Inorg. Chem. **1998,** *37,* 5895−5901

The Structures of [24-Pyrimidinium crown-6][$Au(CN)_2$]$_4$(NO_3)$_2$·$2H_2O$, [24-Pyrimidinium crown-6][$Au(CN)_2$]$_6$·$5H_2O$, and [16-Pyrimidinium crown-4][$Au(CN)_2$]$_4$·6.5 H_2O, in Which Aurophilic Interactions Produce Trimers, Tetramers, and Chains of $Au(CN)_2^-$ Ions

Roger E. Cramer,*,[†] David W. Smith,[†] and William VanDoorne[‡]

Departments of Chemistry, University of Hawaii at Manoa, 2545 The Mall, Honolulu, Hawaii 96822, and Calvin College, Grand Rapids, Michigan 49546

Received April 3, 1998

The cyclic polypyrimidinium cations [24-pyrimidinium crown-6], [$(C_6H_8N_3)_6$]$^{6+}$, and [16-pyrimidinium crown-4], [$(C_6H_8N_3)_4$]$^{4+}$, form colorless salts with the dicyanoaurate(I) anion. [24-Pyrimidinium crown-6][$Au(CN)_2$]$_4$(NO_3)$_2$·$2H_2O$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell dimensions $a = 10.64(1)$ Å, $b = 10.73(1)$ Å, $c = 13.57(1)$ Å, $\alpha = 71.72(8)°$, $\beta = 82.01(9)°$, $\gamma = 83.90(9)°$, and $V = 1455(3)$ Å^3. [24-Pyrimidinium crown-6][$Au(CN)_2$]$_6$·$5H_2O$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell dimensions $a = 11.780(5)$ Å, $b = 12.064(4)$ Å, $c = 13.268(4)$ Å, $\alpha = 102.56(1)°$, $\beta = 112.14(1)°$, $\gamma = 101.82(1)°$, and $V = 1617(1)$ Å^3. [16-Pyrimidinium crown-4][$Au(CN)_2$]$_4$·$6.5H_2O$ (**3**) crystallizes in the monoclinic space group $C2/c$ (No. 15) with unit cell dimensions $a = 39.50(2)$ Å, $b = 13.160(7)$ Å, $c = 17.83(7)$ Å, $\beta = 90.66(3)°$, and $V = 9268(39)$ Å^3. Structures **1** and **3** contain similar centrosymmetric zigzag tetramers of $Au(CN)_2^-$ anions, with a terminal Au−Au distance of 3.271(4) Å and an Au−Au central distance of 3.492(5) Å for structure **1**, as compared to 3.155(7) and 3.501(7) Å, respectively, for **3**. Structure **2** contains a nearly linear trimer of $Au(CN)_2^-$ ions with Au−Au distances of 3.175(1) and 3.234(1) Å. In addition to the $Au(CN)_2^-$ tetramer, structure **3** also contains an infinite chain of $Au(CN)_2^-$ anions consisting of repeating tetrameric units spiraling along a 2-fold axis with internal Au−Au distances of 3.128(3), 3.220(4), and 3.274(5) Å and an Au−Au distance of 3.698(4) Å between tetrameric units.

Introduction

The interaction between metal ions is of interest to chemists, particularly in regard to gold atoms for which theoretical,[1,2,3] structural,[4−10] and spectroscopic studies[11−16] have been reported. The tendency for gold atoms to interact with other gold atoms at distances longer than ordinary bonding distances yet shorter than van der Waals contacts occurs frequently enough to have been bestowed with the term aurophilicity. The interest in aurophilicity stems from the theoretical explanation for this phenomenon and from the potential to use such interactions to build macromolecules. Experimentally, the strength of Au−Au interactions has been estimated to be on the order of 30 kJ/mol, similar to H−O···H hydrogen bonds.[17] For some sulfide, phosphine, and chloro complexes, the experimental value has been found to be as high as 41−46 kJ/mol.[12,18]

One simple system which exhibits aurophilicity is $Au(CN)_2^-$, but there are only three papers which report crystal structures of the dicyanoaurate anion.[19−21] This paper reports the structures of dicyanoaurate oligomers found in salts of the large, cyclic polypyrimidinium cations [24-pyrimidinium crown-6]$^{6+}$, 24PyrC6, and [16-pyrimidinium crown-4]$^{4+}$, 16PyrC4.

Experimental Section

The synthesis of [24-pyrimidinium crown-6](NO_3)$_6$ followed the procedure of Shimahara et al.,[22] as modified by Cramer et al.,[23−25] while [16-pyrimidinium crown-4] nitrate was made as we have previously

---

[†] University of Hawaii.

[‡] Calvin College.

(1) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133−137.

(2) King, C.; Wang, J.-C.; Khan, M. N. I.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2145−2149.

(3) Jiang, Y.; Alvarez, S.; Hoffman, R. *Inorg. Chem.* **1985**, *24*, 749−757.

(4) Weissbart, B.; Larson, L. J.; Olmstead, M. M.; Nash, C. P.; Tinti, D. S. *Inorg. Chem.* **1995**, *34*, 393−395.

(5) Jones, W. B.; Yuan, J.; Narayanaswamy, R.; Young, M. A.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1995**, *34*, 1996−2001.

(6) Raptis, R.; Porter, L. C.; Emrich, R. J.; Murray, H. H.; Fackler, J. P., Jr. *Inorg. Chem.* **1990**, *29*, 4408−4412.

(7) Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P., Jr.; Assman, B.; Angermaier, K.; Schmidbaur, H. *Inorg. Chem.* **1995**, *34*, 75−83.

(8) Heinrich, D. D.; Fackler, J. P., Jr. *Inorg. Chem.* **1990**, *29*, 4402−4404.

(9) Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1990**, *29*, 4404−4407.

(10) Khan, M. N. I.; King, C.; Heinrich, D. D.; Fackler, J. P., Jr.; Porter, L. C. *Inorg. Chem.* **1989**, *28*, 2150−2154.

(11) Assefa, Z.; Shankle, G.; Patterson, H. H.; Reynolds, Y. *Inorg. Chem.* **1994**, *33*, 2187−2195.

(12) Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Ouelette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1993**, *32*, 2506−2517.

(13) McCleskey, T. M.; Gray, H. B. *Inorg. Chem.* **1992**, *31*, 1733−1734.

(14) King, C.; Khan, M. N. I.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1992**, *31*, 3236−3238.

(15) Assefa, Z.; DeStefano, F.; Garepapaghi, M. A.; LaCasce, J. H., Jr.; Ouelette, S.; Corson, M. R.; Nagle, J. K.; Patterson, H. H. *Inorg. Chem.* **1991**, *30*, 2868−2876.

(16) Nagasundaram, N.; Roper, G.; Biscoe, J.; Chai, J. W.; Patterson, H. H; Blom, N; Ludi, A. *Inorg. Chem.* **1986**, *25*, 2947−2951.

(17) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417−419.

(18) Harwell, D. E.; Mortimer, M. D.; Knobler, C, B.; Anet, F. A. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *11*, 2679.

(19) Blom, N.; Ludi, A.; Bürgi, H.-B.; Tichý, K. *Acta Crystallogr.* **1984**, *C40*, 1767−1769.

(20) Rosenzweig, A.; Cromer, D. T. *Acta Crystallogr.* **1959**, *12*, 709.

(21) Hussain, M. S.; Al-Arfaj, A. R.; Akhtar, M. N.; Isab, A. A. *Polyhedron* **1996**, *15*, 2781.

(22) Shimahara, N.; Asakawa, H.; Kawamatsu, Y.; Hirano, H. *Chem. Pharm. Bull.* **1974**, *22*, 2086.

(23) Cramer, R. E.; Waddling, C, A.; Fujimoto, C. H.; Smith, D. W.; Kim, E. *J. Chem. Soc., Dalton Trans.* **1997**, 1675−1683.

10.1021/ic980372x CCC: $15.00

Table 1. Crystal Data and Structure Determination Summary

	1	**2**	**3**
empirical formula	$C_{44}H_{52}Au_4N_{28}O_8$	$C_{48}H_{58}Au_6N_{30}O_5$	$C_{32}H_{45}Au_4N_{20}O_{6.5}$
formula weight	1889.0	2317.04	1601.75
temp (°C)	25(2)	25(2)	25(2)
wavelength (Å)	0.71073	0.71073	0.71073
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
unit cell dimens			
a (Å)	10.644(13)	11.780(5)	39.50(2)
b (Å)	10.733(12)	12.064(4)	13.160(7)
c (Å)	13.576(14)	13.268(4)	17.83(7)
α (deg)	71.72(8)	120.51(1)	
β (deg)	82.01(9)	112.14(1)	90.66(3)
γ (deg)	83.90(9)	101.82(1)	
volume (Å^3)	1455(3)	1617(1)	9268(39)
Z	1	1	8
density (calcd, g/cm^3)	2.155	2.380	2.296
absorp coeff (mm^{-1})	10.124	13.62	12.689
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0561$, $wR_2 = 0.1480$	$R_1 = 0.0517$, $wR_2 = 0.1280$	$R_1 = 0.0643$, $wR_2 = 0.1745$
R indices (all data)	$R_1 = 0.0765$, $wR_2 = 0.1589$	$R_1 = 0.0640$, $wR_2 = 0.1324$	$R_1 = 0.1357$, $wR_2 = 0.2055$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

reported.[26] $KAu(CN)_2$ was synthesized by dissolving 0.25 g (1.12×10^{-3} mol) of AuCN in 5 mL of water containing 1 equiv of KCN (0.073 g); evaporation of the water resulted in large crystals of $KAu(CN)_2$. Synthesis of $KAg(CN)_2$ was accomplished in a manner similar to that of $KAu(CN)_2$.

[24-Pyrimidinium crown-6]$(NO_3)_2$[Au(CN)$_2$]$_4$·2H$_2$O (1). Single crystals suitable for X-ray diffraction were grown in a 20-cm long diffusion tube made of 5-mm o.d. glass tubing. One end of the tube was charged with 0.10 g (7.47×10^{-4} mol) of $KAu(CN)_2$, and the tube was filled with water. Into the other end of the tube was placed 0.10 g (9.05×10^{-5} mol) of 24PyrC6 nitrate, and the tube was capped and left undisturbed for several days. Suitable crystals grew in the center of the tube. Elemental analysis, found (calcd for $C_{44}H_{52}Au_4N_{28}O_8$): C, 27.68 (27.97); H, 3.00 (2.77); N, 20.47 (20.75).

[24-Pyrimidinium crown-6][Au(CN)$_2$]$_6$·5H$_2$O (2). Crystals suitable for X-ray diffraction were grown in a manner similar to that used for **1**. One end of the diffusion tube was charged with 0.10 g of a 6:1 mole ratio mixture of $KAu(CN)_2$ and $KAg(CN)_2$, respectively, and 0.10 g of 24PyrC6 nitrate was placed in the other end of the tube. Elemental analysis, found (calcd for $C_{48}H_{58}Au_6N_{30}O_5$): C, 24.67 (24.87); H, 2.33 (2.52); N, 17.89 (18.13).

[16-Pyrimidinium crown-4][Au(CN)$_2$]$_4$·6.5H$_2$O (3). Single crystals of **3** were obtained in two ways. In each case, a diffusion tube similar to that described above was used. In the first method, one end of the tube was charged with 0.10 g of a 1:1 mole ratio mixture of $KAu(CN)_2$ and $KAg(CN)_2$ and 0.10 g of 24PyrC6 nitrate was added to the other end of the tube. In the second method, 0.10 g of $KAu(CN)_2$ was placed in one end of the tube and 0.10 g of 16PyrC4 nitrate was placed in the other end. With both procedures, crystals grew in the center of the tube after several days. Data were collected from crystals grown both ways, yielding similar structural results. The data presented here are from the first method as the crystal was of better quality. Elemental analysis, found (calcd $C_{32}H_{45}Au_4N_{20}O_{6.5}$): C, 23.70 (23.99); H, 2.19 (2.84); N, 16.97 (17.49).

X-ray Data Collection and Treatment. The structures of **1**−**3** were determined from data collected on a Siemens R3mv diffractometer, using monochromatic Mo Kα radiation ($\lambda = 0.710\,73$ Å). For all structures, colorless crystals were mounted on glass fibers with epoxy cement at room temperature. The SHELXTL autoindexing routine was used to indicate the appropriate unit cell for each sample. During the data collection, three reflections were monitored for each structure and showed no decrease in intensity. The data were corrected for Lorentz and polarization effects using the SHELXTL system. An absorption correction was applied using Ψ scans, five for **1**, three for **2**, and four for **3**. Full-matrix least-squares refinement was carried on weighted values of F_o^2 for all $F_o^2 > 0$ using SHELXL-93,[27] as suggested in the documentation for the program. In Table 1 we have included R values calculated for all data as well as for 2σ data for comparison purposes. A summary of data collection and crystal parameters for structures **1**−**3** is given in Table 1.

Structure Solution and Refinement for 1. The structure of **1** was solved using Patterson methods, which located the two gold atoms in the asymmetric unit. The carbon and nitrogen atoms in the ring system and the cyanide groups were located from a series of Fourier difference maps. All these atoms were refined using anisotropic thermal parameters. During refinement, the nitrate ion in the asymmetric unit was found to be disordered about two positions. These nitrate ions were treated as planar rigid groups using a bond length of 1.24 Å, which is the average value found in the structure of [24-pyrimidinium crown-6]$(NO_3)_6$.[23] The occupancies of the nitrates were constrained so that the combined occupancy did not exceed one. The more highly occupied site refined to an occupancy of 0.63(2). Finally, an oxygen atom was located which appeared to be a water of crystallization. Hydrogen atoms were included at calculated positions, except for those of the water molecule. Hydrogen atoms of each type, methyl, methylene, amine, and aromatic, were given separate group thermal parameters which were refined. Water hydrogens were found from the Fourier map and allowed to refine separately. After the final cycle of refinement, the largest peak in the difference Fourier map was 2.0 e Å^{-3}, close to one of the gold atoms. Final atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and hydrogen bonding parameters are available in the Supporting Information.

Structure Solution and Refinement for 2. The structure of **2** was solved using Patterson methods, which located the three gold atoms in the asymmetric unit. The carbon and nitrogen atoms in the ring system and the cyanide groups were located from a series of Fourier difference maps. Three oxygen atoms of water molecules were located. Oxygen O(1) is near the inversion center at (0, 0, 0) and its occupancy was refined and then fixed at 50%. Oxygen O(2) was found to be disordered over two positions, the higher occupancy being 80(10)%, and O(3) is fully occupied. All of these atoms were refined using anisotropic thermal parameters. Hydrogen atoms were treated as for **1** above. After the final cycle of refinement, the largest peak in the difference Fourier map was 1.9 e Å^{-3}, close to Au(2). Final atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and hydrogen bonding parameters are available in the Supporting Information.

Structure Solution and Refinement for 3. The structure of **3** was solved using Patterson methods, which located two gold atoms at

---

(24) Cramer, R. E.; Carrie, M. J. *Inorg. Chem.* **1990**, *29*, 3902−3904.

(25) Cramer, R. E.; Mitchell, K, A.; Hirazumi, Y. A.; Smith, S. L. *J. Chem. Soc., Dalton Trans.* **1994**, 563−569.

(26) Cramer, R. E.; Fermin, V.; Kuwabara, E.; Kirkup, R.; Selman, M.; Aoki, K.; Adeyemo, A.; Yamazaki, H. *J. Am. Chem. Soc.* **1991**, *113*, 7033−7034.

(27) Sheldrick, G. M. *SHELXL-93*: *A Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1993.

general positions, three gold atoms on the 2-fold axis, and one more gold atom, Au(4), disordered about the 2-fold axis. The carbon and nitrogen atoms in the ring system and the cyanide groups were located from a series of Fourier difference maps. Seven separate water molecule locations were found, and their occupancies were allowed to refine. One water molecule, O(5), was found to be disordered over two positions and refined to an equal occupancy at each site. Another water molecule, O(6), was found by refinement to be 50% occupied. All fully occupied, non-hydrogen atoms, as well as Au(4), were refined using anisotropic thermal parameters. Hydrogen atoms were treated as in **1** above. The geometry of the disordered, half-occupied dicyanoaurate molecule containing Au(4) was restrained to be similar to that of the ordered, fully occupied dicyanoaurate which contains Au(5). The isotropic thermal parameters of the half-occupied C(24) and N(24) atoms of this disordered dicyanoaurate were restrained to be similar to those of Au(4). Finally, atoms C(16) and N(16) were restrained to have thermal ellipsoids similar to that of Au(6). It is not surprising that some such restraints were necessary due to the large differences in the atomic numbers of Au, C, and N and due to the disorder resulting from Au(4) falling just off the 2-fold axis. After the final cycle of refinement, the largest peak in the difference Fourier map was 1.14 e Å^{-3}, close to Au(2). Final atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and hydrogen bonding parameters are available in the Supporting Information.

Results

Selected bond lengths and angles for structures **1**−**3** are given in Table 2.

Table 2. Selected Bond Lengths and Angles for Structures **1**−**3**[a]

	1		
Au(1)−Au(2)	3.271(4)	Au(2)−Au(2)$^{\#1}$	3.492(5)
Au(1)−C(11)	1.94(2)	Au(1)−C(12)	1.97(1)
Au(2)−C(21)	1.99(1)	Au(2)−C(22)	1.99(2)
C(11)−N(11)	1.18(2)	C(12)−N(12)	1.14(2)
C(21)−N(21)	1.10(2)	C(22)−N(22)	1.11(2)
C(11)−Au(1)−C(12)	175.1(5)	C(22)−Au(2)−C(21)	175.0(6)
N(11)−C(11)−Au(1)	178(2)	N(12)−C(12)−Au(1)	175(1)
N(21)−C(21)−Au(2)	174.5(14)	N(22)−C(22)−Au(2)	175(2)
	2		
Au(1)−Au(2)	3.234(1)	Au(1)−Au(3)	3.175(1)
Au(1)−C(10)	1.99(2)	Au(1)−C(11)	1.98(2)
Au(2)−C(20)	1.94(2)	Au(2)−C(21)	1.92(3)
Au(3)−C(30)	2.05(2)	Au(3)−C(31)	2.03(2)
C(10)−N(10)	1.16(2)	C(11)−N(11)	1.11(2)
C(20)−N(20)	1.15(2)	C(21)−N(21)	1.22(3)
C(30)−N(30)	1.11(2)	C(31)−N(31)	1.10(2)
Au(3)−Au(1)−Au(2)	163.73(3)	C(11)−Au(1)−C(10)	179.1(7)
C(21)−Au(2)−C(20)	179.1(8)	C(31)−Au(3)−C(30)	177.2(7)
N(10)−C(10)−Au(1)	178(2)	N(11)−C(11)−Au(1)	176(2)
N(20)−C(20)−Au(2)	177(2)	N(21)−C(21)−Au(2)	174(2)
N(30)−C(30)−Au(3)	174(2)	N(31)−C(31)−Au(3)	176(2)
	3		
Au(1)−Au(2)	3.128(3)	Au(2)−Au(3)	3.220(4)
Au(3)−Au(4)	3.274(5)	Au(5)−Au(6)	3.155(7)
Au(6)−Au(6)$^{\#2}$	3.501(7)	Au(1)−C(11)	2.04(3)
Au(2)−C(12)	1.96(3)	Au(3)−C(13)	2.20(4)
Au(4)−C(14)	2.05(4)	Au(4)−C(24)	1.92(3)
Au(5)−C(15)	2.03(3)	Au(5)−C(25)	1.95(3)
Au(6)−C(16)	1.97(4)	Au(6)−C(26)	2.01(3)
C(11)−N(11)	1.14(3)	C(12)−N(12)	1.16(3)
C(13)−N(13)	1.10(4)	C(14)−N(14)	0.99(4)
C(24)−N(24)	1.11(4)	C(15)−N(15)	1.01(3)
C(25)−N(25)	1.10(3)	C(16)−N(16)	1.13(4)
C(26)−N(26)	1.12(3)		
Au(2)−Au(3)−Au(4)	166.99(8)	C(24)−Au(4)−C(14)	170(2)
C(25)−Au(5)−C(15)	177.9(13)	C(26)−Au(6)−C(16)	176.2(12)
N(11)−C(11)−Au(1)	175(3)	N(12)−C(12)−Au(2)	175(3)
N(13)−C(13)−Au(3)	167(3)	N(14)−C(14)−Au(4)	172(6)
N(24)−C(24)−Au(4)	165(5)	N(15)−C(15)−Au(5)	170(4)
N(25)−C(25)−Au(5)	179(4)	N(16)−C(16)−Au(6)	179(3)
N(26)−C(26)−Au(6)	175(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $1 - z$; #2, $0.5 - x$, $-0.5 - y$, $1 - z$.

Crystal Structure of 1. The asymmetric unit contains one-half of the hexapyrimidinium cation, two dicyanoaurate(I) ions, one disordered nitrate ion, and one water molecule. After application of inversion symmetry, the contents of the unit cell are a complete hexapyrimidinium cation, four dicyanoaurate(I) ions, two disordered nitrate ions, and two water molecules. The center of the macrocycle is located at the inversion center at (0.5, 0.5, 0). The bond lengths and the angles within the cation are statistically the same as those reported previously.[25] A view of the 24PyrC6 cation and the disordered nitrate is given in Figure 1.

The two positions of the disordered nitrate are shown in Figure 1, with the larger spheres representing the more highly occupied site. The two positions are nearly coplanar (angle 15.9°), with the lower occupancy nitrate rotated approximately 30° and displaced by 0.63 Å from the higher. Both nitrate positions are nearly parallel to the "a" pyrimidinium ring (angle 3.7°, 16.1°), with the nitrate nitrogen atom N(10a) 3.32 Å from the nearest ring carbon atom (C(5a) in Figure 1), while N(10b) is 3.43 Å from C(6a). The more occupied nitrate ion occupies one side of the 24PyrC6 cavity, with one oxygen atom, O(13a), directed toward the center of the cavity, at a distance of 1.73 Å from the center. An oxygen, O(11a), of this nitrate is hydrogen-bonded to an aromatic carbon, C(6ca), at a distance of 2.977 Å, as well as an exocyclic amine from a 24PyrC6 ion at x, $1 + y$, z with a distance of 2.988 Å to N(41b). The last oxygen of this nitrate is hydrogen-bonded at a distance of 2.833 Å to another exocyclic amine, N(41c), located at $-x$, $1 - y$, $-z$. The oxygen atoms of the less occupied nitrate all have hydrogen-bonding contacts: O(11b)−N(41c) at $-x$, $1 - y$, $-z$, 2.759 Å, O(12b) to two aromatic hydrogens at C(6ca) and C(6ba) with distances of 3.054 and 2.756 Å, respectively, and O(13b) to N(41b) at x, $1 + y$, z, with a distance of 3.221 Å. The more fully occupied nitrate makes an angle of 44.8° with the mean plane of the 24PyrC6 (as defined by the mean plane formed by the C6 atoms from each pyrimidinium ring), whereas the angle from the same plane to the less occupied nitrate is 58.4°. In all previously reported structures in which a nitrate ion associates with the cavity of the 24PyC6 cation, these nitrates were parallel to the mean plane of 24PyrC6.[24,25] An inversion-related disordered nitrate is similarly located on the other side of the 24PyrC6 cation cavity.

The two dicyanoaurate ions in the asymmetric unit form a dimer with an Au(1)−Au(2) distance of 3.272(4) Å. These two ions are rotated around the Au(1)−Au(2) vector by 68.5° as defined by the dihedral angle between the C(11)−Au(1)−C(12)−Au(2) plane and the C(21)−Au(2)−C(22)−Au(1) plane. The Au(2) atom of this dimer lies near the inversion center at ($^1/_2$, 0, $^1/_2$) so that two dimers are loosely associated to form a tetramer or, more precisely, a dimer of dimers, as seen in Figure 2. The central Au(2)−Au(2a) distance in this tetramer is 3.492(5) Å, and the nearly linear dicyanoaurate ions are eclipsed with the cyanides bent slightly away from each other. The four gold atoms of this tetramer are not collinear. The unique angle Au(1)−Au(2)−Au(2a) is 109.3°.

The three-dimensional packing of this salt consists of layers of 24PyrC6 cations in an ABAB pattern stacked along the *ab* diagonal of the unit cell. The dicyanoaurate dimer of dimers lies mostly within the layers of 24PryC6 molecules, but there are hydrogen-bonding contacts with the layer above. One of

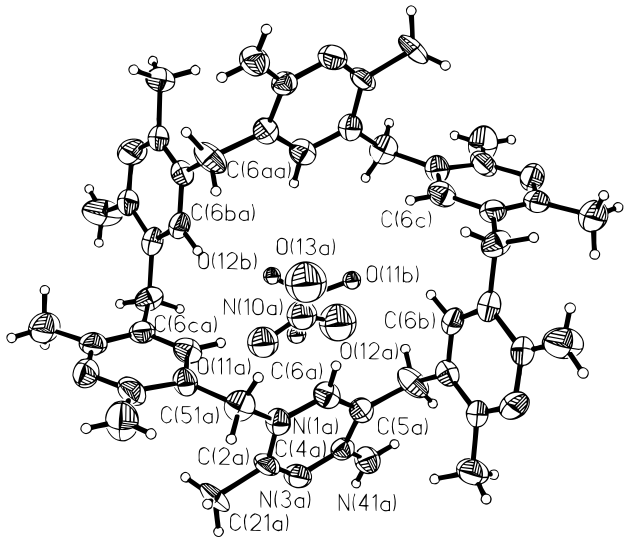

Figure 1. A perspective view of the 24PyrC6 cation and the disordered nitrate in **1**, with 50% probability thermal elipsoids shown. The lesser occupied nitrate, designated as "b", is shown with 12.5% ellipsoids.

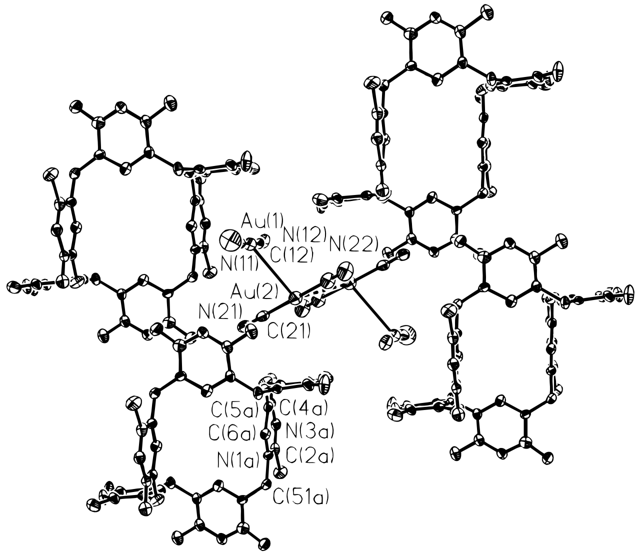

Figure 2. Interaction of the dicyanoaurate dimer of dimers in **1** with surrounding 24PyrC6 cations. The 30% probability thermal elipsoids are shown (C(22) and C(11) are not labeled).

the cyanide groups also interacts electrostatically with a cation in the layer above. In all, five cations interact with the unique Au(1)−Au(2) pair of dicyanoaurate ions. The Au(2) ion lies within the fold between pyrimidinium rings "b" and "c" of cation "1" located at *x*, *y*, *z*. The closest contact is with N(21), which is about 3.2 Å from the b ring, while the distance of C(21) to the c ring is longer, about 3.6 Å. The vector made by the Au(2)−C(21) bond makes an angle of 5.4° to the b ring and an angle of 17.8° to the c ring. The Au(1) ion, in a similar fashion, lies within the fold of the b and c rings of cation 2 located at −*x*, −*y*, −*z* in the same layer, as can be seen in Figure 2. In this case the Au(1)−C(12) bond makes angles of 1.1° and 1.2° with rings b and c, respectively, with N(11) coming as close as 2.9 Å to ring c and C(11) is 3.5 Å from ring b. The second cyanide ligand bound to Au(1) extends up and out of the layer and lies over ring "a" of a third cation in the next layer located at *x* − 1, *y*, *z* (not shown in Figure 2). Here the contacts between both C(12) and N(12) and the a ring are between 3.2 and 3.3 Å. The cyanide nitrogen, N(12), forms a hydrogen bond to the exocyclic amine of a fourth cation located at −*x*, 1 − *y*, 1 − *z*, with an N(12)−N(41a) distance of 2.90 Å. There is another similar hydrogen bond between N(21) and an exocyclic amine of a fifth cation, also located in the layer above at −*x*, 1 − *y*, −*z* with an N(21)−N(41c) distance of 2.94 Å. Finally, N(22) forms a hydrogen bond to each of two equivalent water molecules located in two different unit cells.

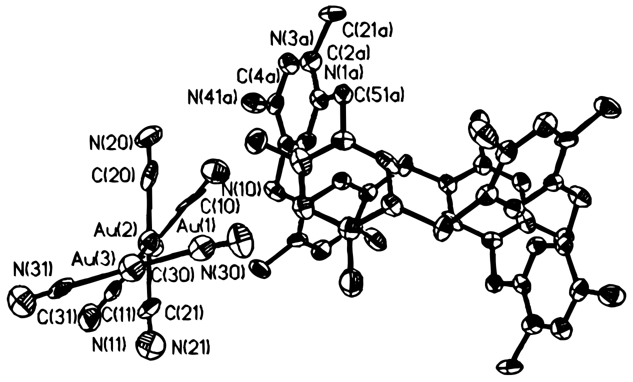

Figure 3. A perspective view of the 24PyrC6 cation and one dicyanoaurate trimer in structure **2**. Hydrogen atoms and water molecules have been excluded. The 50% probability thermal elipsoids are shown.

Crystal Structure of 2. The asymmetric unit contains one-half of the hexapyrimidinium cation and three dicyanoaurate(I) ions. There are also three positions for water molecules, one of which is fully occupied, one which is disordered over two closely situated positions, and a third which is near the inversion center at (0, 0, 0) is half occupied. The inversion symmetry then generates the contents of the unit cell: a complete hexapyrimidinium cation, six dicyanoaurate(I) ions, and five water molecules. The macrocycle is located around the inversion center at (0, 0, 0), and therefore the O(1) water molecule is disordered over two sites near the center of the cavity. The bond lengths and the angles within the cation are statistically the same as those reported for the $Ba(NO_3)_6^{4-}$ and $Pb(NO_3)_6^{4-}$ salts.[25] A general view of this structure without water molecules and hydrogen atoms is given in Figure 3.

The three dicyanoaurate(I) molecules in the asymmetric unit form a nearly linear, spiraling trimer (Au1−Au2−Au3 angle of 163.73(3)°). The rotation angles between dicyanoaurate ions, defined as in the previous structure, are 40.8° between the Au(1) and Au(2) ions and 76.1 between the Au(2) and Au(3) ions. The distances between the gold(I) atoms fall within the previously reported range of gold−gold distances,[4−10] with the distance between Au(1) and Au(2) being 3.234(1) Å and the distance between Au(2) and Au(3) being 3.175(1) Å. Note that the larger rotation angle between the two dicyanoaurate molecules corresponds with the shorter Au−Au distance.

The structure is composed of alternating layers of 24PyrC6 molecules and dicyanoaurate trimers. The 24PyrC6 rings are packed in an ABAB fashion along the cell diagonal. The dicyanoaurate trimeric anions lie between 24PyrC6 layers with the distance between individual trimers being greater than 5.5 Å. The dicyanoaurate trimer lies above a 24PryC6 cation and interacts with it in two ways. The central dicyanoaurate, Au(2), interacts with the cavity of the 24PyrC6 cation and the water contained therein with a hydrogen-bonding distance of 3.29 Å from water O(1) to N(21) at *x*, 1 + *y*, *z*. This same water is hydrogen-bonded to the inversion-related dicyanoaurate N(21) at −*x*, 1 − *y*, −*z*, at a distance of 3.20 Å. The other end of this dicyanoaurate is hydrogen-bonded to an exocyclic amine from a second cation, in the next layer, N(20) to N(41b) at 1 − *x*, 1

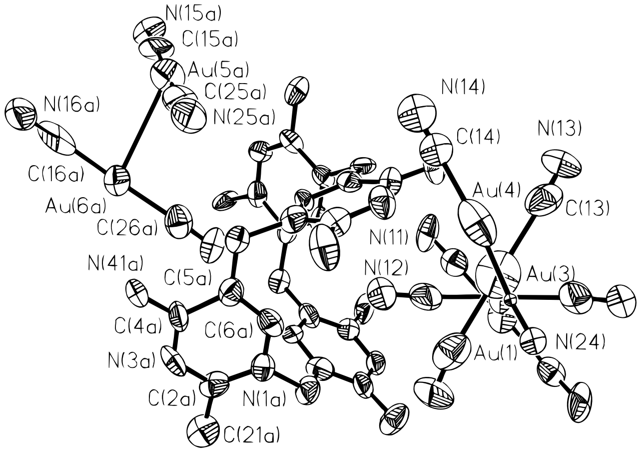

Figure 4. Structure **3** showing the spiraling dicyanoaurate tetramer (right), the 16PyrC4 cation less its hydrogen atoms (middle), and a dicyanoaurate dimer (left). The 50% probability thermal elipsoids are shown. Only one location for the disordered Au(4) ion is shown.

− *y*, 1 − *z*, with a distance of 2.95 Å. The dicyanoaurate containing Au(1) is hydrogen-bonded on both ends; atom N(10) is hydrogen-bonded to the exocyclic amine N(41c) of the first cation, distance 2.90 Å, and atom N(11) is hydrogen-bonded to the aromatic carbon C(6c)of the second cation at −*x*, 1 − *y*, −*z*, a distance of 3.21 Å. The other dicyanoaurate, which contains Au(3) is also hydrogen-bonded on both ends. Atom N(30) is hydrogen-bonded to water molecule O(3) located at −*x*, 1 − *y*, 1 − *z* with a distance of 2.79 Å, and atom N(31) is hydrogen-bonded to the exocyclic amine N(41c) of a third cation located at −*x*, 1 − *y*, 1 − *z* with a distance of 2.94 Å.

Water molecule O2 is disordered between two sites, with the more occupied site being 80(10)% occupied and 0.826 Å away from the less occupied site. Each site is hydrogen-bonded to the same amine group from two [24-pyrimidinium crown-6] rings [O(2a)−N(41a)(1 − *x*, 1 − *y*, 1 − *z*) 3.012 Å, O(2a)−N(41b) 3.162 Å, O(2b)−N(41a)(1 − *x*, 1 − *y*, 1 − *z*) 3.281 Å, and O(2b)−N(41b) 3.091 Å]. Last, there is a hydrogen bond between water molecules O(1) and O(3) at 2.938 Å.

Crystal Structure of 3. The asymmetric unit contains one tetrapyrimidinium cation, two complete dicyanoaurate(I) ions, and six and a half water molecules, one of which is disordered over two positions. In addition, three dicyanoaurate ions lie on the 2-fold axis, and a final dicyanoaurate ion lies just off the 2-fold axis and is therefore 2-fold disordered. The tetrapositive charge of the cation is thus balanced by the negative charges of the two dicyanoaurate ions at general positions and the total of two negative charges contributed by the four dicyanoaurate ions which lie on or, in one case, slightly off of the 2-fold axis. A general view is given in Figure 4.

This structure contains two different clusters of dicyanoaurate(I) ions. One of these clusters is a zigzag dimer of dimers, similar to that found in structure **1**, including an inversion center relating the two dimers. The terminal Au(5)−Au(6) interaction occurs at a distance of 3.155(7) Å, and the central Au(6)−Au(6a) distance is 3.501(7) Å. The terminal $Au(CN)_2^-$ ions are rotated with respect to the central ones so that the plane defined by the atoms Au(6)−C(51)−Au(5)−C(52) forms an angle of 74.0° with the plane defined by Au(5)−C(61)−Au(6)−C(62). As was the case for structure **1**, the central dicyanoaurate ions are centrosymmetrically related and are essentially eclipsed, with the CN^- units bent away from each other. Figure 5 shows this dimer of dimers and the closest 16PyrC4 cationic neighbors.

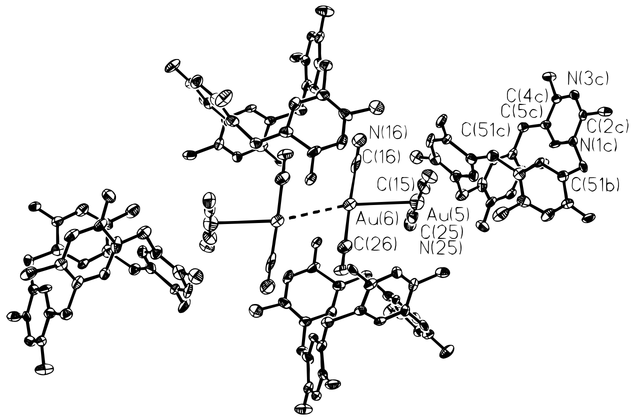

Figure 5. Interaction of the dicyanoaurate dimer of dimers in **3** with surrounding 16PyrC4 cations. The 30% probability thermal elipsoids are shown.

The other cluster of $Au(CN)_2^-$ ions is an infinite chain consisting of repeating, spiraling tetrameric units running along a 2-fold axis. Three of the $Au(CN)_2^-$ ions of each tetrameric unit lie on the axis, and the fourth, Au(4), is slightly displaced from it. The rotation angles between dicyanoaurate ions, as defined above, are Au(1)−Au(2), 48.4°; Au(2)−Au(3), 59.1°; Au(3)−Au(4), 59.3°; and Au(4)−Au(1a), 13.7°. The distance between the gold atoms progressively increases with the distance between Au(1) and Au(2) being 3.128(3) Å. From Au(2) to Au(3) the distance is 3.220(4) Å, and the distance from Au(3) to Au(4) is 3.274(5) Å. Last, the distance from one tetrameric unit to the next, Au(4)−Au(1a), is 3.698(7) Å.

This structure consists of four repeating layers perpendicular to the *b*-axis. Every other layer contains 16PyrC4 molecules which border alternating layers of dicyanoaurate molecules. One of these layers consists of the dicyanoaurate tetrameric chains which run along the 2-fold axes, and the other layer contains the dimer of dimers of dicyanoaurate molecules. This contrasts with structure **1**, where the dimer of dimers lies within the 24PyrC6 layer. However, this structure is similar in that one of the dicyanoaurate ions lies almost parallel with one of the pyrimidinium rings. The Au(5)−C(15) vector forms an angle of 4.3° with the plane of the pyrimidinium ring a. The closest contact between these two is 3.53 Å, between Au(5) and C(5a). Each end of this dicyanoaurate is hydrogen-bonded to different water molecules (for all hydrogen bonds in this molecule see Supporting Information). The dicyanoaurate containing Au(6) hydrogen-bonds to a water, O(1), and the other end points into the cavity of the 16PryC4 molecule. Similarly, a cyanide from Au(2) points into the other side of the 16PryC4 molecule and is hydrogen-bonded to the aromatic hydrogen of carbon C(6c). The disordered dicyanoaurate is related to water O(7) so that when the dicyanoaurate is on one side of the 2-fold axis, the water molecule is on the other side. Both cyanides from this dicyanoaurate are hydrogen-bonded to waters or amine groups. A summary of all hydrogen bonding is given in the Supporting Information.

Discussion

Cations. There is nothing unusual or remarkable about the bond distances and angles in the polypyrimidinium cations reported in this paper as they are statistically the same as those reported previously.[23−26] In addition, due to the abundance of heavy gold atoms in these structures, the structural parameters for the light atoms are of limited accuracy. On the other hand, the conformation of the cations is of some interest as it relates to the ability of the cations to act as host molecules. We have previously discussed these conformations by reference to the angles formed with the mean plane of the entire cation, as defined by the mean plane of all of the C(6) atoms.[23] The structure of 24PyrC6$(NO_3)_6$ has a partially occupied nitrate ion inside the cavity lying parallel to the mean plane of the cation, and the angle between the unique pyrimidinium plane and the mean cation plane is 57.6°.[23] In the structure of 24PyrC6$(NO_3)_2$-$Pb(NO_3)_6$, which has a fully occupied nitrate ion in a similar location within the cavity, this angle in nearly unchanged at 57.5°. On the other hand, in a structure in which an iodo ligand of an HgI_4^{2-} ion lies at the center of the cavity of a 24PyrC6 cation, this angle is 66.2°, 64.3°, and 67.0° for the three independent pyrimidinium rings. In structure **1** reported here, in which the nitrate stacks parallel to one of the pyrimidinium rings and is at an angle of 57.9° to the mean plane, the three unique angles of this type are 45.5°, 57.6°, and 58.0°. In structure **2**, which has a water molecule near the center of the cavity, the three unique angles of this type are 66.8°, 68.5°, and 69.9°. Thus, the presence of a molecule or ion such as water or iodide in the center of the 24PyrC6 cation causes the angles of the pyrimidinium planes with respect to the mean plane to “open up” or become larger. On the other hand, in the structure of **1**, in which the nitrate ion stacks parallel to one pyrimidinium ring rather than parallel to the mean plane of the entire cation, the cavity of the host is less symmetric and somewhat contracted.

Anions. The structures of a number of aurophilic compounds have been published. In most cases, the Au−Au interactions occur between gold atoms in neutral, uncharged complexes.[1−10,12−14] However, in two recent cases, Au−Au interactions were discovered between ionic complexes with like charges. In the case of $[(pyr)_2Au][AuX_2]$, where X = Cl, Br, I,[28,29] the ions are arranged in tetramers with a [− + + −] sequence of charges, and in $[(Me_2PhP)_2Au][Au(GeCl_3)_2]$ tetramers with a [+ − − +] arrangement occur.[30] In both of these cases, the ions are staggered with a 90° rotation angle. In this paper, we report three new patterns, a trimer with [− − −], a dimer of dimers with [− − − −], and an infinite chain of anions. In addition, the rotation angles between ions are less than 90° in many cases.

Pathaneni and Desiraju[31] have analyzed a group of 693 gold-containing structures from the Cambridge Structural Database in order to correlate the Au−Au distance with other structural parameters such as the dihedral angle between ligands on adjacent gold atoms. For dinuclear, two-coordinate structures with Au−Au distances in the range of 3−4 Å, it was found that a strong correlation exists between the Au−Au distance and the dihedral angle, τ, between the donor atoms attached to the two adjacent gold atoms. Eclipsed ($\tau = 0°$ or 180°) and staggered ($\tau = 90°$) conformations predominate, with the eclipsed conformations having longer Au−Au distances and the staggered conformations the shorter distances. Rotation by intermediate angles is rare, and only one exception was found, with a “long” Au−Au distance of 3.615(2) Å.[32]

Of all the gold structures showing the property of aurophilicity, only a couple deal with the dicyanoaurate molecule. In 1959, Rosenzweig and Cromer determined the structure of $KAu(CN)_2$.[20] This structure consists of alternating layers of potassium and dicyanoaurate molecules in which the gold atoms of one layer are 3.64 Å away from the nearest neighbor in the same layer. To our knowledge, the only other structures in which the dicyanoaurate ion exhibits aurophilicity are the thallium and cesium salts described by Blom *et al.*[19] The structure of the thallium salt contains three crystallographically different dicyanoaurate ions. Dicyanoaurate molecules containing Au(1) and Au(2) form infinite chains in which the dicyanoaurates are parallel at a distance of 3.560(1) Å. Also in this structure is a spiraling infinite chain with repeating units of Au(1)−Au(3)−Au(3a). The angle between Au(1) and Au(3) is 51°, with a correspondingly short distance of 3.037(4) Å, and the angle between Au(3) and Au(3a) is 90°, with a distance of 3.068(4) Å. The cesium salt is isostructural with the thallium salt, but the internal distances are longer: Au(1)−Au(2) = 3.72(1) Å, Au(1)−Au(3) = 3.11(1) Å, and Au(3)−Au(3a) = 3.14(1) Å. These structures are further examples of gold−gold interactions in which the torsion angles are not the normal 0° or 90°.

The structures reported in this paper exhibit three different patterns of chains of interacting gold atoms. The most prevalent pattern is a zigzag chain of four gold(I) atoms forming a dimer of dimers. The two central $Au(CN)_2^-$ anions are eclipsed with distances of 3.492(5) and 3.501(7) Å for **1** and **3**, respectively, and the terminal $Au(CN)_2^-$ anions are rotated with respect to the central ones (at torsion angles of 66.4° in **1** and 74.0° in **3**), with distances of 3.271(4) Å and 3.155(7) Å for **1** and **3**, respectively. To our knowledge, this is the first occurrence of such an arrangement for cyano-gold(I) compounds, although a similar pattern was found for $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$, where the gold(III) atoms are bridged by sulfur atoms.[9] The second arrangement reported here is a spiraling, slightly bent trimer (Au(1)−Au(2)−Au(3) angle of 163.73(3)°). This pattern exhibits shorter gold−gold interactions of 3.234(1) and 3.175(1) Å, with torsion angles of 40.8° (Au1−Au2) and 76.1°(Au2−Au3). This structure is unique in that it is a trimer. No other trimers of aurophilic gold atoms have yet been reported to our knowledge. Last, structure **3** contains an infinite chain of spiraling $Au(CN)_2^-$ anions. Although infinite chains of gold atoms have been reported, such as the ones in the thallium structure,[15] the infinite chain in **3** has two remarkable features. The first of these is the spiraling of the $Au(CN)_2^-$ anions which contains four unique angles, none of which are 0° or 90°. The rotation angle between consecutive dicyanoaurate ions varies from 48.4° to 59.1° to 59.3°, with the final $Au(CN)_2^-$ anion rotated only 13.2°. The other remarkable feature is that the fourth $Au(CN)_2^-$ anion in the chain lies slightly off of the axis defined by the previous three anions. Thus, when the symmetry of the C_2 axis is applied, this produces an infinite chain that has a kink in the chain every fourth $Au(CN)_2^-$ anion, where the kink has an equal probability of being on either side of the 2-fold axis.

The structures reported in this paper contain six statistically different rotation angles. The rotation angles for the two central dicyanoaurates of the twinned dimers in compounds **1** and **3** are zero by symmetry and exhibit longer distances between gold atoms of 3.492(5) Å for **1** and 3.501(7) Å for **3**, consistent with the pattern observed by Pathaneni and Desiraju.[31] The rotation angles for all of the other gold−gold interactions fall within the range of $13.2° \le \tau \le 74.0°$ and represent new, uncommon structures with rotation angles intermediate between staggered and eclipsed. The Au−Au distances are shorter, falling in the range of 3.128(4)−3.274(4) Å, again consistent with the statistically observed pattern, yet shorter and different from the only other, previously known intermediate-angle structures.[15,32]

The interactions of the dicyanoaurate ions in these structures

---

(28) Conzelmann, W.; Hiller, W.; Strahle, J.; Sheldrick, G. M. *Z. Anorg. Allg. Chem.* **1984**, *512*, 169−176.

(29) Adams, H.-N.; Hiller, W.; Strahle, J. *Z. Anorg. Allg. Chem.* **1982**, *485*, 81−91.

(30) Bauer, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 5324−5325.

(31) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319−322.

(32) Tiekink, E. R. T. *Acta Crystallogr., Sect. C* **1989**, *45*, 1233.

are remarkable. If electrostatic forces were solely present, one would expect the positively charged gold atoms to approach the negatively charged cyanides of a neighboring ion. However, the ions arrange in patterns which invariably places the positively charged gold atoms close to each other, and in a couple of cases, pairs of the dicyanoaurate ions are eclipsed so that the mutually negative cyanide ions are also in contact. Clearly, this arrangement is not dominated by electrostatic forces, and there must be some attractive force which overcomes the electrostatic repulsion. This attractive force must result from some sort of bonding interaction between the gold atoms that is stronger than the repulsive electrostatic forces. When the dicyanoaurate ions are eclipsed, the distances are long, about 3.50 Å. However, even at these long distances, it is evident that an Au−Au attraction is present because the two ions are held together in the presence of a repulsion between the cyanide ions that bends the cyanide moieties away from each other. From the relationship between other dicyanoaurate ions in these structures, we see that as the two ions rotate away from the eclipsed conformation, thus decreasing the repulsion between cyanide ions, the Au−Au distance decreases as the attractive Au−Au interaction meets less repulsion from the cyanide ions.

It is likely that these structures result from the stereochemistry of the 24PyrC6 and 16PyrC4 cations. The three structures reported here display three types of interactions between the polypyrimidinium cations and the $Au(CN)_2^-$ anions. In both structures **2** and **3**, dicyanoaurate ions associate with the cavity of the polypyrimidinium cations, where they hydrogen-bond to either the C(6)−H bond or to a water molecule located within the cavity. In structure **1**, which has a nitrate ion inside the cavity, no dicyanoaurate ions are associated with the cavity. Instead, some of the cyanide ions stack over pyrimidinium rings or, more exactly, lie in the fold of two adjacent pyrimidinium rings, stacking over both of them. This produces favorable Coulombic interactions between the cation and the anion. Similar stacking is also seen in structure **3** for one of the dicyanoaurate ions that is not associated with the cavity. Also, there are numerous hydrogen bonds between the cyanide ions of the dicyanoaurate anions and the exocyclic amines of the polypyrimidinium cations. These hydrogen bonds play a prominent role in tying the layers of these structures together. Last, the large charges on the 24PyrC6 and 16PyrC4 molecules serve as stabilizing forces for the new anionic dicyanoaurate(I) clusters. The structures are therefore the result of a set of complex interactions including the Au−Au interaction.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**−**3** are available on the Internet only. Access information is given on any current masthead page.

IC980372X