ELSEVIER

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 298 (2000) 24–32

Inorganica Chimica Acta

Synthesis and crystal structure of coinage metal(I) complexes with tetrazole (Htetz) and triphenylphosphine ligands, and their antimicrobial activities. A helical polymer of silver(I) complex $[Ag(tetz)(PPh_3)_2]_n$ and a monomeric gold(I) complex $[Au(tetz)(PPh_3)]$

Kenji Nomiya [a,*], Ryusuke Noguchi [a], Munehiro Oda [b]

[a] *Department of Materials Science, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan*
[b] *Meiji Cell Technology Center, Meiji Milk Products Co., Ltd., Odawara, Kanagawa 250-0862, Japan*

Received 1 July 1999; accepted 28 July 1999

Abstract

Two novel coinage metal(I)-triphenylphosphine complexes with a heterocyclic ligand, $[Ag(tetz)(PPh_3)_2]_n$ (**1**) and $[Au(tetz)(PPh_3)]$ (**2**) (Htetz = tetrazole) were synthesized from a reaction in dichloromethane of the precursor complex $[Ag(tetz)]_n$ with PPh_3 and from a reaction in acetone of $[AuCl(PPh_3)]$ with Htetz in the presence of aqueous NaOH, respectively, and isolated as colorless needle crystals for both **1** and **2**. The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction. These d^{10} complexes were also fully characterized by elemental analyses, TG/DTA and FT-IR in the solid-state, solution NMR (^{31}P, ^{1}H and ^{13}C, as well as ^{109}Ag for **1**) spectroscopies and solution molecular weight measurements. Complex **1**, is composed of a helical polymer, a 2_1 helix with a pitch 9.471 Å, formed by a bridged tetrazolate of an $AgNP_2$ core in the solid-state, but it was present as a monomer in solution. In contrast to **1**, complex **2** consisted of a monomeric two-coordinate AuNP core without gold(I)–gold(I) interaction both in the solid-state and in solution. The molecular structures of **1** and **2** were compared with those of the corresponding triazole complexes, i.e. silver(I) complexes $[Ag(1,2,3\text{-triz})(PPh_3)_2]_n$ (**3**) and $[Ag(1,2,4\text{-triz})(PPh_3)_2]_n$ (**4**) both as helical polymers, a monomeric gold(I) complex $[Au(1,2,3\text{-triz})(PPh_3)]$ (**5**) and a dimeric gold(I) complex $[Au(1,2,4\text{-triz})(PPh_3)]_2$ (**6**) through an intramolecular gold(I)–gold(I) bond; the structures of complexes **3**–**6** being recently determined by X-ray crystallography. The antimicrobial activities of **1**, its precursor $[Ag(tetz)]_n$ and **2** were compared and key factors affecting them discussed.

Keywords: Tetrazole; Triphenylphosphine; Silver(I) complexes; Gold(I) complexes; Crystal structures

1. Introduction

There is currently considerable interest in the coordination chemistry of coinage metals such as silver(I) and gold(I) with biological or medicinal activities [1–11]. The molecular design and structural determination of such silver(I) and gold(I) complexes composed of the same ligands are an intriguing aspect of bioinorganic chemistry, inorganic syntheses and metal-based drugs. We have been interested in the structure-biological activity correlation of the coinage metal complexes [12–17].

One recently highlighted topic in the coordination chemistry of coinage metal(I) atoms is concerned with the helicity (Table 1) [18–25], i.e. properties as helical polymers of d^{10} metals, most of which have been recently observed in silver(I) complexes, e.g. several single-stranded helices such as $[Ag(pydz)](NO_3)$ (pydz = pyridazine), $[Ag(pydz)](OTf)$ ($OTf = CF_3SO_3$) and $[Ag(pydz)_2](BF_4)$ [18], $[Ag(2,2'\text{-biimidazole})](NO_3)$ [23], and the double helix of $[Ag(bpp)](OTf)$ (bpp = 1,3-bis(4-pyridyl)propane) [22]. Chiral helical polymers

---

* Corresponding author. Tel.: +81-463-59 4111; fax: +81-463-58 9684.

E-mail address: nomiya@info.kanagawa-u.ac.jp (K. Nomiya)

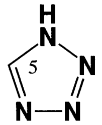
0020-1693/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0020-1693(99)00401-6

such as $[Ag(S\text{-}Hpyrrld)]_n$ (H_2pyrrld = (*S*)-(−)-2-pyrrolidone-5-carboxylic acid) [17], $[Ag(R,R\text{-}DIOP)(NO_3)]_n$ (*R*,*R*-DIOP = (4*R*,5*R*)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane) [20], and $\{[Ag(R,R\text{-}J)](OTf)\}_n$ (*R*,*R*-J = (4*R*,5*R*)-4,5-bis(2-(2-pyridyl)ethyl)-1,3-dioxolane) [24], have been recently found. Also, the double helical polymer in the gold(I) complex has been elucidated for $Cs_2Na[Au_2(tma)(Htma)]$ (myocrisine; H_3tma = thiomalic acid) showing antiarthritic action [25]. A second topic of interest is the d^{10}–d^{10} interaction between two closed shell cations, or the aurophilic interaction, many examples of which have been recently reported and reviewed [26–33].

Transformation of polymeric silver(I) complexes composed of N-heterocyclic ligands to their tertiary phosphine derivatives has resulted in the formation of monomers, oligomers, or helical polymers [14,16,34,35]; e.g. a reaction of a polymer $[Ag(im)]_n$ (Him = imidazole) with 3 equiv. of PPh_3 gave a monomeric species $[Ag(im)(PPh_3)_3]$ [14,16], a reaction of a polymer $[Ag(pz)]_n$ (Hpz = pyrazole) with PPh_3 formed the dinuclear $[Ag_2(pz)_2(PPh_3)_2]$ and $[Ag_2(pz)_2(PPh_3)_3]$ complexes [34], and a reaction of polymers $[Ag(1,2,3\text{-}triz)]_n$ (Htriz = triazole) and $[Ag(1,2,4\text{-}triz)]_n$ with 3 equiv. of PPh_3 provided single-stranded helical polymers $[Ag(1,2,3\text{-}triz)(PPh_3)_2]_n$ (**3**) and $[Ag(1,2,4\text{-}triz)(PPh_3)_2]_n$ (**4**) [13]. These PPh_3 derivatives have never been isolated from reactions of the precursors such as $[AgCl(PPh_3)_3]$ and $[AgCl(PPh_3)_2]_2$ with N-heterocycles under alkaline conditions. On the other hand, the corresponding gold(I) complexes have been isolated as monomers or dimers, but not as polymers, such as $[Au(im)(PPh_3)]$ [14], $[Au(pz)(PPh_3)]$ [15], $[Au(1,2,3\text{-}triz)(PPh_3)]$ (**5**) and $[Au(1,2,4\text{-}triz)(PPh_3)]_2$ (**6**) [12], all of which have been derived from reactions of the precursor $[AuCl(PPh_3)]$ with N-heterocycles. In the dimeric complex **6**, the aurophilic interaction with gold(I)–gold(I) bond distance 3.1971(6) Å has been found, whereas in the closely related gold(I) complex **5**, it has not been observed.

Thus, from a synthetic viewpoint, the helicity of the PPh_3 derivatives and the different reactivity of the precursors have been found as significant differences in the silver(I) and gold(I) complexes. In a viewpoint of the biological activities, e.g. antimicrobial activities, the polymeric silver(I) precursors $[Ag(im)]_n$ and $[Ag(triz)]_n$ have shown wide spectra of antimicrobial activities against bacteria, yeast and even mold, whereas their PPh_3 derivatives have shown poor activities [16]. On the other hand, the antimicrobial test of the gold(I) complexes has been scarcely reported.

In this work, we have examined synthesis and X-ray crystallography of the silver(I) and gold(I) complexes using another heterocyclic ligand, tetrazole (Htetz), in the presence of auxiliary ligand PPh_3. From a reaction of the polymeric precursor $[Ag(tetz)]_n$ with 3 equiv. of PPh_3 in dichloromethane, light- and thermally-stable, colorless needle crystals of $[Ag(tetz)(PPh_3)_2]_n$ (**1**) were obtained in good yield. The analogous gold(I) complex $[Au(tetz)(PPh_3)]$ (**2**) was obtained as colorless needle crystals in good yield from a stoichiometric reaction of the precursor $[AuCl(PPh_3)]$ with Htetz in acetone in the presence of aqueous NaOH.



tetrazole

Table 1
Comparison of silver(I) and gold(I) complexes with helical polymer structures

Complexes	Screw axis	A pitch of the helix (Å)	Ref.
$[Ag(pydz)](NO_3)$	2_1	3.68	[18]
$[Ag(pydz)](CF_3SO_3)$	2_1	5.40	[18]
$[Ag(pydz)_2](BF_4)$	4_1	11.166	[18]
$[Ag(R,R\text{-}DIOP)(NO_3)]_n$ [a]	2_1	16.186	[20]
$\{[Ag(R,R\text{-}J)](OTf)\}_n$ [a]	2_1	[c]	[24]
$[Ag(2,2'\text{-}biimidazole)](NO_3)$	3_1	[c]	[23]
$[Ag(2,4'\text{-}bipy)]X$ ($X = NO_3^-$, ClO_4^-)	[c]	[c]	[19]
$\{[Ag(bpp)](OTf)\}_n$	double helix	21.1	[22]
$[Ag(1,2,3\text{-}triz)(PPh_3)_2]_n$ (**3**)	2_1	9.12	[13]
$[Ag(1,2,4\text{-}triz)(PPh_3)_2]_n$ (**4**)	2_1	9.53	[13]
$[Ag(S\text{-}Hpyrrld)]_n$ [a]	2_1	12.736	[17]
$Cs_2Na[Au_2(tma)(Htma)]$	double helix	[c]	[25]
$[Ag(tetz)(PPh_3)_2]_n$ (**1**)	2_1	9.471	[b]

[a] Chiral helical polymer.
[b] This work.
[c] Not described.

Herein, we report the full details of the synthesis, crystallization and structural characterization of **1** and **2**, as well as the results of their antimicrobial tests. Their crystal structures were determined by single-crystal X-ray diffraction. Complex **1** was a novel helical polymer, a 2_1 helix, formed by a bridged tetrazolate of the $AgNP_2$ core in the solid-state, while **2** consisted of a monomeric two-coordinate AuNP core. In **2**, no gold(I)–gold(I) interaction was observed. Solution molecular weight measurement revealed that complex **1** was a monomer in solution. The compositional characterization of **1** and **2** was also performed by elemental analysis, thermogravimetric and differential thermal analysis (TG/DTA) and the structural characterization by FT-IR and solution NMR (^{31}P, ^{1}H and ^{13}C, as well as ^{109}Ag for **1**). The molecular structures of **1** and **2** were compared with those of related silver(I) and gold(I) complexes **3**–**6**, the structures of which have been recently determined by X-ray crystallography. Mention is also made of the antimicrobial activities of complexes **1** and **2**, and of the precursor complex $[Ag(tetz)]_n$, evaluated by MIC (minimum inhibitory concentration).

2. Experimental

2.1. Materials and reagents

The following were used as received: tetrazole, $AgNO_3$, $NaAuCl_4{\cdot}2H_2O$, NaOH, triphenylphosphine, dichloromethane, ethanol, diethyl ether, hexane, light petroleum (b.p.: 30–60°C), hexane, acetone, benzene (all from Wako); CD_2Cl_2, $CDCl_3$, D_2O (Isotec). $[AuCl(PPh_3)]$ was prepared according to literature methods [36–38]. Benzene should be used in a fume hood as it is toxic.

2.2. Instrumentation/analytical procedures

CHNS elemental analyses were performed using a Perkin–Elmer PE2400 series II CHNS/O analyzer. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Rigaku TG 8101D and TAS 300 data processing system. TG/DTA measurements were run under air with a temperature ramp of 1°C min^{-1} between 20 and 500°C. IR spectra were recorded on a Jasco FT-IR 300 spectrometer in KBr discs at room temperature (r.t.).

Molecular weight measurements in solution based on the vaporimetric method using a vapor pressure osmometer were done by Mikroanalytishes Labor Pascher (Remagen, Germany) and evaluated for 13.50 mg of complex **1** dissolved in 1.1262 g of chloroform.

^{1}H NMR (399.65 MHz), $^{13}C\{^{1}H\}$ NMR (100.40 MHz) and $^{31}P\{^{1}H\}$ NMR (161.70 MHz) spectra in solution were recorded at 25°C in 5 mm outer diameter tubes on a Jeol JNM-EX 400 FT-NMR spectrometer with a Jeol EX-400 NMR data processing system. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the complex were measured in $CDCl_3$ or CD_2Cl_2 solution with reference to an internal TMS. Chemical shifts are reported on the δ scale and resonances downfield of TMS ($\delta = 0$) are recorded as positive. $^{31}P\{^{1}H\}$ NMR spectra were measured in $CDCl_3$ or CD_2Cl_2 solution with reference to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H_3PO_4 ($\delta = 0$).

^{109}Ag NMR (18.45 MHz) were recorded at 25°C in 10 mm outer diameter tubes on a Jeol JNM-EX 400 FT-NMR spectrometer equipped with a Jeol NM-40T10L low-frequency tunable probe. ^{109}Ag NMR spectra of the complexes were measured in $CDCl_3$ solution with reference to an external standard of saturated $AgNO_3$–D_2O solution by a substitution method. Chemical shifts were recorded as positive for resonances downfield of $AgNO_3$ ($\delta = 0$). Spectral parameters for ^{109}Ag NMR include: pulse width 13.2 μs; acquisition time 0.390 s; recycle time 1.39 s; sweep width 21008 Hz.

2.3. Syntheses

2.3.1. Preparation of precursor complex $[Ag(tetz)]_n$

To a clear solution of 0.700 g (10.0 mmol) of tetrazole in 20 ml water was added a colorless solution of 0.849 g (5.0 mmol) of $AgNO_3$ dissolved in 10 ml water. To the white suspension formed were added 5.0 ml of 1.0 M aqueous NaOH (5.0 mmol), followed by stirring for 1 h. White precipitates were collected on a Buchner funnel (Whatman No. 5), washed twice each with 100 ml water, 100 ml ethanol and 100 ml acetone, and dried in vacuo for 2 h. Colorless powder obtained in 0.85 g (95.9%) yield was light-stable, insoluble in most solvents, and explosive around 230°C when the sample is rapidly heated, i.e. at a rate of 4°C min^{-1}. (Note: no explosion occurred on slow heating at a rate of 1°C min^{-1}.) *Anal.* Calc. for CHN_4Ag or [Ag(tetz)] as a monomeric unit: C, 6.79; H, 0.57; N, 31.67. Found: C, 6.85; H, 0.64; N, 31.14%. TG/DTA data: no weight loss was observed before decomposition temperature; decomposition began around 225°C with exothermic peaks at 225 and 361°C, which were observed at a rate of heating of 1°C min^{-1}. Some prominent IR bands at 1700–400 cm^{-1} region (KBr disc): 1636w, 1443w, 1430m, 1275m, 1180m, 1147s, 1120m, 1053w, 1010m, 995m, 892vs, 708vs cm^{-1}.

2.3.2. Preparation of $[Ag(tetz)(PPh_3)_2]_n$ (1)

$[Ag(tetz)]_n$ (0.177 g, 1.0 mmol) and 0.787 g (3.0 mmol) of PPh_3 were dissolved in 50 ml dichloromethane.

After the solution was stirred for 1 h, it was filtered through a folded filter paper (Whatman No. 2). The clear colorless filtrate was added dropwise to 250 ml diethyl ether. During 2 h-standing, colorless needle crystals formed. They were collected on a membrane filter (JG 0.2 μm), washed twice with 100 ml diethyl ether, and dried in vacuo for 2 h. Light- and thermally-stable, colorless needle crystals obtained in 0.68 g (96.7%) yield were soluble in chloroform and dichloromethane, but insoluble in water, diethyl ether, light petroleum and hexane. *Anal.* Calc. for $C_{37}H_{31}N_4P_2Ag$ or [Ag(tetz)(PPh_3)$_2$] as a monomer unit: C, 63.35; H, 4.45; N, 7.99. Found: C, 63.58; H, 4.50; N, 8.00%. TG/DTA data: no weight loss was observed before decomposition temperature; decomposition began gradually around 229°C with an exothermic peak at 229°C. Molecular weight measurement: 710 in $CHCl_3$; calc. 701.5 for [Ag(tetz)(PPh_3)$_2$]. Some prominent IR bands at 1700–400 cm^{-1} region (KBr disc): 1487m, 1434s, 1177w, 1128w, 1094m, 1073w, 1025w, 994w, 742s, 694vs, 510m, 504m, 435w cm^{-1}. ^1H NMR ($CDCl_3$, 25°C): δ 7.17 (30H, m, aryl), 8.07 (1H, s, H5) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ 128.8 (d, J_{CP} 11.1 Hz, phenyl), 129.9 (s, phenyl), 132.9 (d, J_{CP} 20.2 Hz, phenyl), 133.8 (d, J_{CP} 16.6 Hz, phenyl), 150.5 (C5) ppm. ^{31}P NMR ($CDCl_3$, 25°C): δ 7.23 ppm. ^{109}Ag NMR ($CDCl_3$, 25°C): δ 1036.5 ppm.

2.3.3. Preparation of [Au(tetz)(PPh_3)] (2)

[AuCl(PPh_3)] (0.495 g, 1.0 mmol) and 0.070 g (1.0 mmol) of tetrazole were dissolved in 80 ml acetone. To this solution was added 1.0 ml of 1.0 M aqueous NaOH (1.0 mmol). During 4 h stirring, white powder of NaCl was produced and it was removed through a folded filter paper (Whatman No. 2). The obtained colorless clear filtrate was evaporated to dryness at 50°C with a rotary evaporator. The residue was dissolved in 30 ml benzene, followed by filtering through a folded filter paper (Whatman No. 2). The clear filtrate was added dropwise into 250 ml hexane. White precipitates formed, which were collected on a membrane filter (JG 0.2 μm), washed with light petroleum (2 × 20 ml) and dried in vacuo for 2 h.

Crystallization was performed by a vapor diffusion method. The obtained white powder was redissolved in 10 ml benzene and the solution was filtered through a folded filter paper (Whatman No. 2). The colorless filtrate was used as an internal solution and hexane as an external solvent for the vapor diffusion. After 6 h at r.t., colorless needle crystals began to form. After 24 h, the crystals were collected on a membrane filter (JG 0.2 μm), washed twice with 100 ml light petroleum, and dried in vacuo for 2 h. Yield was 0.28 g (52.3%). Relatively light- and thermally-stable, colorless needle crystals obtained as compound **2** were soluble in acetone, benzene, dichloromethane, chloroform and DMSO, but insoluble in diethyl ether, light petroleum, hexane and water. *Anal.* Calc. for $C_{19}H_{16}N_4PAu$ or [Au(tetz)(PPh_3)]: C, 43.20; H, 3.05; N, 10.60. Found: C, 43.46; H, 2.74; N, 10.30%. TG/DTA data: no weight loss was observed below decomposition temperature; decomposition began around 190°C with exothermic peaks at 190 and 433°C. Some prominent IR bands in the 1700–400 cm^{-1} region (KBr disc): 1478m, 1434vs, 1310w, 1179w, 1169w, 1150w, 1101vs, 1061m, 1021m, 997m, 968w, 745s, 711m, 691vs, 546vs, 511s, 499s cm^{-1}. ^1H NMR (CD_2Cl_2, 25°C): δ 7.54 (15H, m, aryl), 8.55 (1H, s, H5) ppm. ^{13}C NMR (CD_2Cl_2, 25°C): δ 128.4 (d, J_{CP} 64.3 Hz, phenyl), 129.9 (d, J_{CP} 11.0 Hz, phenyl), 132.8 (s, phenyl), 134.7 (d, J_{CP} 12.9 Hz, phenyl), 149.1 (C5) ppm. ^{31}P NMR (CD_2Cl_2, 25°C): δ 31.0 ppm.

2.4. X-ray crystallography

The two compounds [Ag(tetz)(PPh_3)$_2$]$_n$ (**1**) and [Au(tetz)(PPh_3)] (**2**) formed colorless, needle crystals by a slow evaporation in the solvent mixture of dichloromethane–diethyl ether and by a vapor diffusion with benzene/hexane as the internal/external solvent system, respectively. Within one day's standing of the solutions at r.t., crystals of sufficient quality suitable for single-crystal X-ray diffraction studies were grown.

Each of the single crystal **1** and **2** was mounted on glass fiber and transferred to a Rigaku AFC5S diffractometer. Cell contents and orientation matrix of **1** and **2** were obtained from the least-squares refinement of 25 reflections. The reflection data were collected using ω–2θ scan with graphite-monochromated Mo Kα radiation at r.t. The intensities of three standard reflections that were measured after every 150 reflections remained constant throughout the data collection. The data were corrected for Lorentz and polarization effects and empirical absorption corrections based on PSI scan were applied to the data. For the overall averaged transmission curve, the transmission factors of **1** and **2** were in the range 0.924–0.999 and 0.688–1.000, respectively. For complex **2**, secondary extinction effects were corrected to the data (coefficient 4.78850e-08). The structures were solved by direct methods followed by subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using the TEXSAN package [39]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Switching the position of C5/N2 in tetrazole produced higher R and R' factors.

A summary of crystal data, data collection, and refinement for **1** and **2** is given in Table 2.

2.5. Antimicrobial activities

Antimicrobial activities of silver(I) and gold(I) compounds were estimated by a minimum inhibitory concentration (MIC: μg ml^{-1}) as usual [13,14,16].

Table 2
Summary of crystal data of the complexes $[Ag(tetz)(PPh_3)_2]_n$ (**1**) and $[Au(tetz)(PPh_3)]$ (**2**) [a,b]

	1	**2**
Formula	$C_{37}H_{31}N_4P_2Ag$	$C_{19}H_{16}N_4PAu$
M	701.49	528.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 4)
a (Å)	14.587(2)	9.650(3)
b (Å)	9.471(3)	16.860(2)
c (Å)	24.653(2)	11.866(4)
β (°)	92.104(9)	108.56(3)
V (Å^3)	3403(1)	1830.1(9)
$F(000)$	1432	1008
Z	4	4
D_{calc} (g cm^{-3})	1.369	1.917
Crystal size (mm)	$0.2 \times 0.1 \times 0.1$	$0.3 \times 0.1 \times 0.1$
No. of reflections used for unit cell dimension (2θ range (°))	25 (20.1–23.7)	25 (27.2–29.8)
Radiation (λ/Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
Scan mode	ω–2θ	ω–2θ
Scan width (°)	$0.63 + 0.30 \tan \theta$	$1.21 + 0.30 \tan \theta$
Scan speed (min^{-1})	8	8
2θ Range (°)	6–55	6–55
μ (cm^{-1})	7.16	81.62
Total reflections	8606	4559
Unique reflections	8289	4363
Observed reflections	3915 ($I > 2.00\sigma(I)$)	2566 ($I > 2.00\sigma(I)$)
R, R'	0.044, 0.036	0.030, 0.019
Goodness-of-fit	1.32	1.24

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.

[b] $R' = [\Sigma(w[|F_o| - |F_c|]^2/[\Sigma w(|F_o|)^2]^{1/2}$, with $w = 4F_o^2/[\sigma^2(F_o^2)]$.

Bacteria and yeast were inoculated into 5 ml of liquid medium (SCD medium for bacteria and GP medium for yeast), and cultured for 24 h at 35°C and 48 h at 30°C, respectively. The cultured fluids were adjusted to the cell concentration of 10^6–10^7 ml^{-1} and used for inoculation in the MIC test. As for the mold culture, the agar slant (PD agar medium) for one week cultivation at 27°C was washed with saline containing 0.05% Tween 80. The spore suspension obtained was adjusted to the concentration of 10^6 ml^{-1} and used for inoculation in the MIC test.

The test materials, $[Ag(tetz)]_n$, $[Ag(tetz)(PPh_3)_2]_n$ (**1**), $[Au(tetz)(PPh_3)]$ (**2**) and the free ligand, Htetz, were added to each culture medium and then diluted two times with each culture medium. Each one ml of culture medium containing various concentrations of test materials was inoculated with 0.1 ml of the microorganism suspension prepared above.

Bacteria were cultured for 24 h at 35°C, yeast for 48 h at 30°C and mold were cultured for one week at 25°C, then the growth of microorganism was observed. When no growth of microorganism was observed in the medium containing the lowest concentration of test materials, the MIC of the test material was defined at this point of dilution.

SCD, GP and PD media were purchased from Nissui.

3. Results and discussion

3.1. Compositional characterization

The molecular formulas of the precursor $[Ag(tetz)]_n$ obtained as a white powder, $[Ag(tetz)(PPh_3)_2]_n$ (**1**) isolated in 96.7% (0.68 g) yield as colorless needle crystals, and $[Au(tetz)(PPh_3)]$ (**2**) isolated in 52.3% (0.28 g) as colorless needle crystals, were consistent with all data of the elemental analysis, TG/DTA, FT-IR and ^1H, ^{13}C and ^{31}P NMR spectra presented in Section 2.3. In these complexes, the IR measurements showed that the tetz ligand coordinated to the metal(I) center as a tetrazolate anion, but not as a neutral tetrazole, because the multiple vibrational bands due to N–H stretchings observed in the free Htetz in the 3100–2600 cm^{-1} region disappeared.

From the single-crystal X-ray analysis described later, the silver(I) and gold(I) compounds **1** and **2** are shown to be polymer and monomer in the solid-state, respectively.

On the other hand, molecular weight measurement in $CHCl_3$ solution revealed that complex **1** was present as a monomeric species in solution. Although the gold(I) complexes with an AuNP core have been present as monomers and/or dimers in the solid-state, as observed in **5** and **6**, all of them are present as a monomer in solution. It is possible that complex **2** is also present as a monomer in solution.

3.2. Crystal and molecular structures

Single crystals suitable for single-crystal X-ray analysis were obtained for **1** and **2**. The molecular structures of **1** and **2** with the atom numbering scheme are depicted in Figs. 1 and 2, respectively. Selected bond distances and angles with their estimated standard deviations are listed in Table 3.

Complex **1** was a helical polymer, a 2_1 helix, consisting of the $Ag^I(PPh_3)_2$ fragments bridged by tetrazolate anions as shown in Fig. 1(a) and (b). The bond angles around the silver(I) atom decrease in the order: P–Ag–P > P–Ag–N > N–Ag–N. The geometry of the silver(I) atom is described as distorted tetrahedral coordination. In complex **1**, two PPh_3 and two tetrazolates coordinate to a silver(I) center via P1, P2, N1 and $N3^i$ atoms. The $N1^i$ and N3 atoms coordinate to the adjacent silver(I) atoms (symmetry operation, (i) $-x + 3/2$, $y - 1/2$, $-z + 3/2$). Thus, the $[Ag(tetz)(PPh_3)_2]$ moiety is arranged helically along the b axis. The pitch of the

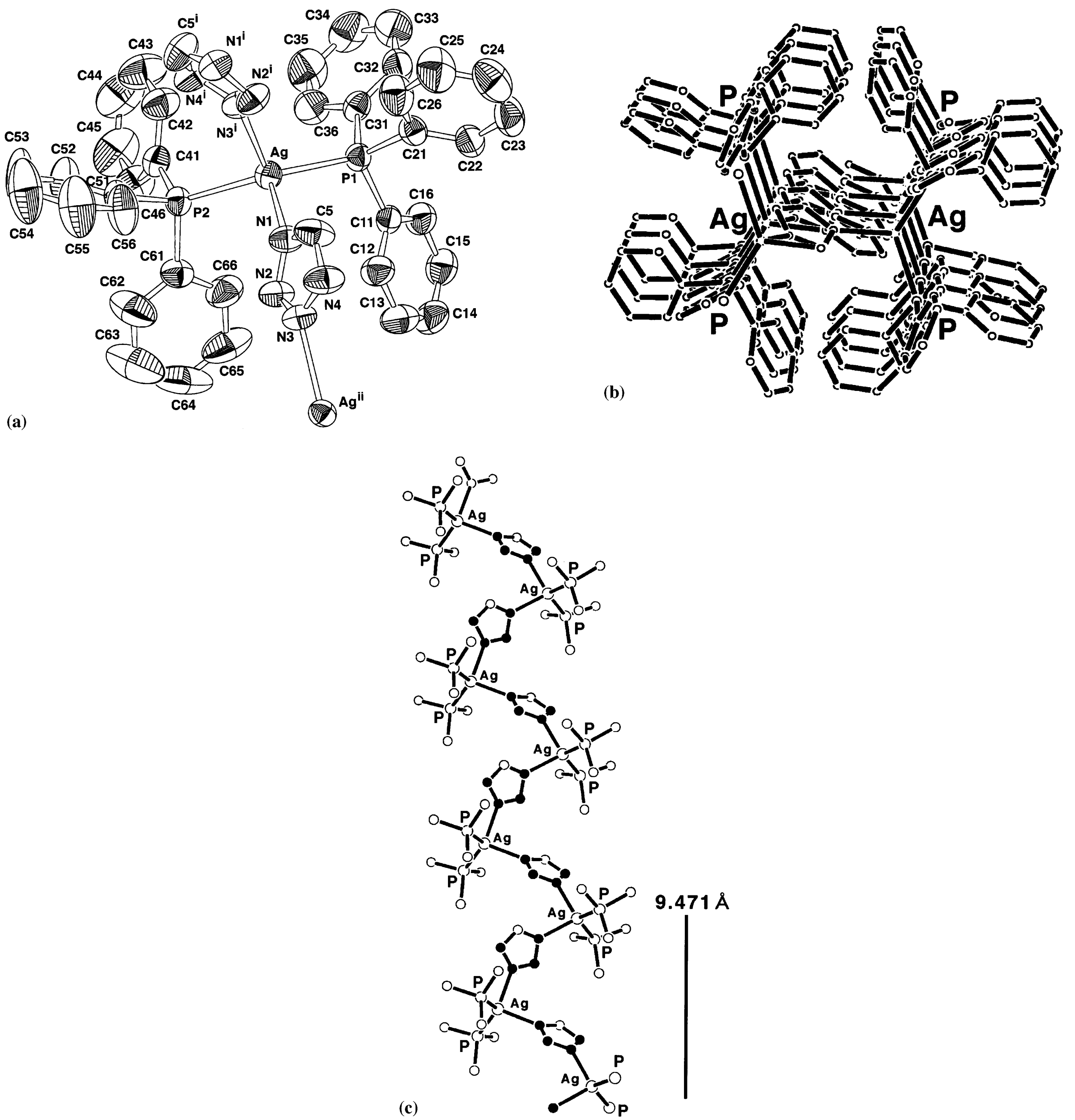


Fig. 1. (a) Molecular structure of the local coordination around each silver(I) center of $[Ag(tetz)(PPh_3)_2]_n$ (**1**) with 50% probability ellipsoids (symmetry operations: (i) $-x+3/2$, $y-1/2$, $-z+3/2$; (ii) $-x+3/2$, $y+1/2$, $-z+3/2$); (b) top and (c) side views of the helical polymer structure. In (c), black and small open circles represent nitrogen and carbon atoms, respectively.

helix, i.e. the distance between the silver(I) atoms of *Ag*-tetz-Ag-tetz-*Ag* is 9.471 Å (Fig. 1(c)). Among the four nitrogen atoms of tetrazolate, N1 and N3 atomsfl participate in the coordination. A single-stranded helical polymer of **1** has been accomplished with bridging tetrazolates of the $[Ag(PPh_3)_2]$ core. The formation of this polymer is similar to that of $[Ag(1,2,3\text{-triz})(PPh_3)_2]_n$ (**3**) and $[Ag(1,2,4\text{-triz})(PPh_3)_2]_n$ (**4**), both 2_1 helices.

The helical polymer **1**, a 2_1 helix, can be compared with several examples of infinite helical species of silver(I) and gold(I) complexes listed in Table 1.

The Ag–P1 and Ag–P2 distances are 2.441(1) and 2.456(1) Å, respectively in complex **1**. These distances are longer than that of $[Ag_2(pz)_2(PPh_3)_2]$ (2.376(1) Å) [34], and similar to those of $[Ag(1,2,4\text{-triz})(PPh_3)_2]_n$ (**4**) (2.441–2.469 Å) [13], $[AgCl(PPh_3)_2]_2$ (2.467–2.472 Å) [40] and $[Ag_2(pz)_2(PPh_3)_3]$ (2.370–2.484 Å) [34], but

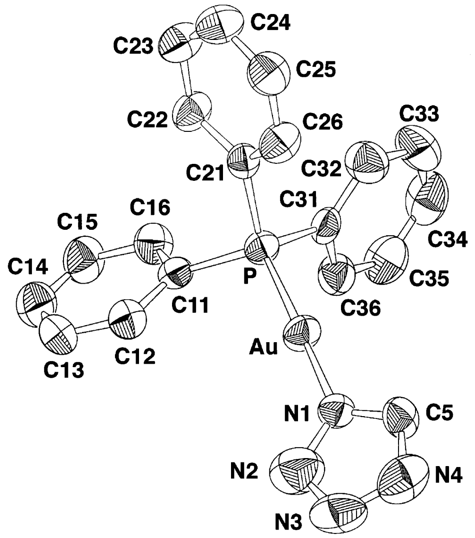


Fig. 2. Molecular structure of [Au(tetz)(PPh$_3$)] (**2**) with 50% probability ellipsoids.

Table 3
Selected bond distances (Å) and angles (°) for the complexes [Ag(tetz)(PPh$_3$)$_2$]$_n$ (**1**) and [Au(tetz)(PPh$_3$)] (**2**) [a]

	1		**2**
Ag–P1	2.441(1)	Au–P1	2.239(2)
Ag–P2	2.456(1)	Au–N1	2.043(5)
Ag–N1	2.316(4)	P–C	1.811 – 1.815
Ag–N3^i	2.337(4)		
P–C	1.818 – 1.826	N1–N2	1.339(7)
		N1–C5	1.310(7)
N1–N2	1.336(6)	N2–N3	1.342(8)
N1–C5	1.306(7)	N3–N4	1.322(8)
N2–N3	1.297(6)	N4–C5	1.298(8)
N3–N4	1.326(6)		
N4–C5	1.316(7)		
P1–Ag–P2	127.41(5)	P1–Au–N1	178.4(1)
P1–Ag–N1	107.0(1)	Au–N1–N2	124.5(5)
P1–Ag–N3	114.3(1)	Au–N1–C5	129.0(5)
P2–Ag–N1	107.4(1)	N1–N2–N3	108.4(7)
P2–Ag–N3	101.5(1)	N1–C5–N4	110.1(6)
N1–Ag–N3	94.3(2)	N2–N1–C5	106.3(5)
Ag–N1–N2	125.8(4)	N2–N3–N4	106.4(6)
Ag–N1–C5	129.7(4)	N3–N4–C5	108.8(6)
Ag–N3–N2	127.1(4)		
Ag–N3–N4	119.3(4)		

[a] Symmetry operations: (i) $-x+3/2$, $y-3/2$, $-x+3/2$; (ii) $-x+3/2$, $y+1/2$, $-z+3/2$.

shorter than those of [Ag(1,2,3-triz)(PPh$_3$)$_2$]$_n$ (**3**) (2.460–2.512 Å) [13], and [AgCl(PPh$_3$)$_3$] (2.520–2.556 Å) [41]. The Ag–N1 and Ag–N3^i distances of complex **1** are 2.316(4) and 2.337(4) Å, respectively. These Ag–N distances are longer than those of [Ag$_2$(pz)$_2$(PPh$_3$)$_2$] (2.204–2.213 Å) [34], those of [Ag$_2$(pz)$_2$(PPh$_3$)$_3$] (2.176–2.323 Å) [34], and also those of [Ag(im)]$_n$ (2.05–2.08 Å), the structure of which has been recently solved by the Rietveld analysis using conventional X-ray powder diffraction data [35], but similar to those of **3** (2.326–2.327 Å) [13] and of **4** (2.309–2.321 Å) [13].

The neutral complex **2** was a discrete monomer consisting of the AuN(PPh$_3$) core coordinated by a tetrazolate anion, in which the geometry around the gold(I) atom is described as almost linear coordination, the P–Au–N angle being 178.4(1)°. Among the four nitrogen atoms of tetrazolate, only one N1 atom participates in the coordination. As to the gold(I)–gold(I) interaction observed in the recently reported complex [Au(1,2,4-triz)(PPh$_3$)]$_2$ (**6**) [12], the possibility of stabilization by a stacking interaction between one triazolate ring and one of the phenyl rings in the PPh$_3$ group has been suggested. Thus, in **2**, which contains a closely related heterocyclic ligand, it should be noted that the gold(I)–gold(I) interaction was absent.

The bond distances Au–N and Au–P (2.043(5) and 2.239(2) Å, respectively) in **2** are compared with those of the reported neutral complexes, **5** (1.98(2) and 2.229(5) Å) [12] and **6** (Au1–N1a and Au2–N1b 2.026(7) and 2.037(7) Å; Au1–P1 and Au2–P2 2.243(2) and 2.238(2) Å) [12], [Au(methym)(PPh$_3$)] (Hmethym = 1-methylthymine) (Au–N and Au–P, 2.20(1) and 2.240(5) Å) [42], [Au(mpyrid)(PPh$_3$)] (Hmpyrid = 6-methylpyridone) (2.077(9) and 2.236(3) Å) [43], [Au(pyrmd)(PPh$_3$)] (Hpyrmd = 5-fluoro-1-(tetrahydro-2-furanyl)-2,4(1*H*, 3*H*)-pyrimidinedione) (2.042(24) and 2.235(7) Å) [44], [Au(theophyl)(PPh$_3$)] (Htheophyl = theophylline) (2.047(6) and 2.231(2) Å) [45], and [Au(7-azaindolato)(PPh$_3$)] (2.033(5) and 2.233(1) Å) [46].

3.3. Solution NMR (^{31}P, ^{1}H and ^{13}C) spectroscopies

The ^{31}P NMR spectrum measured at r.t. in CDCl$_3$ of **1** has shown only one resonance at δ 7.23, the chemical shift of which is in the region usually observed for the PPh$_3$ ligands coordinated to the silver(I) center and can be compared with those of related silver(I) compounds: at δ 3.71 for [Ag(im)(PPh$_3$)$_3$] [14], δ 9.87 for [Ag$_2$(pz)$_2$(PPh$_3$)$_2$] and δ 6.13 for [Ag$_2$(pz)$_2$(PPh$_3$)$_3$] [34], at δ 6.48 for **3** and δ 4.84 for **4** [13].

These resonances are observed in much higher field than those of the coordinated PPh$_3$ to the gold(I) center. In fact, the ^{31}P NMR spectrum of **2** in CD$_2$Cl$_2$ has shown one resonance for the PPh$_3$ coordinated to the gold(I) center at δ 31.0, the chemical shift of which is compared with those of related gold(I) complexes, e.g. at δ 32.46 for [Au(im)(PPh$_3$)], at δ 33.40 for [AuCl(PPh$_3$)] [14], at δ 31.1 for **5** and at δ 31.5 for **6** [12].

The ^{1}H NMR spectra measured at r.t. of **1** in CDCl$_3$ and **2** in CD$_2$Cl$_2$ exhibited only one resonance H5 of the coordinating tetrazolate anion at δ 8.07 and 8.55, respectively, and the ^{13}C NMR spectra showed only one resonance C5 of the coordinating tetz$^-$ ligand at δ

Table 4
Antibacterial and antifungal activities of $[Ag(tetz)]_n$, $[Ag(tetz)(PPh_3)_2]_n$ (**1**), $[Au(tetz)(PPh_3)]$ (**2**) and the free ligand Htetz, evaluated by MIC [a]

	Htetz	$[Ag(tetz)]_n$	$[Ag(tetz)(PPh_3)_2]_n$ (**1**)	$[Au(tetz)(PPh_3)]$ (**2**)
Escherichia coli	>1000	4	>1000	>1000
Bacillus subtilis	500	15.7	>1000	250
Staphylococcus aureus	>1000	15.7	>1000	500
Pseudomonas aeruginosa	>1000	15.7	>1000	>1000
Candida albicans	>1000	31.3	>1000	>1000
Saccharomyces cerevisiae	>1000	15.7	>1000	>1000
Aspergillus niger	>1000	>1000	>1000	>1000
Penicillium citrinum	>1000	>1000	>1000	>1000

[a] Minimum inhibitory concentration (MIC) (μg ml^{-1}).

150.5 and 149.1, respectively. The ^{109}Ag NMR spectrum measured at r.t. of **1** in $CDCl_3$ showed only one resonance at δ 1036.5, which can be compared with those of **3** and **4** in $CDCl_3$ at r.t. at δ 994 and 925, respectively. The solution NMR (^{31}P, ^{109}Ag, ^1H and ^{13}C) spectra at r.t. of the previous silver(I) complexes **3** and **4**, both of which are present as monomers in solution, have been interpreted as averaged signals resulting from the rapid dynamic exchange among several unequivalent ^{109}Ag species containing an ionic species such as $[Ag(PPh_3)_4]^+(triz)^-$ and $[Ag(PPh_3)_2]^+(triz)^-$ [13].

3.4. Antimicrobial activities

Antimicrobial activities of the precursor $[Ag(tetz)]_n$ and the two complexes **1** and **2** described here, together with those of the free Htetz ligand are listed in Table 4, as estimated by the minimum inhibitory concentration (MIC, μg ml^{-1}).

Antimicrobial activities of complex **1** were estimated as > 1000 μg ml^{-1} for bacteria, yeast and mold, showing no activity. The free Htetz ligand and complex **2** showed only poor activities against Gram-positive bacteria (*B. subtilis*, *S. aureus*). On the other hand, the precursor $[Ag(tetz)]_n$ has shown effective activities against Gram-positive and negative bacteria, and yeast, but no activities against mold. These facts are consistent with the recently observed results; the polymeric silver(I) complexes without a PPh_3 ligand such as $[Ag(im)]_n$ [16], $[Ag(1,2,3\text{-triz})]_n$ and $[Ag(1,2,4\text{-triz})]_n$ [13] have shown effective antimicrobial activities, while almost all of their triphenylphosphine derivatives such as $[Ag(im)(PPh_3)_3]$, **3**, and **4** have shown no activity (> 1000 μg ml^{-1}). These facts have been attributed to the restricted ligand exchange ability of the Ag–P bonding complexes [13,14,16]. From a viewpoint of metal-based drug design, no activity of the PPh_3 derivatives is also crucial and can be utilized.

4. Conclusions

Transformation of polymeric silver(I) tetrazolate $[Ag(tetz)]_n$ to its PPh_3 derivatives resulted in the formation of a helical polymer $[Ag(tetz)(PPh_3)_2]_n$ (**1**), a 2_1 helix with a pitch 9.471 Å, formed by a bridged tetrazolate of an $AgNP_2$ core in the solid-state. The two silver(I) triazolate complexes $[Ag(1,2,3\text{-triz})(PPh_3)_2]_n$ (**3**) and $[Ag(1,2,4\text{-triz})(PPh_3)_2]_n$ (**4**) are helical polymers, a pitch of helix being 9.12 and 9.53 Å, respectively. On the other hand, the gold(I) tetrazolate $[Au(tetz)(PPh_3)]$ (**2**) was a discrete monomer with a two-coordinate AuNP core without gold(I)–gold(I) interaction. The two gold(I) triazolate complexes, $[Au(1,2,3\text{-triz})(PPh_3)]$ (**5**) and $[Au(1,2,4\text{-triz})(PPh_3)]_2$ (**6**) are a monomer and a dimer through a gold(I)–gold(I) interaction, respectively. Thus, in comparison with anionic N-heterocyclic ligands such as imidazolate, pyrazolate, and 1,2,3- and 1,2,4-triazolates, *it is likely that the tetrazolate ligand in **1** acts similarly to the 1,2,4-triazolate*, *while that in **2** acts similarly to 1,2,3-triazolate*. In contrast to the precursor $[Ag(tetz)]_n$ complexes **1** and **2** did not show effective antimicrobial activities. These facts can be also utilized in the design of a new type of metal-based drug.

5. Supplementary material

Supplementary crystallographic data sets for both structures are available through the Cambridge Structural Data base. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, New York, 1994, p. 373.

[2] M.J. Abrams, B.A. Murrer, Science 261 (1993) 725.
[3] E.J. Corey, M. Mehrotra, A.U. Khan, Science 236 (1987) 68.
[4] R.C. Elder, M.K. Eidsness, Chem. Rev. 87 (1987) 1027.
[5] D.H. Brown, W.E. Smith, Chem. Soc. Rev. 3 (1980) 217.
[6] C.F. Shaw, Inorg. Perspect. Biol. Med. 2 (1978) 287.
[7] P.J. Sadler, Struct. Bonding (Berlin) 29 (1976) 171.
[8] R.B. Thurman, C.P. Gerba, CRC Crit. Rev. Environ. Control. 18 (1989) 295.
[9] K.M. Davies, G.E. Hobson, D. Grierson, Plant Cell Environ. 11 (1988) 729.
[10] H. Veen, A.A.M. Kwakkenbos, Sci. Hortic. (Amsterdam) 18 (1982, 1983) 277.
[11] H. Veen, Sci. Hortic. (Amsterdam) 20 (1983) 211.
[12] K. Nomiya, R. Noguchi, K. Ohsawa, K. Tsuda, J. Chem. Soc., Dalton Trans. (1998) 4101.
[13] K. Nomiya, K. Tsuda, N.C. Kasuga, J. Chem. Soc., Dalton Trans. (1998) 1653.
[14] K. Nomiya, K. Tsuda, Y. Tanabe, H. Nagano, J. Inorg. Biochem. 69 (1998) 9.
[15] K. Nomiya, R. Noguchi, K. Ohsawa, K. Tsuda, 74th Annual Meeting of Chemical Society of Japan, Kyoto 1998, Abstr. No. 1PA113.
[16] K. Nomiya, K. Tsuda, T. Sudoh, M. Oda, J. Inorg. Biochem. 68 (1997) 39.
[17] K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama, M. Oda, submitted.
[18] L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, Inorg. Chem. 37 (1998) 5941.
[19] M.-L. Tong, X.-M. Chen, B.-H. Ye, S.W. Ng, Inorg. Chem. 37 (1998) 5278.
[20] B. Wu, W.-J. Zhang, S.-Y. Yu, X.-T. Wu, J. Chem. Soc., Dalton Trans. (1997) 1795.
[21] E. Psillakis, J.C. Jeffery, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Dalton Trans. (1997) 1645.
[22] L. Carlucci, G. Ciani, D.W. v. Gudenberg, D.M. Proserpio, Inorg. Chem. 36 (1997) 3812.
[23] C.A. Hester, R.G. Baughman, H.L. Collier, Polyhedron 16 (1997) 2893.
[24] T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa, M. Ochi, Inorg. Chem. 34 (1995) 530.
[25] R. Bau, J. Am. Chem. Soc. 120 (1998) 9380.
[26] P. Pyykko, Chem. Rev. 97 (1997) 597.
[27] P. Pyykko, N. Runeberg, F. Mendizabal, Chem. Eur. J. 3 (1997) 1451.
[28] P. Pyykko, F. Mendizabal, Chem. Eur. J. 3 (1997) 1458.
[29] S.S. Pathaneni, G.R. Desiraju, J. Chem. Soc., Dalton Trans. (1993) 319.
[30] H. Schmidbaur, Chem. Soc. Rev. 24 (1995) 391.
[31] M. Jansen, Angew. Chem., Int. Ed. Engl. 26 (1987) 1098.
[32] I.G. Dance, Polyhedron 5 (1986) 1037.
[33] I.G. Dance, L.J. Fitzpatrick, A.D. Rae, M.L. Scudder, Inorg. Chem. 22 (1983) 3785.
[34] G.A. Ardizzoia, G. La Monica, A. Maspero, M. Moret, N. Masciocchi, Inorg. Chem. 36 (1997) 2321.
[35] N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G.A. Ardizzoia, G. La Monica, J. Chem. Soc., Dalton Trans. (1995) 1671.
[36] M.I. Bruce, B.K. Nicholson, O.B. Shawkataly, Inorg. Synth. 26 (1989) 324.
[37] N.C. Baenziger, W.E. Bennett, D.M. Soboroff, Acta Crystallogr., Sect. B 32 (1976) 962.
[38] D.M.L. Goodgame, C.A. O'Mahoney, S.D. Plank, D.J. Williams, Polyhedron 12 (1993) 2705.
[39] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.
[40] A. Cassel, Acta Crystallogr., Sect. B 35 (1979) 174.
[41] A. Cassel, Acta Crystallogr., Sect. B 37 (1981) 229.
[42] R. Faggiani, H.E. Howard-Lock, C.J.L. Lock, M.A. Turner, Can. J. Chem. 65 (1987) 1568.
[43] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 296 (1985) 301.
[44] T. Amagi, T.K. Miyamoto, H. Ichida, Y. Sasaki, Bull. Chem. Soc. Jpn. 62 (1989) 1078.
[45] E. Colacio, A. Romerosa, J. Ruiz, P. Roman, J.M. Gutierrez-Zorrilla, M. Martinez-Ripoll, J. Chem. Soc., Dalton Trans. (1989) 2323.
[46] C.-K. Chan, C.-X. Guo, K.-K. Cheung, D. Li, C.-M. Che, J. Chem. Soc., Dalton Trans. (1994) 3677.