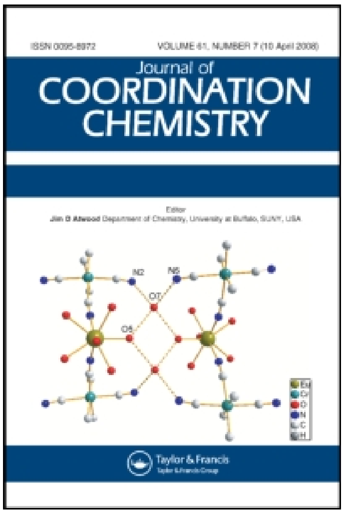

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and luminescent properties of two complexes containing $[Au(CN)_2]^{-}$ building blocks

Jie Qu[a]; Wen Gu[a]; Xin Liu[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

To cite this Article Qu, Jie , Gu, Wen and Liu, Xin(2008) 'Synthesis, crystal structure and luminescent properties of two complexes containing $[Au(CN)_2]^{-}$ building blocks', Journal of Coordination Chemistry, 61: 4, 618 — 626, First published on: 27 August 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701367712

URL: http://dx.doi.org/10.1080/00958970701367712

Journal of Coordination Chemistry
Vol. 61, No. 4, 20 February 2008, 618–626

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Synthesis, crystal structure and luminescent properties of two complexes containing $[Au(CN)_2]^-$ building blocks

JIE QU, WEN GU and XIN LIU*

Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

(*Received 19 December 2006; in final form 12 March 2007*)

Two supramolecular complexes, $\{\{Ni(H_2O)(phen)_2[Au(CN)_2]\}[Au(CN)_2]\cdot 1.5H_2O\}_n$ (**1**) (phen = 1,10-phenanthroline) and $[H_2teta][Au_2(CN)_4]\cdot 2H_2O$ (**2**) (teta = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyocloteradeca-4,11-diene) have been synthesized and structurally characterized. Complex **1** was a one-dimensional infinite chain constructed by $[Au(CN)_2]^-$ building blocks. In complex **2**, there are one cation, one anion, and two water molecules in the asymmetric unit. The two complexes are interconnected through a combination of aurophilic attractions and hydrogen bonds and formed into 3D supramolecular structures. The aqueous solutions of **1** and **2** display interesting luminescence at room temperature.

Keywords: Crystal structure; Aurophilic attractions; Luminescence

1. Introduction

Self-assembled supramolecular architectures have become of interest due to their fascinating structures with potential applications in catalysis, host-guest chemistry, molecule-based magnets, optical materials, ion-exchange, gas absorption, *etc*. [1–4]. Hydrogen-bonding interactions between moieties are well-developed methods to increase structural dimensionality of supramolecular systems in the crystal engineering 'toolbox' [5–8]. This increase is important because one or higher dimensional systems often show useful magnetic [9], nonlinear optical [10], volatile organic compound (VOCs), sensors [11, 12], conducting [13], or zeolitic [14] properties.

M–M interactions such as Au–Au interactions, which have strengths comparable to hydrogen bonds, also play an important role in determining the supramolecular structure and increasing the supramolecular dimensionality [15–19]. The linear and chemically stable dicyanoaurate anion $[Au(CN)_2]^-$ is well known as a good building block for construction of multidimensional frameworks and can be involved in self-association through aurophilic interactions [18–20]. Many homometallic Au (I) polymers formed by these "aurophilic" interactions have been widely studied [21]. Several studies by Patterson and co-workers have shown that $[Au(CN)_2]^-$ aggregates under a variety of conditions in both the solid state and in solution [22–24], and these

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*Corresponding author. Tel.: +86-022-23505020. Email: liuxin64@nankai.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701367712

aggregated forms show variations in their luminescence. This characteristic property in aqueous solution has special importance in monitoring and probing biological processes associated with the luminescent material [25–27]. Here, we report the crystal structures and luminescent properties of two self-assembled supramolecular architectures formed by $[Au(CN)_2]^-$ building blocks.

2. Experimental

All starting materials were of reagent grade and used without further purification. The macrocycle ligand $[Ni(teta)](ClO_4)_2$ was prepared according to the procedures previously described [28, 29]. IR spectra were obtained using a Shimadzu IR-408 infrared spectrometer in the 4000–600 cm^{-1} regions. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C analyzer. The ultraviolet and visible spectra were measured on a Shimadzu UV-570 spectrophotometer. The luminescent spectrum was measured on a Shimadzu RF-540 PC spectrophotometer. Cyanide salts are toxic and should be handled with caution!

3. Synthesis

3.1. *The single crystal synthesis of* $\{\{Ni(H_2O)(phen)_2[Au(CN)_2]\}[Au(CN)_2] \cdot 1.5H_2O\}_n$ *(1)*

A 10 mL aqueous solution of $K[Au(CN)_2]$ (0.0288 g, 0.1 mmol) was added dropwise to a 10 mL aqueous solution of $[Ni(phen)_2(H_2O)_2](NO_3)_2$ (0.0615 g, 0.1 mmol). The mixture was stirred for about 3 h at room temperature and then filtered. After a few days of slow evaporation, pink crystals suitable for X-ray crystallography were formed. Yield: 40.9%. Anal. Calcd for $C_{28}H_{21}Au_2N_8NiO_{2.5}$ (%): C, 34.92; H, 2.18; N, 11.64. Found: C, 34.86; H, 2.17; N, 11.67.

3.2. *The single crystal synthesis of* $[H_2teta][Au_2(CN)_4] \cdot 2H_2O$ *(2)*

A 10 mL aqueous solution of $K[Au(CN)_2]$ (0.0288 g, 0.1 mmol) was added dropwise to a 10 mL methanol solution of $[Ni(teta)](ClO_4)_2$ (0.0542 g, 0.1 mmol), and the mixture was filtered after stirring for 3 h at room temperature. The resulting solution kept at room temperature for several days afforded orange crystals suitable for X-ray structural analysis. Yield: 83%. Anal. Calcd for $C_{20}H_{42}Au_2N_8O_2$ (%): C, 29.25; H, 5.12; N, 13.65. Found: C, 29.12; H, 5.25; N, 13.56.

3.3. *Crystallographic data collection and refinement*

Details for the crystal data and refinement of the two structures are given in table 1. Selected bond lengths and angles are presented in table 2. Data collection was performed on a Bruker Smart 1000 area detector using graphite monochromated

Table 1. Crystal data and details of experiment for complexes **1** and **2**.

Complex	**1**	**2**
Formula	$C_{28}H_{21}Au_2N_8NiO_{2.5}$	$C_{20}H_{42}Au_2N_8O_2$
Formula weight	962.17	820.55
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Absorption coefficient (mm^{-1})	10.763	10.543
Unit cell dimensions (Å, °)		
a	10.3790(19)	8.989(3)
b	12.194(2)	7.8801(12)
c	12.519(2)	19.028(3)
α	111.281(3)	90
β	109.481(5)	101.737(2)
γ	99.076(3)	90
V (Å^3)	1452.0(5)	2787.7(7)
Z	2	4
Density (mg m^{-3})	2.201	1.955
$F(000)$	902	1568
Crystal size (mm^3)	$0.26 \times 0.20 \times 0.12$	$0.38 \times 0.22 \times 0.16$
θ range for data collection (°)	1.80–25.00	2.19–25.03
Final indices [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0728$	$R_1 = 0.0296$, $wR_2 = 0.0629$
R indices (all data)	$R_1 = 0.0494$, $wR_2 = 0.0767$	$R_1 = 0.0491$, $wR_2 = 0.0684$
Limiting indices	$-11 \le h \le 12$, $-14 \le k \le 14$, $-9 \le l \le 14$	$22 \le h \le 14$, $-8 \le k \le 9$, $-21 \le l \le 21$
Data/restraints/parameters	5095/9/386	4929/6/295
Goodness-of-fit on F^2	1.007	1.074
Largest diff. peak and hole (e Å^{-3})	1.473 and −1.818	0.644 and −0.791
Correction method	Multi-scan	Multi-scan

Table 2. Selected bond lengths (Å) and angles (°) for complexes.

Bond lengths (Å)		Bond angles (°)	
Complex **1**			
Au(1)–C(2)	1.965(12)	C(2)–Au(1)–C(1)	178.0(4)
Au(1)–C(1)	1.997(10)	C(2)–Au(1)–Au(2)	88.9(3)
Au(1)–Au(2)	3.1332(6)	C(1)–Au(1)–Au(3)	95.9(3)
Au(1)–Au(3)	3.2266(7)	Au(2)–Au(1)–Au(3)	159.604(16)
Au(2)–C(3)	1.959(12)	C(3)–Au(2)–C(3)#1	179.997(1)
Au(2)–C(3)#1	1.959(12)	C(3)#1–Au(2)–Au(1)	90.0(3)
Au(2)–Au(1)#1	3.1332(6)	Au(1)–Au(2)–Au(1)#1	180.0
Au(3)–C(4)#2	2.02(2)	C(4)#2–Au(3)–C(4)	179.997(2)
Au(3)–Au(1)#2	3.2266(7)	C(4)#2–Au(3)–Au(1)#2	89.5(4)
Ni(1)–N(1)	2.065(8)	N(1)–Ni(1)–O(1)	92.6(3)
Ni(1)–O(1)	2.073(7)	N(1)–Ni(1)–N(7)	94.4(3)
Ni(1)–N(5)	2.092(8)	O(1)–Ni(1)–N(7)	92.1(3)
Ni(1)–N(8)	2.127(8)	O(1)–Ni(1)–N(6)	173.1(3)
N(1)–C(1)	1.120(12)	N(7)–Ni(1)–N(8)	79.2(3)
N(5)–C(5)	1.326(11)	N(6)–Ni(1)–N(8)	99.3(3)
C(27)–C(28)	1.433(14)	N(5)–Ni(1)–N(8)	89.6(3)
Complex **2**			
Au(1)–C(2)	1.957(7)	C(2)–Au(1)–Au(2)	92.8(2)
Au(1)–Au(2)	3.2343(6)	C(1)–Au(1)–Au(2)	88.15(19)
Au(2)–C(3)	1.958(8)	N(1)–C(1)–Au(1)	177.0(6)
C(2)–Au(1)–C(1)	179.0(3)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+2$, $-y$, $-z$; #2: $-x+2$, $-y$, $-z+1$ for **1** and #1: $-z+1$; #2: $-x+1$, $-y$, $-z+1$ for **2**.

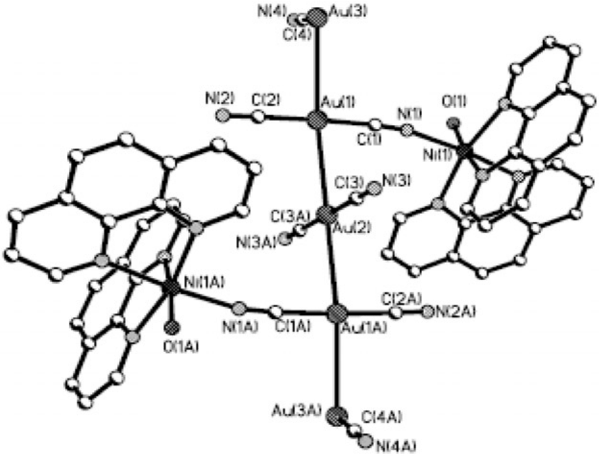

Figure 1. The molecular structure of $\{\{Ni(H_2O)(phen)_2[Au(CN)_2]\}[Au(CN)_2] \cdot 1.5H_2O\}_n$ (H and H_2O not shown for clarity).

Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Intensity data were measured at 293(2) K by the $\omega/2\theta$ technique. Semiempirical absorption analysis was performed using the SADABS program. The structures were solved by direct-method successive Fourier difference analysis (SHELXS-97) and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXS-97). Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters.

4. Results and discussion

4.1. *Crystal structure of 1*

X-ray crystallography shows that **1** is made up of a one-dimensional infinite chain constructed by $[Au(CN)_2]^-$ building blocks and further formed into a 3D supramolecular structure by aurophilic, hydrogen-bonding and π–π interactions. In **1**, each nickel atom is six-coordinate with a distorted octahedron geometry by means of four nitrogen atoms of two phen ligands, a nitrile nitrogen atom from $[Au(CN)_2]^-$ and an oxygen of H_2O (see figure 1). The bond angles are C(2)–Au(1)–C(1) = 178.0(4)°, C(3)–Au(2)–C(3A) = 179.997(1)°, Au(2)–Au(1)–Au(3) = 159.604(16)° and Au(1)–Au(2)–Au(1A) = 180.0°, respectively. The adjacent monocoordinated and the noncoordinated dicyanoaurate anions have a nearly staggered orientation with a torsion angle of 85.8°. The $[Au(CN)_2]^-$ anions are formed into a one-dimensional zig-zag chain through Au $\cdots$ Au interactions (see figure 2). The Au $\cdots$ Au distances of 3.1332(6) Å and 3.2266(7) Å are much shorter than the sum of van der Waals radii of Au (3.60 Å), indicating Au $\cdots$ Au interactions. The distances between parallel phen molecules are 3.56–3.60 Å, which indicate π–π interactions between parallel aryl rings. The uncoordinated water molecules are in the vicinity of the zig-zag chain and hydrogen-bonded to the $[Ni(H_2O)(phen)_2]^{2+}$ and the uncoordinated $[Au(CN)_2]^-$.

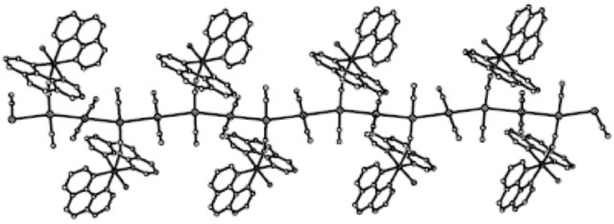

Figure 2. One-dimensional zig-zag chain through Au ··· Au interactions.

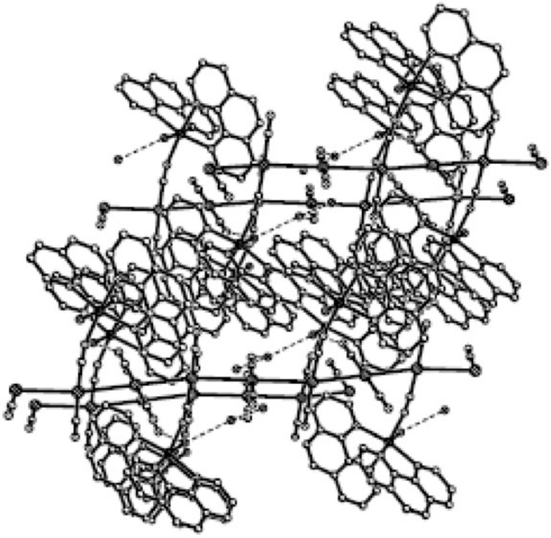

Figure 3. The packing diagram of **1**. The uncoordinated water molecules are positioned in the vicinity of the chains and hydrogen bonded to the uncoordinated nitrogen atoms of the cyanides.

The Au ··· Au and hydrogen-bonding interactions have increased the dimensionality to a 3D supramolecular structure (see figure 3).

4.2. *Crystal structure of [H_2teta][$Au_2(CN)_4$] • $2H_2O$ (2)*

It was unanticipated that Ni(II) ions were not included; through analysis and conjecture, the Ni^{2+} might coordinate with OH^- to form a more stable compound $Ni(OH)_2$, which also balance the H^+ added to the teta ligand.

The crystal structure of **2** is shown in figure 4. One cation, one anion, and two water molecules form the asymmetric unit. $[Au(CN)_2]^-$ forms into $[Au_2(CN)_4]^{2-}$ dimers through Au ··· Au interactions. The Au ··· Au distance is 3.2343(6) Å. The bond angles are C(2)–Au(1)–C(1) = 179.0(3)° and C(3)–Au(2)–C(4) = 178.3(3)°. The torsion angle of adjacent dicyanoaurate anions is 72.1°. The water molecules are in the vicinity of the dimers and hydrogen-bonded to the $[Au_2(CN)_4]^{2-}$ and the teta. Through a combination of aurophilic attractions and hydrogen bonds, $[Au(CN)_2]^-$, teta and water molecules are interconnected and formed into a 3D supramolecular structure (see figure 5).

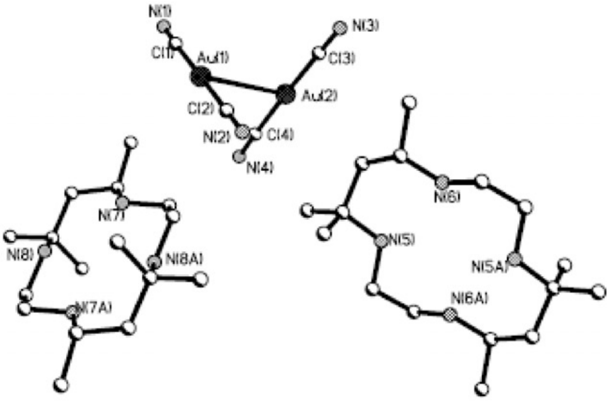

Figure 4. The molecular structure of $[H_2teta][Au_2(CN)_4] \cdot 2H_2O$ (H and H_2O not shown for clarity).

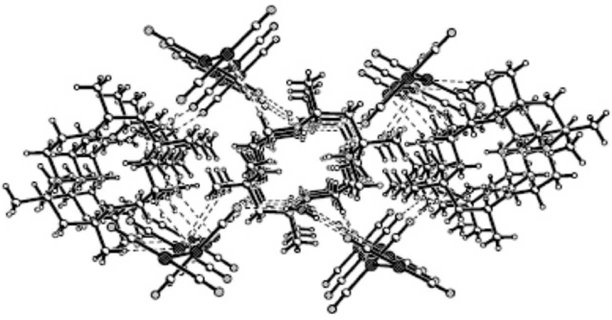

Figure 5. The packing diagram of **2**. The uncoordinated water molecules are hydrogen bonded to the uncoordinated nitrogen atoms of the cyanides.

4.3. *Spectral properties*

The IR spectra of solid phases show the ν_{CN} bands at 2159 and 2146 cm^{-1} for **1**, 2143 cm^{-1} for **2**. The CN bands at 2146 cm^{-1} for **1** and 2143 cm^{-1} for **2** are due to the free $[Au(CN)_2]^-$ anions, the ν_{CN} bands at 2159 cm^{-1} for **1** is due to coordinated $[Au(CN)_2]^-$. The UV spectra of an aqueous solution of **1** shows strong absorption bands in the range 200–280 nm and displays a weak peak at 1174 nm. The peak at 1174 nm may be attributed to the d–d transition of Ni(II).

Aqueous solutions of **1** and **2** are luminescent at room temperature. Figure 6(a) shows emission and excitation spectra of a crystal sample of **1**. The emission spectrum obtained with excitation at 338 nm exhibits one peak with maximum of 400 nm. The results are a little different from that of $K[Au(CN)_2]$ in aqueous solution (0.03 M, $\lambda_{exc} = 290$ nm, maximum at 430 nm) reported by Patterson [26]. Figure 6(b) shows the emission and excitation spectra of a crystal sample of **2**. The emission spectrum obtained with excitation wavelength at 297 nm exhibits a maximum band of 409 nm. In aqueous solutions the polymers may break in some part of oligomers and new oligomers $[Au(CN)_2]_n^{n-}$ may be formed by weak aurophilic attraction [30], and the higher-energy bands (shorter excited wavelength) should be assigned to the smallest

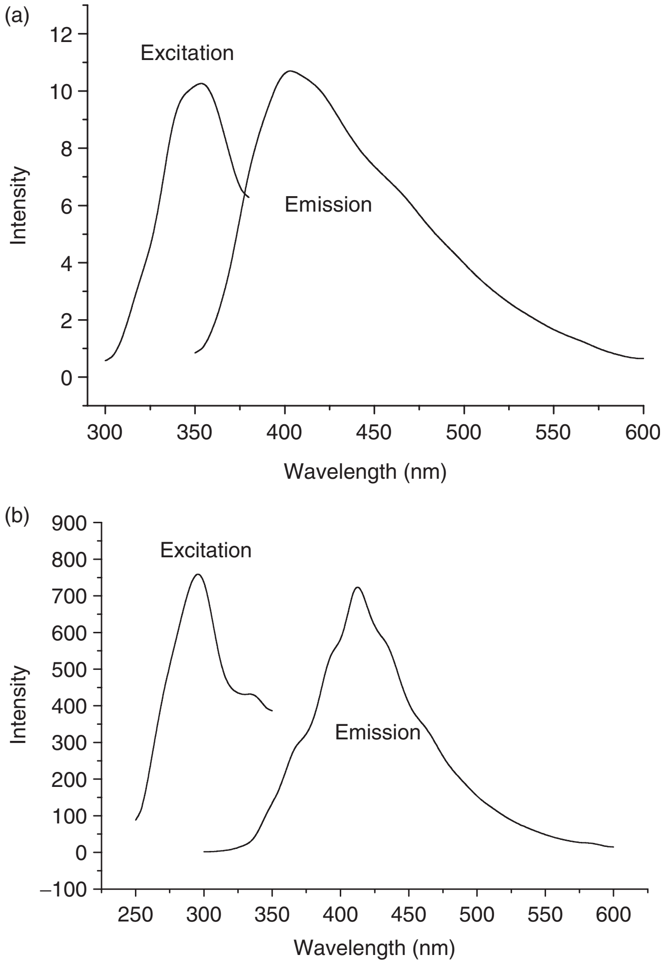

Figure 6. (a) The emission (right) and excitation (left) spectra for **1** at room temperature in aqueous solution; (b) The emission (right) and excitation (left) spectra for **2** at room temperature in aqueous solution.

oligomers $[Au(CN)_2]_n^{n-}$, while the lower-energy bands correspond to larger oligomers in solution [26]. The luminescence observed for **1** and **2** can be attributed to the presence of aurophilic attractions which produce the different oligomers $[Au(CN)_2]_n^{n-}$ in the aqueous solutions. These observations are consistent with the studies of Patterson *et al.* [20, 23, 24, 26] who have attributed the remarkable variations in the luminescence resulting from $[Au(CN)_2]^-$ in different environments to the formation of aggregates.

5. Conclusions

Two supramolecular assemblies **1** and **2** have been synthesized from $[Au(CN)_2]^-$ building block and structurally characterized. Complex **1** shows a 1D infinite chain. In both complexes the incorporation of aurophilic and hydrogen-bonding interactions play an important role in increasing the structural dimensionality. Aqueous solutions of **1** and **2** are luminescent at room temperature, which can be attributed to the presence of aurophilic attractions.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 276387 for **1** and 276658 for **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgement

This work is supported by the National Science Foundation of China (Nos 20071020 and 20371027) and Tianjin Natural Science Foundation (No. 033609211).

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