

Available online at www.sciencedirect.com



Polyhedron 24 (2005) 853-863



Polymer and cage-type structures in silver(I) complexes with heterocyclic thiones and bridging diphosphine ligands. Crystal structures of $[Ag(\mu-dpppent)(tHpymtH)(ONO_2)]_n$ and $[Ag_2(\mu-trans-dppen)_3(pymtH)_2](NO_3)_2 \cdot CH_3CN$

P. Aslanidis ^{a,*}, S. Divanidis ^a, P.J. Cox ^{*,b}, P. Karagiannidis ^a

^a Aristotle University of Thessaloniki, Faculty of Chemistry, Inorganic Chemistry Laboratory, P.O. Box 135, GR- 541 24 Thessaloniki, Greece ^b School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB 10 1FR, Scotland, United Kingdom

> Received 22 February 2005; accepted 16 March 2005 Available online 14 April 2005

Abstract

Reaction of silver(I) nitrate with equimolar amounts of the rigid diphos ligand *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen) and some heterocyclic thiones (L) in acetonitrile/methanol solvent gave rise to triply-bridged coordination cages $[Ag_2(\mu_2 - trans-dppen)_3L_2](NO_3)_2$. On the other hand, the complexes produced when using the flexible 1,5-bis(diphenylphosphino)pentane (dpppent) turned out to be diphosphine-bridged polymers of the type $[Ag(\mu_2 - dpppent)(L)(ONO_2)]_n$ with the diphosphine ligand acting as bridge between two pseudo-tetrahedraly coordinated metal centres. The structures of one representative for each of the two aforementioned series of complex compounds, namely, $[Ag_2(\mu_2 - trans-dppen)_3(pymtH)_2](NO_3)_2$ (pymtH = pyrimidine-2-thione) and $[Ag(\mu_2 - dpppent)(tHpymtH) (ONO_2)]_n$ (tHpymtH = tetrahydropyrimidine-2-thione) have been established by single-crystal X-ray diffraction.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Silver(I) complexes; Heterocyclic thiones; 1,5-Bis(diphenylphosphino)pentane; trans-1,2-Bis(diphenylphosphino)ethene; Crystal structures

1. Introduction

Sulfur donors are known to be good ligands for monovalent group-11 cations [1], and the research field concerning silver(I) in sulfur-dominated coordination spheres is vast and ever expanding. Among the frequently used S-donors, the extended family of heterocyclic thioamides, are of particular interest since their metal complexes are known to have relevance to biological systems [2–4]. The coordination mode of the neutral thioamides, also known as "thiones", towards soft acids is virtually limited to the thione-S monodentate and bidentate (μ_2 -S) types, thus the majority of the Ag(I) complexes bearing simple neutral ligands such as pyridine-2-thione or pyrimidine-2-thione are monomeric or dimeric exhibiting the common trigonal planar or tetrahedral coordination around the metal centre [5]. Our previous approach to this area involved the employment of neutral thioamide ligands in heteroleptic phosphane derivatives of Ag(I) halides or Ag(I) nitrate, whereby some examples of monomers [6,7] or symmetric dimers [8], with pseudo-tetrahedraly coordinated silver(I) have been structurally characterized. On the other hand, oligomeric or polymeric Ag(I) species can be obtained [9–11] for thioamide ligands in their thionate anionic form, generated by deprotonation. It

^{*} Corresponding author. Tel.: +32310997694; fax: +32310997738.

E-mail addresses: p.j.cox@rgu.ac.uk (P.J. Cox), aslanidi@chem. auth.gr (P. Aslanidis).

^{0277-5387/}\$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2005.03.009

should be noted, however, that a few silver-thione polymers of neutral pyridine-2-thione constructed on the basis of μ_2 -S or μ_3 -bridges, are also known [12,13].

Bidentate phosphines exhibit excellent ligating properties towards almost all transition metals [14-16] and diphosphine containing silver(I) complexes have attracted widespread attention [17]. Taking into account that the double bridging coordination mode of both diphosphines and heterocyclic thiones is quite common for univalent group-11 metal complexes, we recently introduced a series of oligomethylene-backboned diphosphines $Ph_2P(CH_2)_nPPh_2$ as a second soft donor with the aim of provoking some variability in the nuclearity of silver-thione complexes. The role of the flexibility of the bridging phosphine in controlling product selectivity in the formation of a multisilver complex is already recognized. Thus, while with long-chained flexible diphosphines, silver(I) salts with oxo-anions selectively form dinuclear (2:2) macrocycles, the rigid bis(diphenvlphosphino) acetylene (dppa) gives stable cationic disilver complexes with triply-bridging diphosphine units [18,19]. On the other hand, by proper selection of thiolato ligands, novel oligonuclear structures can be constructed for Ag(I) complexes containing short bite diphosphines like bis(diphenylphosphino)methane [20]. In this context, our related work was initially devoted to silver(I) nitrate derivatives of some heterocyclic thiones containing bridging 1,2-bis(diphenylphosphino) ethane (dppe) and 1,4-bis(diphenylphosphino)butane (dppb). Interestingly, the only common feature of the two types of structures was the presence of pseudo-tetrahedraly coordinated metal centres exhibiting the same P_2S_2 donor set, since the complexes bearing the longer chained diphosphine (dppb) were found to be quadroubly bridged dimers build by a perfect combination of two kinds of bridges, whereas polymerization occurred in the case of dppe [21]. To prove the role of chain length, bulkines and flexibility of the bidentate phosphine and to gain more information concerning the effect of polymerization, we decided to include further potentially bidentate/bridging diphosphines in our studies. In this paper, we present our results on the use of the long chained 1,5-bis(diphenylphosphino)pentane (dppp) and the rigid *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen).

2. Experimental

2.1. Materials and instruments

Commercially available silver nitrate, *trans*-1,2bis(diphenylphosphino)ethene (*trans*-dppen) and 1,5bis(diphenylphosphino)pentane (dpppent) were used as received while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. All the solvents were purified by respective suitable methods and allowed to stand over molecular sieves. Infra-red spectra, molar conductivities in 10^{-3} M solutions in acetonitrile, magnetic susceptibility measurements and elemental analyses for carbon, nitrogen and hydrogen were performed as described previously [22]. Thermogravimetric analyses were performed on a SETSYS-1200 machine with DTG facility in dry nitrogen atmosphere. Sample sizes were in the range 8–10 mg and open Pt crucibles were used. The heating rate was $10^{\circ}/min$.

2.2. X-ray crystallographic study

Single crystals of **3** and **10** suitable for X-ray crystallographic study were grown by slow concentration of acentonitrile/methanol solutions of the compounds over several days at ambient temperature. X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD area-detector diffractometer. The programs DENZO [23] and COLLECT [24] were used in data collection and cell refinement. Details of crystal and structure refinement are shown in Table 1. The structures were solved using program SIR97 [25] and refined with program SHELX-97 [26]. Molecular plots were obtained with program ORTEP-3 [27].

2.3. Synthesis of complexes 1-14

The complexes were prepared according to the following general procedure. A suspension of silver nitrate (0.5 mmol) and 1,5-bis(diphenylphosphino)pentane or *trans*-1,2-bis(diphenylphosphino)ethene (0.5 mmol) in 20 cm³ acetonitrile was stirred at 50 °C until a white precipitation was formed. A solution of the appropriate thione (0.5 mmol) in methanol was then added and the new suspension was stirred to clearness. The resulting solution was filtered off and the clear solution was kept at room temperature. Slow evaporation of the solvent at room temperature gave the microcrystalline solid, which was filtered off and dried in vacuo.

2.4. $[Ag(\mu-dpppent)(py2SH)(NO_3)]_n$ (1)

Pale yellow crystals. Yield: 263 mg (73%), m.p. 177 °C; *Anal.* Calc. for $C_{34}H_{35}AgN_2O_3P_2S$: C, 56.59; H, 4.89; N, 3.88. Found: C, 56.49; H, 4.79; N, 3.76%; A_m (mho cm² mol⁻¹): 93; IR (cm⁻¹): 3452m, 3049w, 2920w, 1707s, 1601s, 1584vs, 1434vs, 1384vs, 1302vs, 1222s, 1139vs, 1098s, 1025vs, 997s, 741vs, 693vs, 617s, 512vs, 486s, 445s; UV–Vis (λ_{max} , log ε): (CHCl₃); 260 (4.37), 289 (4.29), 361 (3.91).

2.5. $[Ag(\mu - dpppent)(pymtH)(NO_3)]_n$ (2)

Yellow crystals. Yield: 220 mg (61%), m.p.155 °C; Anal. Calc. for $C_{33}H_{34}AgN_3O_3P_2S$: C, 54.86; H, 4.74;

Table 1

Crystal data and structure refinement for $[Ag(dpppent)(tHpymtH)(NO_3)]_n$ (3) and $[Ag_2(trans-dppen)_3(pymtH)]_2](NO_3)_2 \cdot CH_3CN$ (10)

	3	10	
Chemical formula	$[C_{33}H_{38}AgN_{3}O_{3}P_{2}S]_{n}$	$C_{86}H_{76}Ag_2N_4P_6S_2.2NO_3 \cdot CH_3CN$	
Formula weight	726.53 (monomer unit)	1796.26	
Temperature (K)	120(2)	120(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	monoclinic	orthorhombic	
Space group	C2/c	$Pna2_1$	
Unit cell dimensions			
<i>a</i> (Å)	36.7814(10)	31.0485(5)	
b (Å)	9.5500(5)	20.5143(3)	
c (Å)	18.8438(8)	13.2654(3)	
α (°)	90	90	
β (°)	99.209(3)	90	
γ (°)	90	90	
Volume (Å ³)	3529.7(7)	8449.2(3)	
Ζ	8	4	
$D_{\rm calc} ({\rm Mg/m^3})$	1.477	1.412	
Absorption coefficient (mm ⁻¹)	0.817	0.683	
F (000)	2992	3680	
Crystal size (mm)	$0.30 \times 0.28 \times 0.04$	$0.43 \times 0.30 \times 0.20$	
θ Range for data collection (°)	3.03-27.41	3.05-27.48	
Index ranges	$-46 \leq h \leq 47, -12 \leq k \leq 12, -24 \leq l \leq 24$	$-39 \leq h \leq 40, -20 \leq k \leq 26, -17 \leq l \leq 17$	
Reflections collected	34188	62951	
Independent reflections $[R_{int}]$	7393 [0.0822]	18864 [0.0461]	
Completeness to $\theta = 27.47^{\circ}$	99.1%	99.6%	
Maximum and minimum transmission	0.9681 and 0.7917	0.8754 and 0.7576	
Refinement method	full-matrix least-square on F^2	full-matrix least-squares on F^2	
Data/restrains/parameters	7393/11/478	18864/6/1038	
Goodness-of-fit on F^2 (S)	1.009	1.045	
Final <i>R</i> indices $[(I) > 2\sigma(I)]$	$R_1 = 0.0571, wR_2 = 0.1160$	$R_1 = 0.0436, wR_2 = 0.0911$	
R indices (all data)	$R_1 = 0.1215, wR_2 = 0.1365$	$R_1 = 0.0655, wR_2 = 0.0982$	
Final weighting scheme	Calc. $w = 1/[\sigma_2(F_o^2) + (0.0491P)^2 + (21.1062P)]$	Calc. $w = 1/[\sigma_2(F_o^2) + (0.0433P)^2 + (2.2006P)]$	
	where $P = (F_{\rm o}^2 + 2F_{\rm c}^2)/3$	where $P = (F_{o}^{2} + 2F_{c}^{2})/3$	
Largest difference peak and hole ($e \text{ Å}^3$)	0.903 and -0.953	0.926 and -0.627 (close to solvent)	

N, 5.82. Found: C, 54.68; H, 4.81; N, 5.69%; $\Lambda_{\rm m}$ (mho cm² mol⁻¹): 79; IR (cm⁻¹): 3452w, 3048w, 2920m, 1707s, 1603s, 1584vs, 1482s, 1434vs, 1384vs, 1302vs, 1222s, 1178vs, 1098s, 1026s, 997s, 741vs, 693vs, 512s, 486s, 445m; UV–Vis ($\lambda_{\rm max}$, log ε): (CHCl₃); 256 (4.33), 291 (3.95), 350 (3.10).

2.6. $[Ag(\mu - dpppent)(tHpymtH)(NO_3)]_n$ (3)

Colorless crystals. Yield: 207 mg (57%), m.p. 230 °C; Anal. Calc. for $C_{33}H_{38}AgN_3O_3P_2S$: C, 54.55; H, 5.27; N, 5.78. Found: C, 54.27; H, 5.24; N, 5.81%; Λ_m (mho cm² mol⁻¹): 96; IR (cm⁻¹): 3286m, 3049w, 2939w, 1707m, 1608m, 1547vs, 1481s, 1435vs, 1384vs, 1306vs, 1207s, 1098vs, 1025s, 816s, 741vs, 695vs, 511vs, 478s, 418s; UV–Vis (λ_{max} , log ε): (CHCl₃); 253 (4.32), 297 (3.94).

2.7. $[Ag(\mu - dpppent)(mtdztH)(NO_3)]_n$ (4)

Colorless crystals. Yield: 226 mg (61%), m.p. 145 °C; Anal. Calc. for $C_{32}H_{34}AgN_3O_3P_2S_2$: C, 51.76; H, 4.61; N, 5.66. Found: C, 52.05; H, 4.78; N, 5.76%; $A_{\rm m}$ (mho cm² mol⁻¹): 93; IR (cm⁻¹): 3453w, 3050w, 2924m, 1586s, 1482vs, 1435vs, 1385vs, 1284vs, 1197s, 1098s, 1049s, 998s, 740vs, 694vs, 511vs, 480s, 432s; UV–Vis ($\lambda_{\rm max}$, log ε): (CHCl₃); 254 (4.36), 307 (4.29).

2.8. $[Ag(\mu\text{-}dpppent)(mftztH)(NO_3)]_n$ (5)

Colorless crystals. Yield: 266 mg (67%), m.p. 249 °C; Anal. Calc. for $C_{33}H_{34}AgF_{3}N_4O_3P_2S$: C, 49.95; H, 4.32; N, 7.06. Found: C, 49.10; H, 3.99; N, 6.90%; A_m (mho cm² mol⁻¹): 104; IR (cm⁻¹): 3456w, 3051m, 2924m, 1707m, 1616m, 1483vs, 1435vs, 1384vs, 1283s, 1203s, 1149s, 1090s, 741vs, 693vs, 511s, 479m; UV–Vis (λ_{max} , log ε): (CHCl₃); 257 (4.38), 355 (4.09).

2.9. $[Ag(\mu\text{-}dpppent)(bzoxtH)(NO_3)]_n$ (6)

Brownish crystals. Yield: 291 mg (75%), m.p. 135 °C; Anal. Calc. for $C_{36}H_{35}AgN_3O_4P_2S$: C, 56.77; H, 4.63; N, 3.68. Found: C, 57.26; H, 4.83; N, 3.71%; Λ_m (mho cm² mol⁻¹): 103; IR (cm⁻¹): 3440m, 3051m, 2924w, 1616m, 1515vs, 1435vs, 1385vs, 1306vs, 1255s, 1198s, 1136vs, 1096vs, 923s, 740vs, 694vs, 605s, 512vs, 482s, 424s; UV–Vis (λ_{max} , log ε): (CHCl₃); 257 (4.21), 305 (4.22), 335 (3.16).

2.10. $[Ag(\mu\text{-}dpppent)(mbzimtH_2)(NO_3)]_n$ (7)

Colorless crystals. Yield: 225 mg (58%), m.p. 152 °C; Anal. Calc. for $C_{37}H_{38}AgN_3O_3P_2S$: C, 57.37; H, 4.94; N, 5.42. Found: C, 56.97; H, 4.99; N, 5.34%; Λ_m (mho cm² mol⁻¹): 89; IR (cm⁻¹): 3435w, 3051m, 2923w, 1617s, 1520s, 1484vs, 1456vs, 1435vs, 1384vs, 1307vs, 1185s, 1098s, 1026s, 804s, 740vs, 694vs, 628s, 512vs, 479s, 430m; UV–Vis (λ_{max} , log ε): (CHCl₃); 255 (4.37), 303 (4.37).

2.11. $[Ag(\mu-dpppent)(pur6SH)(NO_3)]_n$ (8)

Pale yellow crystals. Yield: 263 mg (69%), m.p. 170 °C; *Anal.* Calc. for $C_{34}H_{34}AgN_5O_3P_2S$: C, 53.55; H, 4.42; N, 9.18. Found: C, 52.98; H, 4.60; N, 8.96%; Λ_m (mho cm² mol⁻¹): 86; IR (cm⁻¹): 3435w, 3050w, 2922w, 1709m, 1594vs, 1570vs, 1482vs, 1435vs, 1384vs, 1207vs, 1158s, 1099vs, 1025s, 999vs, 932vs, 856vs, 741vs, 694vs, 590s, 511vs, 481s, 431s; UV–Vis (λ_{max} , log ε): (CHCl₃); 255 (4.31), 335 (4.25).

2.12. $[Ag_2(\mu - trans-dppen)_3(py2SH)_2](NO_3)_2$ (9)

Pale yellow crystals. Yield: 206 mg (47%), m.p. 224 °C; *Anal.* Calc. for C₈₈H₇₆Ag₂N₄O₆P₆S₂: C, 60.35; H, 4.37; N, 3.20. Found: C, 59.89; H, 4.19; N, 3.16%; $\Lambda_{\rm m}$ (mho cm² mol⁻¹): 137; IR (cm⁻¹): 3446w, 3048w, 2980w, 1583vs, 1481s, 1435vs, 1384vs, 1308vs, 1186s, 1098vs, 1024s, 997vs, 741vs, 693vs, 539vs, 519vs, 493s; UV–Vis ($\lambda_{\rm max}$, log ε): (CHCl₃); 258 (4.34), 282 (4.22), 360 (3.20).

2.13. $[Ag_2(\mu - trans-dppen)_3(pymtH)_2](NO_3)_2$ (10)

Yellow crystals. Yield: 197 mg (45%), m.p. 198 °C; Anal. Calc. for C₈₆H₇₄N₆Ag₂O₆P₆S₂: C, 58.91; H, 4.25; N, 4.79. Found: C, 58.69; H, 4.57; N, 4.58%; $\Lambda_{\rm m}$ (mho cm² mol⁻¹): 124; IR (cm⁻¹): 3445w, 3050w, 2861w, 1600s, 1574vs, 1479vs, 1434vs, 1384vs, 1327vs, 1214s, 1177vs, 1096s, 1026s, 975s, 794m, 743vs, 694vs, 506vs, 488vs, 463s, 335m; UV–Vis ($\lambda_{\rm max}$, log ε): (CHCl₃); 262 (4.30), 286 (4.27), 370 (3.18).

2.14. $[Ag_2(\mu - trans-dppen)_3(tHpymtH)_2](NO_3)_2$ (11)

White crystals. Yield: 247 mg (56%), m.p. 256 °C; Anal. Calc. for $C_{86}H_{82}N_6Ag_2O_6P_6S_2$: C, 58.64; H, 4.69; N, 4.77. Found: C, 58.01; H, 4.49; N, 4.54%; Λ_m (mho cm² mol⁻¹): 121; IR (cm⁻¹): 3060w, 1564vs, 1480vs, 1435vs, 1384vs, 1296vs, 1220vs, 1157vs, 1096vs, 1025vs, 998s, 918s, 812s, 742vs, 692vs, 508vs, 465vs, 416s, 350m; UV–Vis (λ_{max} , log ε): (CHCl₃); 254 (4.32), 279 (3.97), 351 (2.17).

2.15. $[Ag_2(\mu\text{-trans-dppen})_3(bzoxtH)_2](NO_3)_2$ (12)

Braunish crystals. Yield: 256 mg (56%), m.p. 210 °C; Anal. Calc. for $C_{92}H_{76}N_4Ag_2O_8P_6S_2$: C, 60.33; H, 4.18; N, 3.06. Found: C, 59.87; H, 4.18; N, 2.99%; A_m (mho cm² mol⁻¹): 126; IR (cm⁻¹): 3438w, 3051w, 1615m, 1515s, 1479s, 1435vs, 1384vs, 1308s, 1257vs, 1182s, 1138vs, 1097vs, 1026s, 925s, 742vs, 694vs, 507s, 491s, 423s; UV–Vis (λ_{max} , log ε): (CHCl₃); 252 (4.32), 272 (3.15), 355 (2.98).

2.16. $[Ag_2(\mu - trans-dppen)_3(mtdztH)_2](NO_3)_2$ (13)

White crystals. Yield: 233 mg (52%), m.p. 221 °C; *Anal.* Calc. for C₈₄H₇₄N₆Ag₂O₆P₆S₄: C, 56.25; H, 4.16; N, 4.68. Found: C, 56.01; H, 4.10; N, 4.67%; $\Lambda_{\rm m}$ (mho cm² mol⁻¹): 122; IR (cm⁻¹): 3445w, 3050w, 1640s, 1552s, 1480vs, 1435vs, 1384vs, 1308vs, 1197s, 1097vs, 1058vs, 998s, 812m, 741vs, 693vs, 509vs, 476s, 432s, 344m; UV–Vis ($\lambda_{\rm max}$, log ε): (CHCl₃); 251 (4.11), 307 (4.02), 341 (2.87).

2.17. $[Ag_2(\mu - trans-dppen)_3(mftztH)_2](NO_3)_2$ (14)

White crystals. Yield: 270 mg (57%), m.p. 249 °C; *Anal.* Calc. for C₈₆H₇₄N₈Ag₂F₆O₆P₆S₂: C, 54.50; H, 3.93; N, 5.91. Found: C, 53.91; H, 4.08; N, 5.75%; $A_{\rm m}$ (mho cm² mol⁻¹): 115; IR (cm⁻¹): 3.362 w, 3174w, 2965w, 1560vs, 1435vs, 1384vs, 1310vs, 1221vs, 1096s, 997s, 811m, 752s, 742vs, 694vs, 509vs, 479s, 416s; UV– Vis ($\lambda_{\rm max}$, log ε): (CHCl₃); 250 (4.40), 298 (4.19).

3. Results and discussion

3.1. Preparative considerations

Before discussing the experimental results, we should point out that both, 1,5-bis(diphenylphosphino)pentane (dpppent) and *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen) showed a marked preference for the formation of macrocycles in their reactions with Cu(I), in the presence of heterocyclic thione ligands [28–30], whereas *cis*-1,2-bis(diphenylphosphino)ethene yielded predominantly chelated monomeric species [31].

The reaction between equimolar quantities of silver(I) nitrate and 1,5-bis(diphenylphosphino) pentane (dpppent) followed by the addition of one equivalent of the apropriate thione (L) [L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), tetrahydropyrimidinethione (tHpytH), 5-methyl-1,3,4-thiadiazole-2-thione (mtdztH), benz-1,3-oxazoline-2-thione (bzoxtH), 5-methyl-benz-1,3-imidazole-2-thione (mbzimtH₂), 4methyl-5-trifluoromethyl-4H-1,2,4-triazoline-3(2H)-thione (mftztH), and 6-mercaptopurine (pur6SH) in dry acetonitrile/methanol solution at 30 °C afforded microcrystalline solids which, on analysis were found to be of composition [AgNO₃(dpppent)L] (compounds **1–8**).

According to our previous experience with thione/ phosphine complexes of Ag(I) nitrate, Ag^+ tends to adopt a tetrahedral coordination whith the counterion kept outside the coordination sphere, despide its strong coordination ability. Within the meaning of this criterion, two structures (structures **a** and **b**, Scheme 1) come into question that reproduce the above given stoichiometry.

On the other hand, if the coordination of the nitrate anion is weak, the formation of a monomeric, dimeric or polymeric complex (structures **c**–**e**, respectively), could be possible, but formation of **c** is unlikely as it is less compatible with the stereochemical characteristics of the long-chained diphosphine applied. Indeed, the structure determination of the tetrahydropyrimidine-2-thione complex (compound 3) by X-ray diffraction confirmed compounds **1–8** to be coordination polymers of type $[Ag(\mu-dpppent)(L)(ONO_2)]_n$.

In general, diphosphines bearing a long-chained flexible backbone, are expected to bridge metal centres forming dimeric macrocycles of type $[M(diphos)_2M]$ rather than polymeric adducts, the later being continuously favoured upon decreasing the diphosphine chain length. Indeed, the ability of 1,5-bis(diphenylphosphino)pentane to serve as a bridge between two metal centres in monovalent coinage metal complexes is well documented, among others in a recent publication of Pettinari and co-workers [32], where the flexible diphosphine was shown to predominantly form dimers of type $[M(\mu-dpppent)(\mu-X)]_2$ (M = Cu, Ag and X = Br, I). Likewise, treating an acetonitrile solution of Cu(I) chloride with stoichiometric amounts of dpppent and a heterocyclic thione ligand, the complexes formed were of the formula [CuCl(dpppent)L], whereby the thione-free dimer $[Cu(\mu-dpppent)(\mu-Br)]_2$ was found to be the only product of the analogous reactions when copper(I) bromide was used [30]. Consequently, the formation of the polymers under investigation was considered as unpredictable with respect to the geometrical features of the diphos ligand applied. Moreover, it contrasted, regarding the stoichiometric composition of the products formed, with the findings of our recent work on analogous AgNO₃ compounds, where the use of 1,2-bis(diphenylphosphino)ethane (dppe) afforded polymers of general formula $[Ag(dppe)(L)_2]_n(NO_3)_n$ [21], with the latter containing ionic outer-sphere nitrate groups. Thus, following the same procedure, we repeated the reactions using the apropriate thione in a twofold excess, aiming to attain cationic complexes, but we obtained once more compounds 1-8. Likewise, we treated compounds 1-8 with two equivalents of an apropriate thione per formula unit, however the products isolated in all the cases turned out to be once more the polymeric complexes initially used as starting materials.

The second series of mixed ligand complexes obtained on treating silver(I) nitrate with equimolar quantities of *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen) and the same set of heterocyclic thiones was of the composition $[(AgNO_3)_2(trans-dppen)_3(L)_2]$. On the basis of the above composition it was presumed that these compounds could be phosphine-bridged dinuclear cages. This was indeed found for six of the thiones applied (compounds **9–14**), but not for mbzimtH₂ or



Scheme 1.

pur6SH, where the reaction, carried out under the same experimental conditions as usual, gave in both cases a powder of uncertain stoichiometry.

Complexes 1–14 are diamagnetic, air stable, microcrystalline solids, only slightly soluble in common organic solvents. In accordance with their polymeric nature, the molar conductivities of complexes containing dpppent (compounds 1–8) in dry acetonitrile solutions are somewhat lower than those of the dinuclear compounds 9–14, but still fairly high to suggest complete ionization in solution.

3.2. Spectroscopic characterization

The solid state FT-IR spectra of complexes 1-14, recorded in the range $4000-250 \text{ cm}^{-1}$ provide useful information regarding the mode of thione ligand coordination. They show the disappearance of the S-H stretching band around 2560 cm⁻¹ due to the "free" ligands and the presence of the v(NH) band in the 3190–3230 cm⁻¹ region, suggesting M-S bond formation. Moreover, they contain all of the bands required by the presence of heterocyclic thioamides occurring in their thione form, with shifts indicating the exclusive S-coordination mode of these ligands. Further, they show all the expected strong phosphine bands, which remain practically unshifted upon coordination. The asymmetric N-O stretching mode (v_1) of the NO₃ anion appears as a band of medium intensity in the 1375–1285 cm^{-1} range, in some cases not recognizable because of overlapping with strong absorptions due to the thione and phosphine ligands. Unfortunately, nothing certain can be stated about the coordination mode of the nitrate ion since the thione ligands strongly absorb in the regions where the bands associated with coordinated nitrate occur.

The electronic absorption spectra of the complexes in chloroform solutions appear to be mainly of intraligand character, consisting of two intense sharp bands in the 250–260 and 282–307 nm regions, as well as an additional rather broad band with maximum at 335–370 nm. The first two bands can be attributed to intraligand $\pi^* \leftarrow \pi$ transitions on the phenyl group of the phosphine ligands, since the uncoordinated 1,5-bis(diphenylphosphino)pentane and *trans*-1,2-bis(diphenylphosphino) ethene both reveal two strong absorptions at 259 and 287.5 nm and 258.5 and 296 nm, respectively, which are known to undergo small shifts upon coordination to Ag(I). The lower energy band lies in the region where the free thiones absorb, expressing a small red shift as a consequence of the coordination to Ag(I) and should be, therefore, considered as a thione-originating intraligand transition which possess some MLCT character [33,34] (Fig. 1).

3.3. Thermal decomposition

Thermal analysis in nitrogen atmosphere shows the complexes 1–8 decompose in three or four stages. Fig. 2 illustrates TG and DTA data curves for the polymeric $[Ag(NO_3)(dpppent)(tHpymtH)]_n$ (compound 3). The three low temperature initial stages involve a weak endothermic and a very strong exothermic effect in the temperature range 240–360 °C and are connected with an overall weight loss of ~16% which is consistent with gradually thermal breakdown of the tetrahydropyrimidine-2-thione ligand. Note that the very strong exothermic effect is an attribute of the decomposition of complexes bearing non-aromatic thione ligands, whereby the corresponding DTA courve in the case of aromatic thione compounds allways show endothermic events instead.

The observed mass loss (\sim 67%) in the final, slightly endothermic stage, show excellent agreement for simultaneous loss of the diphosphine molecule and conversion of the resultant silver nitrate to Ag₂O under NO₂ evolution. However no clear distinction between these



Fig. 1. The heterocyclic thione ligands used with their abbreviations.



Fig. 2. TG and DTG curves for compound 3.

two processes can be made, thus this stage must be somewhat complicated in character.

Complexes 9–14 show an analogous decomposition patern but they are in general thermally less stable, decomposition being usually completed at 450 °C. Noticeable is the particular short final stage, that extends over a temperature range of only 60 °C. In the majority of the cases solvent retention occurs at the temperature of 190 °C indicated by a strong exothermic effect connected with a weight loss corresponding to one molecule of CH₃CN per formula unit.

3.4. Crystal structures

Colorless crystals of 3 suitable for X-ray were obtained by slow evaporation of a CH₃CN/CH₃OH solution of the compound. The complex crystallizes in the monoclinic space group C2/c, with eight monomer units in the unit cell. Details regarding the crystal data collection and refinement for the complex are reported in Table 1. Bond lengths and angles around the Ag(I) are listed in Table 2. Fig. 3 shows the monomeric unit of the complex with the labelling of the atoms, and Fig. 4 the resultant polymer. The structure is substantially disordered, with each of the individual components of the monomeric entity being affected in some degree. Four of the five carbon atoms (C5-C8) in the pentane chain are disordered over two sites, whereas disorder in the thione ligand involves three carbons (C3–C5). Similarly the three oxygen atoms in the NO₃ ion are highly disordered. Moreover, there are high displacement parameters associated with an aryl group attached to P2, which had to be restricted to a hexagon with ideal bond lengths and angles.

Complex 3 is a coordination polymer consisting of Ag(I) cations linked through the phosphorous atoms of the 1,5-bis(diphenylphosphino)pentane ligand. Each silver nucleus completes the familiar tetrahedral coordination environment considering the S-atom from the tetrahydropyrimidine-2-thione ligand, one O-atom from the weakly coordinated nitrate anion and the two bridging P-atoms belonging to two different diphosphine units. The repeating unit extends into an infinite one-dimensional chain formed by linking Ag and P1 atoms by unit cell translations along the *b* axis, in which the tetrahydropyrimidine-thione units are ordered in a *syn* configuration.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

Bond lengths (\mathring{A})			
Ag–P(2)	2.4541(14)	P(1)–C(9)	1.837(5)
$Ag-P(1)^a$	2.4666(14)	P(2)–C(5B)	1.70(3)
Ag-S(1)	2.5623(15)	N(3)–O(1A)	1.232(9)
Ag–O(1A)	2.535(8)	N(3)–O(2A)	1.148(8)
S(1) - C(1)	1.712(6)	N(3)–O(3A)	1.227(9)
Bond angles (°)			
$P(2)-Ag-P(1)^a$	132.75(5)	$P(1)^{a}$ -Ag-O(1A)	99.7(2)
P(2)-Ag-S(1)	110.07(6)	Ag-S(1)-C(1)	113.92(19)
$P(1)^{a}$ -Ag-S(1)	108.25(6)	O(2A)-N(3)-O(1A)	120.7(9)
P(2)-Ag-O(1A)	103.6(3)	O(2A)-N(3)-O(3A)	125.2(9)
S(1)–Ag–O(1A)	94.64(18)	O(3A)-N(3)-O(1A)	113.9(8)
Hydrogen bridges			
$O(1A) \cdots N(1)$	2.721(9)	N(1)–H(1)	0.88
$O(1A) \cdots H(1)$	1.90	$O(1A) \cdot \cdot \cdot H(1) - N(1)$	155°
$O(2A)^{b} \cdots N(2)$	3.034(11)	N(2)–H(2)	0.88
$O(2A)^{b} \cdots H(2)$	2.23	$O(2A)^{b} \cdots H(2) - N(2)$	153°

^a Atom coordinates transposed by x, y - 1, z.

^b Atom coordinates transposed by x, -2 - y, 0.5 + z.



Fig. 3. The monomeric unit $[Ag(\mu-dpppent)(tHpymtH)(ONO_2)]$ of **3** with atom labels (disorder removed). Displacement ellipsoids are shown in the 50% probability level.



Fig. 4. A view of the polymeric chain $[Ag(dpppent)(tHpymtH)(NO_3)]_n$ with hydrogen atoms removed for clarity. Displacement ellipsoids are shown at the 50% probability level.

Considering the angles involving the central metal atom, there are considerable distortions from the ideal tetrahedral geometry, the most remarkable being the P(1)#-Ag-P(2) angle, with a large value of 132.75(5)° which can be partly accounted for the steric hindrance induced by the bulky phenyl-rings of the two phosphine units, but probably also for the presence of the weakly coordinated nitrate. Namely, the weak anion-cation interaction, indicated by the large Ag-O distance of 2.535(8) A, is associated with angles involving the coordinated nitrate oxygen-atom that are less than the ideal tetrahedral value of 109.4°, thus allowing an appropriate opening up of the angle between the sterically demanding groups. Another remarkable feature in the structure of 3 is the quite large Ag–S–C angle of 113.92(19)°, which may be attributed to the presence of a strong hydrogen N–H···O bridge (Table 2).

The Ag–S bond distance of 2.5623(15) A, coincident with the sum of the corresponding atomic radii, is typical for this bonding arrangement. Likewise, the two Ag– P distances lie within the limits of 2.426–2.504 Å found for a number of complexes containing tetracoordinated silver atoms bonded to two phosphorus atoms [35,36] and vary little [Ag(1)-P(1) = 2.4501(5), [Ag(1)-P(2) = 2.4658(5) Å]. Finally, the geometrical characteristics of the tetrahydropyrimidine-thione ligand, where the sexmembered ring adopts an envelope conformation, are not altered noticeable upon coordination.

Compound 10 crystallizes in the orthorhombic space group $Pna2_1$, with 4 discrete molecules in the unit cell as well as four lattice CH₃CN molecules. Main bond lengths and angles are given in Table 3 and a perspective drawing showing the atom numbering is shown in Fig. 5.

The crystal structure of **10** is built by dinuclear units in which the two tetrahedral silver centres are linked by three bridging diphosphine units, whereby the fourth position of each tetrahedron is occupied by the S-atom of a thione unit. Interestingly, the two thione rings are almost parallel to each other adopting a relative *cis* orientation. Each of the two nitrate anions is placed near to a thione unit and is adjusted to its nitrogen-bound hydrogen atom via hydrogen bonding interactions (see Table 3). Furthermore, each of these counterions is close

Table 3					
Selected bond lengths (Å) and angles (°) for 10					
Bond lengths (Å)					
Ag(1) - P(1)	2.4979(14)	P(2)–C(13)	1.804(4)		
Ag(1)–P(2)	2.5131(11)	P(3)–C(11)	1.813(4)		
Ag(1) - P(3)	2.5211(13)	P(4)–C(10)	1.808(4)		
Ag(1) - S(1)	2.5660(10)	P(5)-C(12)	1.808(4)		
Ag(2)–P(5)	2.5123(12)	P(6)-C(14)	1.810(4)		
Ag(2)–P(4)	2.5370(12)	O(1)–N(5)	1.264(7)		
Ag(2)–P(6)	2.5379(11)	O(2)–N(5)	1.236(6)		
Ag(2)–S(2)	2.5923(10)	O(3)–N(5)	1.253(5)		
S(1)–C(1)	1.693(4)	O(4)–N(6)	1.191(6)		
S(2)–C(5)	1.689(4)	O(5)–N(6)	1.247(8)		
P(1)–C(9)	1.825(4)	O(6)–N(6)	1.332(7)		
Bond angles (°)					
P(1)-Ag(1)-P(2)	111.56(4)	P(4)-Ag(2)-S(2)	110.82(4)		
P(1)-Ag(1)-P(3)	113.12(4)	P(6)-Ag(2)-S(2)	101.48(3)		
P(2)-Ag(1)-P(3)	100.39(4)	C(1)-S(1)-Ag(1)	102.78(13)		
P(1)-Ag(1)-S(1)	109.69(4)	C(5)–S(2)–Ag(2)	103.60(14)		
P(2)-Ag(1)-S(1)	104.65(3)	O(2)–N(5)–O(3)	123.1(5)		
P(3)-Ag(1)-S(1)	116.71(4)	O(2)–N(5)–O(1)	119.9(4)		
P(5)–Ag(2)–P(4)	111.00(4)	O(3)–N(5)–O(1)	117.1(5)		
P(5)–Ag(2)–P(6)	114.65(4)	O(4)–N(6)–O(5)	124.0(7)		
P(4)–Ag(2)–P(6)	108.78(4)	O(4)–N(6)–O(6)	119.3(7)		
P(5)-Ag(2)-S(2)	109.75(5)	O(5)–N(6)–O(6)	116.6(5)		
Hydrogen bridges					
$O(2)^{a} \cdot \cdot \cdot N(2)$	2.831	N(2)–H(2)	0.88		
$O(2^a) \cdot \cdot \cdot H(2)$	1.956	$O(2)^{a} \cdots H(2) - N(2)$	173°		
$O(1)^{a} \cdots N(2)$	3.063				
$O(1)^{a} \cdots H(2)$	2.539	$O(1)^a \cdots H(2) - N(1)$	119		
$O(3)^{b} \cdots N(4)$	2.871	N(4)–H(4)	0.88		
$O(3)^{b} \cdots H(4)$	2.018	$O(3) \cdot \cdot \cdot H(4) - N(4)$	163°		
$O(1)^{b} \cdots N(4)$	3.102				
$O(1)^{b} \cdots H(4)$	2.532	$O(1)^{b} \cdots H(4) - N(4)$	123		

T 11

^a Atom coordinates transposed by -x + 1, -y + 1, z + 0.5.

^b Atom coordinates transposed by -x + 1, -y, z + 0.5.

to a lattice CH_3CN molecule, which will not be further discussed as there is no evidence of any specific interaction involving this latter solvent molecule. One of the nitrate ions is hydrogen bonded to both thione units (Fig. 6). As well as the N-H···O bonds (Fig. 6, Table 3) there is also evidence of N-H···N interactions.

trans-1,2-Bis(diphenylphosphino)ethene (*trans*-dppen) is well known to serve as a phosphorus(σ) donor bridge between metal centres in coordination compounds [28,29,37,38]. However, in view of the rigidity of the diphosphine backbone, the formation of the three-fold bridging motif realized in the complex under discussion should be considered as quite strained, the more so as this rigidity is accompanied with a remarkable accumulation of stericaly demanding Ph₂PCH₂-units around the metal centres. Nevertheless, some related triply bridged $[M_2L_3]$ complexes with rigid bridging diphosphines such as $Ph_2P-C\equiv C-PPh_2$ [39] and $Ph_2P-C\equiv C-C\equiv$ C-PPh₂ [40] have been characterised in the solid state. Among the Ag(I) complexes, this cage structure is known to exist, with no terminal ligands and thus with trigonal coordination of the two metal atoms, in the triply-bridged disilver helical complexes $[Ag_2(\mu_2-dppa)_3]^{2+}$



Fig. 5. A view of $[Ag_2(trans-dppen)_3(tHpymtH)_2](NO_3)_2 \cdot CH_3CN$ (10) with hydrogen atoms and disorder removed for clarity. Displacement ellipsoids are shown at the 50% probability level.

bearing the rigid bis-(diphenylphosphino)acetylene (dppa) [19]. Some examples of such cages with more or less strong anion-cation interactions, thus exhibiting tetrahedrally coordinated Ag(I) centres have been also reported recently [41]. Further related $[Ag_2L_3]$ complexes involve 2,6-bis(diphenylphosphino)pyridine [42], 3,6-bis(diphenylphosphino)pyridazine [42] and 2,9-bis(diphenylphosphino)-1,8-naphthyridine [43]. With *trans*-dppen, evidence for the formation of discrete $[Ag_2L_3]$ cages was found in solution, although, on crystallization, only the corresponding ring-opened polymeric structures could be obtained [41].

The geometrical characteristics of the structure under investigation generally refer to those of other silver(I) complexes tetrahedrally coordinated by phosphine and thione ligands. There are six different Ag-P bond distances around the two Ag(I) centres, each of them within the limits expected for a complex containing a tetracoordinated silver atom bearing phosphorus and sulfur donor ligands [44]. Likewise the two Ag-S distances [2.5660(10) and 2.5923(10) Å] are typical for this type of ligation. Interestingtly, the formation of the Ag(PP)₃Ag cage does not require significant conformational rearrangements on the part of the diphosphine ligands; upon coordination the two P atoms of each diphosphine unit twist about the ethene bridge altering the dihedral angle through the four atoms by about 8°, taken as the average of the torsion angles P(1)-C(9)-C(10)-P(4), P(3)-C(11)-C(12)-P(5)and P(2)-C(13)-C(14)-P(6), with respect to the corresponding value (176.6°) in the free trans-dppen [45], thus only moderately modifying the bite size of the diphosphine.



Fig. 6. Plot showing the N–H \cdots O hydrogen bonds linking a nitrate ion to two thione units. Phenyl rings and hydrogen atoms are removed for clarity.

4. Conclusion

Two series of heterocyclic thione ligated silver(I) nitrate complexes in which Ag(I) centres are bridged either by 1,5-bis(diphenylphosphino)pentane or trans-1,2bis(diphenylphosphino)ethene have been prepared and spectroscopically characterised. The complexes bearing the former long chained dpppent contain weakly coordinated nitrate groups and are polymeric. This contrast with the hitherto observed coordination behaviour of this flexible diphos ligand, since the majority of its univalent group I_B metal complexes are dinuclear macrocycles. Likewise as non-predictable should be considered the behaviour of the rigid bridging ligand *trans*-dppen, which is known to preferably form dinuclear macrocycles, as it favours in the present case the selective formation of triply bridged disilver derivatives, indepentend from the metal-to-ligand ratio applied. These results clearly demonstrate that factors other than the chain length, flexibility or stereochemical constrains between bulky groups on the part of the bridging ligand additionally play an important role in determining the structure being formed in each case. In this context, at least the effect of polymerization observed seems to be of particular interest and will be, therefore, object of more extensive studies.

5. Supplementary material

CCDC- 263254 (3) and CCDC-263255 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We thank the EPSRC X-ray crystallography service at the University of Southampton for collecting the X-ray data.

References

- H. Sigel, V.M. Rheinberger, B.E. Fischer, Inorg. Chem. 18 (1979) 3334.
- [2] R.H. Holm, E.I. Solomon, Chem. Rev. (1996) 96.
- [3] J.A. Garcia-Vazquez, J. Romero, A. Sousa, Coord. Chem. Rev. 193–195 (1999) 691, and references therein.
- [4] P.D. Akrivos, Coord. Chem. Rev. 181-210 (2001) 213.
- [5] (a) E.S. Raper, Coord. Chem. Rev. 61 (1985) 115;
 (b) G. Giusti, G. Geier, A. Currao, R. Nesper, Acta Cryst. C 52 (1996) 1914.
- [6] P. Karagiannidis, P. Aslanidis, S. Kokkou, C.J. Cheer, Inorg. Chim. Acta 172 (1990) 247.
- [7] W. McFarlane, P.D. Akrivos, P. Aslanidis, P. Karagiannidis, C. Hatzisymeon, M. Numan, S. Kokkou, Inorg. Chim. Acta 281 (1998) 121.
- [8] P.J. Cox, P. Aslanidis, P. Karagiannidis, S. Hadjikakou, Inorg. Chim. Acta 310 (2000) 268.
- [9] P.A. Perez-Jourido, J.A. Garcia-Vazquez, J. Romero, M.S. Louro, A. Sousa, Q. Chen, Y. Chang, J. Zubieta, J. Chem. Soc., Dalton Trans. (1996) 2047.
- [10] L. Zhang, H.-X. Zhang, C.-L. Chen, L.-R. Deng, B.-S. Kang, Inorg. Chim. Acta 355 (2003) 49.
- [11] I.C. Dance, L.J. Fitzpatrick, A.D. Rae, M.L. Scudder, Inorg. Chem. 22 (1983) 3785.
- [12] W. Su, M. Hong, J. Weng, Y. Liang, Y. Zhao, R. Cao, Z. Zhou, A.S.S. Chan, Inorg. Chim. Acta 331 (2002) 8.
- [13] W. Su, R. Cao, M. Hong, W.-T. Wong, J. Lu, Inorg. Chem. Commun. 2 (1999) 241.
- [14] C.A. McAuliffe, W. Levason, Phosphine, Arsine and Stibine Complexes of the Transition Elements, Elsevier, Amsterdam, 1979.
- [15] R.J. Puddephatt, Chem. Soc. Rev. (1983) 99.
- [16] B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 191.
- [17] Effendy, C. di Nicola, M. Fianchini, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 748.
- [18] S.L. James, E. Lozano, M. Nieuwenhuyzen, Chem. Commun. (2000) 617.
- [19] E. Lozano, M. Nieuwenhuyzen, S.L. James, Chem. Eur. J. (2001) 2644.
- [20] L. Zhang, H.-X. Zhang, C.-L. Chen, L.-R. Deng, B.-S. Kang, Inorg. Chim. Acta 355 (2003) 49.
- [21] P. Aslanidis, P.J. Cox, S. Divanidis, P. Karagiannidis, Inorg. Chim. Acta 357 (2004) 2677.
- [22] P. Karagiannidis, S.K. Hadjikakou, P. Aslanidis, A. Hountas, Inorg. Chim. Acta 178 (1990) 27.
- [23] Z. Otwinowski, W. Minor, Methods in enzymology, in: C.W. Carter Jr., R.M. Sweet (Eds.), Macromolecular Crystallography, vol. 276, Academic Press, 1997, Part A, p. 307.
- [24] R. Hooft, COLLECT Data Collection Software, Nonius B.V., 1998.
- [25] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 27 (1994) 434.

- [26] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Analysis (Release 97-2), University of Goettingen, Germany, 1997.
- [27] L.J. Farrugia, J. Appl. Crystallogr. 30 (1977) 565.
- [28] P. Aslanidis, P.J. Cox, S. Divanidis, P. Karagiannidis, Inorg. Chim. Acta 357 (2004) 4231.
- [29] S. Divanidis, P.J. Cox, P. Karagiannidis, P. Aslanidis, Polyhedron 24 (2004) 351.
- [30] S. Divanidis, PhD Thesis, University of Thessaloniki, 2004.
- [31] P. Aslanidis, P.J. Cox, S. Divanidis, P. Karagiannidis, Inorg. Chim. Acta 357 (2004) 1063.
- [32] Effendy, C.D. Nicola, M. Fianchini, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 763.
- [33] A.A. Del Paggio, D.R. McMillin, Inorg. Chem. 22 (1983) 691.
- [34] C. Kutal, Coord. Chem.Rev. 99 (1990) 213.
- [35] D. Coucouvanis, N.C. Benzinger, S.M. Johnson, Inorg. Chem. 13 (1974) 1191.
- [36] D.D. Heinrich, J.P. Fackler Jr., P. Lahuerta, Inorg. Chim. Acta 116 (1986) 15.

- [37] W. Oberhauser, T. Stampfl, C. Bachmann, R. Haid, C. Langes, H. Kopacka, K.-H. Ongania, P. Brüggeller, Polyhedron 19 (2000) 913.
- [38] G.B. Jacobsen, B.L. Shaw, M. Thornton-Pett, J. Organomet. Chem. 323 (1987) 313.
- [39] G. Hogarth, T. Norman, Polyhedron 15 (1996) 2859.
- [40] M. Semmelmann, D. Fenske, J.F. Corrigan, J. Chem. Soc. Dalton Trans. (1998) 2541.
- [41] E. Lozano, M. Nieuwenhuyzen, S.L. James, Chem. Eur. J. 7 (2001) 2644.
- [42] S.-M. Kuang, L.-M. Zhang, Z.Z. Zhang, B.-M. Wu, C.W. Mak, Inorg. Chim. Acta 284 (1999) 278.
- [43] V.J. Catalano, H.M. Kar, B.L. Bennett, Inorg. Chem. 39 (2000) 121.
- [44] W. McFerlane, P.D. Akrivos, P. Aslanidis, P. Karagiannidis, C. Hatzisymeon, M. Numan, S. Kokkou, Inorg. Chim. Acta 281 (1998) 121.
- [45] H. Schmidbaur, G. Reber, A. Schier, F.E. Wagner, G. Müller, Inorg. Chim. Acta 147 (1988) 143.