).

X-ray diffraction (XRD)[33] pattern in Figure 2a refers to a thin silver film obtained by curing for 30 min at T = 220 °C a 2 wt % Ag (hfa)·tetraglyme in $CHCl_3$ solution spin coated on a silicon substrate. All the typical metallic silver reflections[34] are present. The corresponding scanning electron microscopy (SEM) micrograph, shown in Figure 2b, reveals a nanostructured film in which the silver grain dimensions are of the order of 70 nm. Note that, to obtain crystalline metallic silver films by MOCVD it is mandatory to use a reducing atmosphere, i.e., to use H_2 as reaction gas.[35] Metal particles whose diameters are less than 100 nm have singular properties[36,37] with respect to bulk materials, due to their small size, shape, high specific surface area, and quantum size effects. Therefore size effects can be expedient to change the properties of a nanostructured material by reducing the dimension of the constituent clusters. Unexpected properties can be built up in nanocomposites by using host matrixes that control the dimension of the embedded silver particles. The present

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(30) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallographr.* **1994**, *27*, 1045.

(31) Sheldrick, G. M. *SHELXL93, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, 1993.

(32) (a) Doppelt, P.; Baum, T. H.; Ricard, L. Inorg. Chem., **1996**, *35*, 1286. (b) Xu, C.; Corbitt, T. S.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *J. Chem. Soc., Dalton Trans.* **1994**, 2841. (c) Bailey, A.; Corbitt, T. S.; Hampden-Smith, M. J.; Duesler, E. N.; Kodas, T. T. *Polyhedron* **1993**, *12*, 1785. (d) Xu, C.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N.; Rheingold, A. L.; Yap, G. *Inorg. Chem.* **1995**, *34*, 4767. (e) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1994**, *72*, 1605. (f) Darr, J. A.; Poliakoff, M.; Li, W. S.; Blake, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2869.

(33) X-ray diffraction $\theta - 2\theta$ scans were recorded on a Bruker-AXS D5005 $\theta - \theta$ X-ray diffractometer using Cu Kα radiation operating at 40 kV/30 mA.

(34) JCPDS no. 1-1167.

(35) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *J. Mater. Chem.* **1995**, *5*, 303.

(36) Special issue: *Science* **1996**, *271*, 920.

(37) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.

film fabrication strategy allows the production of silver nanocomposites, in which the cluster dimensions can be tailored by the presence of an insulating medium. The XRD patterns (Figure 3) of a polyimide thin film (thickness ~1 μm) and of a silica thin film (thickness ~0.5 μm), containing silver nanoclusters, only show the most intense reflection of Ag metal. The corresponding transmission electron microscopy (TEM) and SEM images (Figure 4a,b) show nanoclusters 30 and 20 nm wide, respectively. It, therefore, transpires that this precursor opens a very attracting and intriguing route for the fabrication of new nanocomposites whose silver particle dimensions can be easily tuned by changing the host matrix nature, the metal concentration in the starting mixture, and the annealing temperature. Finally it is worthy of note that the present one-pot synthesis proved capable of synthesizing, with a great reproducibility, good yields (~80%) and through a viable low-cost route, a silver precursor that represents a pure, final product with no foreign species introduced in the procedure. This synthetic strategy, successfully applied to the preparation of alkaline earth[38] and lanthanide[39−41] precursors, opens a new route to an interesting generation of silver precursors.

In summary, the new adduct Ag(hfa)·tetraglyme has been successfully applied to the fabrication of silver-based films through a single-step route involving its thermal reduction to metallic silver. To our knowledge, this adduct represents the first example of a glyme adduct of a 1B (11) transition metal. Further studies are focusing on the coordination of other glymes and on the effect of polyether length on the adduct formation and stability.

Acknowledgment. The authors thank, Professor F. Castelli for the TGA analysis, Dr. Massimiliano Cantiano for the SEM images, Dr. Corrado Spinella for the TEM image, and Dr. Giuseppe Compagnini for the useful discussions.

Supporting Information Available: TGA analysis, complete list of crystal structure analysis, atom positions, thermal parameters, bond distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Malandrino, G.; Castelli, F.; Fragalà, I. L. *Inorg. Chim. Acta* **1994**, *224*, 203.

(39) Malandrino, G.; Licata, R.; Castelli, F.; Fragalà, I. L.; Benelli, C. *Inorg. Chem.* **1995**, *34*, 6223.

(40) Malandrino, G.; Incontro, O.; Castelli, F.; Fragalà, I. L.; Benelli, C. *Chem. Mater.* **1996**, *8*, 1292.

(41) Malandrino, G.; Benelli, C.; Castelli, F.; Fragalà, I. L. *Chem. Mater.* **1998**, *10*, 3434.