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Reversible Depolymerization of Silver Pyrimidinolate into Cyclic Hexamers

Norberto Masciocchi,*[,1a] Eleonora Corradi,[1a] Massimo Moret,[1a] G. Attilio Ardizzoia,*[,1b] Angelo Maspero,[1b] Girolamo La Monica,[1b] and Angelo Sironi*[,1a]

Dipartimento di Chimica Strutturale e Stereochimica
Inorganica—Centro CNR and Dipartimento di Chimica
Inorganica, Metallorganica e Analitica—Centro CNR,
Università di Milano, via Venezian 21, 20133 Milano, Italy

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Introduction

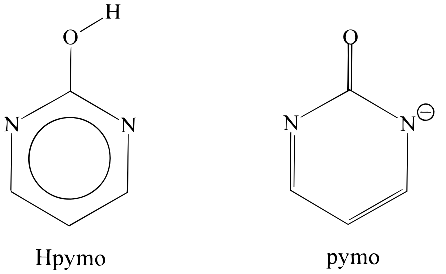
One-dimensional polymers containing transition metal ions were recently studied with the aim of discovering new materials with specific magnetic, optical, catalytic, and structural properties.[2] New fundamental science can be expected to emerge as structure−property correlations are established for these systems. Unfortunately, neither spectroscopic nor chemical methods can be considered as definitive structural tools until several analogues have been properly characterized by diffraction techniques. However, the negligible solubility in most organic solvents and the thermal instability of many of these polymers hamper the growth of suitable single crystals (from solution or from the melt) and require all structural information to be extracted from microcrystalline samples.

After having studied the syntheses and crystal structures of several group 11 metal azolates,[3−5] showing, *inter alia*, that the nuclearity of these species is heavily dependent on the synthetic approach and on the nature of ring substituents, we learned[6] of the existence of a hydrated polymer, $[Ag(pymo)]_n{\cdot}2nH_2O$, **1** (Hpymo = 2-hydroxypyrimidine; see Chart 1), whose structure is partially reminiscent of that of the $[M(pz)]_n$ (M = Cu, Ag; Hpz = pyrazole) phases.[3] Accordingly, we decided to attempt the synthesis of the hypothetical $[Ag(pymo)]_n$ phase by thermally induced dehydration of **1** (monitored by DSC, TGA, FTIR, and XRPD) or by direct means from anhydrous components.

Experimental Section

Synthesis of $[Ag(pymo)]_6$. Solid Hpymo (0.43 g, 4.48 mmol) was added, under N_2 atmosphere, to a solution of $AgNO_3$ (0.50 g, 2.94 mmol) in 40 mL of freshly distilled acetonitrile. The suspension was stirred for 10 min, and then NEt_3 (0.690 mL, 5 mmol) was added. The suspension was stirred for an additional 0.5 h; then the white solid was filtered off, washed with acetonitrile, and dried under vacuum at room temperature (0.58 g, 97% yield, based on $AgNO_3$). Anal. Calcd (found) for $C_4H_3AgN_2O$: C, 23.64 (23.63); H, 1.48 (1.43); N, 13.79 (13.36). Significant IR absorptions for $[Ag(pymo)]_6$, **3** (Nujol mull, cm^{-1}): 1618 (s), 1375 (s), 1280 (s), 1142 (w), 1085 (w), 1023 (m), 983 (m), 970 (m), 797 (s), 771 (s), 757 (s), 674 (s). IR absorptions of $[Ag(pymo)]_n{\cdot}2nH_2O$ for comparison (Nujol mull, cm^{-1}): 3340 (br, s), 3210 (br, s), 1636 (br, s), 1366 (s), 1268 (s), 1140 (w), 1100 (w), 1038 (w), 884 (w), 807 (s), 793 (s).

Chart 1



XRPD Analysis. X-ray powder diffraction data were obtained with Cu Kα radiation ($\lambda = 1.5418$ Å) on a Rigaku D-III MAX horizontal-scan powder diffractometer equipped with parallel (Soller) slits, a graphite monochromator in the diffracted beam, a Na(Tl)I scintillation counter, and a pulse height amplifier. The generator was operated at 40 kV and 40 mA. Slits used: DS, 1.0°; AS, 1.0°; RS, 0.3 mm.

The white powder was gently ground in an agate mortar to ensure homogeneity in particle size and then cautiosly deposited on a quartz monocrystal (zero background holder) with the aid of a binder (5% collodion in amyl acetate). Data were collected at room temperature in the 4−104° range, in the $\theta-2\theta$ mode, using a step scan method with $\Delta 2\theta = 0.02°$ and a fixed time of 10 s.

Since the diffraction peaks were rather broad, with fwhm's up to 0.40°, the few (orthorhombic) unit cells suggested by TREOR,[7] despite being consistent with 8 [Ag(pymo)] formula units (*V ca.* 1000 $Å^3$), were found to be misleading and did not lead to any successful structural model. After the sample was annealed, under nitrogen atmosphere, for 2 h at 260 °C, a new data collection, performed exactly as described above, afforded fwhm's as low as 0.20°, allowing a better definition of several peaks, previously overlapped. The lowest 22 peak positions (located by standard peak-search methods) were fed to the trial and error indexing routines of TREOR. The program found a reasonable agreement within the monoclinic system, with the following approximate cell parameters and figures of merit: $a = 9.01$ Å; $b = 18.78$ Å; $c = 8.90$ Å; $\beta = 95.7°$; $M(22) = 12$; $F(22) = 20$ (0.0089; 123). No rational transformations of this unit cell into higher symmetries could be found. Systematic absences indicated the $I2/m$ space group, subsequently confirmed by successful refinement. ALLHKL[8] was used to extract intensities in the 4−45° (2θ) range. SIRPOW[9] provided the initial atomic coordinates of two independent Ag atoms, one of which lies on the 2-fold axis. Remaining atoms were located by difference Fourier techniques and geometrical model building. The final refinements were performed using GSAS,[10] which permits bond parameters (Ag−N, N−N, C−C, C−O) to be restrained to known values. Low-angle data ($2\theta < 17°$), being those most affected by instrumental aberrations, were discarded. Two sets of isotropic thermal parameters were used, one for the metal atoms and one for all the atoms of the ligands. The contribution of the hydrogen atoms to the scattering factors was neglected. Atomic scattering factors were taken from the internal library of GSAS. The background was refined by using a six-term cosine Fourier series; a pseudo-Voigt function was found to best fit the peak shapes. The angular dependence of the peak widths was modeled using the dependence of Caglioti *et al.* with the *V* and *Z* (tan θ dependent) parameters set to zero. Final R_p, R_{wp}, and $R(\mathrm{Bragg})$ values were 0.061, 0.080, and 0.043, respectively. Table 1 contains the relevant crystallographic data for compound **3**. A detailed description of the methodology used can be found in ref 11, which reports the complete *ab-initio* structural analysis, from XRPD data only, of the cyclic $[Ag(dmpz)]_3$ trimer (Hdmpz = 3,5-dimethylpyrazole).

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(1) (a) Dipartimento di Chimica Strutturale e Stereochimica Inorganica e Centro CNR. (b) Dipartimento di Chimica Inorganica, Metallorganica e Analitica e Centro CNR.

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Table 1. Summary of Crystallographic Data and Experimental Details for **3**

formula	$C_{24}H_{18}Ag_6N_{12}O_6$
fw	1217.70
crystal system	monoclinic
space group	I2/m
a, Å	9.0149(4)
b, Å	18.808(1)
c, Å	8.9114(3)
β, deg	95.776(3)
V, Å^3	1503.3(2)
D_c, g cm^{-3}	2.69
Z	2
T, K	298(2)
radiation (*λ*, Å)	Cu Kα (1.5418)
no. of observns	4301
no. of reflns	1820
2*θ* range, deg	17−104
R_p	0.061
R_{wp}	0.080
R_F	0.043

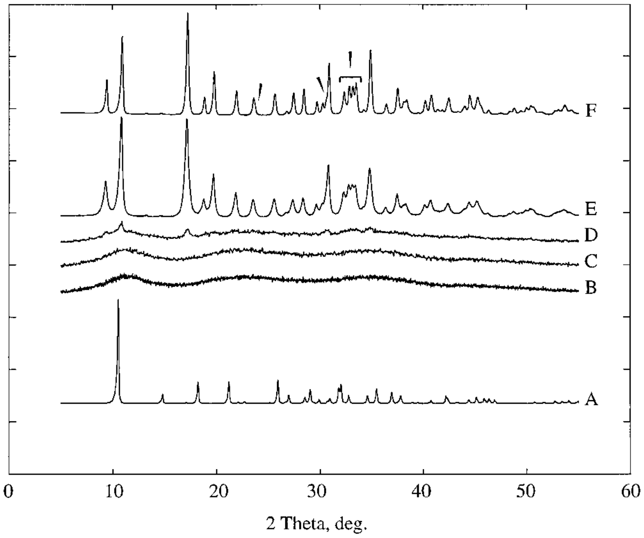


Figure 1. Raw XRPD data showing (bottom to top) the [Ag(pymo)]$_n$·2nH$_2$O dehydration (and amorphization) process and subsequent devitrification to crystalline [Ag(pymo)]$_6$: A = as synthesized; B = 15 min at 80 °C; C = 15 min at 120 °C; D = 15 min at 140 °C; E = 1 h at 180 °C; F = 2 h at 260 °C. Note that the top first and second curves possess fwhm's of 0.20 and 0.40° (2*θ*), respectively. Arrows indicate peaks which allowed, after annealing, assessment of the correct lattice parameters (see Experimental Section).

Results and Discussion

DSC and TGA of pristine **1**, under N$_2$, showed that (i) it readily loses water in the 80−110 °C range (ΔH = 101 kJ mol^{-1}), (ii) a weak exothermic peak, not accompanied by weight losses, is present at about 150 °C (ΔH = −4.9 kJ mol^{-1}), and (iii) complete thermal decomposition (to metallic silver) occurs at about 300 °C. Following by X-ray powder diffraction (XRPD) processes i and ii on powders of **1** deposited on a quartz monocrystal, we observed (Figure 1) that progressive heating generates an amorphous phase, **2**, which transforms, above 150 °C, into a white (poly)crystalline phase, **3**. This transformation is under kinetic control since it can be achieved also at lower temperatures by longer heating times. IR monitoring (Nujol mulls) confirmed the loss of water and the formation of a slightly different absorption pattern, which we originally attributed to the anhydrous [Ag(pymo)]$_n$ polymer.

Direct synthesis of a microcrystalline, insoluble material, possessing the same spectroscopic and diffraction patterns as **3**, was also accomplished by adding Et$_3$N to a CH$_3$CN solution of 2-hydroxypyrimidine and AgNO$_3$ or by suspending, at room temperature, **1** in anhydrous HC(OEt)$_3$ for 12 h under magnetic stirring. The reversibility of the latter process has been verified by the quantitative production of **1** on stirring **3** in wet acetone for one night (as checked by XRPD measurements). Scheme 1 graphically illustrates on such transformations.

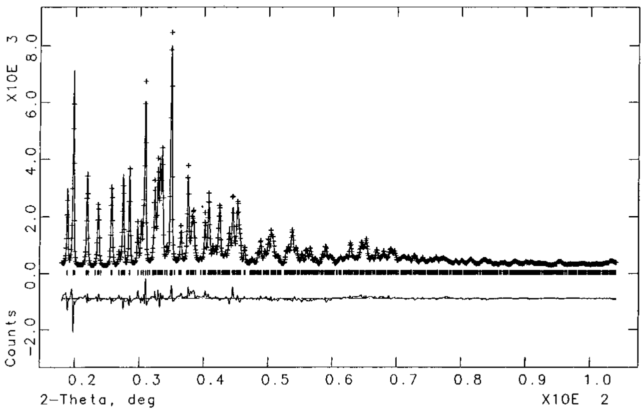
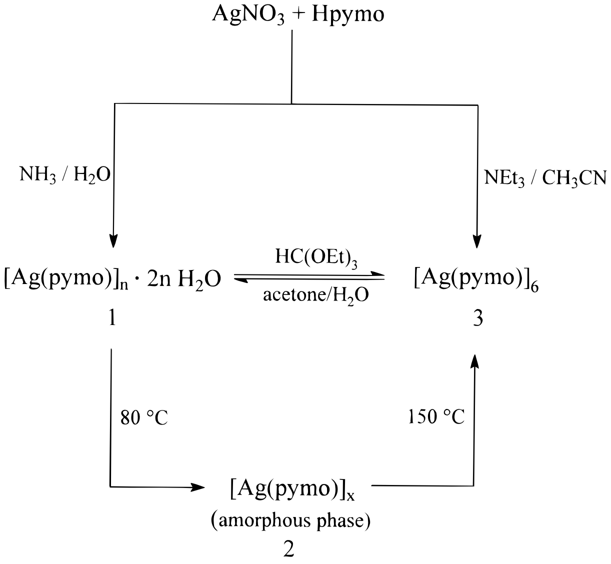


Figure 2. Final Rietveld refinement plot for [Ag(pymo)]$_6$, with peak markers and the difference plot at the bottom.

Scheme 1



The (micro)crystalline nature of **3** prompted us to attempt its structural characterization via XRPD.[12] Rather surprisingly, our XRPD analysis (see Figure 2) led to the discovery of a novel cyclic, hexameric compound, [Ag(pymo)]$_6$, of crystallographic C_{2h} symmetry (see Figure 3). The silver ions, lying approximately at the vertices of a nonbonded (Ag···Ag 6.117(6) and 5.909(5) Å) hexagon, are linearly coordinated by nitrogen atoms of the N,N′ bidentate ligands and have short contacts (of the aurophilic type) with neighboring molecules (Ag···Ag 2.962(2) and 3.061(5) Å). Whether or not these interactions are responsible for the very low solubility of the complex is not yet understood; indeed, in contrast to the situation for gold complexes, where relativistic effects are also at work,[13] the repulsive or attractive nature of "short" Ag···Ag interactions is still in debate: somewhat shorter contacts of this kind have been considered attractive in some cases, *e.g.* in [Ag(4,4′-bipyridine)]NO$_3$,[14] but also repulsive, as in [Ag(SCEt$_2$Me)].[15]

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(12) We also synthetized the Cu(I) and Au(I) analogues, which proved to be crystalline but *not* isomorphous. Their *ab-initio* XRPD structure determination has been attempted, but has not been, so far, successful.

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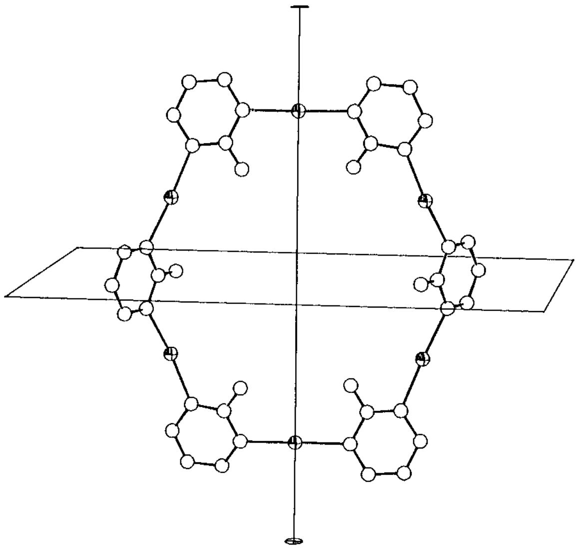

Figure 3. ORTEP drawing of the $[Ag(pymo)]_6$ molecule possessing crystallographic C_{2h} symmetry. Note the folded character of the whole ring.

The possibility of an N,O coordination of the pymo ligand, similar to that found in the $[Cu(mpyo)]_4$ (Hmpyo = 2-hydroxy-6-methylpyridine) tetramer,[16] was also originally considered, but IR evidence, hard/soft acid/base considerations, and successful refinement led to a more plausible N,N′ link.

The conformation of the six pymo ligands about the Ag_6 hexagon is markedly nonplanar, with dihedral angles between adjacent pymo rings of about 20 or 70°, in agreement with the structure observed for the cyclic $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2S)Au]_6$ hexamer.[17] According to the schematic conformational analysis put forward for binary pyrazolates in ref 3 (c = cis, s = staggered, t = trans), $[Ag(pymo)]_6$ possesses a [*csscss*] sequence, which contrasts with that of the only other hexamer known within this family, Fackler's gold 3,5-diphenylpyrazolate,[18] [*cctcct*]. The planar conformation of the whole molecule has been experimentally rejected, since, by imposing geometric restraints on the O···O distances, the XRPD fitting resulted in much worse agreement factors ($R_{wp} = 0.189$ *vs* 0.080; $R_F = 0.085$ *vs* 0.043). However, it is worth noting that both planar [*cccccc*] and folded conformations lack short (unconventional) *inter*molecular interactions and are consistent with the given cell. Indeed, molecular mechanics computations within a periodically updated crystal lattice, performed by a locally developed method[19] based on Allinger's MM3 program and force field,[20] show a possible plastic character of $[Ag(pymo)]_6$ crystals, *i.e.* that cooperative inversion of the wing-tips through a planar intermediate (at least in principle) could dynamically occur. The apparently large cavity present in the center of the hexamer (see Figure 3), actually, does not exist, since the analysis of the crystal packing clearly reveals that it is occupied by the tails of neighboring *nonplanar* molecules.

Comparison of the IR spectrum of the amorphous phase, **2**, with those of the crystalline phases **1** and **3** suggests that, on heating, its local structure, initially similar to that of **1**, smoothly evolves into cyclic hexamers (much like **3**). This could, at least in principle, be confirmed an XRPD study of the (Ag/Ag) radial distribution function (RDF), since second neighbor contacts within the open or cyclic sequences should differ by about 2 Å (the overall picture is, however, rather complicated by the likely existence of short(er) *inter*molecular Ag···Ag contacts); a similar approach has indeed been used in the tentative estimation of the nuclearity of amorphous sodium gold(I) thiomalate (myochrisin) using synchrotron radiation.[21]

The *reversible* transformation of **3** into the polymeric phase **1** represents a rare case of ring-opening polymerization (ROP), which was recently presented as a promising method for the synthesis of high molecular weight inorganic polymers.[2] The competitive formation of polymeric phases or cyclic, oligomeric species has structural analogues in the inorganic (sulfur allotropes[22]), coordination ($[Ag(pz)]_n$ *vs* $[Ag(pz)]_3$),[3] organic (polyethylene *vs* cycloalkanes), and organometallic ($[Ru(CO)_4]_n$[23] *vs* $[Ru_3(CO)_{12}]$) chemistry fields. Since bonding within these *molecular* fragments is mostly covalent and is very different from the *inter*molecular interactions, these couples are not usually considered, in the solid state, polymorphic forms of the same species or clusters of the simple basic motif. Therefore, although the stability field of the different forms might have been studied, it is unlikely that easily accessible interconversion paths exist. Alternatively, we have found a reversible chemical system, for which the presence of hydrogen-bonded water molecules (*i.e.*, of a vigorous enthalpic gain) stabilizes the polymer, rather than the (cyclic) hexameric form, which, on the contrary, is stabilized by anhydrous conditions.

Conclusions

This paper, besides contributing to a deeper understanding of the coordination chemistry of the Hpymo ligand, demonstrates that *ab-initio* powder diffraction analysis, even on standard (but well-conditioned) laboratory equipment, can be taken as an *active* structural tool, particularly valuable when other more conventional structural methods do not work; indeed, XRPD allowed us to discard a prefigured model, the $[Ag(pymo)]_n$ polymer, in favor of a new one, the cyclic $[Ag(pymo)]_6$ species. Moreover, the present structure determination led, at the same time, to the gross molecular features of (i) a solid state reaction product and (ii) a coordination compound failing to afford suitable single crystals. This has some general relevance since it can be easily foreseen that these two classes of compounds, together with twinned[24] and metastable[25] phases, are the best candidates for the meaningful use of *ab-initio* XRPD analysis.

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Supporting Information Available: FTIR spectra of **1**−**3** and tables listing crystallographic data, fractional atomic coordinates, and bonding parameters (5 pages). Ordering information is given on any current masthead page.

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