This article was downloaded by: [Boston University] On: 21 February 2013, At: 05:24 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

Strong Silver-Silver Interactions in Three Silver(I) Carboxylate Complexes with High Cytotoxicity Properties

Xiu-Ying Liu^a & Hai-Liang Zhu^b

^a Department of Chemistry, Wuhan University of Science & Engineering, Wuhan, P.R. China ^b Institute of Functional Biomolecules and State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing, P.R. China Version of record first published: 16 Aug 2006.

To cite this article: Xiu-Ying Liu & Hai-Liang Zhu (2005): Strong Silver-Silver Interactions in Three Silver(I) Carboxylate Complexes with High Cytotoxicity Properties, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 35:4, 325-332

To link to this article: http://dx.doi.org/10.1081/SIM-200055672

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Strong Silver-Silver Interactions in Three Silver(I) Carboxylate Complexes with High Cytotoxicity Properties

Xiu-Ying Liu

Department of Chemistry, Wuhan University of Science & Engineering, Wuhan, P.R. China

Hai-Liang Zhu

Institute of Functional Biomolecules and State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing, P.R. China

Three carboxylate silver(I) complexes, [Ag(fbc)]n, (1), [Ag2(cpd)]n (2) and [Ag2(idc)]n (3), were prepared and characterized by X-ray single crystal analysis, where fbcH is 4-fluorobenzoic acid, cpdH2 is cyclopentane-1,1-dicarboxylic acid and idcH2 is iminodiacetic acid. The three coordination polymers show clear Ag-Ag bonds in their structures. The Ag-Ag bond length 2.850Å both in 1 and 2 is much shorter than that (2.89Å) in metal silver, which is the shortest silver-silver interaction reported. The result of cytotoxicity of the three complexes indicates that they have very high crytotoxicity properties to normal cells and carcinoma cells.

Keywords carcinoma cells, crystal structures, cytotoxicity, silver complexes, silver-silver bonds

INTRODUCTION

One of the recent hot topics in the coordination chemistry of coinage metals(I) is the d¹⁰-d¹⁰ interactions between two closed-shell cations, many examples of which have been reported and reviewed in silver(I) complexes (Dance, 1986; Dance et al., 1983; Guo et al., 1999; Jansen, 1987; Jaw et al., 1989; Leung et al., 1999; Tong et al., 1999; Wang and Mak, 2000, 2001a, 2001b; Yam and Lee, 1993; Yam and Lo, 1999; Yam et al., 1994, 1998). Silver(I) complexes with organic ligands containing donors such as O, N, and S atoms are also of great interest in bioinorganic chemistry (Lopez-Garzon et al., 1990; Veen, 1983) We have been investigating the cytotoxicity of silver(I) complexes (Chen et al., 2001a, 2001b; Zhu et al., 2003) and, as an extension of this work, report herein the syntheses, structures and cytotoxicities of

three silver(I) complexes with carboxylate ligands, $[Ag(fbc)]_n$ (1), $[Ag_2(cpd)]_n$ (2) and $[Ag_2(idc)]_n$ (3), where fbcH is 4-fluorobenzoic acid, cpdH₂ is cyclopentane-1,1-dicarboxylic acid and idcH₂ is iminodiacetic acid. The three coordination polymers show clear Ag-Ag bonds in their structures and high cytotoxicity properties to normal cells and carcinoma cells.

EXPERIMENTAL

Materials and Measurements

Commercially available Ag_2O , 4-fluorobenzoic acid, cyclopentane-1,1-dicarboxylic acid and iminodiacetic acid were purchased from Aldrich and used without further purification. Other solvents and reagents were used as obtained from The Second Chemicals Factory of Shanghai, P.R. China. C, H and N elemental analyses were performed with a Perkin-Elmer elemental analyzer.

Syntheses of the Ag^I Complexes $[Ag(fbc)]_n$ (1)

A solution of Ag_2O (0.12 g, 0.5 mmol) in 30% aqueous ammonia solution (5 mL) was added drop-wise with stirring at room temperature to a solution of 4-fluorobenzoic acid (fbcH) (0.14 g, 1 mmol) in 30% aqueous ammonia solution (5 mL). The mixture was let to stand still in the air to vaporize about three-quarters of the solvents and filtered. Crystals were obtained and washed three times with water, and then dried in a vacuum desiccator over drying CaCl₂. The yield, melting/decomposition point and the analytical data of elemental analyses and IR determination are presented in Table 1.

Syntheses of the Ag^I Complexes [Ag₂(cpd)]_n (2)

A solution of Ag_2O (0.12 g, 0.5 mmol) in 30% aqueous ammonia solution (5 mL) was added drop-wise with stirring at room temperature to a solution of



Received 13 July 2004; accepted 13 January 2005.

Address correspondence to Hai-Liang Zhu, Department of Chemistry, Wuhan University of Science & Engineering, Wuhan 430073, P.R. China. E-mail: hailiang_zhu@fync.edu.cn

 TABLE 1

 Analytical data for complexes (1), (2) and (3)

Compound (1)	Formula	C ₇ H ₄ AgFO ₂
1 ()	FW	246.97
	Yield (%)	32
	EA	Anal. Calcd.: C, 34.04;
		H, 1.63 (%) Found: C,
		33.83; H, 1.70(%)
	IR (KBr, cm^{-1})	3290 w, 1603 m,
		1559–1557 vs, 1425 m
		1411 m, 1384 s, 1329 m,
		1292 m, 1279 m,
		1109 m, 1106 m,
		1035 m, 966 w, 915 m,
		730 m, 700 w
Compound (2)	Formula	$C_7H_8Ag_2O_4$
	FW	371.87
	Yield (%)	38
	EA	Anal. Calcd.: C, 22.61;
		H, 2.17(%) Found: C,
		22.55; H, 2.25(%)
	IR (KBr, cm^{-1})	2941 m, 1529 vs, 1439 s,
		1395 s, 1360 vs, 1268 m,
		1203 w, 882 w, 801 m,
		775 w, 711 m
Compound (3)	Formula	$C_4H_5Ag_2NO_4$
	FW	346.83
	Yield (%)	69
	EA	Anal. Calcd.: C, 13.85;
		H, 1.45; N, 4.04(%)
		Found: C, 14.01; H,
		1.50; N, 3.95(%)
	IR (KBr, cm^{-1})	3290 w, 1603 m,
		1559–1557 vs, 1425 m
		1411 m, 1384 s, 1329 m,
		1292 m, 1279 m,
		1109 m, 1106 m,
		1035 m, 966 w, 915 m,
		730 m, 700 w

cyclopentane-1,1-dicarboxylic acid $(cpdH_2)$ (0.08 g, 0.5 mmol) in 30% aqueous ammonia solution (mL). The mixture was let to stand still in the air to vaporize about three-quarters of the solvents and filtered. Crystals were obtained and washed three times with water, and then dried in a vacuum desiccator over drying CaCl₂. The yield, melting/decomposition point and the analytical data of elemental analyses and IR determination are presented in Table 1.

Syntheses of the Ag^{I} Complexes $[Ag_{2}(idc)]_{n}$ (3)

A solution of Ag_2O (0.12 g, 0.5 mmol) in 30% aqueous ammonia solution (5 mL) was added drop-wise with stirring

at room temperature to a solution of iminodiacetic acid $(idcH_2)$ (0.07 g, 0.5 mmol) in 30% aqueous ammonia solution (5 mL). The mixture was let to stand still in the air to vaporize about three-quarters of the solvents and filtered. Crystals were obtained and washed three times with water, and then dried in a vacuum desiccator over drying CaCl₂. The yields and the analytical data of elemental analyses and IR determination are presented in Table 1.

Data Collection, Structural Determination and Refinement

Diffraction intensities were collected on a CCD area detector for compounds (1) and (3), and on a Siemens R3m diffractometer for compound (2) using Mo-Ka radiation $(\lambda = 71.073 \text{ pm})$. Absorption corrections were applied (North, A. C. T., Phillips, D. C., Mathews, F. S. Acta Crystallogr. Sect. A 24, 351(1968)). The structure solutions and fullmatrix least-squares refinements based on F² were performed with the SHELX-97 program package (Sheldrick, G. M. SHELX-97, Program for Crystal Structure Determination, University of Göttingen (1997)). All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically and allowed to ride on their parent carbon atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data for the three compounds are summarized in Table 2. Selected bond distances and bond angles are given in Table 3.

RESULTS AND DISCUSSION

Syntheses of the Complexes $[Ag(fbc)]_n$ (1), $[Ag_2(cpd)]_n$ (2) and $[Ag_2(idc)]_n$ (3).

The formation of the three complexes (1)-(3) can be expressed as the following equations:

$$nAg_2O + 2nfbcH = nH_2O + 2[Ag(fbc)]_n(1)$$

 $nAg_2O + ncpdH_2 = nH_2O + [Ag_2(cpd)]_n(2)$
 $nAg_2O + nidcH_2 = nH_2O + [Ag_2(idc)]_n(3)$

The compounds were prepared by mixing the solutions of Ag_2O and bi-equimolar 4-fluorobenzoic acid (fbcH) for (1), or equimolar cyclopentane-1,1-dicarboxylic acid (cpdH₂) and iminodiacetic acid (idcH₂) for (2) and (3), respectively. 30% aqueous ammonia solution is the most suitable solvent for the syntheses of the complexes and crystals generated by evaporations of the solvents of the mixtures.

Structure Description of Complex (1)

The X-ray crystallographic study reveals that compound (1) crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit consists of one Ag ion and one 4-fluorobenzoate anion ligand (fbc). The Ag ion in (1) has a distorted trigonal geometry, being coordinated by three oxygen atoms from

246.97	371.87		
Long rod	5/1.0/	346.83	
Long rou	Cube	Long rod	
$0.29 \times 0.13 \times 0.08$	$0.40 \times 0.40 \times 0.40$	$0.19 \times 0.12 \times 0.00$	
Monoclinic	Orthorhombic	Orthorhombic	
$P2_1/c$	Pbcn	Pbca	
15.619(17)	6.447(2)	6.955(4)	
3.699(4)	10.893(3)	9.527(5)	
11.178(12)	23.536(10)	19.384(11)	
90	90	90	
98.951(15)	90	90	
90	90	90	
638.0(12)	1652.9(10)	1284.4(12)	
4	8	8	
298(2)	293(2)	298(2)	
3.102	4.712	6.053	
2.446	2.989	3.587	
1311	1305	1263	
972	991	1000	
448	1408	1296	
0.7894	1.0082	0.7128	
0.4665	0.9860	0.3926	
1.025	1.079	0.879	
0.0407, 0.1029	0.0388, 0.0879	0.0211, 0.0368	
0.0564, 0.1092	0.0602, 0.0979	0.0317, 0.0389	
	Monoclinic $P2_1/c$ 15.619(17) 3.699(4) 11.178(12) 90 98.951(15) 90 638.0(12) 4 298(2) 3.102 2.446 1311 972 448 0.7894 0.4665 1.025 0.0407, 0.1029 0.0564, 0.1092 $wR_2 = [\sum w(F_o^2 - F_o^2)]$	MonoclinicOrthorhombic $P2_1/c$ $Pbcn$ 15.619(17) $6.447(2)$ $3.699(4)$ $10.893(3)$ $11.178(12)$ $23.536(10)$ 90 90 90 90 90 90 90 90 90 90 90 90 90 90 90 90 90 90 91 $1652.9(10)$ 4 8 $298(2)$ $293(2)$ 3.102 4.712 2.446 2.989 1311 1305 972 991 448 1408 0.7894 1.0082 0.4665 0.9860 1.025 1.079 $0.0407, 0.1029$ $0.0388, 0.0879$ $0.0564, 0.1092$ $0.0602, 0.0979$	

 TABLE 2

 Crystallographic and experimental data for complexes (1), (2) and (3)

three fbc ligands. Figure 1 displays the coordination environment of the silver atoms in complex (1). The Ag-O distances are in the range of 2.210(4)-2.512(4) Å, which are slightly longer than common Ag-O bonds in silver(I) complexes with similar aromatic carboxylic acids, and the O-Ag-O angles are in the range of 90.0-157.9°. The Ag-Ag distance of 2.850(3) Å is significantly shorter than that (2.89 Å) in silver metal, indicating a more clear Ag-Ag bond. The fbc anion in (1) adopts a μ_3 coordination mode. Adjacent Ag ions in (1), via sharing O(2) and its equivalents result in Ag-O chains with the sequence of ··· Ag-O-Ag-O..., and the Ag-O chains are further linked by Ag-Ag bonds to build up a two-dimensional layer with (6,3)topology, as shown in Figure 2. The three-connected nodes are provided by Ag ions and the two-connectors are provided by oxygen bridges and Ag-Ag bonding interaction. The fbc ligands are located on both sides of the layers, which are stacked via aromatic rings to form hydrophobic regions between layers (Figure 3).

Structure Description of Complex (2)

Compound (2) crystallizes in the orthorhombic space group Pbcn, and the asymmetric unit is composed of two Ag ions and one cyclopentane-1,1-dicarboxylate dianion ligands (cpd), as shown in Figure 4. The Ag(1) ion in (2) has a distorted tetrahedral geometry, being coordinated by four oxygen atoms from three cpd ligands. The Ag(2) ion in (2) has a distorted trigonal geometry, being coordinated by three oxygen atoms from three cpd dianions. The Ag-O bond lengths are in the range of 2.213(6) - 2.400(6) Å, which are longer than those in silver(I) complexes with aromatic carboxylic acids, but slightly shorter than those Ag-O bonds in complex (1). The O-Ag-O angles are in the range $74.2(2)-143.7(2)^{\circ}$. It should be noted that each Ag ion in (2) has two other Ag ions approaching it with Ag-Ag distances 2.789(2), 2.850(1) and 2.996(2) Å. The Ag-Ag distance of 2.789(2) Å is among the shortest Ag-Ag separations ever reported, indicating clear evidence of the existence of Ag-Ag bonding interactions. The cpd ligand in (2) adopts a μ_7 coordination mode (Figure 5).

	8	\mathbf{I}	- /
	(1	1)	
Ag(1)-O(2B)	2.196(4)	Ag(1) - O(1)	2.512(4)
Ag(1) - O(1A)	2.210(4)	$Ag(1) \cdots Ag(1A)$	2.850(3)
O(2B) - Ag(1) - O(1A)	157.9(2)	O(1) - Ag(1) - O(1A)	93.5(1)
O(2B) - Ag(1) - O(1)	99.0(2)		
	(2	2)	
Ag(1)-O(4B)	2.213(6)	Ag(1)-O(3A)	2.404(6)
Ag(1) - O(1)	2.342(7)	Ag(1)-O(2A)	2.591(7)
$Ag(1)\cdots Ag(1A)$	2.789(2)	$Ag(1) \cdots Ag(2)$	2.850(1)
Ag(2) - O(2)	2.215(6)	Ag(2)-O(1C)	2.353(6)
Ag(2)–O(3B)	2.400(6)	$Ag(2) \cdots Ag(2A)$	2.996(2)
O(4B) - Ag(1) - O(1)	151.7(2)	O(4B)-Ag(1)-O(2A)	84.1(2)
O(4B) - Ag(1) - O(3A)	128.0(2)	O(1) - Ag(1) - O(2A)	116.8(2)
O(1) - Ag(1) - O(3A)	74.3(2)	O(3A)-Ag(1)-O(2A)	88.4(2)
O(2) - Ag(2) - O(1C)	140.3(3)	O(1C) - Ag(2) - O(3B)	74.2(2)
O(2) - Ag(2) - O(3B)	143.8(2)		
	(3	3)	
Ag(1)-O(3A)	2.201(2)	Ag(1)-O(4B)	2.488(3)
Ag(1) - O(1)	2.213(3)	$Ag(1) \cdots Ag(2)$	2.939(1)
Ag(2)-N(1C)	2.284(3)	Ag(2)-O(1D)	2.382(3)
Ag(2) - O(4A)	2.365(3)	Ag(2) - O(2)	2.489(3)
O(3A) - Ag(1) - O(1)	172.5(1)	O(1) - Ag(1) - O(4B)	77.07(9)
O(3A) - Ag(1) - O(4B)	100.3 (1)	N(1C)-Ag(2)-O(4A)	116.6(1)
N(1C) - Ag(2) - O(1D)	146.2(1)	O(4A) - Ag(2) - O(2)	127.8(1)
O(4A) - Ag(2) - O(1D)	76.44(9)	O(1D) - Ag(2) - O(2)	96.82(8)
N(1C) - Ag(2) - O(2)	97.7(1)		

TABLE 3Selected bond lengths (Å) and angles (°) for complexes (1), (2) and (3)

More interestingly, adjacent Ag ions via Ag–Ag bonding interaction generate silver chains and adjacent silver chains are further linked by sharing oxygen atoms to result in a twodimensional Ag–O layer, as shown in Figure 5. The cpd



FIG. 1. Perspective view of the coordination environments of Ag in (1).

ligands are located on both sides of the Ag–O layer to result in a two-dimensional layer.

Structure Description of Complex (3)

The asymmetric unit in (3) consists of two crystallographically distinct Ag ions and one iminodiacetate dianion ligand (idc). As shown in Figure 6, the Ag(1) ion is coordinated by three carboxylate oxygen atoms from three idc ligands with the Ag-O bond distances of 2.201(2)-2.488(3) Å. The O-Ag-O angles are 172.5(1), 77.1(1) and $100.3(1)^{\circ}$, which indicate the coordination geometry of Ag(1) is closer to a "T-shape" than a triangle "Y-shape." The Ag(2) atom is coordinated by three carboxylate oxygen atoms and one nitrogen atom from four idc dianions. The Ag-O distances around the Ag(2) atom are in the range of 2.365(3) - 2.489(3) Å and the Ag-N distance is 2.284(3) Å. The O-Ag-O and N-Ag-O angles are in the range of 76.4(1)-146.2(1), indicating a distorted tetrahedral geometry for Ag(2). The Ag(1) and Ag(2) ions are linked by O,O'-bridges of carboxylate with Ag-Ag distance of 2.939(1) Å. The Ag-Ag distance in (3), which is comparable with those reported by Bosch, is below the sum of van der Waals radii of two Ag ions (3.44 Å) and



FIG. 2. Perspective view of the two-dimensional layer of (1) showing Ag-Ag bonds. For clarity, the carbon and fluorine atoms of fbc are omitted. The balls with diagonal lines represent the Ag atoms and the hollow balls are the oxygen atoms.

is close to the Ag-Ag distance in silver metal (2.89 Å), indicating a strong interaction of Ag \cdots Ag in (3) (Bosch and Barnes, 2002; Schultheiss et al., 2003). The idc ligand in (3) employs one nitrogen and four oxygen atoms to coordinate the Ag ions and thus adopts a μ_7 coordination mode (Figure 7). The compound is a dimeric motifs formed by silver(I) carboxylates



FIG. 4. Perspective view of the coordination environments of Ag in (2).

and is an analog of that reported by Brammer (Brammer et al., 2001). The adjacent Ag(1) and Ag(2) atoms also form a dimeric unit via sharing of carboyxlate oxygen atoms, and the dimeric units are further linked by Ag-Ag bonding interactions to generate one-dimensional Ag-Ag-O chains. The Ag-Ag-O chains are connected by idc anions to form a



FIG. 3. Perspective view of the stacking array of (1).



FIG. 5. Perspective view of the two-dimensional layer of (2) showing Ag-Ag bonds. For clarity, some carbon atoms of cpd are omitted and the others are shown with smaller hollow balls. The balls with diagonal lines represent the Ag atoms and the bigger hollow balls are the oxygen atoms.



FIG. 6. Perspective view of the coordination environments of Ag in (3).



FIG. 7. The three-dimensional structure of (3). The balls with diagonal lines represent the Ag atoms and the bigger hollow balls are the oxygen atoms and the smaller hollow balls are carbon atoms.

three-dimensional framework, as shown in Figure 7. The Ag-Ag bonds in (3) are shown in Figure 8.

Cytotoxicity

Five human solid carcinoma cell lines, Hela (cervix adenocarcinoma), HepG2 (hepatocellular carcinoma), BGC (gastric carcinoma), 95-D (lung carcinoma), CNE (rhinocarcinoma) and two normal cell lines, NIH 3T3 (mouse normal fibroblast), and L-02 (human normal liver cell), were obtained from Shanghai Cell Institute of the Chinese Science Academy. These cells were subcultured in media RMPI 1640 (GIBCO BRL product) with 10% fetal bovine serum (Hyclone



FIG. 8. The Ag-Ag bonds in (3).

		Cytotoxicities of complexes (1) , (2) and (3)						
Complex	IC ₅₀ (µM)							
	Hela	HepG2	BGC	95-D	CNE	L-02	NIH3T3	
(1)	8.1	8.7	9.3	8.7	16.2	17.4	41.6	
(2)	4.2	4.2	6.3	4.2	10.8	4.2	4.2	
(3)	20.6	13.4	25.4	26.8	60.1	25.8	11.7	

TABLE 4Cytotoxicities of complexes (1), (2) and (3)

product), at 37°C with 5% CO₂. Cells were adjusted to a concentration of 10^5 cells · mL⁻¹ and were planted in 96-well tissue culture plate, and were then exposed to the test compounds ranging in concentrations from 2.5 to $100 \,\mu g \cdot mL^{-1}$ for 48 hours. The cells were pigmented by MTT [3-(4,5dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide], and the O.D. values were measured by an ELX800 universal microplate reader (BIO-TEK Instruments, Inc.) under 490 nm wave length. The IC₅₀ value (concentration of drug required to inhibit 50% growth) was calculated from linear regression of the percent viable cells versus the log of the drug concentration. The results are shown in Table 4.

The cytotoxicity properties of (1)-(3) were studied and the concentrations required to yield 50% inhibition of the viable cells (IC₅₀) (Carmichael et al., 1987) are listed in Table 4. The low IC₅₀ concentrations of the three complexes show that they are strong cytotoxic *in vitro* (Baird et al., 1997; Rosenberg et al., 1969) to normal cells and carcinoma cells. The high cytotoxicities to cells and good stability both in air and in light of these complexes imply that they are potential candidates for antitumor agents. On the other hand, different kinds of the cells have different sensitivities to these compounds; therefore, further exploration in generating analogous silver(I) complexes through appropriate chemical modification is required for higher selectivity as well as for understanding the structure-function relation.

REFERENCES

- Baird, C. L.; Griffitts, A. E.; Baffic, S.; Bryant, P.; Wolf, B.; Lutton, J.; Berardini, M.; Arvanitis, G. M. Synthesis, characterization and antitumor activity of platinum triamine complexes containing imidazothiazole ligands. *Inorg. Chim. Acta* **1997**, *256*, 253–262.
- Bosch, E.; Barnes, C. L. One- and two-dimensional silvercoordination networks containing π-sandwiched silver-silver interactions. *Inorg. Chem.* 2002, 41 (9), 2543–2547.
- Brammer, L.; Burgard, M. D.; Rodger, C. S.; Swearingen, J. K.; Rath, N. P. Silver(I) carboxylates: versatile inorganic analogs of carboxylic acids for supramolecular network formation. *Chem. Commun.* 2001, 23, 2468–2469.
- Carmichael, J.; DeGrafp, W. C.; Gazdar, A. F.; Minna, J. D.; Mitchell, J. B. Evaluation of a tetrazolium-based semiautomated colorimetric assay: assessment of chemosensitivity testing. *Cancer Res.* **1987**, *47*, 936–942.

- Chen, Q.; Zhu, H.-L.; Qi, S.-J.; Peng, W.-L.; Xu, A.-L. Studies on antitumor activity of several complexes of hexaaza-macrocyclic Schiff base with silver(I). *Acta Scient. Nat. Univ. Sunyatseni* 2001, 40 (2), 65–67CA 366309a, Vol. 135, 2001.
- Chen, Q.; Qi, S.-J.; Zhu, H.-L.; Peng, W.-L.; Xu, A.-L. Syntheses and cytotoxicity evaluation of silver(I) compounds of propandioic acid: dimension structure analogues of carboplatin. *Chem. Chin. J. Med. Chem.* 2001, *11* (1), 5–8, CA 144160b, Vol. 136, 2002.
- Dance, I. G. The structural chemistry of metal thiolate complexes. *Polyhedron.* **1986**, *5*, 1037–1104.
- Dance, I. G.; Fitzpatrick, L. J.; Rae, A. D.; Scudder, M. The intertwined double-(-Ag-SR)-strand chain structure of crystalline 3-methylpentane-3-thiolatosilver, in relation to molecules (AgSR)₈ in solution. *Inorg. Chem.* **1983**, *22*, 3785–3788.
- Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. Structural variation in novel double salts of silver acetylide with silver titrate: fully encapsulated acetylide dianion in different polyhedral silver cages. J. Am. Chem. Soc. 1999, 121, 3136–3141.
- Jansen, J. Homoatomic d10-d10 interactions: their effects on structure and chemical and physical properties. *Angew. Chem. Int. Ed. Engl.* 1987, 26, 1098–1110.
- Jaw, H. R. C.; Savas, M. M.; Mason, W. R. Electronic absorption and MCD spectra for the binuclear three-coordinate gold(I) complex Au₂(dmpm)₃²⁺ (dmpm = bis(dimethylphosphino)methane). *Inorg. Chem.* **1989**, *28*, 4366–4369.
- Leung, K. H.; Phillips, D. L.; Tse, M. C.; Che, C. M.; Miskowski, V. M. Resonance Raman investigation of the Au(I)-Au(I) interaction of the 1 [d*p] excited state of Au₂(dcpm)₂(ClO₄)₂ [dcpm = bis(dicyclohexylphosphino)methane]. *J. Am. Chem. Soc.* **1999**, *121* (20), 4799–4803.
- Lopez-Garzon, R.; Romero-Molina, M. A.; Navarrete-Guijosa, A.; Lopez-Gonzalez, J. M.; Alvarez-Cienfuegos, G.; Herradcr-Pino, M. M. Synthesis, molecular structure determination, and biological studies on E-1-p-ethoxyphenyl-4-hydrox-iminomethyl imidazole metal complexes. J. Inorg. Biochem. 1990, 38, 139–151.
- Rosenberg, B.; Camp, L.; van Trosko, J. E.; Mansour, V. H. Platinum compounds: a new class of potent antitumour agents. *Nature* 1969, 222, 385–386.
- Schultheiss, N.; Powell, D. R.; Bosch, E. Silver(I) coordination chemistry of 2,6-diarylpyrazines. *π*-stacking, anion coordination, and steric control. *Inorg. Chem.* **2003**, *42* (17), 5304–5310.
- Tong, M.-L.; Chen, X.-M.; Ye, B.-H.; Ji, L.-N. Syntheses, structures, and luminescent properties. *Angew. Chem. Int. Ed. Engl.* 1999, 38, 2237–2240.
- Veen, H. Silver thiosulfate: an experimental tool in plant science. *Hortic Sci. (Amsterdam)* 1983, 20, 211–224.

- Wang, Q.-M.; Mak, T. C. W. Novel honeycomb-like layered structure: The first isomorphous triple salts of silver acetylide. J. Am. Chem. Soc. 2000, 122, 7608–7609.
- Wang, Q.-M.; Mak, T. C. W. Elliptic column consolidated by acetylide dianion, cyanide and trifluoroacetate in a novel quadruple salt of silver(I). J. Am. Chem. Soc. 2001, 123, 1501–1502.
- Wang, Q.-M.; Mak, T. C. W. Argentophilicity and solvent-induced structural diversity in double salts of silver acetylide with silver perfluoroalkyl carboxylate. J. Am. Chem. Soc. 2001, 123, 7594–7600.
- Yam, V. W. W.; Lee, W. K. Synthesis, spectroscopy and excited-state redox properties of novel luminescent trinuclear three-co-ordinate gold(I) phosphine complexes. J. Chem. Soc., Dalton Trans. 1993, 2097–2100.

- Yam, V. W.-W.; Lo, K. K.-W. Luminescent polynuclear d10 metal complexes. *Chem. Soc. Rev.* **1999**, 28 (5), 323–334.
- Yam, V. W. W.; Choi, S. W. K.; Lo, K. K. W.; Dung, W. F.; Kong, R. Y. C. Photolytic cleavage of DNA by [Au₃(dmmp)₂]³⁺. *J. Chem. Soc., Chem. Commun.* **1994**, 2379–2380.
- Yam, V. W. W.; Li, C. K.; Chan, C. L. Proof of potassium ions by luminescence signaling based on weak gold-gold interactions in dinuclear gold(I) complexes. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 2857–2859.
- Zhu, H.-L.; Zhang, X.-M.; Liu, G.-F.; Wang, D.-Q. Syntheses, crystal structures, and cytotoxicity evaluation of two chain-like and diamond-like silver(I) complexes, Z. Anorg. Allg. Chem. 2003, 629, 1059–1062.