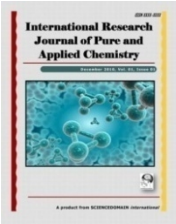

International Research Journal of Pure & Applied Chemistry
5(2): 185-201, 2015, Article no.IRJPAC.2015.017
ISSN: 2231-3443

SCIENCEDOMAIN *international*
www.sciencedomain.org

SCIENCEDOMAIN

Crystallographic and Structural Analysis of Heterometallic FeAg Complexes

M. Melník[1*] and P. Mikuš[1]

[1]Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic.

Authors' contributions

This work was carried out in collaboration between the authors, each section in the ratio 1:1. The authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2015/13420
Editor(s):
(1) Monica Butnariu, Department of Chemistry & Biochemistry, Banat's University of Agricultural Sciences and Veterinary Medicine from Timisoara, Romania.
(2) SungCheal Moon, Korea Institute of Materials Science (KIMS), Industrial Technology Support Division, Changwon, Republic of Korea.
Reviewers:
(1) Anonymous, Gulbarga University, India.
(2) Anonymous, Southwest University of Science and Technology, China.
(3) Anonymous, Quaid-i-Azam University, Pakistan.
(4) Olga Kovalchukova, General Chemistry Department, Science Faculty, Peoples' Friendship University of Russia, Russia.
(5) Anonymous, Fukushima University, Japan.
Complete Peer review History: http://www.sciencedomain.org/review-history.php?iid=807&id=7&aid=6838

Review Article

Received 16th August 2014
Accepted 9th October 2014
Published 6th November 2014

ABSTRACT

There are 30 heterometallic Fe/Ag complexes in this review. The complexes contain the following metallic cores: FeAg, Fe_2Ag, $FeAg_2$, FeAgW, Fe_2Ag_2, $FeAg_3$, Fe_4Ag, Fe_3Ag_2, Fe_2Ag_4, $Fe_2Ag_2Pd_2$, Fe_6Ag, Fe_4Ag_4, Fe_4Ag_5, Fe_3Ag_6 and $\{FeAg\}_n$. The mean M-M bond distance elongated in the order: 2.614Å (Fe-Fe) < 2.660Å (Fe-Ag) < 2.806Å (Ag-Ag). The most common type of ligands is C donor for iron atoms, while for silver atoms are O and N donors. The inner coordination spheres about the iron atoms range from four to seven and ten (sandwiched) which is the most common. About the silver atoms from two to six, the four are the most common. The structural parameters are analyzed and compared with those of FeCu and FeAu complexes.

Keywords: Structure; heterometallics; Fe/Ag; classification; review.

**Corresponding author: Email: qmelnik@stuba.sk;*

ABBREVIATIONS

Acac- acetylacetonate; bz- benzoate; $C_{13}H_{14}S_2$- bis(cyclopentadienyl)-1,5-dithiopentane; C_4H_4N- pyrrolyl; $C_5H_4PPh_2$- diphenylphosphinecyclopentadienyl; C_5H_4py- cyclopentadienylpyridine; C_6H_6- benzene; Dptpc- diphenylthiophosphoryl cyclopentadienyl; Edta- ethylenediaminetetraacetate; Eimp- bis(3-ethylenedimino-4-methoxyphenyl)cyclopentadienyl; m- monoclinic; Me- methyl; $O_2C_2S_2$ - dithiooxalate(2-); or - orthorhombic; PBu^t_2- di-tera-butylphosphido; Ph_2Ppy- 2-(diphenylphosphino)pyridine; Phen- 1,10-phenanthroline; PMe_3- trimethylphosphine; PPh_2(tol)- diphenyltoluenephosphine; PPh_3 – triphenylphosphine; Si(Me)Ph_2- diphenylmethylsilicium; tol-toluene; tr- triclinic; trg- trigonal;

1. INTRODUCTION

The chemistry of heterometallic iron complexes is an extensive and active area of study, with the relationships between structure, reactivity and catalytic activity of major importance. There have been many structural studies of such complexes [1]. Heterometallic iron gold as well as iron copper complexes have been summarized and classified from a structural point of view [2]. The aim of this review is to classify and analyze of heterometallic iron silver complexes from a structural point of view. There are thirty heterometallic iron / silver complexes for which structural data are available. Variations and trends in bond distances and angles were found and their importance is discussed in this review. The factors relevant to the stereochemical interactions around the these metals are discussed and where appropriate comparisons are made with heterometallic FeAu and FeCu complexes and show a general view on an interaction between iron and 1 B metal atoms.

2. HETERODIMERIC COMPLEXES

There are three yellow FeAg complexes [3-5] and their structural parameters are gathered in Table 1A. In [3] two fragments, $(PMe_3)\{Si(Me)Ph_2\}(CO)_3Fe$ and $Ag\{PPh_2(tol)\}$ are held together via direct Fe-Ag bond (2.581(1)Å). The iron atom is six- FeC_3PSiAg and silver atom is two- AgPFe coordinated with Fe-Ag-P bond angle of 175.49(7)º. In [4] beside direct Fe-Ag bond (2.760(1)Å), a carbon atom of CO group and two Ph_2Ppy ligands in the manner $\eta^1(P):\eta^1(N)$ serve as bridges between $(CO)_2Fe$ and $Ag(\eta^1\text{-}Ph_2Ppy)$ fragments. The iron atom is six- FeC_3P_2Ag and silver atom is five- AgN_2CPFe coordinated. The Fe-C-Ag bridge angle is 86.2(2)º. In [5] pair of equivalent dptpc ligands is coordinated to iron atom via the cyclopentadienyl rings and forms a sandwich (FeC_{10}) and to silver atom via the two S atoms (AgS_2). The S-Ag-S angle is 176.83(5)º (Fig. 1). In golden FeAg complex [6] a pair of $C_5H_4PPh_2$ ligands serve as bridges between Fe atom and $Ag(\eta^2\text{-phen})$ unit. Each of the ligand coordinated to the iron atom via five carbon atoms and via the phosphorous to the silver atom. The iron atom is sandwiched (FeC_{10}) and the silver atom is four- AgN_2P_2 coordinated.

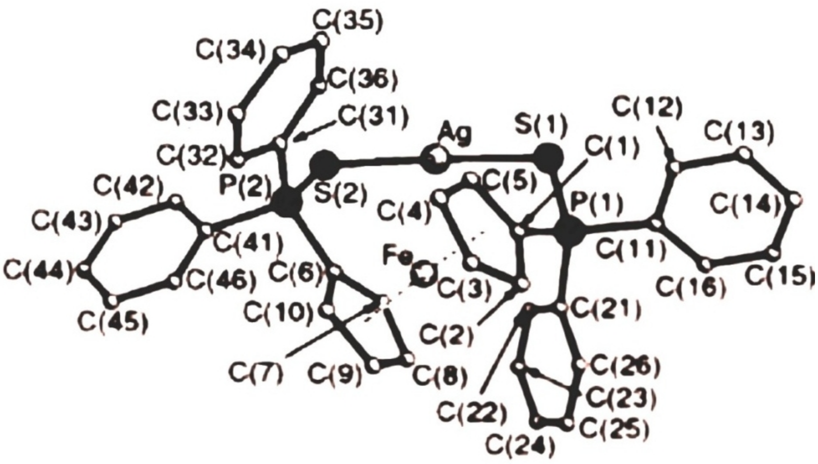

Fig. 1. Structure of $[Fe(dptpc)Ag]^+$ [5]

3. HETEROTRIMERIC COMPLEXES

There are eight heterotrimeric (Fe_2Ag (6 examples), $FeAg_2$ (1 example), FeAgW (1 example)) complexes and their structural parameters are summarized in Table 1B. Structure of red – violet complex [7] consists of a trimer cluster built up of two iron atoms and a silver atom which are positioned at the corners of an almost equilateral triangle, with the bond lengths: Fe-Fe 2.656(1), Fe(1)-Ag 2.693(1)Å, and Fe(2)-Ag 2.670(1)Å. The Fe-Fe bond is double - bridged by both a di-tert-butylphosphido ligand and a carbonyl group. Besides, the Ag atom is coordinated by a PPh_3 ligand and to each iron atom three terminal CO groups are attached.

The basic structural skeleton of dark red cluster [8] consists of an almost equilateral triangle of two iron atoms and a silver atom (Fe-Fe 2.682(1)Å, Fe-Ag 2.685(1) and 2.703(1)Å) with the Fe-Fe bond bridged by a diphenylphosphido group and a single carbon atom of a dipolar μ-η^1-alkylidene ligand $Me(H)^+N=C(Ph\ )CH$. The alkylidene ligand also coordinated to the silver atom via carbon atoms (Table 1B). In yellow Fe_2Ag complex [9] the two ferrocenophane ligands form a distorted tetrahedral arrangement about the silver atom (AgS_4). Each ferrocenophane acts as a bidentate chelate ligand. The mean Fe···Ag separation of 4.149Å ruled out a direct metal-metal bond. In the remaining three Fe_2Ag complexes [6,10,11] the four P atoms of four ferroceno phosphine ligands are directly bonded to the silver center (AgP_4).

Yellow $FeAg_2$ complex [12] is the only example which contains two silver atoms and one iron atom. In the complex two benzoate anions serve as bridges in syn-syn configuration between the silver atoms (Ag···Ag 3.346(4)Å). In addition, the 1,1´-bis (diphenylphosphino)ferrocene fragment bridges the {Ag(μ-η^2-bz)$_2$Ag} fragment via P atoms. Each silver atom has trigonal planar geometry (AgO_2P) (Fig. 2).

Dark red FeWAg complex [13] is the only example which contains three different metal atoms. The tungsten atom is „real“ center atom. The two satellites Br_2Fe and $(PPh_3)_2Ag$ are connected with the tungsten center via pairs of sulfur atoms in the manner: $Br_2Fe(\mu\text{-}S)_2W(\mu\text{-}S)_2Ag(PPh_3)_2$. The Fe-W bond distance of 2.779(1)Å is much shorter than the W-Ag distance (3.0788(7)Å). The mean Fe-S-W bridge angles of 75.5º are about 3.7º smaller than the W-S-Ag (79.2º).

4. HETEROTETRAMERIC COMPLEXES

There are four heterotetrameric (Fe_2Ag_2 (3 examples), $FeAg_3$ (1 example)) complexes and their structural parameters are gathered in Table 1C. In the orange Fe_2Ag_2 complex [14] is a bridge of azaferrocene ligands with a nearly linear coordination for the silver atoms. The Ag···Ag distance is 3.257(1)Å. Each methanol coordinated to each silver atom and completes the T-shape geometry (AgN_2O).

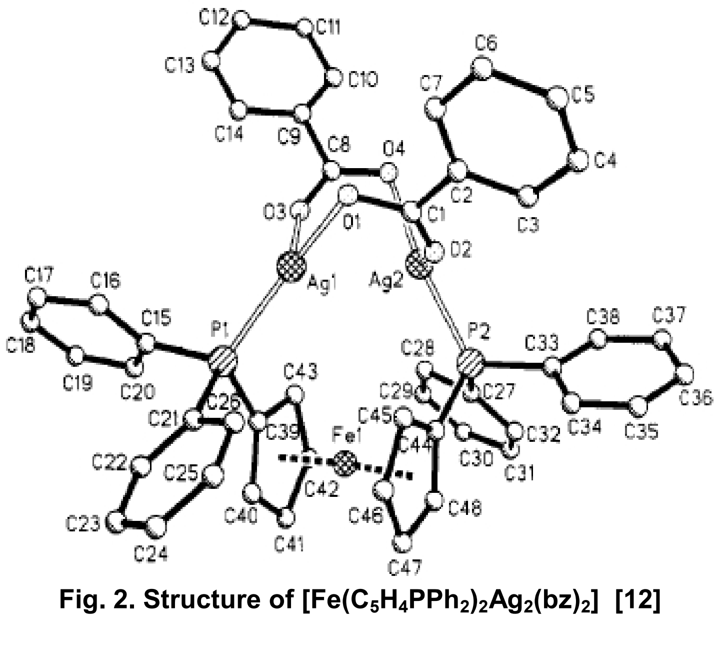

Fig. 2. Structure of [Fe(C$_5$H$_4$PPh$_2$)$_2$Ag$_2$(bz)$_2$] [12]

Table 1. Crystallographic and structural Data of heterodi-, heterotri-, heterotetra- and heteropentameric complexes[a]

Complex (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo- phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
A: Dimers								
$(PMe_3)\{Si(Me)Ph_2\}$. $(CO)_3FeAg\{PPh_2(tol)\}$ (light yellow)	tr P1̄ 2	10.931(2) 12.837(4) 15.863(7)	74.95(3) 76.63(2) 74.31(2)	FeC_3PSiAg	OC[b]1.734(9,24) Me_3P 2.199(3) Si 2.327(3)	Ag 2.581(1)	C,C[b] 140.0(4) P,Si 173.7(1) C,Ag 70.2(3,6) 173.2(3) P,Ag 96.08(9) Si,Ag 90.14(7)	3
				AgPFe	P 2.393(2)		P,Fe 175.49(7)	
$[(CO)_2Fe(\mu\text{-}\eta^1:\eta^1$- $Ph_2Ppy)_2(\mu\text{-CO})$. $Ag(\eta^1\text{-}Ph_2Ppy)]$. ClO_4 (yellow)	m $P2_1/n$ 4	14.701(1) 13.349(1) 27.780(1)	 100.03(1)	FeC_3P_2Ag	OC 1.787(7,5) µLP2.224(2,1) µOC 1.804(7)	Ag2.760(1) C 76.2(2)	C,C 110.2(3,5.1) 139.7(3) P,P 173.4(1) C,Ag 69.9(2,5.5) 169.3(3)	4
				AgN_2CPFe	µLN2.467(6,11) µOC 2.565(6) P 2.449(2)		N,N 122.5(2) N,P 108.0(1,2.5) N,Fe 85.4(1,5) P,Fe 149.6(1)	
$[Fe(\mu\text{-}\eta^5:\eta^1\text{-dptpc})_2$. $Ag]CH_2Cl_2$ (yellow) (at 173 K)	or $Pna2_1$ 4	25.943(2) 12.121(1) 11.292(2)		FeC_{10}	η^5C not given		not given	5
				AgS_2	η^1S 2.381(1,0)		S,S 176.83(5)	
$Fe(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4PPh_2)_2$. $Ag(\eta^2$-phen) (yellow) (at 143 K)	m $P2_1/n$ 4	11.027(2) 17.050(3) 21.029(5)	 95.09(3)	FeC_{10}	η^5C not given		not given	6
				AgN_2P_2	η^2N 2.352(3,9) η^1P 2.411(1) 2.507(1)		N,N 70.85(10)[c] P,P 110.59(3) N,P 94.52(7) 118.7(1,1) 138.69(7)	
B: Trimers								
$(CO)_4(\mu\text{-CO})(\mu\text{-}PBu^t_2)$.	tr	12.714(2)	96.79(1)	FeC_4PAgFe	OC 1.783(9,34)	Ag2.682(1,12)	C,C 93.1(4,9.5)	7

Complex (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo- phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
$Fe_2Ag(PPh_3)$ (red violet)	$P\bar{1}$ 2	14.667(2) 10.121(2)	113.14(2) 88.68(1)	(x2) $AgPFe_2$	μOC 1.964(7,22) μP 2.273(2,2) Ph_3P 2.404(2)	Fe 2.656(1) C not given P 71.51(6)	169.4(3,2.3) μC,P 81.6(2,4) C,P 99.1(3,2.7) μC,Ag 96.5(2,9) μC,Fe 47.5(2,7) P,Fe 149.9(1,4.7) Fe,Fe 59.36(2)	
$[(CO)_6Fe_2\{\mu\text{-}CHC.(NHMe)Ph\}(\mu\text{-}PPh_2).Ag]ClO_4.C_6H_6.tol$ (dark red)	tr $P\bar{1}$ 2	14.101(3) 10.654(4) 15.777(4)	93.68(2) 114.27(2) 95.03(3)	FeC_4PAgFe (x2) AgC_2Fe_2	OC 1.794(7,32) μC 2.066(6,18) μP 2.226(2,9) C 2.505(12,2)	Ag2.694(1,9) Fe 2.682(1) C 81.0(0) P 74.1(0)	C,C 93.7(3,4.5) 168.7(2,8) μC,P 77.2(1,5) C,P 96.1(2,3.7) 166.0(2,1.5) μC,Ag 97.2(1,2) μC,Fe 49.6(1,6) Fe,Fe 59.7(0)	8
$[\{Fe(\mu\text{-}\eta^{10}:\eta^2\text{-}C_{13}H_{14}S_2)\}_2Ag]BF_4$ (yellow)	tr $P\bar{1}$ 2	11.347(2) 11.849(5) 12.025(8)	62.66(3) 81.68(3) 81.87(3)	FeC_{10}(x2) AgS_4	C 2.054 S 2.611(3,30)	Ag4.149(2,44)	not given S,S 91.7(1,9)[d] 103.9-144.9(1)	9
$[\{Fe(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4.PPh_2)_2\}_2Ag].2CHCl_3$ (yellow) (at 143 K)	tr $P\bar{1}$ 2	11.411(2) 16.517(3) 18.600(4)	98.20(2) 94.59(2) 107.45(2)	FeC_{10}(x2) AgP_4	C not given P 2.555(2,6) 2.593(2,9)		not given P,P 109.4(-,8.4)	6
$[\{Fe(\mu\text{-}\eta^5:\eta^1\text{-}Me_4.C_4P)_2\}_2Ag].(tcnq)$ (dark blue)	tr $P\bar{1}$ 1	13.547(2) 13.729(1) 15.415(3)	98.55(1) 106.33(1) 113.92(1)	FeC_{10}(x2) AgP_4	C not given P 2.500(5,7) 2.529(3,5)		not given P,P 95.4(2,1) 116.9(2,5.3)	10
$[\{Fe\{\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4PO_2(CH_2)_2C.Me_2\}_2\}_2Ag]BF_4$				FeC_{10}(x2) AgP_4	C not given P not given		not given P,P 99.11(-,8)	11

Complex (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo- phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
(yellow)								
Fe(μ-η^5:η^1-C_5H_4.	or	10.532(2)		FeC_{10}	C not given		not given	12
$PPh_2)_2Ag_2$(μ-bz)$_2$	Pbca	18.851(9)						
(yellow)	8	41.74(2)		AgO_2P	O 2.201(9,19)	Ag 3.346(4)	O,O 103.7(4,3.0)	
				(x2)	2.439(8,39)		O,P 103.0(3,4.9)	
					η^1P 2.352(4,12)		151.6(2,7)	
Br_2Fe(μ-S)$_2$W.	tr	13.527(4)	104.91(3)	FeS_2Br_2W	μS 2.305(3,1)	W 2.779(1)	S,S 102.06(9)	13
(μ-S)$_2$Ag($PPh_3)_2$	$P\bar{1}$	15.592(5)	94.72(3)		Br 2.351(2,0)	S 75.5(1,1)	Br,Br 110.68(8)	
(dark red)	2	12.429(6)	101.19(2)				S,Br 111.0(1,1.6)	
				WS_4	μS 2.189(2,5)	Ag3.0788(7)	S,S 109.5(1,3.6)	
					2.232(2,5)	S 79.2(1,7)		
				AgS_2P_2	μS 2.616(2,27)		S,S 88.56(7)	
					Ph_3P 2.487(3,1)		P,P 118.27(7)	
							S,P 111.4(1,5.2)	
C. Tetramers								
[Fe(μ-η^5:η^1-$C_4H_4N)_2$.	tr	8.333(1)	76.02(1)	FeC_8N_2	η^5C 2.057(2,31)		N,N 108.3(1)	14
Ag(MeOH)]$_2$($BF_4)_2$	$P\bar{1}$	9.602(1)	77.89(1)	(x2)	μN 2.014(2,1)			
(orange)	1	13.522(2)	81.15(1)	AgN_2O	η^1N 2.108(2,1)	Ag 3.257(1)	N,N 178.3(1)	
				(x2)	O 2.631(2)		N,O 90.3(1,2.3)	
[Fe(μ-η^5:η^1-C_5H_4P.	m	13.908(5)		FeC_{10}	η^5C 2.04(1,1)		not given	12
$Ph_2)_2$Ag(ONO_2)]$_2$.	$P2_1/n$	15.629(9)	102.07(2)	(x2)				
$2CHCl_3$	2	18.674(9)		AgP_2O	η^1P 2.434(3,1)	Ag 3.936(2)	P,P 140.1(1)	
(yellow)				(x2)	O 2.476(8)		P,O 103.3(2,3.1)	
[Fe(μ-η^5:η^1-C_5H_4.	tr	10.489(2)	91.60(2)	FeC_{10}	η^5C not given		not given	15
Py)$_2$Ag(μ-$OClO_3$)]$_2$	$P\bar{1}$	11.340(3)	113.29(1)	(x2)				
(orange red)	1	8.789(2)	83.52(2)	AgO_2N_2	μO 2.81(1,8)	O 111.9(2)	O,O 68.1(2)	
				(x2)	2.16(1,2)		N,N 163.1(2)	
							O,N 96.4(2,3.6)	
[Fe(μ-η^2:η^2-	trg	19.984(6)		FeO_6	η^2O 2.003(6,7)		O,O 77.8(3)[c]	16
$O_2C_2S_2)_3${Ag($PPh_3)_2$}$_3$]	P3						95.1(3,9.1)	
(not given)	2	15.302(11)					161.0(4)	
				AgS_2P_2	η^2S 2.587(3,12)		S,S 83.3(1)[c]	

Complex (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
				(x3)	Ph_3P 2.468(2,13)		P,P 115.2(1) S,P 107.8(1,8.2) 121.7(1,4.3)	
D: Pentamers								
[{(η^5-cp)$_2$Fe$_2$(μ-η^{10}:η^2-eimp)$_2$}$_2$Ag] (orange)		not given		FeC_{10} (x4) AgN_4	C not given η^2N 2.344(6,0)		not given N,N 76.3(2)^c 128.2(2)	17
[Fe$_3$(μ-η^5:η^1-C$_5$H$_4$PPh$_2$)$_6$Ag$_2$].(PF$_6$)$_2$ (golden)	tr P$\bar{1}$ 1	13.410(4) 13.417(4) 15.163(5)	77.74(3) 75.94(3) 72.58(3)	FeC_{10} (x3) AgP_3 (x2)	η^5C 2.07(3,1) η^1P 2.486(7,32)		not given P,P 105.6(2) 127.2(2,3.5)	18
[Fe$_3$(μ-η^5:η^1-C$_5$H$_4$ PPh$_2$)$_6$Ag$_2$.(HCOO)$_2$].2CH$_2$Cl$_2$ (not given)	m C2/c 4	41.79(1) 10.70(1) 24.73(1)	 110.43(2)	FeC_{10} (x3) AgP_3O (x2)	η^5C 2.05(2,1) η^1P 2.521(5,25) O 2.65(2)		not given P,P 113.6(2,4.3) P,O 89.9(3) 111.4(3,8.4)	12

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated, The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean value, b. The chemical identity of coordinated atom / ligand is specified in these columns. c. The five-membered metallocyclic ring, d. The six-membered metallocyclic ring.

Yellow Fe_2Ag_2 complex [12] has the bridging coordination mode of $Fe(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4PPh_2)_2$ moieties with a bent P-Ag-P angle of 140.1(1)º. The Ag-Ag distance is 3.936(2)Å. There is a three coordination sphere around the silver atoms, with the third coordination site occupied by an oxygen atom of nitrate anion (AgP_2O). Structure of orange red Fe_2Ag_2 complex [15] consists of two $Fe(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4py)_2Ag$ fragments linked by two perchlorate anions. Each iron atom is sandwiched and both silver atoms are four-AgO_2N_2 coordinated. The Ag-O-Ag bridge angle is 111.9(2)º.

In an $FeAg_3$ complex [16] (Fig. 3) the central iron(III) atom is octahedral coordinated by three dithiooxalate ligands via oxygen atoms (FeO_6). The $Ag(PPh_3)_2$ moieties interact also with the dithiooxalate ligands, but now via the sulphur atoms. Each silver atom is four- AgS_2P_2 coordinated. The chelate angle of 77.8º for O-Fe-O is narrower than that for the S-Ag-S´ (83.3º).

5. HETEROPENTAMERIC COMPLEXES

There are three heteropentameric (Fe_4Ag (1 example), Fe_3Ag_2 (2 examples)) complexes (Table 1D). Crystals of the orange [{(cp)$_2$Fe$_2$(μ-eimp)}$_2$Ag] [17] belongs to the highly unusual cubic system (F43d) (Fig. 4). The complex involves a distorted tetrahedral configuration of the four imino nitrogens of the two eimp ligands around the central silver atom in a helical arrangement. The ferrocene units and the aromatic rings are situated in an α-helical array around silver atom.

Structure of golden Fe_3Ag_2 complex [18] contains well separated $[Fe_3(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4PPh_2)_6Ag_2]^{2+}$ cations and PF_6 anions. In a dicationic molecular core compressing two $\{Fe(C_5H_4PPh_2)_2\}$ moieties singly bridged by a $Fe(C_5H_4PPh_2)_2$ group. The crystallographically imposed C_2 symmetry of the structure implies a symmetrical disposition of the bridging $Fe(C_5H_4PPh_2)_2$ group with respect to the two Ag(1) moieties (cp···cp torsion twist 180º). The different steric demands of $Fe(C_5H_4PPh_2)_2$ groups in bridging and chelating modes impose some significant distortion on the trigonal planar Ag(1) centers (P-Ag-P bond angles range from 105.6(2) to 130.7(2)º).

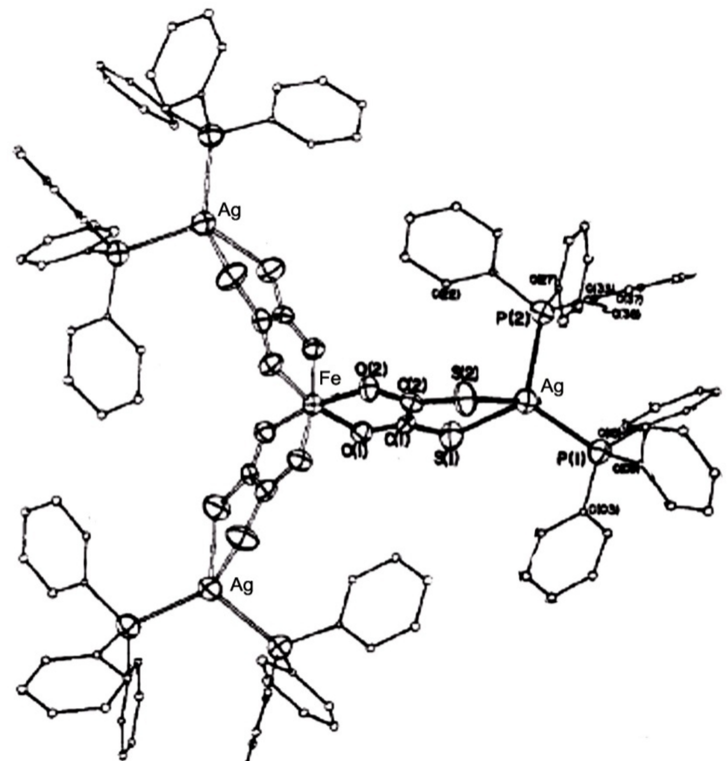

Fig. 3. Structure of $[Fe(O_2C_2S_2)_3\{Ag(PPh_3)_2\}_3]$ [16]

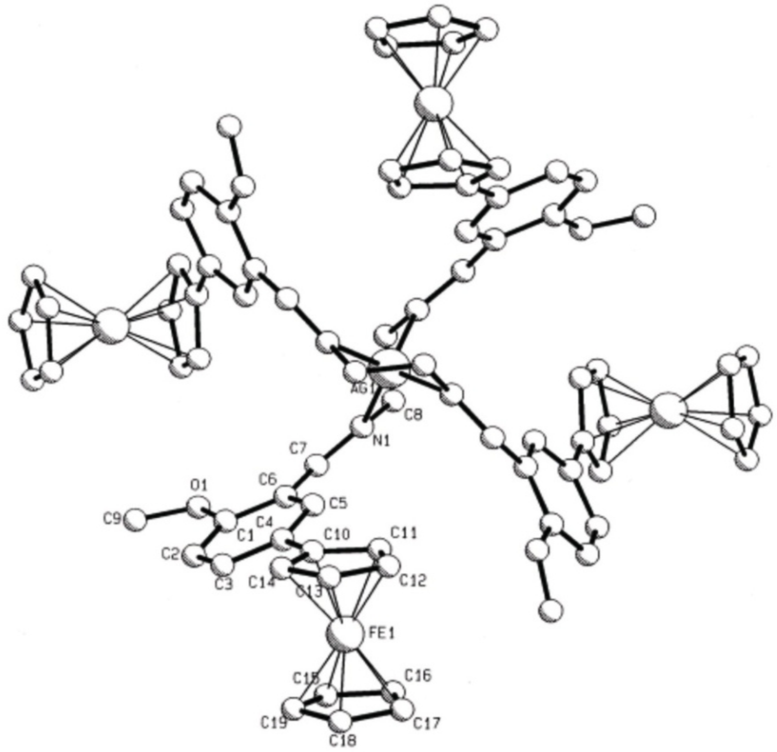

Fig. 4. Structure of [{(cp)$_2$Fe$_2$(eimp)$_2$}$_2$Ag] [17]

Structure of another Fe_3Ag_2 complex [12] consists of a {Fe($C_5H_4PPh_2)_2$} ligand symmetrically bridged between two {Fe($C_5H_4PPh_2)_2$Ag(HCOO)} moieties. The molecule is centrosymmetric with Fe(2) lying on a center of symmetry. Each Ag(1) atom is four-AgP_3O coordinated, and iron atoms are sandwiched (FeC_{10}).

Inspection of the data in Table 1 reveals that here are heterometallics which contains the following metal cores: FeAg; Fe_2Ag, $FeAg_2$, FeAgW; Fe_2Ag_2, $FeAg_3$; Fe_4Ag. Fe_3Ag_2. The inner coordination spheres about the iron atoms are: FeS_2Br_2W, FeO_6, FeC_4Ag_2, FeC_3P_2Ag, FeC_3PSiAg, FeO_5N_2, FeC_4Ag_3, FeC_4PAgFe, FeC_{10} and FeC_8N_2. The mean Fe-L bond distance elongated in the order: 1.795Å (CO) < 1.965Å (μ-CO) < 2.11Å (OL) < 2.20Å (PPh_3)< 2.225Å (μ-PL) < 2.327Å (SiL) < 2.35Å (Br). The inner coordination spheres about the silver atoms are: AgS_2, $AgFe_2$; AgPFe; AgP_3, AgO_2X (X=C or P), AgN_2O, AgP_2O, $AgPFe_2$; AgX_4 (X=N, S or P), AgP_3O, AgN_2X_2 (X=O, P or Ag), AgS_2P_2, AgC_3Fe_2; AgN_2CPFe; AgO_6, AgC_4S_2, $AgFe_2Ag_4$. The mean Ag-L bond distance elongated in the order: 2.35Å (bi-OL) < 2.35Å (bi-NL) < 2.440Å (PL) < 2.52Å (OL) < 2.525Å (bi-SL) < 2.81Å (μ-OL). There are heterodonor ligands which serve as bridge'/s between Fe and Ag in the manner (Fe:Ag):η^1P:η^1N, η^1C:η^2C, η^2O:η^1C, η^2O:η^2S, η^5C:η^1N, η^5C:η^1S; η^5C:η^1P, η^{10}C:η^2N and η^{10}C:η^2S. The mean M-M bond distance elongated in the order 2.664Å (Fe-Ag) < 2.670Å (Fe-Fe) < 2.790Å (Ag-Ag) < 2.780Å (Fe-W) < 3.08Å (Ag-W). The complexes crystallized in the crystal classes: triclinic (x10), monoclinic (x5), orthorhombic (x2) and trigonal (x1).

6. HETEROOLIGO- AND HETEROPOLYMERIC COMPLEXES

Crystalographic and structural parameters for heterooligo - complexes are gathered in Table 2A. Structure of the orange Fe_2Ag_4 complex [19] which is centrosymmetric, comprises two {(Fe($C_5H_4PPh_2)_2Ag_2(ac)_2$}$_2$ moieties linked by two oxygen sites [O(1) and O(1a)], thus resulting in two triple bridging acetates. The four Ag(1) centers are arranged in an approximate chair conformation together with the acetates. The structure may also be viewed in a fashion of three metallocyclic rings, consisting of a planar four- membered {Ag_2O_2} ring sandwiched by two six- membered rings. The silver atoms are tetrahedrally coordinated by three basal oxygen atoms and an apical phosphorus atom. Iron atoms are sandwiched. The Ag···Ag separation is 3.104(1)Å.

Structure of $Fe_2Pd_2Ag_2$ aggregate [20] consists of a $\{Pd_2S_2\}$ molecular square with two AgCl „fails" dangling from the sulfur sites on opposite faces of the plane. A chelating $\{Fe(C_5H_4PPh_2)_2\}$ molecule is on each Pd atom. Each iron is sandwiched (FeC_{10}), the Pd atoms have a square-planar arrangement (PdS_2P_2) and each Ag atom is an almost linear (Cl-Ag-S, 178.1(1)º).

Structure of dark red Fe_6Ag complex [21] contains well separated $[\{(cp)_2(CO)_2(\mu\text{-}CO)Fe_2(\mu\text{-}\eta^2\text{-}CS)\}_3Ag]^+$ cations and BF_4 anions. In the complex cation, three $\{(cp)_2(\mu\text{-}CO)Fe_2(\mu\text{-}\eta^2\text{-}CS)\}$ fragments are connected by a silver atom, which is surrounded by three S atoms of the CS ligands (Fig. 5). The mean Fe-Fe bond distance is 2.503Å.

In $[(cp)Fe(C_5H_4CH_2NMe_2)Ag]_4$ [22] each $\{(cp)Fe(C_5H_4CH_2NMe_2\}$ moiety serves as bridge between two Ag(1) atoms by amine donor. Four Ag(1) atoms form plane square. Unfortunately, structural parameters are not available. Structure of pale yellow Fe_4Ag_4 cluster [23] contains well separated $(NMeCH_2Ph)^+$ cations and $[Ag_4\{\mu\text{-}Fe(CO)_4\}_4]^{4-}$ anion. The molecular structure of the anion consists of an Ag_4 square, spanned on all the edges, by $Fe(CO)_4$ groups. The idealized molecular symmetry is D_{4h}. The Ag-Fe bond distances range from 2.570(2) to 2.600(2)Å (av. 2.581Å). The Ag-Ag interactions are distributed over the range 3.036 – 3.334(1)Å.

Structure of $[Ag_5\{\mu\text{-}Fe(CO)_4\}_2\{\mu\text{-}Fe(CO)_4\}_2]^{3-}$ [23] contains a planar cluster of nine metal atoms packed in a rhombus. The iron atoms define the vertices and the silver atoms are placed almost midway along the edges and in the center. Both the idealized and crystallographic symmetry of the anion is D_{2h}. The silver atoms define a bow tie with four equivalent atoms at the corners and unique central atoms. The latter is six-coordinated to four silver and two iron atoms. (Ag(1) – Ag(2) 2.975(1)Å and Ag(1) – Fe 2.727(1)Å. The corner atoms are four-coordinated with two Ag···Ag and two Ag···Fe interactions. The Ag···Ag distance bridged by the $Fe(CO)_4$ group of 3.017(1)Å is longer than the values above. The $Fe(CO)_4$ groups form two independent pairs, both form to a precise C_{2v} symmetry. The Fe(1) and Fe(1)' are three connected to the silver atoms resulting in the distorted pentagonal - bipyramid (FeC_4Ag_3). The Fe(2) and Fe(2)' atoms are two connected and realize octahedral like coordination (FeC_4Ag_2). The values of Ag-Fe bond distances are 2.585(1)Å for the six coordination Fe(2) and for the seven coordination Fe(1) the values are 2.650(1) and 2.727(1)Å.

The molecule of dark red $[\{(CO)_4Fe\}_3Ag_6\{\mu\text{-}\eta^3\text{-}CH(PPh_2)_3\}].2Me_2CO$ [24] has no crystallographically imposed symmetry, but the skeletal atoms have approximately C_3 symmetry. The silver atoms define a distorted octahedron with the trigonal $CH(PPh_2)_3$ ligand coordinated to three silver atoms on the face of the octahedron. These silver atoms {Ag(1), Ag(2) and Ag(3)} are separated by 3.288(1)Å.

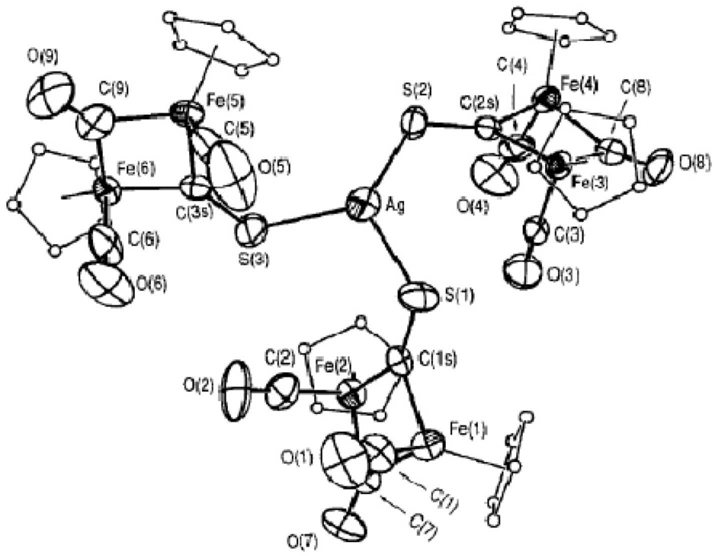

Fig. 5. Structure of $[\{(cp)_2(CO)_3Fe_2(CS)\}_3Ag]$ [21]

The remaining Ag···Ag distances lie in the range 2.817(1) – 3.065(1)Å (av. 2.909(1)Å). The three $Fe(CO)_4$ fragments cap three of the faces of the octahedron in a symmetrical fashion. The Fe-Ag bond distances lie in a narrow range 2.660(1) – 2.720(1)Å. In view of the long Ag...Ag distances associated with the silver atoms coordinated to the tripodal ligand, the cluster geometry can be described as a triangle of vertex linked Ag_3Fe tetrahedral.

There are four heteropolymeric $\{FeAg\}_n$ complexes (Table 2B). In dark red monoclinic $[Fe(acac)_3Ag(OClO)_3(H_2O)]$ [25] the $Fe(acac)_3$ moieties arranged in a staggered array along 2 axis to form a bulky sheet – like structure parallel to the bc plane. These sheets create „cylindrical holes“ in a direction parallel to y. These „holes“ are filled with Ag(I) and perchlorate ions. The Fe(III) atom is six- (FeO_6) coordinated build up by three bidentate chelating acac ligands. Each Ag(I) atom is surrounded by a monodentate perchlorate oxygen, the hydrate oxygen and the central carbon atom of one acac ring (AgO_2C). In yellow brown monoclinic $\{Fe(edta)Ag(H_2O)_3\}_n$ complex (Fig. 6) [26] the Fe(III) atom is surrounded by four O atoms and two N atom of an edta ligand, which acts in a six- dentate fashion and by a water molecule (FeO_5N_2). The coordination polyhedron is of roughly pentagonal bipyramid shape. Each Ag(I) atom is six- AgO_6, coordinated. The anions form layers along a crystallographic plane. Single layers are loosely linked by the cations into neutral double layers.

In linear one- dimensional polymeric $[Fe(C_5H_4S_2CNEt_2)_2Ag]ClO_4.CH_2Cl_2$ [27], the Ag(I) centers are bonded to two sulphur atoms of different ferrocene moieties and also to the cyclopentadienyl ring in an η^2-fashion. The silver atom lies on an inversion centre and the iron atom on a two-fold axis. In structure of orange $[Fe\{CH_2(Ph_2PS)_2Ag\}_2(\mu\text{-dptdf})_2](ClO_4)_2.CH_2Cl_2$ [28] the complex cationic units to form a polymeric chain (Fig. 7). The single Ag(I) atom displays a distorted tetrahedral geometry forms by a chelating $CH_2(Ph_2PS)_2$ ligand (atoms S2 and S3) whereby one sulfur atom (S2) also forms a bridge to an adjacent silver atom leading to four-membered Ag_2S_2 rings with inversion symmetry. The Ag···Ag separation of 3.554(1)Å ruled out a direct bond. The mean Ag-S-Ag bond angle is 83.43(6)º.

Inspection of the data in Table 2 reveals that the complexes prefer to crystallized in monoclinic (x8), tetragonal (x2) and orthorhombic (x1) crystal classes. The inner coordination spheres about the iron atoms are: FeO_6, FeO_5N_2, FeC_4Ag_3 and FeC_{10} (most common). The Ag atoms: AgClS, $AgFe_2$; AgS_3, AgO_2C; AgS_4, AgO_3P; AgN_2Ag_2, $AgFe_2Ag_2$; AgO_6, AgC_4S_2, $AgFe_2Ag_4$. The mean M-M bond distance elongated in the order: 2.503Å (Fe-Fe) < 2.654Å (Fe-Ag) < 2.806Å (Ag-Ag).

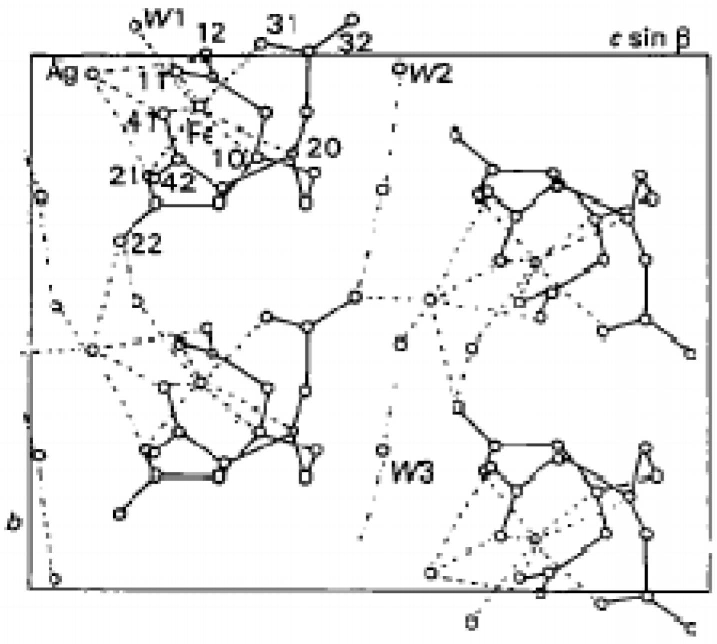

Fig. 6. Structure of $[(H_2O)Fe(edta)Ag(H_2O)_2]$ [26]

Table 2. Crystallographic and structural data for heterooligo- and heteropolymeric complexes[a]

Complex (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
A: Oligomers								
[{Fe(μ-η^5:η^1-$C_5H_4PPh_2)_2$. {Ag(μ-η^3-ac$)_2\}_2]_2$ (orange)	m $P2_1/n$ 2	10.373(2) 17.593(5) 19.754(8)	 100.66(2)	FeC_{10}(x2) AgO_3P(x4)	η^5C^b not given ac 2.376(5) μO 2.395(5,2) η^1P 2.667(5)	 Ag 3.104(1) O 75.5(1) 103.6(1)	C,C^b not given O,O 51.2-114.1(2) O,P 114.5-137.9(1)	19
[{Fe(μ-η^5:η^1-C_5H_4. $PPh_2)_2$Pd(μ_3-S)$\}_2$. $(AgCl)_2].4CH_2Cl_2$ (not given)	m $P2_1/c$ 2	13.090(1) 20.539(1) 15.744(1)	 113.16(1)	FeC_{10}(x2) PdS_2P_2(x2) AgClS(2)	η^5C not given μ_3S 2.368(1,14) η^1P 2.336(1,3) Cl 2.348(2) μ_3S 2.397(1)	 S 97.3(1) S 81.2(1,1.7)	not given S,S 82.7(1) P,P 98.1(1) S,P 89.6(1,1.9) Cl,S 178.1(1)	20
[{(η^5-cp$)_2$(CO$)_2$(μ-CO). Fe_2(μ-η^2-CS)$\}_3$Ag]BF_4 (dark red)	tr P$\bar{1}$ 2	13.771(4) 15.047(7) 12.544(4)	109.55(3) 93.77(3) 90.76(3)	FeC_8Fe (x6) AgS_3	OC 1.76(2,4) η^5C not given μOC 1.87(1,2) μSC 1.91(2,2) μCS 2.498(6,19)	Fe 2.503(2,4) C 81.6(7,1.3) 84.0(7,1.3)	C,μC 90.0(7,1.7) η^5C,μC 95.8(7,7) C,Fe 99.4(5,5) μC,Fe 48.6(6,9) S,S 109.9(2) 122.4(4,5.2)	21
[{η^5-cp)Fe(μ-η^5:η^1- $C_5H_4CH_2NMe_2$)Ag$]_4$ (not given)	tg $P42_1c$ 2	15.817 10.186		FeC_{10}(x4) AgN_2Ag_2 (x4)				22
$(PhCH_2NMe_3)_4$. [(CO$)_4$FeAg$]_4$ (pale yellow)	m $P2_1/n$ 4	11.419(4) 29.714(5) 19.227(3)	 92.40(2)	FeC_4Ag_2 (x4) $AgFe_2$(x4)	OC 1.75(1,8)	Ag2.581(2,19) Ag3.043(1,7) 3.254(1,80)	C,C 103.0(6,2.9) 135.4(6,2.5) Ag,Ag 75.2(1,5.5) Fe,Fe 165.4(1,3.9) Ag,Ag 90.0(1,2.6)	23
$(NEt_4)_3[Ag_5$\{μ- Fe(CO$)_4\}_2\{\mu_3$-Fe. (CO$)_4\}_2$] (yellow)	tg $P4_2/mnm$ 2	14.004(1) 14.278(1)		FeC_4Ag_3 (x2) FeC_4Ag_2 (x2)	OC 1.771(7,1) OC 1.740(8,8)	Ag 2.650(1) 2.727(1) Ag 2.585(1)	C,C 94.4(6) 141.4(6) Ag,Ag 62.6(1) C,C 107.3(5) 141.2(7) Ag,Ag 71.4(1)	23

Complex (colour)	Crys.cl Sp.Gr. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo- phore	M-L [Å]	M-M [Å] M-L-M [°]	L-M-L [°]	Ref
				$AgFe_2Ag_2$ (x4) $AgFe_2Ag_4$		Ag 2.795(1) 3.017(1)	 Ag,Ag 65.3(1)	
[{$(CO)_4Fe$})$_3Ag_6$. {μ-η^3-CH($PPh_2)_3$}]. $2Me_2CO$ (dark red)	m $P2_1/c$ 4	12.168(2) 20.473(4) 24.425(3)	 91.65(2)	FeC_4Ag_3 (x3) AgPFe (x6)	OC not given P not given	Ag2.670(1,15) 2.711(1,9) Ag 2.817- 3.415(1)	C,C 99-120(2)	24
B: Polymers								
[Fe(μ-acac)$_3$Ag. ($OClO_3$)(H_2O)] (dark red)	m $P2_1/c$ 4	12.274(5) 11.751(5) 17.235(5)	 120.64(12)	$Fe^{III}O_6$ Ag^IO_2C	η^2O 2.00(1,3) H_2O 2.25(2) O_3ClO 2.50(2) LC 2.29(2)		O,O 88.0(4,1.6)[c] 90.5(4,3.2) 176.7(4,3.1) O,O 100.5(4) O,C 86.0(4)	25
[(H_2O)Fe(μ-edta). Ag($H_2O)_2$] (yellow brown)	m C_c 4	8.928(4) 11.871(1) 15.116(2	 99.85(2)	$Fe^{III}O_5N_2$ Ag^IO_6	LO 1.957(7) 2.052(7,49) LμO2.079(6) LμN 2.340(8,2) H_2O 2.109(7) LO 2.351(7) 2.558(7,56) LμO 2.673(6) H_2O 2.334(7)		not given not given	26
[Fe(μ-cpS $_2$CNEt$_2)_2$. Ag]$ClO_4.CH_2Cl_2$ (yellow) (at 173 K)	m P2/c 4	20.066(5) 9.859(3) 18.463(5)	 113.02(2)	FeC_{10} Ag´C_4S_2	cpC not given cpμC 2.972(8) 3.027(8) S 2.286(3,0)		not given not given	27
[{$CH_2(Ph_2PS)_2Ag$}$_2$. (μ-dptdf)$_2$]($ClO_4)_2$. CH_2Cl_2 (orange) (at 173 K)	m C2/c 4	26.933(4) 11.209(2) 31.404(3)	 105.74(1)	FeC_{10} Ag^IS_4	cpC not given S 2.524(2,2) μS 2.530(2) 2.801(2)		not given S,S 99.3(1,5.7) 125.0(1,4.8)	28

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated, The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean, b. The chemical identity of coordinated atom / ligand is specified in these columns, c. The six-membered metallocyclic ring

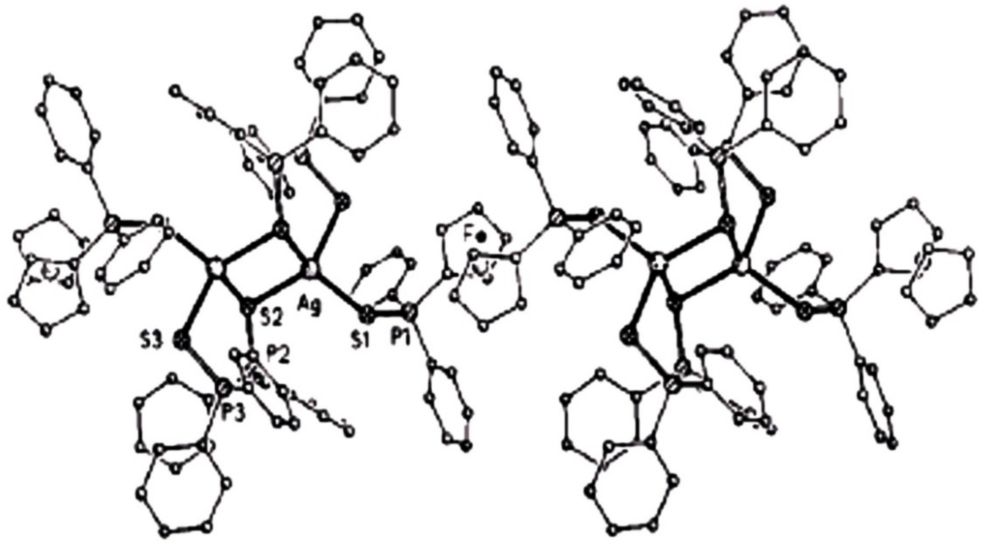

Fig. 7. Structure of $[\{CH_2(Ph_2PS)_2Ag\}_2(dptdf)_2]_n^{2+}$ [28]

7. CONCLUSION

There are thirty heterometallic iron/silver complexes in this review. The numbers of the FeAg examples are much less than those of the FeAu [1] and FeCu [2] with over 90 examples of each of the respective complexes. However, it is interesting that the heterometallic FeM (M=Cu, Ag, Au) complexes prefer to crystallized in the two crystal classes: monoclinic (43% (M=Cu), 43.3% (Ag), 61.7% (Au) and triclinic (41%, 36.7%, 29.8%)), respectively. Similar trend exists in the chemistry of the heterometallic PtM (M=Ag [29], Au [30], Cu [31]). These complexes also prefer crystallized in the same crystal classes: monoclinic (48%) and triclinic (35%). The coordination numbers about the metal atoms are: around iron atoms from five to ten, (FeC_{10}) is the most common; around copper atoms from two to six, with six is the most common; around silver and gold atoms from two to six, with four is the most common. The ligands can be divided into the three groups, the first one which are coordinated only to the iron atoms and the second group which bound only to M atom. The mean Fe-L and M-L bond distances elongated in the orders:

(Fe-L) : 1.77Å (μ-O, CO) < 1.925Å (CN) < 1.95Å (μ-CO) < 1.97Å (tetra-OL) < 2.01Å (CL) < 2.02Å (NL) < 2.04Å (penta-CL) < 2.045Å (OL) < 2.07Å (ter-CL) < 2.09Å (tetra-NL, ter-CL) < 2.21Å (PL) < 2.215Å (di-NL) < 2.225Å (μ-PL) < 2.235Å (Cl) < 2.33Å (SiL);

(Cu-L): 2.00Å (NL) < 2.01Å (di-NL, tetra-NL) < 2.02Å (ter-NL) < 2.15Å (Cl) < 2.22Å (di-SL) < 2.235Å (PL) < 2.34Å (OL) < 2.355Å (AsL) < 2.41Å (μ-Cl) < 2.44Å (I) < 2.74Å (μ-I); (Ag-L): 2.35Å (di-OL), di-NL, Cl) < 2.44Å (PL) < 2.45Å (OL) < 2.525Å (di-Sl) < 2.81Å (μ-OL);

(Au-L): 2.02Å (di-Cl) < 2.065Å (CL) < 2.08Å (OL) < 2.15Å (di-NL) < 2.25Å (μ_3-CL) < 2.29Å (Cl, PPh_3; di-SL) < 2.305Å (di-PL)< 2.335Å (μ-S) < 2.35Å (μ_3-S, I).

The third type of the ligands which serve as bridge / s are mostly heterodonors, coordinated in the manner (Fe : M) : η^1C : η^1N, η^1O : η^1O; η^1P : η^1N, η^1C : η^2C, η^2O : η^1O, η^2O : η^1C, η^2O : η^2S, η^5C :

η^1O, η^5C : η^1N, η^5C : η^1S, η^5C : η^1P, η^5C : η^1S, η^5C : η^2S, η^{10}C : η^2N and η^{10}C : η^2S.

The mean M-M bond distances elongated in the sequences:

in Fe/Cu complexes: 2.520Å (Fe-Cu) < 2.638Å (Cu-Cu) < 2.663Å (Fe-Fe);
in Fe/Ag complexes: 2.614Å (Fe-Fe) < 2.660Å (Fe-Ag) < 2.806Å (Ag-Ag);
in Fe/Au complexes: 2.668Å (Fe-Fe) < 2.680Å (Fe-Au) < 2.898Å (Au-Au).

As can be seen, the Fe-M as well as M-M bond distances elongated in the order of M (Cu < Ag < Au), and the mean Fe-Fe bonds (Ag < Cu < Au).

In PtM complexes the mean M-M bond distances elongated in the sequences:

in PtCu complexes: 2.673Å (Cu-Cu) < 2.693Å (Pt-Pt) < 2.727Å (Pt-Cu);
in PtAg complexes: 2.740Å (Pt-Pt) < 2.820Å (Pt-Ag) < 2.943Å (Pt-Au);
in PtAu complexes: 2.720Å (Pt-Au) < 2.742Å (Pt-Pt) < 2.802Å (Pt-Au)

In the series of PtM complexes, the order of Pt-M and M-M bond distances is: M = Cu < Au < Ag; and the mean of Pt-Pt bonds (Cu < Ag < Au).

It is hoped that such review will help to focus attention on areas of heterometallic complexes that could be enhanced by further study and assist in allowing comparative behaviors of the iron and the 1 B subgroup metal atoms which can arise from the widespread use of the respective heterometal atoms.

ACKNOWLEDGEMENTS

This work was supported by the projects VEGA 1/0664/12 and KEGA 031UK-4/2012.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1a. Holloway CE, Melník M. Crystallographic and Structural Characterization of Heterometallic Platinum Compounds. Part I. Heterobinuclear Pt Compounds, Centr. Eur. J. Chem. 2011;9:5601-549.

1b. Melník M, Mikuš P, Part II. Heterobinuclear Pt Compounds, ibid. 2012;10:1709-1759.

1c. Melník M, Mikuš P. Part III. Heterotrinuclear Pt Clusters, ibid, 2013;11:827-900.

1d. Melník M, Mikuš P. Part IV. Heterotetranuclear Pt Clusters, ibid, 2013;11:1902-1953.

1e. Melník M, Mikuš P. Part V. Heteropentanuclear Pt Clusters, ibid, 2014;12:283- 316.

1f. Melník M, Mikuš P. Part VI. Heterohexanuclear Pt Clusters, ibid, 2014;12:1101-1126.

2a. Melník M, Mikuš P. Structural Characterization of Heterometallic Gold – Iron Clusters. Int. Res. J. Pure Appl. Chem. in press.

2b. Melník M, Mikuš P. Structural Characterization of Heterometallic FeCu Complexes. Int. Res. J. Pure Appl. Chem. in press.

3. Reinhard G, Hirle B, Schubert U. Übergangsmetall-silyl-komplexe: XLII. Einfluβ des phosphan-liganden auf bildung, struktur und stabilität der hetero-zweikernkomplexe $(CO)_3(R'_3P)(R_3Si)Fe$—ML_n (M = Cu, Ag, Au, Hg). J. Organomet. Chem. 1992;427(2):173-192.

4. Li SL, Mak TC, Zhang ZZ. Synthesis and crystal structures of heterobimetallic 2-(diphenylphosphino)-pyridine complexes containing an Fe→M (M = CuI, AgI or HgII) donor–acceptor bond and a mononuclear iron(II) complex bearing a pair of planar strained four-membered chelate rings. J. Chem. Soc. Dalton Trans. 1996;16:3475-3483.

5. Gimeno MC, Jones PG, Laguna A. Sarroca C., 1,1′-Bis(diphenylthiophosphoryl) ferrocene as a *trans*- chelating ligand in gold(I) and silver(I) complexes. J. Chem. Soc. Dalton Trans. 1995;21:3563-3564.

6. Gimeno MC, Jones PG, Laguna A, Sarroca C. Synthesis of silver(I) complexes with 1,1′-bis(diphenyl-phosphino)ferrocene (dppf). Crystal structures of $[Ag(dppf)(PPh_3)]ClO_4{\cdot}2CH_2Cl_2$, $[Ag(dppf)_2]ClO_4{\cdot}2CHCl_3$ and $[Ag(dppf)(phen)]$ ClO_4(phen = 1,10-phenanthroline). J. Chem. Soc., Dalton Trans. 1995;9:1473-1481.

7. Walther B, Hartung H, Bötcher HC, Baumeister U, Böhland U, Reihold J, Sieler J, Ladriere J, Schiebel HM. Unexpected Reaction of [ni(co)4-n(r2pcl)n] (n=1, 2, R=bu-tert, Cy, Ph) With Na2[fe2(co)8] - Synthesis and Electronic-structure of the Anions [fe2(mu-co)(co)6(mu-pr2)]- and Their Reactions With H+ and [m(pph3)]+

(m=cu, Ag, Au). Polyhedron. 1991;10(20-21):2423-2435.

8. Mott GN, Taylor NJ, Carty AJ. Triangular Iron-Silver Clusters via the Addition of Silver Electrophiles to Electron-Rich Iron-Iron Bonds. Organometallics. 1983;2:447-452; Carty A.J., Mott G.N., Taylor N.J., Triangular Iron-Silver Clusters. J. Amer. Chem. Soc. 1979;101(11):3131-3133.
9. Sato M., Anano H., The transition-metal complexes of the thiamacrocycle containing two ferrocene nuclei in the main chain. Synthesis, properties, and molecular structure of Ag(I), Cu(I), Pd(II), and Pt(II) complexes of 1,5,16,21-tetrathia[5.5]ferrocenophane. J. Organomet. Chem. 1998;555(2):167-175.
10. Atwood DA, Cocley AH, Dennis SM. A diphosphaferrocene as a chelating ligand for silver(I). Inorg. Chem. 1993;32(8):1527-1528.
11. Nifantev IE, Mazhukova LF, Antipin MY, Struchkov YT, Nifantev EE. Ferrocenylenediphosphonites as ligands in the synthesis of oligonuclear heterometallic complexes. Zh. Obsch. Khim. 1995;659(5):756-760.
12. Hor TSA, Neo SP, Tan Ch. S, Mak TCW, Leung KWP, Wang RJ. Metal-metal cooperation via 1,1'-bis(diphenylphosphino)ferrocene (dppf). 1. Structurally distinctive silver(I) dppf complexes of nitrato and carboxylato ligands in variable coordination modes. Crystal structures of $[Ag(NO_3)(dppf)]_2.2CHCl_3$, $[Ag_2(HCOO)_2(dppf)_3].2CH_2Cl_2$, $[Ag_2(CH_3COO)_2(dppf)]_2$, and $Ag_2(C_6H_5COO)_2(dppf)$. Inorg. Chem. 1992;31(22):4510-4516.
13. Lin P, Huang Q, Sheng T, Wu X. The Heterotrimetallic Linear Complex Tetraethylammonium Dibromo-2κ^2Br-tetra-κ-sulfido-1:2κ^4S;1:3κ^4S-bis(triphenylphosphine-3κP)-2-iron-3-silver-1-tungsten, $[Et_4N][Br_2FeS_2WS_2Ag(PPh_3)_2]$. Acta Cryst., Sect. C. 1996;52:27-29.
14. Kuhn N, Horn EM, Boese R, Bläser D. Heterocyclen als Liganden, VI: Die verbrückende Koordination eines 1,1′-Diazaferrocens in einem zweikernigen Silberkomplex — eine ungewöhnliche Struktur. Chem. Ber. 1989;122(12):2275-2277.
15. Tani K, Mihana T, Yamagata T, Saito T. Transition metal complexes of 1,1′-Bis(2-pyridyl)ferrocene. A Cationic Rhodium(I) and a Silver(I) Complex. Preparation and Structure . Chem. Lett. 1991;20(12):2047-2050.
16. Hollander FJ, Coucouvanis D. Metal complexes as ligands. V. Crystal and molecular structures of tris(bis(triphenylphosphine)silver(I)) tris(dithiooxalato)iron(III) and -aluminum(III). Inorg. Chem. 1974;13(10):2381-2386.
17. Hall CD, Sachsinger N, Nyburg SC. Steed J.W., Redox-active schiff-base ligands. J. Organomet. Chem. 1998;561(1-2):209-219.
18. Neo SP, Hor TSA, Zhou ZJ, Mak TCW. Nitrato displacement in $[Ag_2(NO_3)_2(\mu\text{-}dppf)_2]$. Molecular structure of a homoleptic dppf complex, $[Ag_2(\mu\text{-}dppf)(dppf)_2](PF_6)_2$(dppf = 1,1′-bis(diphenylphosphino)ferrocene). J. Organomet. Chem. 1994;464(1):113-119.
19. Liu Q, Huang L, Liu H, Wu D, Ang B, Lu J. Structural chemistry of molybdenum-iron-sulfur cluster compounds with a single-cubane $[MoFe_3S_4]$n+ (n = 4-6) core and crystal structure of $[MoFe_3S_4(Me_2dtc)_5].2CH_2Cl_2$. Inorg. Chem. 1990;29(20):4131-4137.
20. Li GM, Li S, Tan AL, Wip WH, Mak TCW, Hor TSA. Heteropolymetallic aggregates from $[Pd_2(dppf)_2(\mu\text{-}S)_2]$. Bonding and structural analysis of $[Ag_2Pd_2Cl_2(dppf)_2(\mu_3\text{-}S)_2]\cdot 4CH_2Cl_2$[dppf = $Fe(C_5H_4PPh_2)_2$]—a flat $\{Pd_2S_2\}$ core with two AgCl ‘tails’. J. Chem. Soc. Dalton Trans. 1996;23:4315-4316.
21. Choi MG, Daniels LM, Angelici RJ. Cyclopentadienyl thiocarbonyl complexes of iron: $[Cp^\star Fe(CO)_2CS]^+$, $Cp^\star{}_2Fe_2(CO)_2(CS)_2$, $Cp_2Fe_2(CO)_3(CS)$, and $Cp_2Fe_2(CO)_2(CS)_2$. J. Organomet. Chem. 1990;383(1-3):321-337.
22. Moiseev SK, Meleshonkova NN, Spiridonov FM. Solid-solutions of organocopper and organosilver compounds - tetrakis-[2-(N,N-dimethylaminomethyl) ferrocenylcopper]-tetrakis-[2-(N,N-dimethylaminomethyl)ferrocenylsilver] system. Koord. Khim. 1987;13(12):1589-1592.
23. Albano VG, Azzaroni F, Iapalucci MC, Longoni G, Monari M, Mulley S, Proserpio DM, Sironi A. Synthesis, Chemical Characterization, and Bonding Analysis of the $[Ag\{Fe(CO)_4\}_2]^{3-}$, $[Ag_4\{\mu^2\text{-}Fe(CO)_4\}_4]^{4-}$, and $[Ag_5\{\mu^2\text{-}Fe(CO)_4\}_2\{\mu^3\text{-}Fe(CO)_4\}_2]^{3-}$

Cluster Anions. X-ray Structural Determination of $[NMe_3CH_2Ph]_4[Ag_4Fe_4(CO)_{16}]$ and $[NEt_4]_3[Ag_5Fe_4(CO)_{16}]$. Inorg. Chem. 1994;33(23):5320-5328.

24. Briant CF, Smith RG, Mingos DMP. Synthesis and structural characterisation of [Ag6{Fe(CO)4}(Ph2P)3CH] - A Distorted Tricapped Octahedral Silver Cluster. J. Chem. Soc. Chem. Commun. 1984;9:586-588.
25. Nasimbeni LR, Thackeray MM. Synthesis and crystal structure of the silver perchlorate adduct of iron(III) triacetylacetonate monohydrate. Acta Cryst. Sect. B. 1974;30:1072-1076.
26. Solans X, Altaba MF, Garcia OJ. Crystal structures of ethylenediaminetetraacetato metal complexes. V. Structures containing the $[Fe(C_{10}H_{12}N_2O_8)(H_2O)]^-$ anion. Acta Cryst. Sect. C. 1984;40:635-638.
27. Crespo O, Gimeno MC, Jones PG, Laguna A, Sarroca C. A double sandwich silver(I) polymer with 1,1'-bis(diethyldithiocarbamate)-ferrocene, Chemical Commun. 1998;14:1481-1482.
28. Gimeno MC, Jones PG, Laguna A, Sarroca C. Co-ordination chemistry of 1,1′-bis(diphenylthiophosphoryl)ferrocene (dptpf) towards silver(I). Crystal structure of the polymeric complex $[Ag_2(\mu\text{-dptpf})\{(SPPh_2)_2CH_2\}_2]_n[ClO_4]_{2n}$‡. J. Chem.Soc., Dalton Trans. 1998;8:1277-1280.
29. Melník M, Mikuš P. Structural Characterization of heterometallic PtAg complexes. New developments in chromophore research. Editors: A. Moliere and E. Vigneron, Chapter 3, Nova Science Publishers Inc. 2013, ISBN: 978-1-62417-154-3
30. Melník M, Mikuš P. Structural characterization of heterometallic PtAu complexes. New developments in chromophore research. Editors: A. Moliere and E. Vigneron, Chapter 6, Nova Science Publishers Inc. 2013, ISBN: 978-1-62417-154-3.
31. Melník M, Mikuš P. Structural characterization of heterometallic PtCu Complexes. New developments in chromophore research. Editors: A. Moliere and E. Vigneron, Chapter 9, Nova Science Publishers Inc. 2013, ISBN: 978-1-62417-154-3

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=807&id=7&aid=6838