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CLASSIFICATION AND ANALYSIS OF GOLD COMPOUNDS ON THE BASIS OF THEIR X-RAY STRUCTURAL AND MÖSSBAUER SPECTROSCOPIC DATA

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CONTENTS

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ABBREVIATIONS

ae	2-aminoethyl
aliz	alizarinsulphonate
AP	(*o*-allylphenyl)diphenylphosphine
$AsPh_3$	triphenylarsine
$AsPh_4$	tetraphenylarsonium
azt	4,4′-azotoluene
$bbzim^{2-}$	2,2′-bibenzimidazolate
$BH_2[P(CH_3)_2CH_2]_2$	boronato-bis(dimethylphosphoniummethylide)
bipy	2,2′-bipyridyl
biq	2,2′-biquinolyl
BPh_4^-	tetraphenylborate
bpte	1,2-bis(phenylthio)ethane
$Bu_2MeP(CH_2)_2$	di-(t-butyl)-methylphosphoniummethylide
$n\text{-}Bu_4N^+$	tetra-n-butylammonium
$[HC(CF_3)]_2$	(trifluoromethyl)ethylene
$C_5(CO_2Me)_5$	pentakis(methoxycarbonyl)cyclopentadiene
C_4F_6	hexafluorobut-2-yne
$C_6F_5^-$	pentafluorophenyl
C_5H_5	cyclopentadienyl
$(C_6H_5CH_2)_2S$	dibenzylsulfide
$(t,t\text{-}p\text{-}CH_3C_6H_4NH)_2C$	(*trans,trans-p*-tolylimino)methyl
CH_3CSS^-	dithioacetate
$C_2H_{10}N_2^{2+}$	ethylenediammonium
$(i\text{-}C_3H_7O)_2PS_2$	bis(μ-*O,O′*-diisopropyl)dithiophosphate
$(CH_2)_4P(CH_2)_2$	1-methyl-1-methylen-1λ^5-phospholane
$CH[P(CH_3)_2CH_2]_2$	methanido-bis(dimethylphosphoniummethylide)
$C_{12}H_8S_2$	thianthrene
$CH_2SO(CH_3)_2$	trimethylsulfonium
$C(ma)_2$	bis(*N-p*-methylanilino)methylide
$CN_4i\text{-}pt$	1-isopropyltetrazol-5-ate
CN-xylyl	2,6-dimethylphenylisocyanide
cod	cycloocta-1,5-diene
COMe	methoxymethylidine
C_4Ph_4	1,2,3,4-tetraphenylbuta-1,3-diene-1,4-diyl
C_4S_4	tetrathioquadrate
cy	cyclohexyl
t-db	*trans,trans*-1,4-diphenyl-1,3-butadiene
1,2-dcb	1,2-dicarbollyl
dhd^-	dodecahydrido-6-thia-nido-decaborate
dmg^-	dimethylglyoximate

dmp	2,9-dimethyl-1,10-phenanthroline
dmph	2,6-dimethoxyphenyl
dpdt	dipropyldithiocarbamate
dpk	di-2-pyridylketone
dppe	bis(diphenylphosphino)ethylene
dppm	bis(diphenylphosphino)methane
dppp	diphenyl(2-pyridyl)phosphine
1,3-dppp	1,3-bis(diphenylphosphino)propane
dpt	α,α-di-2-pyridyltoluene
dtc	*N*,*N*-di-n-butyldithiocarbamate
EtO^-	ethoxy
Et_2O	diethylether
$Et_2P(CH_2)_2$	diethylphosphoniumbis(methylide)
etu	ethylenethiourea
$HB(pz)_3^-$	tris(pyrazol-1-yl)borate
$H(dma)_2$	hydrogenbis(*N*,*N*-dimethylacetamide)
hyp	hypoxanthine
L_{eq}	equatorial ligand
L_{ax}	axial ligand
m	monoclinic
$(MeC_6H_4N{=})C$	(*N*-*p*-tolylimino)methyl
Me_2CO	acetone
$Me_2P(CH_2)_2$	dimethylphosphoniumbis(methylide)
mes	mesityl
mhd	*N*-methylhydantoinate
mn	malonitrile
na	n-nonylamine
$N(ae)^-$	bis(2-aminoethyl)amide
NH(ae)	bis(2-aminoethyl)amine
$N[P(CH_3)_2CH_2]_2$	nitrido-bis(dimethylphosphoniummethylide)
$[N(PPh_3)_2]^+$	bis(triphenylphosphine)iminium
OAc	acetate
or	orthorhombic
Otf	trifluoromethanesulfonate
pa	isopropylamine
pap	2-(phenylazo)phenyl
$P(p\text{-}C_6H_4OMe)_3$	tri(*p*-methoxyphenyl)phosphine
$PClPh_3^+$	chlorotriphenylphosphonium
$P(p\text{-}ClPh)_3$	tri(*p*-chlorophenyl)phosphine
Pcy_3	tricyclohexylphosphine
Pcy_2Ph	dicyclohexylphenylphosphine
pdma	*o*-phenylenebis(dimethylarsine)

Pe	phenylethyl
Pen	D-penicillaminate
PEt_3	triethylphosphine
$P(p\text{-}FPh)_3$	tri(*p*-fluorophenyl)phosphine
Ph_4HC_5	tetraphenylcyclopentadienyl
phen	1,10-phenanthroline
$(Ph_2P)CH$	bis(diphenylphosphine)methanide
$Ph_2P(CH_2)S$	diphenylmethylenethiophosphinate
$PhPr^n_2S^+$	phenyl(di-n-propyl)sulphonium
pip	piperidine
pna	n-pentylamine
$P(OPh)_3$	triphenylphosphite
PP	2,11-bis(diphenylphosphinomethyl)benzo-[c]-phenanthrene
PPh_3	triphenylphosphine
PPh_2Me	diphenylmethylphosphine
$PPhMe_2$	dimethylphenylphosphine
PPr_3	tripropylphosphine
pq	2-(2′-pyridyl)quinoline
prazepam	1,4-benzo-diazepin-2-one-6-chlorine
ptdby	3-phenyl-1,4-bis(*p*-toluidino)-2,3-diazabut-1-en-1-yl-4-ylidene
$P(tol)_3$	tri(*p*-tolyl)phosphine
py	pyridine
pya	2-pyridylamide
rh	rhombohedral
$SbPh_3$	triphenylstibine
$S_2C_2(CF_3)_2$	*cis*-1,2-bis(trifluoromethyl)ethene-1,2-dithiolate
$S_2C_2(CN)_2$	1,2-dicyanoethane-1,2-dithiolate
$SCH_2CH_2PEt_2$	diethylphosphinoethylthio
$S_2C_6H_3Me$	toluene-3,4-dithiolate
S_2CNBu_2	*N*,*N*-di-n-butyldithiocarbamate
S_2CNEt_2	*N*,*N*-diethyldithiocarbamate
$(SO_3)_2en^{4-}$	*cis*-ethylenediaminedisulphite
SP	*o*-styryldiphenylphosphine
t-stb	*trans*-stilbene
tag	2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosate-S
tdme	1,1,1-tris(diphenylphosphinomethyl)ethane
terpy	2,2′,2″-terpyridine
tg	tetragonal
tmtcp	5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclo-tetradeca-4,6,9,12,13-pentaenate

tmtct	5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenate
tpm	tri-2-pyridylmethane
tpp	($\alpha,\beta,\gamma,\delta$-tetraphenyl)porphinate
tpzm	tri-1-pyrazolylmethane
tr	triclinic
trg	trigonal

A. INTRODUCTION

Gold is widely distributed in nature and the chemistry of gold remains an active research area, with emphasis on the production of new compounds. Gold is not essential for any living organism, though some plants concentrate the element [1,2]. Various gold(I) compounds are biologically active and used as anti-inflammatory drugs in rheumatoid arthritis treatment [2,3]. Colloidal gold also has commonly been used for labelling enzymes and proteins for X-ray diffraction study, since it can be readily located. Moreover, there have been many contributions to try and understand the nature of the relatively facile redox processes, to define the ability of gold to coordinate with various complexing groups and to establish the major types of complex which can be formed by each gold oxidation state [4].

During recent years there have been many structural studies and some reviews of gold compounds [5], but a comprehensive study of these structural results and their classification has not been given. The basic crystal and structural data, obtained by X-ray (neutron) diffraction analyses together with the relevant Mössbauer spectroscopic data through the year 1984 are reviewed in detail.

The review includes a classification on the basis of coordination number, comparison of the X-ray data with those obtained by Mössbauer spectroscopy, and a discussion of the factors which will lead to better understanding of the stereochemical interactions in gold compounds.

B. STRUCTURAL DATA FOR GOLD COMPOUNDS WITH COORDINATION NUMBER TWO

(i) Mononuclear compounds

The lowest and highest coordination numbers found in coordination compounds of gold, are two and six, respectively, with the intermediate number four being the most frequent for gold(III) and number two for gold(I) compounds. A wider range of coordination numbers exists in organometallic (cluster) gold compounds, ranging from two to twelve.

TABLE 1

Structural data for mononuclear gold compounds with coordination number two

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L (°)	Ref.
$[Au^{I}(mhd)_2]Na\cdot 4\ H_2O$	tr	$P\bar{1}$	2	AuN_2	6.111 (1) 13.378 (2) 10.174 (2)	81.98 (2) 103.90 (2) 99.37 (2)	N 1.94 (2×) [a]	180	6
$[Au^{I}(CN)_2]K\cdot(bipy)$	m	$P2_1$	2	AuC_2	3.789 (1) 18.871 (6) 9.293 (3)	 101.73 (2)	C 1.98 (4) 2.04 (4)	176 (2)	7
$[Au^{I}\{(t,t\text{-}p\text{-}CH_3C_6H_4NH)_2C\}_2]\cdot(BF_4)$	m	$P2_1/n$	4	AuC_2	14.506 (6) 20.753 (9) 10.344 (5)	 105.7 (3)	C 2.02 (2) (2×)	177.4 (7)	8
$[Au^{I}(C_6F_5)_2][Au^{I}(pdma)_2]$ [b]	tr	$P\bar{1}$	2	AuC_2	10.340 (3) 10.982 (3) 17.612 (5)	75.45 (2) 82.35 (2) 87.23 (2)	C 2.04 (2) (2×)	180	9
$[Au^{I}(C_6F_5)_2][Au^{I}(Ph_3Sb)_4]$ [c]	trg	$P3c1$	6	AuC_2 AuC_2	21.615 (3) – 28.598 (4)		C 2.06 (2) (2×) C 2.072 (24) 2.095 (21)	180 177.9 (11)	10
$[Au^{I}Cl_2][Au^{I}(dmg)_2]$ [d]	or	$Pnnm$	2	$AuCl_2$	11.52 10.59 6.52		[e]	[e]	11
$[Au^{I}(etu)_2]Cl\cdot H_2O$	tr	$P\bar{1}$	2	AuS_2	8.828 (6) 9.017 (4) 10.414 (6)	114.63 (4) 92.14 (6) 116.05 (4)	S 2.278 (9) 2.279 (8)	167.1 (2)	12
$[Au^{I}(S_2O_3)_2]Na_3\cdot 2\ H_2O$	m	$P2_1/a$	4	AuS_2	18.206 (6) 11.355 (6) 5.430 (4)	 97.87 (5)	S 2.272 (3) 2.280 (3)	176.5 (2)	13
$[Au^{I}(PMePh_2)_2](PF_6)$	m	$C2/c$	4	AuP_2	23.23 (2) 10.33 (1) 15.31 (2)	 131.28 (10)	P 2.316 (4) (2×)	180	14
$[Au^{I}\{P(cy)_3\}_2](SCN)$	or	$Pnma$	4	AuP_2	15.151 (19) 15.737 (14) 9.630 (9)		P 2.295 (11) 2.316 (13)	177.2 (4)	15
$[Au^{I}\{P(cy)_3\}_2](PF_6)$	or	$Pbca$	8	AuP_2	19.347 (2) 26.805 (3) 15.530 (2)		P 2.324 (6) 2.325 (6)	178.0 (2)	16
$Au^{I}\{C_5(CO_2Me)_5\}(PPh_3)\cdot CH_3OH$	tr	$P\bar{1}$	2	AuP_2	21.04 (1) 12.936 (8) 9.376 (5)	82.85 (4) 76.95 (4) 76.95 (4)	P 2.297 (3) 2.300 (3)	170.4 (2)	17

$Au^{I}(pip)Cl$	tg	$P\bar{4}2_1c$	8	AuClN	12.474 (20) – 9.694 (10)		N 2.068 (18) Cl 2.256 (8)	176.0 (5)	19
$Au^{I}(PPh_3)(CN)$	or	$P2_12_12_1$	4	AuCP	10.39 (2) 12.40 (2) 12.99 (2)		C P 2.27 (1)	169 (2)	20
$Au^{I}(C_6F_5)(PPh_3)$	m	$P2_1/c$	4	AuCP	8.340 (3) 11.991 (4) 22.146 (7)	98.33	C 2.07 (2) P 2.27 (1)	178 (1)	21
$Au^{I}(CH_3)(PPh_3)$	m	$P2_1/n$	4	AuCP	17.29 (1) 11.27 (1) 8.92 (1)	104.5 (1)	C 2.124 (28) P 2.279 (8)	179.1 (8)	22
$Au^{I}(dmph)(PPh_3)$ [f]	m	$P2_1/n$	4	AuCP	13.040 (2) 19.268 (3) 9.013 (3)	96.98 (1)	C 2.050 (4) P 2.284 (1)	172.7 (1)	23
$Au^{I}(C_5H_5)(PPr_3)$ [g]	m	$P2_1/c$	4	AuCP	8.225 (2) 15.623 (2) 12.483 (3)	106.81 (2)	C 2.175 (9) P 2.267 (2)	177.0 (2)	24
$Au^{I}(Ph_4HC_5)(PPh_3)$ [g]	m	$P2_1/c$	4	AuCP	13.303 (2) 12.951 (2) 21.117 (4)	96.60 (1)	C 2.15 (1) P 2.239 (3)	178.6 (3)	25, 26
$Au^{I}\{C_5(CO_2Me)_5\}(PPh_3)$	m	$P2_1/c$	4	AuCP	10.959 (3) 14.691 (3) 20.889 (5)	105.70 (2)	C 2.199 (4) P 2.253 (1)	169.7 (1)	17
$Au^{I}\{S(CH_2C_6H_5)_2\}Cl$	tg	$P4_1$	4	AuClS	10.462 (3) – 12.885 (6)		Cl 2.222(9) S 2.290 (9)	172.3 (3)	27
$Au^{I}\{S(CH_2C_6H_5)_2\}Br$	tg	$P4_1$	4	AuBrS	10.567 (2) – 12.863 (3)		Br 2.387 (2) S 2.275 (4)	178.7 (1)	27
$Au^{I}(PPh_3)(OAC)$	or	$P2_12_12_1$	4	AuOP	11.088 (3) 12.050 (4) 13.839 (5)		O 2.063 (6) P 2.207 (3)	177.3 (2)	28
$Au^{I}\{P(OPh)_3\}Cl$	tr	$P\bar{1}$	2	AuClP	9.539 (6) 10.438 (5) 9.634 (4)	82.27 (3) 84.56 (4)	Cl 2.273 (5) P 2.192 (5)	178.5 (2)	29
$Au^{I}(dppp)Cl$	or	*Pnma*	4	AuClP	11.774 (3) 12.617 (3) 11.114 (6)	90	Cl 2.286 (4) P 2.234 (4)	178.0 (2)	30
$Au^{I}(PPh_3)Cl$	or	$P2_12_12_1$	4	AuClP	12.300 (4) 13.084 (4) 10.170 (3)		Cl 2.279 (3) P 2.235 (3)	179.63 (8)	31

TABLE 1 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L (°)	Ref.
$Au^{I}(PCl_3)Cl$	m	$P2_1/c$	4	AuClP	7.23 14.62 6.19	 96.4	Cl 2.33 P 2.19	180	32
$Au^{I}\{SSCN(Et)_2\}(PPh_3)$	m	$P2_1/c$	4	AuSP	13.547 (1) 12.277 (1) 14.013 (1)	 90.81 (1)	S 2.338 (3) P 2.251 (3)	175.7 (1)	33
$Au^{I}(tag)(PEt_3)$	m	$P2_1$	2	AuSP	10.331 (1) 8.231 (1) 16.203 (2)	90 105.31 (1) 90	S 2.293 (3) P 2.259 (3)	173.6 (1)	34
$Au^{I}(AsPh_3)Br$	or	$P2_12_12_1$	4	AuBrAs	12.438 (1) 13.637 (1) 10.191 (1)		Br 2.377 (6) As 2.342 (5)	179 (1)	35
$(\eta^3\text{-}C_3H_5)(CO)_3FeAu(PPh_3)$	m	$C2/c$	8	AuPFe	30.76 (2) 11.60 (1) 13.54 (2)	 110.38 (1)	P 2.273 (5) Fe 2.519 (1)	174.4 (2)	36
$(CO)_4CoAu(PPh_3)$	tr	$P\bar{1}$	2	AuPCo	9.76 (1) 13.10 (1) 10.82 (1)	108.9 (3) 110.0 (3) 62.9 (3)	P 2.23 (2) Co 2.50 (1)	177.5 (5)	37
$(CO)_4\{P(OPh)_3\}MnAu(PPh_3)$	tr	$P\bar{1}$	2	AuPMn	10.76 (1) 10.63 (1) 16.74 (1)	93.6 (1) 97.0 (1) 77.8 (1)	P 2.33 (1) Mn 2.573 (7)	166.5 (3)	38
$(PPh_3)_3(\mu\text{-}H)_2IrHAu(PPh_3)\cdot(BF_4)$	tr	$P\bar{1}$	2	AuPIr	17.482 (5) 15.617 (5) 13.218 (4)	91.9 (2) 71.4 (2) 103.9 (3)	P 2.265 (5) Ir 2.765 (1)	155.3 (1)	39
$(CO)_3(\pi\text{-}C_5H_5)WAu(PPh_3)$	or	*Pbca*	8	AuPW	15.545 (7) 26.54 (1) 11.515 (5)		P 2.25 (1) W 2.698 (3)	173.8 (3)	40
$[Au\{Co(CO)_4\}_2][N(PPh_3)_2]$	tr	$P\bar{1}$	1	$AuCo_2$	9.610 (4) 9.978 (4) 11.506 (5)	97.70 (2) 97.84 (2) 90.97 (2)	Co 2.509 (2) (2×)	180	41
$[Au^{I}\{Cr(CO)_3\text{-}\eta\text{-}C_5H_5\}_2]\cdot(n\text{-}Bu_4N)$ [h]		$P2_1/c$	4	$AuCr_2$	11.106 (6) 16.905 (14) 22.092 (8)	 122.46 (3)	Cr 2.635 (8) 2.641 (2)	162.2 (3)	42

[a] The chemical identity of the coordinated atom (ligand) is specified in this column. [b] Two independent $[Au(C_6F_5)_2]^-$ anions are there. In the $[Au^{I}(pdma)_2]^+$ cation the chromophore $AuAs_4$ will be presented in Table 7. [c] The $[Au(Ph_3Sb)_4]^+$ ion with $AuSb_4$ chromophore will be presented in Table 7. [d] The $[Au(dmg)_2]^+$ ion with AuN_4 chromophore will be presented in Table 7. [e] Not given. [f] At −35°C. [g] At −120°C. [h] At −20°C.

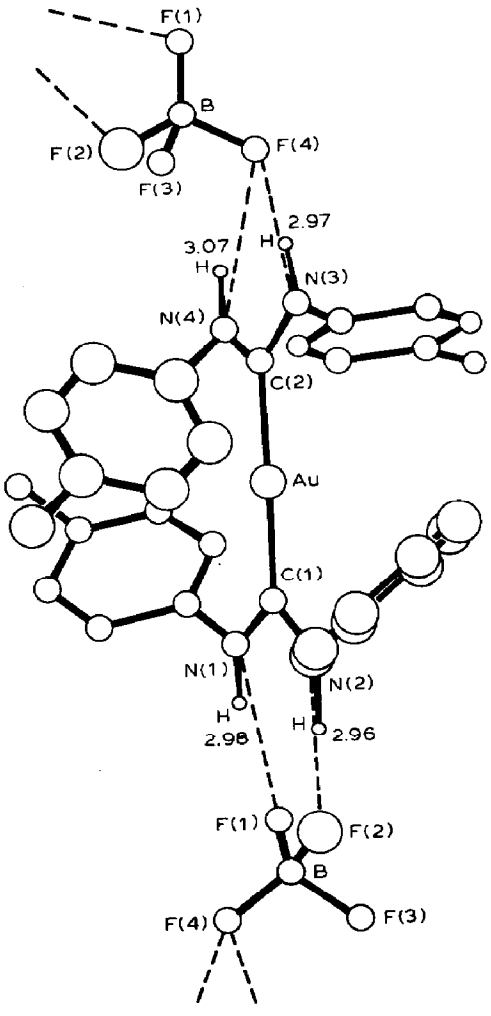

Fig. 1. A perspective view of $[\{p\text{-}CH_3C_6H_4NH)_2C\}_2Au]BF_4$ [8].

Structural data for mononuclear gold compounds with coordination number two are gathered in Table 1. Two common geometries, linear and bent, exist in the chemistry of gold compounds. In Fig. 1 is illustrated the crystal structure of $[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2Au]BF_4$ [8], as a representative example of linear geometry.

From the data summarised in Table 1, we see that the gold atom occurs only in oxidation state one or zero. The Au–L bond distance lengthens with increasing van der Waals' radius of the coordinated atoms (ligands), as expected. The L–Au–L(L') angles are in the range 180–155.3(1)°.

(ii) Binuclear compounds

X-ray data for binuclear gold(0) and gold(I) compounds with coordination number two are summarised in Table 2. The structures are tabulated by

TABLE 2

Structural data for binuclear gold compounds with coordination number two [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M (Å)	L–M–L (°)	Ref.
$[Au(PPh_3)]_2$				AuPAu'			P 2.37 [b] Au' 2.76	2.76	[c]	43
$[Au^I\{Et_2P(CH_2)_2\}]_2$	tr	$P\bar{1}$	1	AuC_2	8.13 (1) 6.87 (1) 7.94 (1)	95.10 (8) 107.00 (8) 89.55 (8)	C 2.09 (3) 2.10 (3)	3.023 (1)	179 (1) 90.3 (7, 5) [d]	44
$[Au^I\{(CH_2)_4P(CH_2)_2\}]_2$	m	$C2$	4	AuC_2	18.45 (1) 10.90 (1) 14.65 (1)	149.04 (8)	C [e]	[e]	[e]	45
$[Au^I\{Ph_2P(CH_2)S\}]_2$	m	C_2/c	4	AuCS	23.874 (4) 9.030 (1) 12.172 (2)	105.61 (1)	C 2.115 (9) S 2.323 (3)	3.040 (1)	[c]	46
$[\{Au^I(PPh_3)\}_2Cl]$-$(ClO_4)\cdot CH_2Cl_2$ [e]	tr	$P\bar{1}$	4	AuClP	11.214 (3) 14.675 (4) 25.505 (6)	85.62 (2) 85.16 (2) 68.25 (2)	Cl 2.334 (5, 6) P 2.235 (5, 5)	3.035	177.2 (2, 1) 82.7 (2) [f]	47
				AuClP			Cl 2.343 (5, 2) P 2.236 (5,4)	3.085	176.9 (3,7) 80.7 (2) [f]	
$[\{Au^I(PPh_3)\}_2S]\cdot CH_2Cl_2$ [g]		$P2_1/c$	4	AuSP	18.516 (4) 22.251 (6) 8.803 (2)	90 96.32 (1) 90	S 2.159 (5,2) P 2.135 (5, 4)	3.018 (1)	177.7 (2, 1.2)	48
$[(Ph_3P)Au^IC(CF_3)]_2$ [h]	m	$P2_1/c$		AuCP	13.78 14.28 21.91	112.3	C 2.05 (6) P 2.28 (1)	3.343 (8)	170 (7)	49
$[Cl_2Au^I_2(dppm)]$ [i]	m	$C2/c$	4	AuClP	22.31 (1) 7.215 (7) 18.12 (1)	120.43 (8)	Cl 2.288 (1) P 2.238 (1)	3.351 (2)	175.2 (2)	50
$(\mu\text{-bpte})Au^I_2Cl_2$ [j]	tr	$P\bar{1}$	2	AuClS	6.382 (9) 14.878 (12) 8.975 (9)	85.91 (11) 100.94 (12) 87.46 (13)	Cl 2.311 (9, 18) S 2.259 (12, 1)	3.198 (2, 11)	175.6 (4, 2.2)	51
$(Au^ISCH_2CH_2PEt_2)_2$ [k]		$C2/c$	4	AuSP	21.626 (4) 8.547 (7) 18.12 (1)	145.16 (7)	S 2.31 P 2.27	3.104	173.5	52
$(\mu\text{-dppe})Au^I_2Cl_2$ [l]	m	Cc	4	AuClP	13.293 (6) 12.863 (6) 15.497 (7)	101.30 (4)	Cl 2.294 (5, 5) P 2.232 (5, 6)	3.05 (1)	172.9 (2, 4)	53
$[(Ph_3P)_2Au^I_2(\mu\text{-bbzim})$-$Rh(cod)](ClO_4)\cdot CHCl_3$ [m]	tr	$P\bar{1}$	2	AuNP	20.972 (14) 11.324 (9) 14.425 (10)	64.00 (7) 85.84 (6) 91.18 (6)	N 1.97 (3, 1) P 2.22 (1, 1)	3.134 (4)	175 (1, 2)	54

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following an averaged value is the e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Not given. [d] The C–Au–Au angle. [e] There are two independent cations; and Au–Cl–Au bridge. [f] The Au–Cl–Au' angle. [g] There is Au–S–Au bridge; the Au–S–Au angle is 88.7 (1)°. [h] There is Au–C–C–Au bridge. [i] There is Au–P–C–P–Au bridge; the Au–C–P angle is 111.7 (7, 4.4). [j] There is Au–S–C–C–S–Au bridge; the Au–S–C angle is 106.7 (12, 3.5)°. [k] There is Au–S–C–C–P–Au bridge; the Au–S–C angle is 103.8°; and Au–P–C is 112.4°. [l] There is Au–P–C–C–P–Au bridge; the Au–P–C angle is 114.9 (5, 4.9)°. [m] There is Au–N–C–C–N–Au bridge.

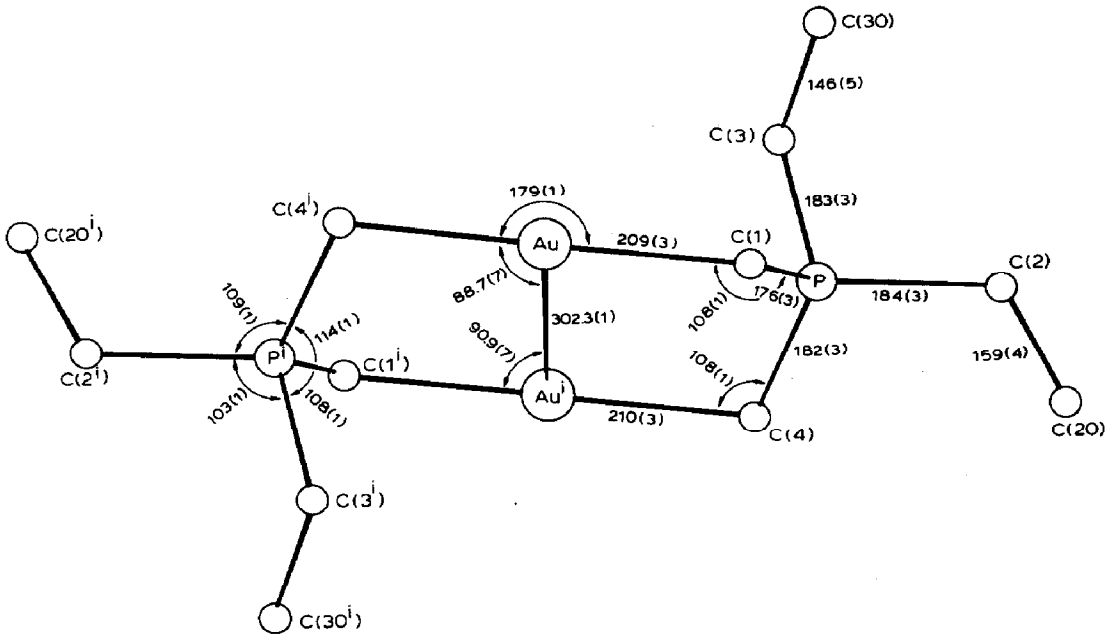

Fig. 2. A schematic view of the crystal structure of $[Au^{I}\{Et_2P(CH_2)_2\}]_2$ [44].

increasing number of bridging atoms between two gold atoms. Six types of gold compound are included. In $[Au(PPh_3)]_2$ the distance between the two Au atoms (2.76 Å) is shorter than in gold metal (2.88 Å) [74] and is one of the shortest reported for gold compounds with coordination number two, supporting a direct Au–Au bond interaction. In the binuclear $[Au^{I}\{Et_2P(CH_2)_2\}]_2$ (Fig. 2), $[Au^{I}\{(CH_2)_4P(CH_2)_2\}]_2$ and $[Au^{I}\{Ph_2P(CH_2)S\}]_2$ the distance between the two Au(I) atoms, namely 3.023(1) Å in the former and 3.040(1) Å in the latter, are well above the Au(I) covalent diameter (1.32 Å), supporting only Au ... Au contacts. In $[\{Au^{I}(PPh_3)\}_2Cl]^+$ and $[\{Au^{I}(PPh_3)\}_2S]$ the two Au(I) atoms are bridged through the chlorine atom (Au–Cl = 2.334(5,6) Å in the former and by the sulphur atom (Au–S = 2.159(5,2) Å) in the second. (The first number in parentheses following is an averaged value of an e.s.d., and the second number is the maximum deviation from the average value.) The two crystallographically independent cations, $[\{Au^{I}(PPh_3)\}_2Cl]^+$, have different Au–Cl(P) bond lengths (Table 2). These results indicate the presence of two distortion isomers [75] of gold(I) in molecules of $[\{Au(PPh_3)\}_2Cl](ClO_4) \cdot (CH_2Cl_2)$ [47].

In $[(Ph_3P)Au^{I}C(CF_3)]_2$ the two Au(I) atoms are bridged through two carbon atoms, and the P–Au–C=C–Au–P moiety is substantially planar, where the Au...Au contact of 3.343(8) Å is too large for any appreciable interaction. A somewhat longer distance, 3.351(2) Å between the two Au(I) atoms was found in $[Cl_2Au^{I}_2(dppm)]$, where the Cl–Au–P–C–P–Au–Cl moiety is observed.

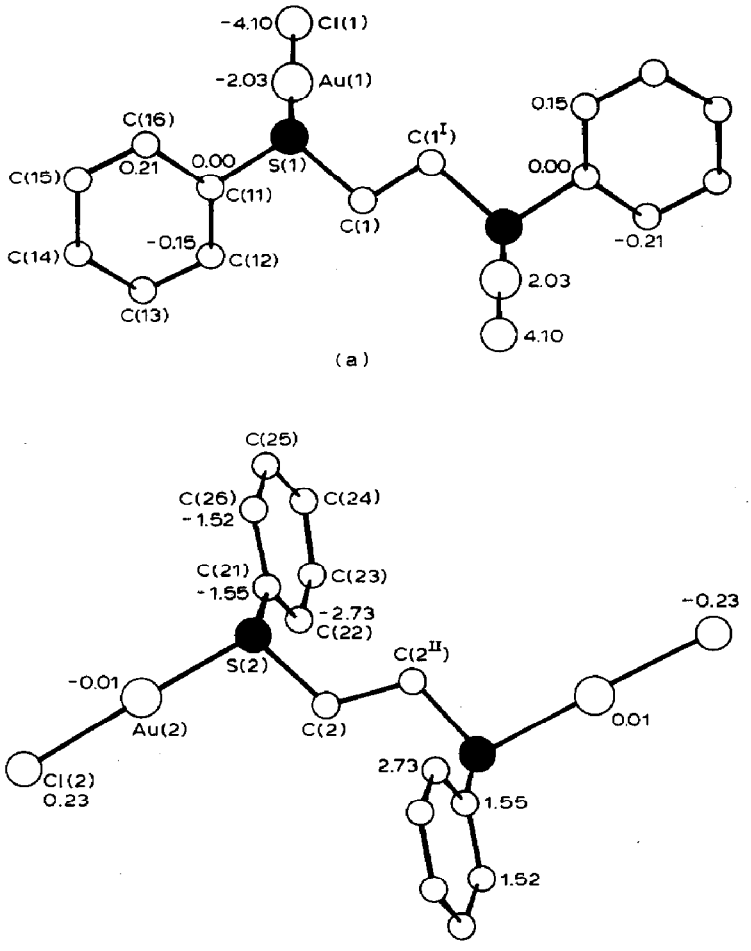

Fig. 3. Projection of the crystal structure of (μ-bpte)$Au^{I}_{2}Cl_{2}$ [51].

In the following four species, (μ-bpte)$Au^{I}_{2}Cl_{2}$ (Fig. 3) $(Au^{I}SCH_{2}CH_{2}PEt_{2})_{2}$, ($\mu$-dppe)$Au^{I}_{2}Cl_{2}$ and $[(Ph_{3}P)_{2}Au^{I}_{2}(\mu\text{-bbzim})Rh(cod)]^{+}$, the two Au(I) atoms are held together through four heteroatoms Au–S–C–C–S–Au. The intramolecular Au...Au contacts (3.12 Å mean value) (Table 2) in the four heteroatom bridged binuclear gold(I) compounds indicate no direct bond between the two gold(I) atoms.

(iii) Tri-, tetra-, penta-, hepta- and polynuclear compounds

Six kinds of trinuclear gold compound exist (Table 3). In $[Ph_{4}C_{5}(Au\text{-}PPh_{3})_{3}]^{+}$ (Fig. 4) the three metal atoms fall into two non-equivalent classes exhibiting different coordination numbers: the central atom Au(1) is two-coordinate (AuCP) and the other two, Au(2) and Au(3), atoms are three-coordinate (AuCPAu') with a direct Au(2)–Au(3) bond of 2.820(1) Å. There is a

TABLE 3

Structural data for tri-, tetra-, penta-, hepta- and polynuclear gold compounds with coordination number two [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M (Å)	L–M–L (°)	Ref.
$[Ph_4C_5(AuPPh_3)_3]\cdot(BF_4)\cdot(C_6H_6)_2$	tr	$P\bar{1}$	2	AuCP (1×)	12.845 (6) 16.042 (8) 22.642 (11)	86.62 (4) 77.51 (4) 76.05 (4)	C 2.21 (2) [b] P 2.257 (5)	3.02 (1)	172.8 (4)	26, 55
				AuCPAu′(2×)			C 2.13 (2, 3) P 2.290 (5, 8) Au 2.820 (1)	2.820 (1)	172.2 (6, 2)	
$[O(Au^IPPh_3)_3](BF_4)$ [c]	m	$P2_1/c$	2	AuOP	12.616 (8) 24.796 (15) 16.151 (1)	97.37 (5)	O 1.98 (8, 6) P 2.26 (3, 1)	3.094 (7) 3.162 (6) [d]	177 (2, 3)	56
$[Se(Au^IPPh_3)_3](PF_6)$ [e]	m	$P\bar{1}$	4	AuSeP	15.395 (6) 18.005 (7) 22.895 (9)	89.35 (3) 72.44 (3) 69.75 (3)	Se 2.444 (2, 19) P 2.270 (5, 13)	3.159 (0, 219) 3.308 (0) [d]	174.3 (2, 2.6)	48
$[S(Au^IPPh_3)_3](PF_6)$ [f]	m	$P2_1/b$	8	AuSP	11.079 (4) 18.642 (7) 55.53 (3)	96.81 (3)	S 2.327 (7, 22) P 2.269 (8, 15)	3.223 (3, 186) 3.298 (3, 63) [d]	174.8 (3, 2.9)	57
$[(Au^ICl)_3(tdme)]$ [g]	m	$P2_1/c$	4	AuClP	13.257 (2) 22.018 (4) 17.206 (3)	99.35 (2)	Cl 2.292 P 2.239	3.091	174.8–178.2	58
$[(EtO)(MeC_6H_4N{=})\cdot CAu^I]_3$ [h]	tr	$P\bar{1}$	2	AuCN	15.110 (13) 14.267 (11) 7.913 (8)	87.6 (1) 108.6 (11) 100.5 (1)	C 1.954 (26, 21) N 2.033 (22, 15)	3.270 (1, 46)	175.0 (10, 1.9)	59
$[Au^I(CH_3CSS)]_4$ [i]		$P\bar{1}$	2	AuS_2	12.200 (5) 9.728 (3) 8.876 (3)	95.32 (2) 110.71 (3) 92.67 (2)	S 2.30 (1, 4)	3.008 (3, 19)	1973 (1)	60
$[(Ph_3P)_4Au_4N](BF_4)$ [j]	m	$P2_1/c$	4	AuNP	17.672 (10) 19.166 (9) 18.985 (10)	96.03 (4)	N 2.02 (2, 9) P 2.230–2.244 (7)	3.270 (2, 258)	171.5–177.0 (6)	61
$[Fe(CO)_4Au_2(dppe)]_2$	m	$C2/c$	4	AuPFe	15.823 (3) 15.858 (4) 25.708 (3)	95.88 (2)	P [k] Fe 2.530 (2, 6)	2.977 (1)	[k]	62
$[Fe(CO)_4Au_2(dppm)]_2$	m	$C2/c$	4	AuPFe	14.250 (5) 19.431 (4) 24.810 (11)	103.44	P [k] Fe 2.573(3, 35)	3.102 (2, 61)	[k]	62

TABLE 3 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M (Å)	L–M–L (°)	Ref.
$[Au^{I}Cl(py)]_4$	m	$C2/c$	16	$AuCl_2$	14.579 (3)		Cl 2.27 (1, 2)	3.332 (4, 84)	177.5 (5)	63
				AuN_2	13.242 (3)	117.16 (5)	N 2.09 (4, 1)		173 (1)	
					15.270 (3)					
$[Au^{I}Br(py)]_4$	tr	$P\bar{1}$	4	$AuBr_2$	7.915 (2)	85.78 (2)	Br 2.385 (3) (2×)	3.344 (2, 125)		64
				AuN_2	9.356 (2)	102.07 (2)	N 2.04 (2, 1)		175.1 (8)	
					10.051 (3)	109.31 (2)				
$[Au^{I}Br(py)]_4$	m	$C2/c$	16	$AuBr_2$	12.259 (2)		Br 2.389 (3, 1)	3.433 (2, 230)	179.4 (3, 2)	64
				AuN_2	15.222 (3)	97.82 (2)	N 2.00 (3, 5)		173 (1)	
					14.597 (3)					
$[Au^{I}I(py)]_4$	or	$Pnnm$	8	AuI_2	7.222 (3)		I 2.543 (1, 5)	3.104 (1, 187)	175.4 (3)	64
				AuN_2	14.250 (4)		N 2.020 (5) (2×)		175.3 (1)	
					14.773 (4)					
$[Au^{I}\{S(Au^{I}PPh_3)_2\}_2]\cdot$ $[(CH_3)_3SnCl_3]$	m	$C2/c$	8	AuS_2	17.134 (5)		S 2.325 (7, 6)	3.093 (2, 20)	179.0 (3)	65
				AuSP	29.967 (12)	102.40 (3)	P 2.257 (6, 7)	3.121 (2, 91)	171.3 (3, 4.0)	
					30.817 (12)		S 2.322 (6, 69)			
$[Au^{I}_7P_{10}I]$	trg	$P\bar{3}1m$	1	AuP_2 (6×)	6.180 (1)		P 2.328 (7, 7)	3.329 (2, 239)	180.0 (2, 0)	66(a)
					–					
					11.122 (2)					
				AuP_3I (1×)			P 2.339 (7) (3×)		118.5 (2, 0)	
$[Au^{I}_7P_{10}I]$	hx	$P\bar{6}2m$	1	AuP_2(6×)	6.173 (7)		P 2.302	3.069	[k]	66(b)
					–					
					11.107 (2)					
				AuP_3I (1×)			P 2.324 (3×)		106.0	
							I 3.065		98.2 [c]	
$\{K[Au^{I}(CN)_2]\}_n$	rh	$R\bar{3}$		AuC_2	9.74	43.9	C 2.12 (4)	[k]		67
$\{Cs[Au^{I}(CN)_2]\}_n$	or	$Pbca$	16	AuC_2	7.42 (1)		C 1.971 (2, 1)	3.32 (1, 40)	177.1 (2)–	68
					32.67 (1)				180.0	
					9.369 (3)				176.2 (4, 4) [m]	
$\{Tl[Au^{I}(CN)_2]\}_n$	or	$Pbcn$	16	AuC_2	7.09 (2)		C 1.971 (2, 1)	3.221 (4, 339)	177.1 (2)–	68
					30.429 (7)				180.0	
					9.140 (5)				176.2 (4, 4) [m]	
$[Cs_2Na[Au(CN)_2]_3\}_n$	hx	$P6_3/mmc$	2	AuC_2	7.0679 (7)		C 1.94 (1)	3.534 (1, 86)	178.3 (3)	69
					–				178.6 (6) [m]	
					18.2566 (56)					
$\{Au^{I}(CN)(CNCH_3)\}_n$	or	$Pbcm$	4	AuC_2	10.989 (6)		C 1.99 (5, 2)	3.613 (3, 111)	176 (2)	70
					6.899 (6)				175 (4) [m]	
					6.359 (5)					

$\{Au^{I}Cl\}_n$	tg	$14_1/a$	8	$AuCl_2$	6.734 – 8.674		Cl 2.36			71
$\{Au^{I}I\}_n$	tg	$P4_2/ncm$	4	AuI_2	4.35 – 13.73		I 2.62 (2×)			18
$\{Au^{I}_2P_3\}_n$	m	$C2/m$	4	AuP_2	5.863 (1) 14.439 (3) 4.674 (1)	108.39 (1)	P 2.335 (8, 4)	3.056 (8, 80)	175.2 (2, 4.8)	66(a)
$\{(pe)Au^{I}(pa)\}_n$	or	$Pccn$	8	AuCN	17.92 (1) 17.15 (2) 7.22 (1)		C 1.935 (19) N 2.028 (13)	3.498 (0, 224)	176.8 (7)	72
$\{(pe)Au^{I}(pna)\}_n$		$P2_1/c$	8	AuCN	22.0 17.0 7.2	98				72
$\{(pe)Au^{I}(na)\}_n$		$Pccn$	8	AuCN	29.0 17.0 7.2					72
$\{(1,3\text{-dppp})Au^{I}_2Cl_2\}_n$	or	$Pbcn$	8	AuClP	19.507 (4) 14.404 (3) 19.827 (4)		Cl 2.300 (7, 6) P 2.234 (7, 3)	3.116 (0, 49)	174.6 (3, 1.1)	73

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d.; and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Three Au atoms are bridged through an oxygen atom, the Au–O–Au angle is 103 (3, 5)°. [d] The value of Au ··· Au interactions between two $[X(AuPPh_3)_3]^+$ cations. [e] Three Au atoms are bridged through an Se atom, the Au–Se–Au angle is 80.5 (1, 6.5)°. [f] Three Au atoms are bridged through an S atom, the Au–S–Au angle is 87.4 (3, 7.6)°. [g] There are only two Au atoms in contact (Au ··· Au = 3.09 Å). [h] There are three Au–C–N–Au bridges, the Au–C–N angle is 120.6 (20, 3.4)°; and Au–N–C is 117.1 (18, 2.0)°. [i] The four Au atoms are at the vertices of a rhomb; the S–Au–Au angle is 94°, and Au–Au–Au angles are 66.3 (1, 3)° and 113.5 (1, 3)°, respectively. [j] At −120°C. A distorted tetrahedral $Au_4(N)$ cluster is built up of four linearly coordinated Au atoms with an interstitial N atom; the Au–N–Au angles are in the range of 94.3–120.7 (8)°. [k] Not given. [l] The value of P–Au–I angle. [m] The value of Au–C–N angle.

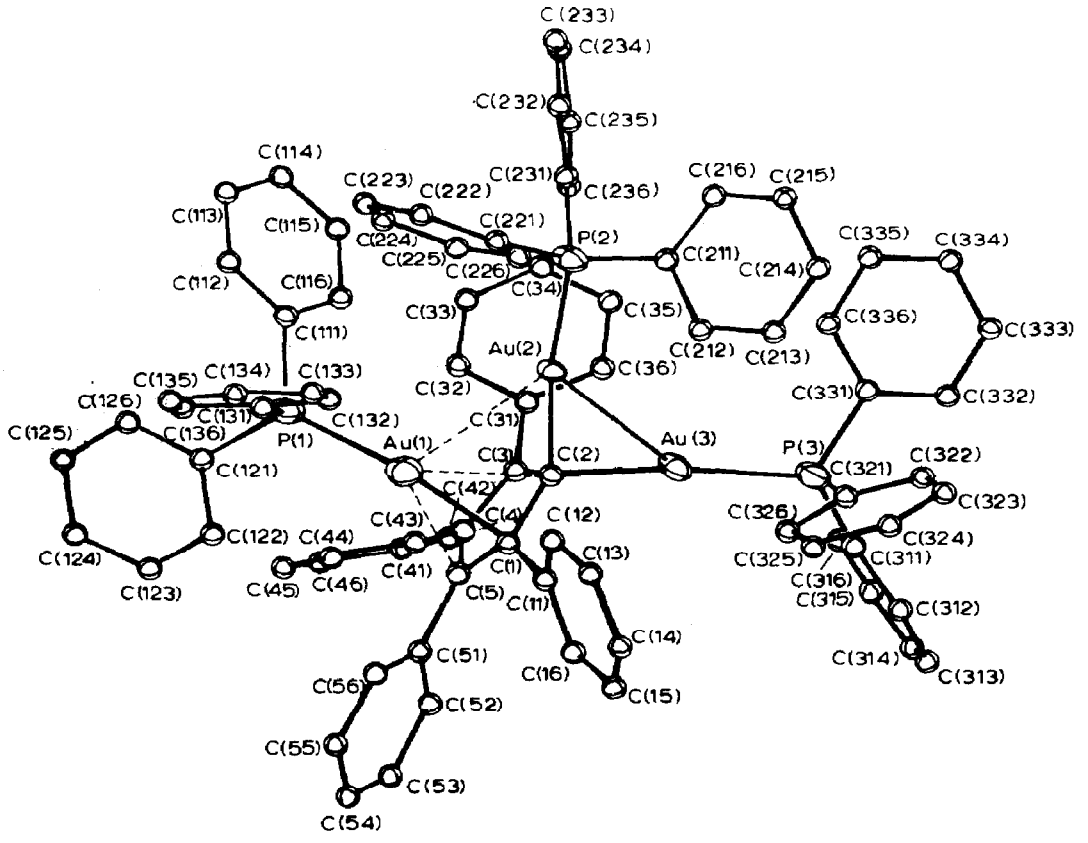

Fig. 4. A schematic outline of the crystal structure of $[Ph_4C_5(AuPPh_3)_3]^+$ [55].

contact between Au(1) and Au(2) of 3.021(1) Å. Differences exist between the Au(1)–L and Au(2)(3)–L bond lengths. While the Au(1)–C bond distance of 2.21(2) Å is longer than those of Au(2)(3)–C (2.16 and 2.10(2),Å), the Au(1)–P of 2.257(5) Å is shorter than those of 2.297 and 2.282(5) Å, respectively, consistent with the difference in coordination number.

In the other five trimer compounds (Table 3), all the metal atoms exhibit the same coordination number i.e. two. From the structural point of view, these five compounds can be divided into three groups. The structure of $[X(Au^IPPh_3)_3]^+$ (X = O, S or Se) is shown in Fig. 5. The Au–X bond lengths increase with increasing ionic radii of X^{2-} in the order; O, 1.98 Å (ionic radius 1.26 Å) < S, 2.33 Å (1.70 Å) < Se, 2.44 Å (1.84 Å). The intramolecular Au...Au contacts do not follow the same order: 3.094 Å(O) < 3.159 Å (Se < 3.22 Å (S); while the intermolecular Au...Au contacts do: 3.162 Å(O) < 3.298 Å (S) < 3.308 Å (Se).

In $[(Au^ICl)_3(tdma)]$, each of the three gold(I) atoms has a linear coordination geometry (P–Au–Cl, 174.8–178.2°), but with only one contact between Au(1)...Au(2) (3.091 Å) [58] (Table 3).

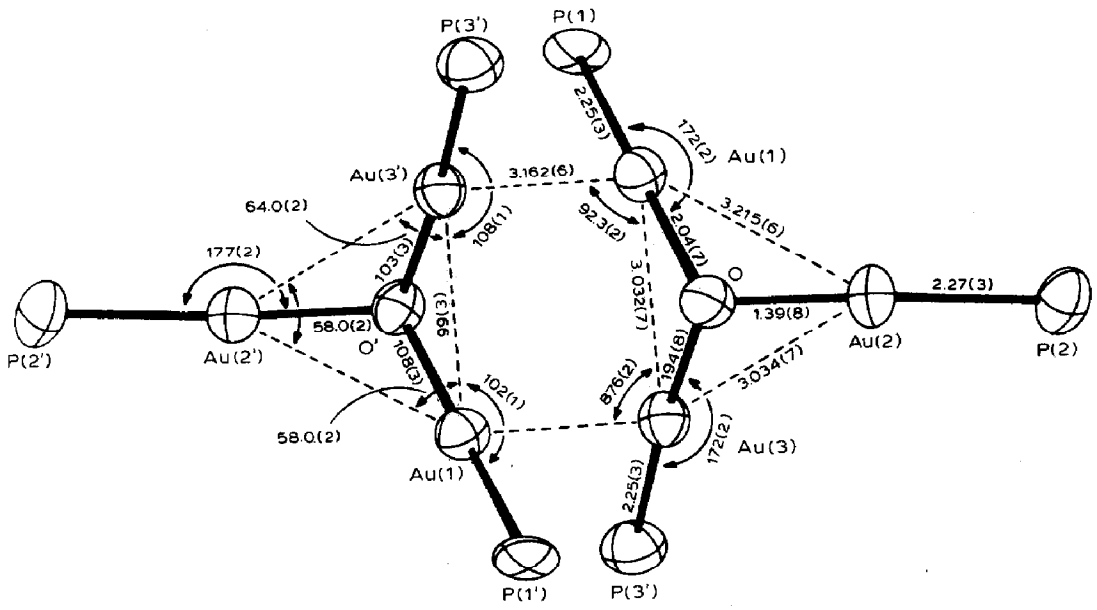

Fig. 5. A schematic outline of the $[O(AuPPh_3)_3]^+$ fragment [56].

Three gold(I) atoms in $[(EtO)(MeC_6H_4N{=})CAu']_3$ [59] are bridged through the N and O atoms of three $C(EtO){=}N(C_6H_4Me)$ groups.

Four types of tetranuclear gold compound (Table 3) are included. In $[Au^I(CH_3CSS)]_4$ [60] the four gold(I) atoms are at the vertices of a rhombohedron. In $[(Ph8d3P)_4AU_4N]^-$ a distorted tetrahedral $Au_4(N)$ cluster is built up of four linearly coordinated gold atoms with an interstitial N atom [61]. Structural analyses on $[Fe(CO)_4Au_2L]_2$ (L = dppm or dppe) [62] have shown that the bite angle of L exerts a profound influence on the cluster geometry, since L = dppm gives a rhomboid of gold atoms with μ_2-$Fe(CO)_4$ moieties, while for L = dppe well separated Au_2Fe triangles are found.

The structures of $[Au^IX(py)]_4$ where X = Cl, Br or I [63,64] are built up of linear $[Aupy_2]^+$ and $[AuX_2]^-$ ions, which are linked together into tetranuclear, chain-like compounds AuX_2–$Aupy_2$–$Aupy_2$–AuX_2. $[AuBr(py)]_4$ was prepared in two isomeric forms, monoclinic and triclinic. Differences in the interatomic distances were observed (Table 3), and this is an another example of distortion isomerism in gold(I) compounds.

In pentanuclear $[Au^I\{S(Au^IPPh_3)_2\}_2]^+$ [65] the metal atoms fall into two non-equivalent chromophores; one Au(I) atom has an AuS_2 chromophore, and four Au(I) atoms an AuSP chromophore (Table 3). Gold(I) atoms are bridged to each other through a sulphur atom $(Au–S–Au)_4$.

Two distortion isomers of heptanuclear, $[Au_7P_{10}I]$ were prepared and

studied by X-ray analysis [66]. There exist two types of chromophore in each of the isomers, AuP_2 (6 ×) and AuP_3I (1 ×), respectively (Table 3).

Several polynuclear gold compounds exhibit coordination number two and are shown in Table 3.

Structural results confirm the sensitivity of the M–L bond length to the degree of aggregation. Usually, the M–L bond lengths are somewhat shorter in mononuclear compounds than those in an oligomer. For instance, the mean Au–N distance in monomers is about 1.98 Å and in oligomers is 2.08 Å; similarly Au–Cl is 2.21 Å and 2.31 Å and Au–S is 2.288 Å and 2.295 Å in monomers and oligomers, respectively.

The data in Table 1 (monomers) reveal that L–Au–L(L') angles lie in the range 180–155°, which spans a wider range than that found for oligomers (Tables 2 and 3).

C. STRUCTURAL DATA FOR GOLD COMPOUNDS WITH COORDINATION NUMBER THREE

(i) Mononuclear compounds

Structural data for mononuclear gold compounds with coordination number three are collected in Table 4 and a crystal structure of $[Au(PPh_3)_3]^+$ [79] is shown in Fig. 6 as a representative example. The compound contains a central AuP_3 unit with a geometry close to an ideal trigonal plane. The Au atom is 0.20 Å out of the least-squares plane through the P atoms.

Inspection of the data in Table 4 reveals that angular distortion from regular trigonal-planar geometry takes place even in compounds where the trigonal plane contains the same ligands (triphenylphosphine). The distortion originates in the steric repulsion between the bulky triphenylphosphine ligands.

Highly distorted three-fold planar coordination occurs if the trigonal plane is built up by two, or three different types of donor atoms (ligands) (Table 4).

Crystallographic analysis of $[AuRu_3(\mu_2\text{-}COMe)(PPh_3)(CO)_{10}]$ [91,92] and $[Ru_5C(CO)_5\{\mu\text{-}AuPPh_3\}Cl]$ [94] provides evidence for the presence of two independent molecules which have significantly different M–L bond lengths (Table 4).

(ii) Bi, tri-, tetra-, penta- and polynuclear compounds

Structural data for oligonuclear gold compounds are given in Table 5. The data are tabulated by increasing degree of aggregation and by elongation of the Au–Au bond (contact) distance.

In eight of 14 binuclear gold compounds there exists a direct Au–Au bond. From the structural point of view these eight compounds can be divided into two groups. The structures of $[Au^{I}(dpdt)]_2$ [100], $[Au^{I}_2Ni_2(pen)_4]Na_2$ [106], and $[Au^{I}_2\{(Ph_2P)_2CH_2\}\{Bu_2MeP(CH_2)_2\}]$ [107] are illustrated by the molecular structure of $[Au^{I}(Ph_2P)_2CH]_2$ [103] as shown in Fig. 7. The molecule contains an eight-membered $Au_2S_4C_2$ ring, in the first; $Au_2S_4N_2$ in the second; $AuP_2C + AuC_2P$ in the third; and $Au_2P_4C_2$ in the molecule illustrated. Their structural data are presented in Table 5. Two independent $[Au^{I}_2Ni_2(pen)_4]^-$ ions, mostly differing in their M–L distances, demonstrate distortion isomerism.

The crystal structure of $[Au_2Pt(PPh_3)_2(PEt_3)_2Cl]$ [101] is shown in Fig. 8 as a representative example of the second type of binuclear gold compound with a direct gold–gold interaction. The three metal atoms [101] lie at the vertices of an approximately isosceles triangle Au_2Pt in which the long edge is defined by the Au–Au vector (Table 5). Similar structures were found for $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au^{I}_2(PPh_3)_2](BF_4)$ [102] and $[\{Au^{I}PPh_3\}_2(mn)]$ [104] in which the Au_2C triangle is defined by the long Au–Au vector, as well as in $[Os(CO)_4\{AuPPh_3\}_2]$ [105] with a Au_2Os triangle, again with the long Au–Au vector.

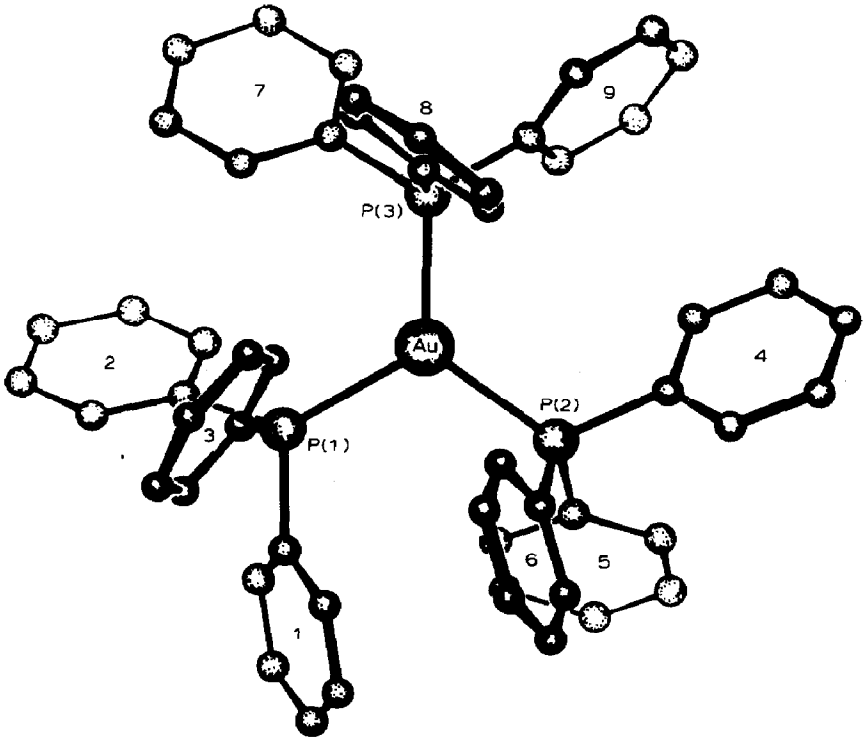

Fig. 6. A perspective of the structure of the $[Au(PPh_3)_3]^+$ cation [79].

TABLE 4

Structural data for mononuclear gold compounds with a coordination number three

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L (°)	Ref.
$[Au^{I}(PPh_3)_3](Ph_4B)$	m	$P2_1/c$	4	AuP_3	16.747 (6)		P 2.365 (3) [a]	115.2 (2)	77
					20.645 (8)	95.06 (2)	2.384 (3)	119.3 (2)	
					18.398 (7)		2.403 (3)	125.4 (2)	
$[Au^{I}_{2/3}Ag^{I}_{1/3}(PPh_3)_3](NO_3)$	tr	$P\bar{1}_1$	4	AuP_3	13.351 (2)	64.23 (2)	P 2.383 (26)	113.4 (8)	78
					13.899 (3)	88.52 (2)	2.391 (29)	115.0 (9)	
					14.361 (2)	75.52 (2)	2.435 (21)	129.7 (8)	
$[Au^{I}(PPh_3)_3](dhd)$	tr	$P\bar{1}$	2	AuP_3	13.086 (12)	103.60 (16)	P 2.373 (14)	112.3 (2)	79
					19.635 (32)	72.10 (9)	2.384 (7)	121.5 (2)	
					11.180 (8)	94.76 (15)	2.389 (6)	124.1 (2)	
$[Au^{I}(PPh_3)_3](PPh_3)\cdot(BPh_4)\cdot CHCl_3$		$P2_1/n$	4	AuP_3	16.009 (6)		P 2.392 (4)	116.0 (2)	80
					30.025 (12)	90.84 (2)	2.406 (4)	119.3 (2)	
					16.893 (6)		2.408 (4)	121.4 (2)	
$Au^{I}(PPh_3)_4\cdot(BPh_4)\cdot EtOH$ [b]		*Ibca*	8	AuP_3	22.161 (1)		P 2.434 (12)		80
					23.111 (11)		2.445 (12)		
					30.651 (14)		2.461 (12)		
				AuP_4			P 2.602 (9) (2×)		
							2.610 (9) (2×)		
$Au^{I}(PPh_3)_4\cdot(BPh_4)\cdot(CH_3CN)$ [c]		*Ibca*	8	AuP_3	21.657 (10)		P 2.359 (6)		80
					22.917 (15)		2.389 (6)		
					30.652 (15)		2.410 (6)		
				AuP_4			P 2.504 (2) (2×)		
							2.561 (2) (2×)		
$[Au^{I}(PPh_3)(bipy)](PF_6)$	tr	$P\bar{1}$	2	AuN_2P	11.025 (1)	81.63 (1)	N 2.166 (2)	71.4 (1) [d]	81
					11.248 (1)	71.98 (1)	2.406 (2)	130.4 (1)	
					12.045 (2)	72.57 (1)	P 2.212	157.1 (1)	
$[Au^{I}(PP)Cl]$				AuP_2Cl			Cl 2.818 (3)	90.4 (1)	82
							P 2.307 (2)	93.4 (1)	
							2.310 (2)	175.7 (1) [e]	
$[Au^{I}(PPh_3)_2Cl]\cdot 0.5\ C_6H_6$	tr	$P\bar{1}$	2	AuP_2Cl	10.187 (1)	52.54 (1)	Cl 2.500 (4)	109.2 (1)	83, 84
					12.997 (1)	90.68 (1)	P 2.323 (4)	118.7 (1)	
					16.596 (1)	75.00 (1)	2.339 (4)	132.1 (1) [e]	
$[Au^{I}(PPh_3)_2Cl]$		$P\bar{1}$	2	AuP_2Cl	11.682	113.65 (2)	Cl 2.526 (10)	108.1 (3)	84
					10.921 (3)	99.35 (3)	P 2.230 (9) [m]	115.1 (3)	
					14.701 (2)	109.31 (3)	2.313 (8)	136.4 (3) [e]	

$[Au^{I}(PPh_3)_2(SCN)]$	m	$P2_1/n$	4	AuP_2S	11.823 (2)		S 2.468 (4)	112.4 (1)	85
					19.795 (6)	91.73 (5)	P 2.346 (4)	119.6 (1)	
					13.887 (5)		2.349 (4)	127.8 (1) [e]	
$(PPhMe_2)_2Au^{I}SnCl_3$	m	$P2_1/m$	2	AuP_2Sn	11.954 (2)		Sn 2.881 (1)	102.2 (1)	86
					9.925 (2)	111.40 (2)	P 2.310 (4)	104.0 (2)	
					10.059 (1)		2.318 (4)	153.8 (2) [e]	
$(CO)_8Os_3Au(PPh_3)_2 \cdot pya$	m	$P2_1/n$	4	$AuOs_2P$	14.567 (5)		P 2.304 (9)	62.7 (1) [f]	87
					18.010 (24)	92.22 (3)	Os 2.738 (2)	141.5 (2)	
					18.456 (7)		2.788 (2)	155.6 (2)	
$Os_4Au^{I}(\mu\text{-}H)(CO)_{13}(PEt_3)$	or	$P2_12_12_1$	4	$AuOs_2P$	23.503 (11)		P 2.288 (12)	63.8 (1) [f]	88
					14.100 (6)		Os 2.745 (2)	146.4 (3)	
					9.012 (4)		2.799 (2)	149.9 (3)	
$Os_4Au^{I}(\mu\text{-}H)_3(CO)_{12}(PEt_3)$	tr	$P\bar{1}$	2	$AuOs_2P$	9.737 (4)	73.40 (2)	P 2.227 (12)	64.0 (1) [f]	88
					10.041 (5)	74.02 (2)	Os 2.783 (2)	146.2 (2)	
					16.256 (8)	89.256 (8)	2.803 (2)	149.8 (2)	
$HOs_4Au^{I}(PPh_3)(CO)_{10}$	m	$P2_1/c$	4	$AuOs_2P$	12.363 (3)		P 2.320 (7)	58.7 (1) [f]	89
					16.128 (4)	109.16 (2)	Os 2.738 (1)	141.8 (2)	
					16.907 (4)		2.772 (2)	159.4 (2)	
$Os_3Au^{I}(PPh_3)(SCN)(CO)_{10}$	m	$P2_1/n$	4	$AuOs_2P$	15.240 (5)		P 2.310 (4)	63.1 (1) [f]	89
					8.962 (4)	106.75 (2)	Os 2.755 (1)	146.5 (1)	
					26.008 (9)		2.768 (1)	148.1 (2)	
$[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2 \cdot (\mu\text{-}AuPPh_3)(CO)_9]$	tr	$P\bar{1}$	2	$AuOs_2P$	13.923 (3)	93.81 (4)	P 2.292 (8)	62.5 (1) [f]	90
					14.213 (4)	105.48 (2)	Os 2.747 (2)	141.5 (2)	
					9.544 (4)	102.83 (2)	2.775 (2)	154.1 (2)	
$[AuRu_3(\mu_2\text{-}COMe) \cdot (PPh_3)(CO)_{10}]$ [g]	tr	$P\bar{1}$	4	$AuRu_2P$	12.952 (7)	107.80 (2)	P 2.301 (6)	62.8 (1) [h]	91, 92
					15.588 (3)	95.46 (3)	Ru 2.760 (2)	144.7 (1)	
					17.386 (3)	90.37 (3)	2.762 (2)	152.5 (1)	
				$AuRu_2P$			P 2.324 (6)	62.4 (1) [h]	
							Ru 2.762 (2)	147.5 (2)	
							2.782 (2)	150.1 (2)	
$[AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe) \cdot (PPh_3)(CO)_9]$	tr	$P\bar{1}$	2	$AuRu_2P$	14.421 (4)	114.02 (2)	P 2.308 (3)	63.2 (1) [h]	92, 93
					14.136 (5)	93.47 (3)	Ru 2.727 (1)	141.3 (1)	
					9.535 (4)	105.19 (2)	2.763 (1)	154.7 (1)	
$[Ru_5C(CO)_{15}\{\mu\text{-}AuPPh_3\}Cl]$ [g]	tr	$P\bar{1}$	4	$AuRu_2P$	15.333 (3)	84.29 (4)	P 2.277 (6)	64.1 (5) [h]	94
					15.865 (3)	84.41 (4)	Ru 2.774 (4)	146.5 (2)	
					18.813 (7)	61.88 (2)	2.811 (3)	147.5 (2)	
				$AuRu_2P$			P 2.283 (7)	64.0 (1) [h]	
							Ru 2.764 (3)	142.9 (2)	
							2.841 (3)	153.0 (2)	

TABLE 4 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L (°)	Ref.
$[Ru_5C(CO)_{14}\{\mu\text{-}AuPPh_3\}\mu\text{-}Br)]$	m	$P2_1/c$	4	$AuRu_2P$	8.967 (1)		P 2.290 (4)	65.0 (1) [h]	94
					29.767 (7)	92.16 (1)	Ru 2.633 (2)	137.2 (1)	
					15.010 (3)		2.850 (2)	157.5 (1)	
$[Ru_3Au(\mu_2\text{-}H)(CO)_9\cdot(PPhMe_2)(\mu_3\text{-}PPh)]$	m	$P2_1/c$	4	$AuRu_2P$	8.805 (3)		P 2.314 (9)		95
					20.195 (7)	100.62 (2)	Ru 2.749 (4)		
					16.683 (6)		2.763 (4)		
$[Ru_5C(CO)_{13}(\eta^5\text{-}C_5H_5)\cdot(AuPPh_3)]$	m	$P2_1/n$		$AuRu_2P$	8.863 (1)		P [i]		96
					16.512 (1)	94.02 (1)	Ru 2.750 (1)		
					27.807 (2)		2.780 (1)		
$[Ru_5C(CO)_{14}(\mu\text{-}\eta^2\text{-}COMe)\cdot(AuPPh_3)]$	m	Pn		$AuRu_2P$	9.613 (1)		P [i]		96
					14.094 (1)	90.70 (1)	Ru 2.721 (3)		
					15.145 (2)		2.764 (3)		
$[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$	tr	$P\bar{1}$	2	AuHPCr	9.310 (3)	112.90 (3)	H 1.72 (11)	34 (4) [j]	97, 98
					12.105 (5)	95.56 (4)	P 2.290 (3)	170 (4)	
					11.967 (4)	109.59 (3)	Cr 2.770 (2)	155.4 (1)	
					9.244 (5)	112.67 (4) [k]			
					12.019 (8)	95.90 (4)			
					11.786 (6)	109.81 (4)			
$[AuW(\mu\text{-}CHC_6H_4Me)(CO)_2\cdot(PPh_3)(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$	tr	$P\bar{1}$	2	AuCPW	9.176 (4)	91.17 (4)	C 2.268 (4)	151.8 (4) [l]	99
					9.837 (5)	104.29 (4)	P 2.262 (4)	159.2 (4)	
					18.319 (11)	87.31 (4)	W 2.729 (1)		

[a] The chemical identity of the coordinated atom (ligand) is specified in this column. [b] The site ratio trigonal: tetrahedral is 1:1. [c] At −150°C; the site ratio trigonal: tetrahedral is 1:7. [d] The value of N–Au–N angle. [e] The value of P–Au–P angle. [f] The value of Os–Au–Os angle. [g] There are two crystallographically independent molecules. [h] The value of Ru–Au–Ru angle. [i] Not given. [j] The values of Cr–Au–H, H–Au–P and Cr–Au–P angles, respectively. [k] Cell dimensions at 210 K. [l] The values of C–Au–P and W–Au–P angles. [m] The original paper may contain a typographical error; this number may be 2.320 (9) Å (M. Khan and D.G. Tuck, personal communication).

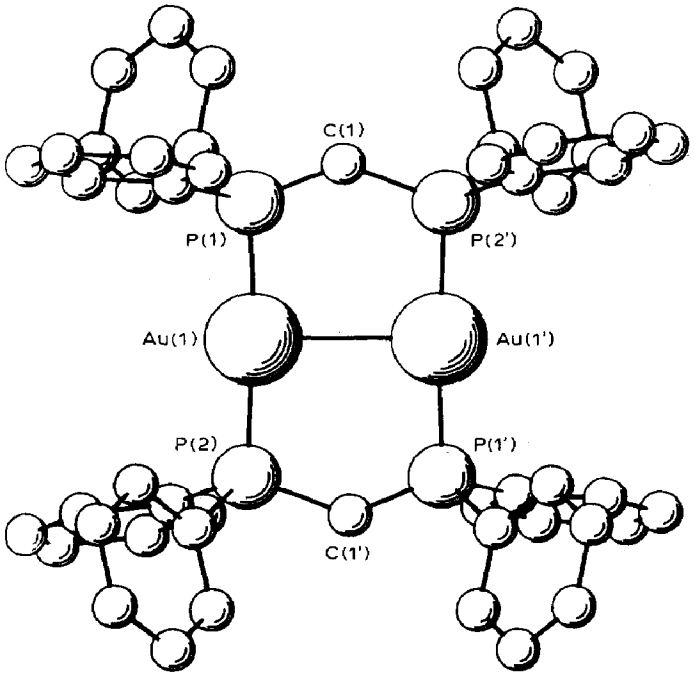

Fig. 7. Molecular structure of $[Au^{I}(Ph_2P)_2CH]_2$ [103].

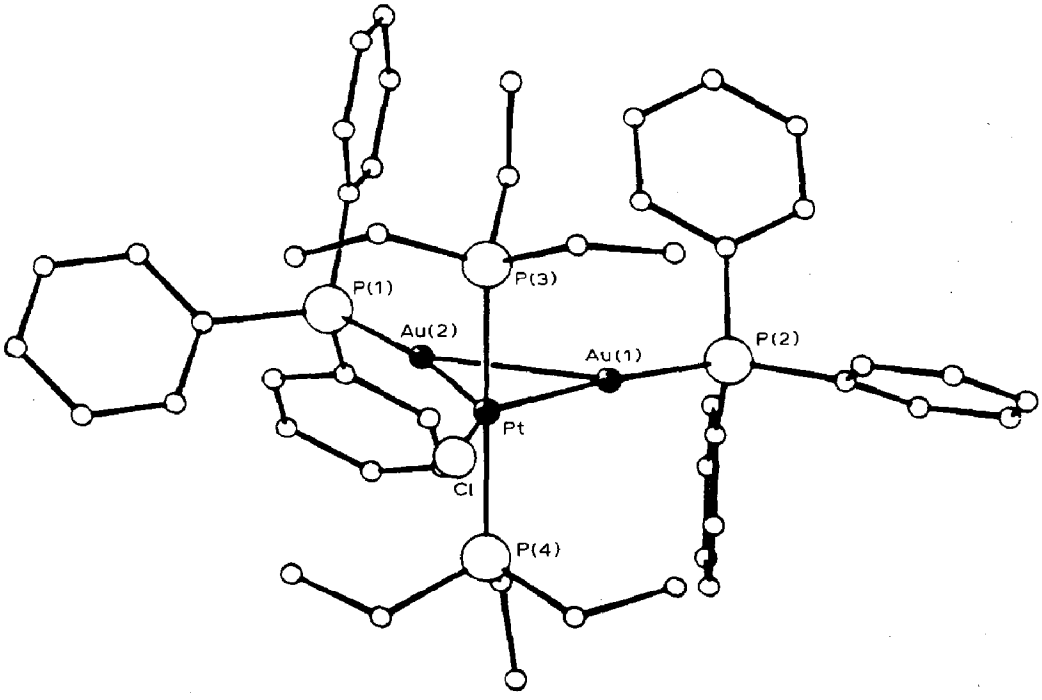

Fig. 8. Structure of $[Au_2Pt(PPh_3)_2(PEt_3)_2Cl]$ [101].

TABLE 5

Structural data for bi, tri-, tetra-, penta- and polynuclear gold compounds with a coordination number three [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M (Å)	L–M–L (°)	Ref.
$[Au^{I}(dpdt)]_2$	tg	$P\bar{4}b2$	2	AuS_2Au'	13.194 (5) – 6.162 (3)		S 2.28 (2) (2×) [b] Au' 2.76 (1)	2.76 (1)		100
$[Au_2Pt(PPh_3)_2(PEt_3)_2Cl]$	tr	$P\bar{1}$	2	AuPPtAu'	14.209 (4) 21.938 (4) 10.614 (5)	81.651 (6) 106.89 (7) 76.57 (7)	P 2.262 (7, 2) Pt 2.600 (4, 1) Au' 2.737 (3)	2.737 (3)	169.1 (3, 4.0)	101
$[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)\cdot Au^{I}_2(PPh_3)_2](BF_4)$	m	$P2_1/a$	4	AuCPAu'	14.460 (11) 30.539 (27) 9.509 (12)	92.61 (5)	C 2.21 (0, 6) P 2.28 (0, 1) Au' 2.768 (3)	2.768 (3)	168 44 [c]	102
				AuCPFeAu'			C 2.27 (4) P 2.283 (12) Fe 2.818 (9) Au 2.768 (3)	2.768 (3)	48 (1) [d] 49 (1) 126.3 (4) 135.6 (4)	
$[Au^{I}(Ph_2P)_2CH]_2$	tr	$P\bar{1}$	1	AuP_2Au'	9.001 (2) 11.407 (5) 11.436 (6)	103.85 (3) 101.89 (3) 74.58 (3)	P 2.290 (7) (2×) Au' 2.883 (3)	2.883 (3)	176.0 (3) 91.8 (2, 8) [e]	103
$[\{Au^{I}PPh_3\}_2(mn)]$	m	$P2_1/c$	4	AuCPAu'	12.055 (6) 14.086 (5) 20.466 (2)	90.32 (4)	C 2.101 (9, 6) P 2.268 (9, 1) Au' 2.912 (1)	2.912 (1)	174.3 (2, 9) [f] 129.61 (6, 78) 46.1 (2, 2)	104
$[Os(CO)_4\{AuPPh_3\}_2]$	or	$Pc2_1/n$	4	AuPOsAu'	13.039 (3) 15.851 (2) 18.499 (3)		P 2.276 (6, 49) Os 2.656 (1, 11) Au' 2.929 (1)	2.929 (1)	171.1 (2, 3.0) [g] 127. 9 (3, 3.4) 56.5 (1, 4)	105
$[Au^{I}_2Ni_2(Pen)_4]Na_2$ [h]	hx	$R3$	18	AuS_2Au'	28.27 (7) – 33.27 (8)		S 2.30 (2) 2.33 (2) Au' 2.94 (1)	2.94 (1)	174 (1, 3)	106
				AuS_2Au'			S 2.28 (2) 2.30 (2) Au' 2.99 (1)	2.99 (1)	176 (1, 0)	
$[Au^{I}_2\{(Ph_2P)_2CH_2\}\cdot\{Bu_2MeP(CH_2)_2\}]$	m	$P2_1/c$	4	AuCPAu'	17.230 (9) 10.232 (3) 23.258 (15)	124.88 (3)	C 2.13 (3, 1) P 2.283 (7, 2) Au' 2.967 (1)	2.967 (1)	173.7 (7, 4.3) 91.2 (2, 7) [i] 89.6 (7, 1.9)	107

$[Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}\cdot(\mu\text{-}AuPEt_3)_2]$	m	$P2_1/c$	4	$AuPFe_2$	12.934 (5) 18.879 (6) 16.425 (9)	106.86 (4)	P 2.276 (5) Fe 2.696 (2) 2.701 (3)		146.9 (2, 1.9) 66.0 (1) [j]	108
				$AuCPFe_4$			C 2.117 (14) P 2.268 (4) Fe 2.935 (3, 107)		176.7 (4)	
$[Os_5C(CO)_{14}\cdot\{Au(PPh_3)\}_2]$	m	$P2_1/c$	4	$AuPOs_2$	20.307 (4) 9.843 (2) 27.980 (6)	90.0 100.53 (2) 90.0	P 2.294 (5, 1) Os 2.771 (1, 109)		66.1 (1.4) [k] 146.6 (1, 16.6)	109
$[Os_3(CO)_{10}(AuPEt_3)_2]$	m	$12/c$	4	$AuPOs_2$	13.701 (3) 14.982 (4) 17.512 (5)	103.47 (2)	P 2.287 (6) Os 2.761 (1, 1)	4.304 (2)	57.4 (1, 8) [k] 151.3 (3)	110
$[WS_4Au_2(PPh_2Me)_2]$	m	$P2_1$		AuS_2P	16.542 (7) 13.504 (4) 6.647 (2)	96.18 (2)	P 2.263 (3, 3) S 2.429 (3, 7)		90.1 (1, 1) [l] 130.9 (1, 9)	111
$[Au^I_2(C_4S_4)(PPh_2Me)_2]$	m	$C2/c$	4	AuS_2P	15.785 (3) 10.723 (2) 18.009 (4)	92.11 (2)	P 2.270 (3) S 2.364 (3, 2) 2.952 (3)		85.9 (2) [l] 111.4 (2) 162.4 (2)	112
$[Ru_6C(CO)_{16}\cdot\{Au(PMePh_2)\}_2]$	m	$P2_1/c$	2	$AuRu_2P$	14.811 (6) 9.698 (4) 18.031 (11)	106.39 (42)	P 2.288 (3) Ru 2.758 (1) 2.788 (1)			113
$[Ph_4C(AuPPh_3)_3(BF_4)]\cdot(C_6H_6)_2$	tr	$P\bar{1}$	2	$AuCPAu'$ (2×)	12.845 (6) 16.042 (8) 22.642 (11)	86.62 (4) 77.51 (4) 76.05 (4)	C 2.13 (2, 3) P 2.290 (5, 8) Au′ 2.820 (1)	2.820 (1)	172.2 (6, 2) 48.5 (5, 9) [m] 131.7 (1, 6.8)	55
				$AuCP$ (1×)			C 2.21 (2) P 2.257 (5)	3.021 (1)	172.8 (4)	
$[Au_3Ir(NO_3)(PPh_3)_5]\cdot(PF_6)$	m	$P2_1/c$	4	$AuPIrAu'$ (2×)	14.042 (3) 13.309 (2) 43.58 (1)	91.07	P 2.258 (0, 5) Ir 2.623 (0, 30) Au′ 2.766 (0, 40)	2.766	161.1 (1, 7) 59.42 (3, 18) [n] 131.0 (1, 1.0)	114
				$AuPIrAu'_2$ (1×)			P 2.281 (1) Ir 2.675 (1) Au′ 2.766 (0, 40)	2.766	115.24 (1) [o] 122.4 (1, 2)	
$[Au_4(dppe)_2Fe_2(CO)_8]$	m	$C2/c$	4	$AuPFeAu'$	15.823 (3) 15.858 (4) 25.708 (3)	95.88 (2)	P not given Fe 2.530 (2, 6) Au′ 2.977 (1)	2.977 (1)		62
$[Au'(mes)]_5$	or	$Pnma$	4	AuC_2Au'	21.864 (10) 27.188 (11) 8.951 (5)		C 2.16 (2, 4) Au′ 2.701(4, 9)	2.701 (4)	150.5 (7, 2.4) 77.4 (6, 1.5) [p]	115

TABLE 5 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M (Å)	L–M–L (°)	Ref.
$[Au_5(dppmH)_3(dppm)]\cdot(NO_3)_2$	m	$P2_1$	2	AuCPAu′ (1×)	15.796 (3) 23.19 (2) 15.280 (4)	 118.47 (2) 	C 2.18 (7) P 2.278 (16) Au′ 3.013 (3)	3.013 (3)	175 (2) 91.6 (4) [q]	116, 117
				$AuP_2Au'_3$ (3×)			P 2.363 (16, 68) Au′ 2.828 (3, 178)	2.828 (3)	134.0 (4, 19.6) [q] 55.4–65.4 [r]	
				$AuPAu'_4$ (1×)			P 2.306 (16) Au′ 2.818 (3, 195)	2.818 (3)	126.4 (4, 37.4) [q] 110.0 (1, 38.5) [r]	
$(Tl_6Au_2I_{10})n$		$P\bar{6}2c$	2	AuI_3	10.569 (1) – 13.431 (2)		I 2.77 (1, 3)	3.358 (1)	120	118
				AuI_6			I 3.25 (2, 11)		85.9 (4, 3.8) 171.1 (9)	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d.; and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] The value of C–Au–Au′ angle. [d] The values of C–Au–Fe, C–Au–Au′, C–Au–P and Fe–Au–P angles, respectively. [e] The value of P–Au–Au′ angle. [f] The values of P–Au–C, P–Au–Au′ and C–Au–Au′ angles, respectively. [g] The values of P–Au–Os, P–Au–Au′ and Os–Au–Au′ angles, respectively. [h] There are two independent anions. [i] The values of P–Au–Au′ and C–Au–Au′ angles. [j] The value of Fe–Au–Fe angle. [k] The values of Os–Au–Os and Os–Au–P angles. [l] The values of S–Au–S and P–Au–S angles. [m] The values of C–Au–Au′ and P–Au–Au′ angles. [n] The values of Au′–Au–Ir and Au′–Au′–P angles. [o] The values of Au′–Au–Au′ and Au′–Au–P angles. [p] The value of Au–C–Au angle. [q] The value of Au′–Au–P angle. [r] The value of Au′–Au–Au angle.

The elongation of the Au–Au distance is also reflected in the simultaneous opening of the Au–L–Au bridging angle. In $[Au^{I}_{2}Pt(PPh_3)_2(PEt_3)_3Cl]$ the Au–Au bond distance is 2.737(3) Å and the Au–Pt–Au angle is 63.5°; in $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au^{I}_{2}(PPh_3)_2]^+$ the Au–Au bond distance is 2.768 Å and Au–C–Au = 77(1)°; in $[\{Au'PPh_3\}_2(mn)]$, Au–Au=2.912Å and Au–C–Au = 87.7(3)°. On the other hand, note that the Au–Au distance, 2.929 Å, found in $[Os(CO)_4\{AuPPh_3\}_2]$, is the highest in the series, in spite of the fact that the bridging Au–Os–Au angle of 66.9(1)° is not the largest; however, the Au–Os bond length of 2.656 Å is the longest in the series. In binuclear $[Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu\text{-}AuPEt_3)_2]$ [108], $[Os_5C(CO)_{14}\{AuPPh_3\}_2]$ [109], $[Os_3(CO)_{10}(AuPEt_3)_2]$ [110], $[WS_4Au_2(PPh_2Me)_2]$ [111], $[Au^{I}_{2}(C_4S_4)(PPh_2Me)_2]$ [112], and $[Ru_6C(CO)_{16}\{AuPMePh_2\}_2]$ [113], for which structural data are given in Table 5, no interaction exists between two gold atoms.

In trinuclear $[Ph_4C_5(AuPPh_3)_3]^+$ [55], only two gold atoms have a coordination number three (AuCPAu') with a Au–Au bond length of 2.820(1) Å. The third atom has a linear coordination (AuCP) and was discussed in Section B(iii). Similar, non-equivalent gold atoms exist in the other trinuclear, $[Au_3Ir(NO_3)(PPh_3)_5]^+$ [114]. Au(1) and Au(3) are three-coordinate (AuPIrAu'), Au(2) is four-coordinate with the $AuPIrAu'_2$ chromophore (Table 5).

Direct Au–Au interactions were found in tetranuclear and pentanuclear compounds, but not in polynuclear $(Tl_6Au_2I_{10})_n$ (Table 5).

There is a tendency for elongation of the M–L bond length from two-coordinate to three-coordinate gold compounds: Au–N (mean value) 2.02 and 2.28 Å; Au–C, 2.05 and 2.21 Å; Au–Cl, 2.26 and 2.62 Å; Au–S, 2.29 and 2.43 Å; Au–P, 2.27 and 2.31 Å, and Au–I, 2.58 and 2.77 Å, respectively. On the other hand, the trend for the Au–Au bond length is opposite, the mean value of 2.84 Å found in two-coordinate oligonuclear compounds, is about 0.03 Å longer than that found in three-coordinate compounds (2.81 Å).

D. STRUCTURAL DATA FOR GOLD COMPOUNDS WITH COORDINATION NUMBER FOUR

(i) Mononuclear gold(I) and gold(0) compounds

Structural data for mononuclear gold(I) and gold(0) compounds are gathered in Table 6. The structures are tabulated by increasing number of hetero-coordinated atoms (ligands). The crystal structure of $[Au^{I}(PPh_2Me)_4]^+$ [119], is shown as a representative example in Fig. 9. The coordination environment about the gold(I) is nearly that of a regular tetrahedron. All Au–P bonds are equivalent (2.449(1) Å, and the two

TABLE 6

Structural data for mononuclear gold(1) and gold(0) compounds with coordination number four [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L (°)	Ref.
$[Au^{I}(PPh_3)_4](BPh_4)EtOH$ [d]		*Ibca*	8	AuP_4	22.161 (1) 23.111 (11) 30.651 (14)		P 2.602 (9) (2×) [b] 2.610 (9) (2×)	[c]	80
				AuP_3			P 2.446 (12, 15)		
$[Au^{I}(PPh_3)_4](BPh_4)(CH_3CN)$ [e]		*Ibca*	8	AuP_4	21.657 (10) 22.917 (15) 30.652 (15)		P 2.504 (2) (2×) 2.561 (2) (2×)	[c]	80
				AuP_3			P 2.383 (9, 24)		
$[Au^{I}(PPh_2Me)_4](PF_6)$		*P4/ncc*	4	AuP_4	14.797 (1) – 22.184 (3)		P 2.449 (1) (4×)	105.24 (4) (2×) 118.32 (4) (2×)	119
$[Au^{I}(dppe)_2](SbF_6)Me_2CO$	m	$P2_1/n$	4	AuP_4	18.685 (2) 19.414 (2) 15.096 (1)	91.69 (1)	P 2.390 (3, 2) 2.416 (3) (2×)	85.7 (1, 4) 122.3 (1, 7.3)	120
$[Au^{I}(pdma)_2][Au^{I}(C_6F_5)_2]$	tr	$P\bar{1}$	2	$AuAs_4$	10.340 (3) 10.982 (3) 17.612 (5)	75.45 (2) 82.35 (2) 87.23 (2)	As 2.471 (2, 11)	87.1 (2, 4) 121.3 (2, 5)	11
				AuC_2			C 2.05 (2, 1)	180	
$[Au^{I}(Ph_3Sb)_4][Au^{I}(C_6F_5)_2]$ [f]	trg	*P3c1*	6	$AuSb_4$	21.615 (3) – 28.598 (4)		Sb 2.630 (7) (2×) 2.669 (14) (2×)	109.0 (3) 109.9 (3)	10
				$AuSb_4$			Sb 2.585 (12) (2×) 2.669 (7) (2×)	109.4 (3) 109.5 (3)	
				$AuSb_4$			Sb 2.627 (6) (2×) 2.648 (12) (2×)	108.5 (3) 110.4 (3)	
				AuC_2			C 2.083 (22, 12)	177.9 (11)	

$[Os_6Au^I(CO)_{20}H_2]\cdot[N(PPh_3)_2]$	m	$C2/c$	8	$AuOs_4$	27.777 (12) 18.273 (8) 26.540 (11)	111.42 (3)	Os 2.807 (1, 2) 2.808 (1, 6)	57.5 (1) 57.1 (1)	121
$[Au^I(PPh_3)_3Cl]$	tr	$P2_1/n$	4	AuP_3Cl	10.197 (2) 33.586 (6) 13.306 (2)	90.04 (2)	P 2.410 (2, 21) Cl 2.710 (2)	117.4 (1, 2.2) 99.3 (1, 8.4)	122
$[Au^I(PPh_3)_3(SCN)]\cdot H_2O$	m	$P2_1/n$	4	AuP_3S	13.806 (6) 22.110 (9) 15.774 (4)	94.68 (4)	P 2.399 (3, 15) S 2.791 (4)	117.6 (1, 4.7) 98.8 (1, 7.8)	123
$[Au^I(PPh_3)_3(SCN)]\cdot H_2O$	or	$P2_12_12_1$	4	AuP_3S	13.95 (5) 30.44 (10) 11.09 (4)		P 2.392 (14, 15) S 2.938 (17)	117.2 (4, 1.9) 99.8 (4, 9.6)	124
$[FeCo_3(CO)_{12}Au^0PPh_3]$		$P2_1$	2	$AuPCo_3$	9.174 (2) 15.103 (2) 12.708 (3)	108.08 (2)	P [c] Co 2.714 (7)	55.3 (3)	125
$[Ru_6C(CO)_{15}(NO)(AuPPh_3)]$	tr	$P\bar{1}$	2	$AuPRu_3$	17.211 (2) 11.851 (2) 10.949 (2)	84.43 (3) 107.2 (3) 104.79 (3)	P 2.296 (5) Ru 2.907 (2, 252)	[c]	126
$[Pt_3Au(\mu_2\text{-}CO)_3(Pcy_3)_4](PF_6)$	m	$C2/c$	8	$AuPPt_3$	19.149 (6) 18.567 (5) 50.968 (12)	95.96 (2)	P 2.27 (3) Pt 2.758 (5, 10)	[c]	127
$[AuW_2(\mu\text{-}C(4\text{-}MeC_6H_4)\cdot(CO)_4(\eta\text{-}C_5H_5)_2](PF_6)$	or	$Pnna$	4	AuC_2W_2	10.024 (11) 22.247 (12) 13.905 (5)		C 2.119 (17) (2×) W 2.752 (1) (2×)	115.4 (10) 162.8 (1)	128
$[RuCo_3(CO)_{12}Au^0PPh_3]$	m	$P2_1/c$	4	$AuPCo_3$	8.921 (3) 14.165 (2) 26.720 (1)	91.95 (4)	P [c] Co 2.721 (4, 42)	[c]	76

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Not given. [d] The site ratio tetragonal : trigonal is 1 : 1. [e] At −150°C; the site ratio tetragonal : trigonal 7 : 1. [f] There are three independent $[Au^I(Ph_3Sb)_4]^+$ cations.

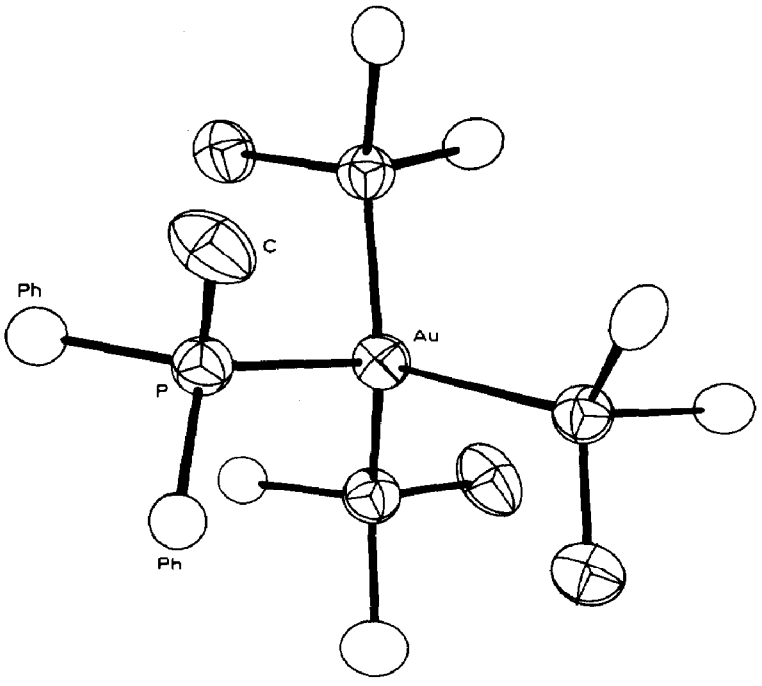

Fig. 9. Structure of the $[Au^{I}(PPh_2Me)_4]^+$ cation [119].

independent P–Au–P angles (105.24(2) and 118.32(4)°) yield a slightly "flattened" tetrahedron. Data (Table 6) confirm the sensitivity of the M–L bond length to the steric bulk of the ligands as well as to the stereochemistry around the metal atoms (Table 4).

The more bulky phosphines force an increase in the Au–P bond length, as seen in the series of gold compounds with a AuP_4 chromophore, where the mean Au–P bond distance increases in the order: dppe (2.403 Å) < PPh_2Me (2.449 Å) < PPh_3 (2.569 Å). The Au–P bonds are longer in the case of the AuP_4 chromophore (2.50 Å) than those found for the AuP_3 chromophore (2.36 Å).

In $[Au^{I}(Ph_3Sb)_4][Au^{I}(C_6F_5)_2]$ [10], three independent $[Au^{I}(Ph_3Sb)_4]^+$ units differ mostly in their Au–Sb bond distances (Table 6) indicating the presence of three distortion isomers.

(ii) Mononuclear gold(III) compounds

There are numerous four-coordinate gold(III) compounds (Table 7). We can see some trends in Table 7. In the series of compounds with the general formula $[AuX_4]M$ (X = F, and M is Li, Na, K or Rb) the value of the unit cell axial ratio c/a increases as the ionic radius (R_{ion}) (Å) of the cation increases in the order: Li^+(c/a, 0.485; R_{ion}, 0.90) < Na^+(1.860; 1.16) <

TABLE 7

Structural data for mononuclear gold(III) compounds with a coordinated number four [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α[°] β[°] γ[°]	M–L (Å)	L–M–L (°)	Ref.
$[Au(NO_3)_4]K$	m	$P2_1/c$	2	AuO_4	9.21 (2) 7.14 (2) 10.04 (2)	 128.6 (3) 	O 1.99 (1) (2×) [b] 2.02 (2) (2×)	89.1 (6) (2×) 90.9 (6) (2×)	129, 130
$[Au(NH_3)_4](NO_3)_3$	or	*Cmmm*	2	AuN_4	7.243 (2) 13.805 (6) 5.302 (2)	 	N 2.02 (1) (4×)	88.6 (6) (2×) 91.4 (6) (2×)	131
$[Au(tmtct)]Cl \cdot 2\ H_2O$	m	$C2/c$	4	AuN_4	23.002 (19) 6.931 (3) 12.828 (8)	 108.66 (9) 	N 1.976 (4) (2×) 1.980 (5) (2×)	96.2 (2)	132
$[Au(tmtcp)](BF_4)$		$P\bar{1}$	2	AuN_4	7.344 (1) 11.192 (2) 11.751 (2)	 106.59 (1) 92.04 (1)	N 1.982 (10, 10) 1.969 (10, 7)	83.9 (5, 3) 96.2 (4, 7)	133
$[Au(CN)_4]H \cdot 2\ H_2O$	m	$P2_1/c$	2	AuC_4	7.881 (5) 10.129 (4) 6.798 (3)	 123.19 (2) 	C 1.95 (2) (2×) 1.99 (2) (2×)	89.9 (7) (2×) 90.1 (7) (2×)	134
$[Au(CN_4i\text{-}pr)](AsPh_4)$	m	$P2_1$	2	AuC_4	11.07 18.66 11.36	 104.5 	C 1.95 (4, 1) 2.00 (4) (2×)	88.4 (14, 1.1) 91.6 (14, 5)	135
$[Au(CH_3)_2\{N(P(CH_3)_2CH_2)_2\}]$		$P2_1/c$	4	AuC_4	6.853 (2) 15.482 (4) 12.708 (4)	 86.58 (2) 	H_3C 2.095 (22, 12) C 2.135 (19, 19)	89.4 (8, 3) 90.6 (8, 2)	136
$[Au(CH_3)_2\{CH(PCH_3)_2CH_2)_2\}]$		*Pbca*	8	AuC_4	10.1602 (15) 13.0519 (14) 20.8249 (30)	 	H_3C 2.090(17, 9) C 2.130 (16, 17)	89.2 (5, 1) 90.8 (6, 6)	136
$[Au(CH_3)_2\{(CH_3)_2SOCH_2\}]$	or	$P2_12_12_1$	4	AuC_4	5.297 (1) 10.953 (3) 17.065 (5)	90.00 90.00 90.00	H_3C 2.14 (5, 2) C 2.12 (6)	86.4 (27, 4) 93.4 (26, 4) 175.7 (32, 3.0)	137, 138
$[Au(CH_3)_2\{(CH_2P(CH_3)_2BH_2\}]$	m	$P2_1/c$	4	AuC_4	6.688 (3) 16.845 (7) 12.686 (8)	 92.23 (5) 	H_3C 2.112 (23, 8) C 2.166 (22.7)	90.36 (82, 1.48) 89.67 (84, 23)	139
$[Au(CH_3)_3(CH_2PPh_3)]$	m	$P2_1/c$	4	AuC_4	9.679 (2) 19.477 (7) 10.713 (3)	90.00 92.71 (2) 90.00	H_3C 2.135 (14, 18) C 2.149 (13)	90.79 (61) 92.20 (63) 177.40 (62)	140

TABLE 7 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α[°] β[°] γ[°]	M–L (Å)	L–M–L (°)	Ref.
cis-[Au(C_6F_5)$_2$(ptdby)]	m	$P2_1/c$	4	AuC_4	12.230 (2) 20.276 (3) 13.123 (2)	 101.21 (2) 	C 2.053 (6) (2×) 2.067 (6) 2.097 (5)	82.4 (3, 5.1) 97.7 (3, 1.1) 171.2 (3, 2.3)	140
[AuF_4]Li	m	$C2/c$	4	AuF_4	11.16 5.39 5.41	 115.7 	F 2.00	[c]	141
[AuF_4]Na	tg		4	AuF_4	5.64 – 10.49		F 2.40	[c]	141
[AuF_4]K	tg		4	AuF_4	5.99 – 11.38		F 2.65	[c]	141
[AuF_4]Rb	tg		4	AuF_4	6.18 – 11.85		F 2.79	[c]	141
[AuF_4]$_2$Mg	or		2	AuF_4	5.32 9.42 6.94				141
[AuF_4]$_2$Ba	tg		2	AuF_4	6.92 – 7.63				141
[$AuCl_4$]H·4 H_2O	m	$C2/m$	2	$AuCl_4$	11.78 4.62 8.89	 101.9 	Cl 2.283 (2×) 2.286 (2×)	[c]	142
[$AuCl_4$]NH_4·2/3 H_2O [d]	m	$C2/c$	12	$AuCl_4$	14.054 (10) 11.519 (5) 14.496 (10)	 102.58 (6) 	Cl 2.267 (8, 14) 2.278 (8, 5)	90.0 (3, 1.9)	143
				$AuCl_4$			Cl 2.264 (8) (2×) 2.253 (12) (2×)	90.5 (5)	
[$AuCl_4$]K [d]	m	Pc	4	$AuCl_4$	8.671 (10) 6.386 (5) 12.243 (10)	 95.37 (8) 	Cl 2.28 (2, 9) 2.29 (3, 4)	90 (1, 4)	144
				$AuCl_4$			Cl 2.28 (3, 8) 2.29 (3, 9)	90 (1, 4)	

$[AuCl_4]K \cdot 2\,H_2O$	or	*Pbcn*	4	$AuCl_4$	11.639 (4)		Cl 2.285 (5) (2×)	90.0 (2, 6)	145
					10.012 (3)		2.291 (6) (2×)	178.4 (2) (2×)	
					7.548 (2)				
$[AuCl_4]Cs$	m	$12/c$	4	$AuCl_4$	9.596 (2)				146
					6.252 (1)	115.65 (2)			
					14.066 (3)				
$[AuCl_4]Rb$	m	$12/c$	4	$AuCl_4$	9.760 (2)		Cl 2.280	[c]	146, 147
					5.902 (1)	120.05 (5)			
					14.116 (3)				
$[AuCl_4]Ag$	m	$12/c$	4	$AuCl_4$	13.223 (9)		Cl 2.281 (6) (2×)	87.5 (3)	147
					4.101 (4)	122.72 (8)	2.284 (7) (2×)	88.8 (3)	
					13.089 (8)				
$Cs_2AgAuCl_6$	tg	$14/mmmm$	2	$AuCl_4$	7.38 (2)				148
					–				
					11.01 (2)				
$[AuCl_4](Hpy)$	m	$C2/m$	2	$AuCl_4$	10.885 (3)		Cl 2.270 (2)	90.9 (2)	149
					11.490 (3)	101.1 (6)			
					4.015 (2)				
$[AuCl_4]\{H(dma)_2\}$	m	$P2_1/a$	2	$AuCl_4$	11.597 (3)		Cl 2.258 (7) (2×)	89.8 (2)	150
					10.404 (2)	108.6 (1)	2.272 (8) (2×)	90.2 (2)	
					7.657 (2)		Cl 2.266 (3) (2×) [e]	89.3 (2)	
							2.263 (3) (2×)	90.7 (2)	
$[AuCl_4][(hyp) \cdot 2\,H_2O$	m	$P2_1/a$	4	$AuCl_4$	7.767 (5)		Cl 2.281 (6, 6)	90.0 (2, 9)	151
					11.338 (5)	97.47 (2)	2.284 (6, 8)	178.5 (2, 3)	
					15.678 (5)				
$[AuCl_4](AsPh_4)$	tg	$P4/n$	2	$AuCl_4$	12.448 (4)		Cl 2.271 (4) (4×)	90.0 (1)	152
					12.448 (4)			179.0 (1)	
					8.034 (2)				
$[AuCl_4][Au(pap)_2]$	tr	$P\bar{1}$	2	$AuCl_4$	18.113 (3)	82.84 (2)	Cl 2.284 (6, 13)	90.3 (3, 3)	153
					9.752 (2)	101.90 (2)			
					7.515 (2)	99.17 (1)			
				AuC_2N_2			C 1.99 (2, 1)	98.1 (9) [f]	
							N 2.17 (2) (2×)	107.1 (6)	
								77.4 (8, 7)	
$[AuBr_4]Rb$	m	$P2_1/a$	2	$AuBr_4$	10.299 (2)				146
					6.214 (1)	121.33 (5)			
					7.436 (1)				
$[AuBr_4]Cs$	m	$I2/c$	4	$AuBr_4$	9.926 (2)				146
					6.510 (1)	114.90 (5)			
					14.769 (3)				

TABLE 7 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α[°] β[°] γ[°]	M–L (Å)	L–M–L (°)	Ref.
$[Au(S_2CNBu_2)_2](AgBr_2)$	m	$C2/c$	4	AuS_4	17.39 (1) 18.65 (1) 9.199 (6)	 93.9 (1)	S 2.324 (8) (2×) 2.357 (8) (2×)	75.5 (3)	154
$[Au(S_2CNBu_2)_2]^+ \cdot [Au\{S_2C_2(CN)_2\}_2]^-$	m	$P2_1/c$	2	AuS_4	9.930 (3) 12.517 (3) 15.632 (3)	 110.46 (3)	S 2.333 (4) (2×) [g] 2.337 (4) (2×) S 2.312 (4) (2×) 2.306 (5) (2×)	75.1 (2) 90.7 (2)	155
$[Au(S_2CNBu_2)\{S_2C_2(CN)_2\}]$	or	$Pbca$	8	AuS_4	14.066 (3) 28.980 (2) 9.192 (2)		S 2.324 (5) [h] 2.329 (5) S 2.284 (5) 2.303 (5)	75.0 (2) 95.1 (2) 90.9 (2) 99.1 (2)	156
$[Au(S_2CNEt_2)_3]$	m	$P2_1/c$	4	AuS_4	7.512 (2) 15.479 (3) 20.762 (3)	 90.46 (10)	S 2.333 (4) (2×) 2.350 (4, 3)	75.0 (2) 92.0 (2) 97.1 (2, 4)	157
$[Au\{S_2C_2(CF_3)_2\}_2]\cdot(PClPh_3)$	m	$P2_1/n$	4	AuS_4	13.166 (10) 11.623 (9) 20.486 (15)	 91.21 (2)	S 2.287 (8, 5) 2.290 (8, 6)	90.0 (3, 6)	158
$[Au(S_2CNBu_2)_2]Br$	m	$P2/c$	2	AuS_4	11.45 (2) 4.97 (1) 22.62 (3)	 97.45 (10)	S 2.309 (6) (2×) 2.334 (6) (2×)	75.4 (2)	159
$[Au(S_2C_6H_3Me)_2](n\text{-}Bu_4N)$	m	$P2_1/a$	4	AuS_4	18.823 (4) 19.126 (5) 9.366 (5)	 96.72 (3)	S 2.299 (4) (2×) 2.306 (4) (2×)	90.0 (1, 1.6) 178.6 (1, 8)	160
$[Au(S_2CNBu_2)_2(CuBr_2)$	m	$C2/c$	4	AuS_4	22.215 (2) 16.231 (4) 8.182 (1)	 97.65 (1)	S [e]	[e]	180
$[Au(terpy)Cl]Cl_2\cdot 3\,H_2O$		$P2_1/c$	4	AuN_3Cl	8.457 (6) 7.084 (2) 31.246 (3)	90 94.748 (7) 90	N 1.993 (6, 62) Cl 2.269 (2)	81.4 (3) (2×) 162.7 (3) 98.6 (2, 1) [j]	161
$[Au\{NH(ae)\}Cl](ClO_4)$	m	$P2_1/n$	4	AuN_3Cl	8.590 (6) 12.745 (8) 12.256 (8)	 113.6 (1)	N 2.00 (2, 5) Cl 2.273 (8)	85.6 (9, 3) [i] 170 (1) 94.4 (8, 6) [j] 176.4 (6)	162
$[Au\{N(ae)\}Cl](ClO_4)$	or	$P2_12_12_1$	4	AuN_3Cl	12.976 (8) 10.029 (7) 8.171 (6)		N 2.04 (4, 3) Cl 2.33 (1)	86 (1, 2) [i] 168 (1) 95 (1, 1) [j] 176 (1)	162

$[AuCl_3(NH_3)]$	m	$P2_1/c$	4	$AuCl_3N$	6.161 (1)		N 2.012 (15)	90.5 (3, 5) [i]	163
					10.969 (2)	126.77 (3)	Cl 2.282 (5, 5)	89.5 (3, 1, 1) [j]	
					9.899 (2)				
$[AuCl_3(azt)]$ [d]	m	$P2_1/n$	4	$AuCl_3N$	15.909 (3)		N 2.134 (2)	91.7 (1, 3) [i]	164
					10.052 (2)	92.17 (2)	Cl 2.268 (3, 4)	88.4 (5, 2.8) [j]	
					10.413 (2)				
				$AuCl_3N$			N 2.022 (13)	91.7 (1, 3) [i]	
							Cl 2.268 (3, 4)	88.2 (4, 2.4) [j]	
$[AuCl_3(prazepam)$	m	$P2_1/n$	4	$AuCl_3N$	12.542 (4)		N 2.031 (17)	91.4 (3, 1) [i]	165
					9.269 (4)	102.67 (2)	Cl 2.270 (8, 11)	88.7 (5, 9) [j]	
					19.574 (6)				
$[AuCl_3(Py)]$	m	$C2/c$	8	$AuCl_3N$	20.58 (2)		N 1.993 (7)	89.8 (2, 10.3) [l]	149
					7.27 (1)	128.10 (5)	Cl 2.278 (4, 18)	89.5 (3, 4) [j]	
					15.23 (2)				
$[AuCl_3(C_{12}H_8S_2)](CHCl_3)$ [k]	m	Cm	2	$AuCl_3S$	12.887 (3)		S 2.351 (15)	89.8 (5) [i]	166
					14.275 (5)	103.05 (2)	Cl 2.289 (11, 16)	179.5 (6)	
					5.331 (2)			90.2 (5) [j]	
								175.9 (7)	
$[AuCl_3(PPh_3)]$	tr	$P\bar{1}$	2	$AuCl_3P$	10.683 (8)	92.19 (8)	P 2.335 (4)	89.2 (2, 7) [i]	167
					9.109 (6)	69.68 (8)	Cl 2.300 (4, 47)	172.7 (2)	168
					10.090 (8)	91.69 (8)		91.5 (1, 2.3) [j]	
								169.9 (1)	
$[Au(CH_3)_3(PPh_3)]$ [d]	tr	$P\bar{1}$	4	AuC_3P	15.569 (8)	103.70 (6)	P 2.350 (6)	91.7 (0, 2.4) [j]	138
					12.652 (4)	99.10 (6)	C 2.064 (25, 141)	177.7	
					10.676 (9)	99.76 (4)			
				AuC_3P			P 2.347 (6)	93.1 (0, 1.6) [j]	
							C 2.066 (27, 45)	174.2	
$[Au(C_6F_5)_3(pdma)]$	m	$P2_1/n$	4	AuC_3As	10.796 (3)		As 2.453 (1)	89.7 (4, 4) [j]	169
					17.347 (6)	94.47 (3)	C 2.085 (11, 20)	179.3 (4)	
					16.275 (5)			90.3 (3, 1.5) [j]	
								176.2 (3)	
$[AuBr_3(PEt_3)]$	m	$P2_1/n$	4	$AuBr_3P$	7.871 (3)		P 2.328 (2)	90.16 (5, 10) [i]	170
					14.171 (5)	94.41 (3)	Br 2.430 (1, 38)	176.05 (4)	
					11.734 (3)			89.80 (7, 2.19) [j]	
								177.43 (7)	

TABLE 7 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α[°] β[°] γ[°]	M–L (Å)	L–M–L (°)	Ref.
$[Au(CH_3)_2(Otf)(H_2O)]$	or	*Abam*	8	AuC_2O_2	17.301 (4) 14.417 (4) 7.076 (2)		C 2.018 (9, 1) O 2.201 (6) H_2O 2.157 (6)	90.1 (4) [l] 88.1 (2) [m] 90.9 (3, 2.0) [j]	171
$[Au(CH_3)_2\{HB(pz)_3\}]$	rh	R_3c			17.98 (1)	117.98 (5)			172
	hx		18	AuC_2N_2	30.82 (1) – 7.739 (2)		C 2.04 (2, 1) N 2.12 (2, 1)	86.5 (1) [l] 88.2 (6) [n] 92.6 (9, 9) [j] 176.7 (10, 3)	
$[Au(CH_3)_2(tpzm)]NO_3$	m	$P2_1/n$	4	AuC_2N_2	16.72 (1) 9.662 (3) 10.700 (4)	107.83 (3)	C 2.027 (8, 4) N 2.135 (5, 6)	87.0 (3) [l] 86.8 (2) [n] 93.0 (3, 3) [j] 177.2 (8, 3)	173
$[Au(CH_3)_2(tpm)]NO_3 \cdot 2\,H_2O$	or	$P2_12_12_1$	4	AuC_2N_2	18.56 (1) 11.150 (7) 9.983 (7)		C 2.034 (13, 7) N 2.132 (9, 5)	87.4 (6) [l] 85.0 (3) [n] 93.8 (5, 6) [j] 178.2 (7, 6)	173
$[Au(CH_3)_2(dpt)]NO_3$	m	$P2_1/n$	4	AuC_2N_2	14.142 (6) 13.012 (7) 10.372 (3)	100.60 (3)	C 2.039 (12, 1) N 2.142 (8, 1)	86.9 (5) [l] 84.8 (3) [n] 94.2 (4, 3) [j] 178.6 (9, 7)	173
$[Au(C_6F_5)_2(dppm)]ClO_4$	or	*Pnma*	4	AuC_2P_2	17.204 (4) 20.053 (4) 11.348 (2)		C 2.071 (10) (2×) P 2.361 (3) (2×)	89.1 (6) [l] 71.5 (2) [o] 99.7 (3) [j] 171.2 (3)	174
$[AuI_2\{C(ma)_2\}_2]ClO_4 \cdot Et_2O$	m	$P2_1/c$	4	AuC_2I_2	10.03 15.915 25.21	101.63	C 2.08 (2, 1) I 2.604 (2, 3)	[c]	175
$[AuCl_2(py)_2]Cl \cdot H_2O$	m	$B2_1/m$	4	$AuCl_2N_2$	14.66 12.64 7.47	91			176
	m	$P2_1/n$	4	$AuCl_2N_2$	13.195 (4) 12.600 (7) 8.231 (3)	95.83 (3)	Cl 2.273 (4, 4) N 1.971 (7, 5)	90.8 (1, 3.2) [p] 90.2 (2, 3.2) [j]	149

$[AuCl_2(dpk \cdot H_2O)]Cl$	m	$P2_1/c$	4	$AuCl_2N_2$	10.398 (10) 7.249 (8) 18.406 (12)	91.60 (8)	Cl 2.257 (7, 1) N 2.04 (2, 4)	89.7 (2) [p] 86.4 (6) [n] 92.0 (5, 4) [j] 178.1 (5, 1)	177, 178
$[Au(SO_3)_2en]_2(C_2H_{10}N_2)$	tr	$P\bar{1}$	1	AuN_2S_2	7.975 (1) 7.872 (1) 9.198 (1)	93.88 (2) 94.90 (2) 100.07 (1)	N 2.126 (7, 7) S 2.305 (2, 4)	95.6 (2) [q] 81.9 (3) [n] 91.3 (2, 1.5) [j]	179
$[Au(S_2CNBu_2)Br_2]$	m	$C2/c$	4	AuS_2Br_2	13.85 (3) 14.94 (3) 7.4 (2)	98.8 (3)	S [c] Br [c]	[c]	181
$[Au(S_2CNBu_2)Br_2]$(t-stb)		$P\bar{1}$	1	AuS_2Br_2	8.168 (2) 10.236 (3) 13.356 (3)	74.97 (3) 103.95 (3) 95.15 (3)	S 2.293 (5, 4) Br 2.439 (2, 4)	75.5 (2) [q] 95.05 (7) [r] 94.7 (2, 1) [j] 170.1 (2, 1)	182
$[Au(S_2CNBu_2)Br_2]$(t-db)		$P\bar{1}$	1	AuS_2Br_2	7.920 (1) 11.104 (1) 13.933 (2)	70.91 (1) 91.71 (1) 110.55 (1)	S 2.306 (2, 3) Br 2.435 (1, 7)	75.27 (7) [q] 90.00 (3) [r] 95.38 (7, 8) [j] 170.5 (1) (2×)	182
$[AuCl(PPh_3)(C_6F_5)_2]$	tg	$P4_2bc$	8	AuC_2ClP	25.56 (1) 25.56 (1) 9.069 (3)		C 2.15 (10, 3) Cl 2.38 (2) P 2.37 (3)	91 (3) [p] 88 (3) [s] 174 (2) 90 (2) [t] 179 (3)	183
$[AuCl_2(Ph)n\text{-}Pr_2S)]$	m	$P2_1/c$	4	$AuCl_2CS$	9.32 (2) 16.10 (3) 10.09 (2)	91.6	C 2.00 (1) Cl 2.33 (1, 6) S 2.31 (1)	[c]	184
$[AuBr_3(SP)]$		$P2_1/n$	4	$AuBr_2CP$	8.59 13.70 17.91	97.3	C 2.10 P 2.26 Br 2.49 (2×)	[c]	185
$[AuBr_3(AP)]$		$Pbca$	8	$AuBr_2CP$	15.23 32.13 8.87		C 2.13 P 2.29 Br 2.49 (0, 3)	[c]	185

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Not given. [d] There are two crystallographically independent species. [e] By neutron diffraction. [f] The values of C–Au–C, N–Au–N and C–Au–N angles. [g] In $[Au(S_2CNBu_2)_2]^+$ cation. [h] The first two values belong to the $(S_2CNBu_2)_2$ ligand. [i] The values of *cis*- and *trans*-L–Au–L angles. [j] The values of *cis*- and *trans*-L–Au–L′ angles. [k] At −70°C. [l] The value of C–Au–C angle. [m] The value of O–Au–O angle. [n] The value of N–Au–N angle. [o] The value of P–Au–P angle. [p] The value of Cl–Au–Cl angle. [q] The value of S–Au–S angle. [r] The value of Br–Au–Br angle. [s] The value of *cis*- and *trans*-C–Au–Cl angles. [t] The value of *cis*- and *trans*-C–Au–P angles.

$K^+(1.899; 1.52) < Rb^+(1.917; 1.66)$; also when X = Cl, and M is Ag, K, Rb or Cs: $Ag^+(0.990; 1.08) < K^+(1.412; 1.52) < Rb^+(1.446; 1.66) < Cs^+(1.466; 1.81)$.

In $[Au(tmtct)]^+$ [132] and $[Au(tmtcp)]^+$ [133] the AuN_4 chromophores are built up by a tetradentate ligand, while in $[Au(terpy)Cl]^{2+}$ [161] as well as [Au{NH(ae)}Cl] and $[Au\{N(ae)\}Cl]^+$ [162] tridentate ligands are present.

In spite of the presence of three potentially bidentate ligands in $[Au(S_2CNEt_2)_3]$ [157], only one is coordinated to the central atom through both its S donor atoms, while the other two are monodentate. An approximate square-planar configuration about the Au(III) atom is built up by two bidentate ligands in $[Au(pap)_2]^+$ [153], $[Au(S_2CNBu_2)_2]^+$ [154,159,180], $[Au(S_2CNBu_2)_2]^-$ and $[Au\{S_2C_2(CN)_2\}_2]$ [155], $[Au(S_2CNBu_2)\{S_2C_2(CN)_2\}]$ [156], $[Au\{S_2C_2(CF_3)_2\}_2]^-$ [158] and $[Au(S_2C_6H_3Me)_2]^-$ [160]. In a few examples [136,139,140,172–175,177–179] three ligands, one bidentate and two monodentate, build up a four-coordinate environment about the Au(III) atoms.

Four monodentate ligands are the most common framework for four-coordinate gold(III) compounds (Table 7). The mean Au(III)–P bond length of 2.33 Å is about 0.17 Å smaller than that found in mononuclear Au(I) compounds (2.50 Å) (Table 6).

In $[AuCl_4]^-$ [143,144], $[Au(CH_3)_3(PPh_3)]$ [138] and [AuCl(azt)] [164], two crystallographically independent distortion isomers are present.

(iii) Binuclear compounds

Structural data for binuclear gold compounds are summarised in Table 8. The data are tabulated via increasing Au–Au bond length (contact). The gold compounds in Table 8 can be divided into a few groups. The structures of $[Au_2Pt_2(PPh_3)_4(CN\text{-xylyl})_4]^{2+}$ [186], $[Au^{III}\{N(CH_3)_2\}(CH_3)_2]_2$ [191] (Fig. 10), $[Au_2^{III}O_6]^{6+}$ [192], $[Au^{III}Cl_3]_2$ [193], $[Au^{III}Br_3]_2$ [194], $[Au_2Br_4(CH_3)_2]$ [195], $[Au^{III}(Et)_2Br]_2$ [196] and $[Au_2^{III}Sr(OH)_8]$ [198], consist of a planar Au_2L_6 unit, in which two Au atoms are bridged by two other atoms (ligands) (Table 8). The extension of the Au–Au distance is reflected in simultaneous opening of the Au–L–Au bridging angle.

The molecules of $[Au^{III}\{Et_2P(CH_2)_2\}Cl]_2$ [187], $[Au^{II}\{Ph_2P(CH_2)S\}I]_2$ [46] and $[Au'\{(Ph_2P)_2CH_2\}Cl]_2$ [190] contain an eight membered $Au_2C_4P_2$, $Au_2C_2S_2P_2$ and $Au_2P_4C_2$ ring, respectively. The Au–Au bond length increases with a decrease in oxidation state of the central atom (Table 8).

The two gold atoms in $[Au_2^{III}Br_4(CH_3)_2]$ [195] fall into two non-equivalent classes exhibiting different coordination patterns, $AuBr_4$ and AuC_2Br_2, respectively. Different coordination numbers, three and four, have been found in $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2^I(PPh_3)_2]^+$ [102]; and four and five in

TABLE 8

Structural data for binuclear gold compounds with a coordination number four [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	Au–L (Å)	Au–Au′ (Å) (°)	L–Au–L Au′–Au–L (°)	Ref.
$[Au^{I}_2Pt_2(PPh_3)_4 \cdot (CN\text{-}xylyl)_4] \cdot (PF_6)_2$	tr	$P\bar{1}$	2	$AuPPt_2Au'$	13.882 (4) 15.460 (2) 27.578 (5)	77.99 (5) 88.95 (2) 67.42 (5)	P [c,b] Pt 2.714 (2, 3) 2.974 (2, 52) Au′ 2.590 (2)	2.590 (2)	125.0 (2, 10.1) 57.8 (1, 6); 68.2 (1, 1.3) 54.0 (1, 7) [d]	186
$[Au^{II}[Et_2P(CH_2)_2\}Cl]_2$	tr	$P\bar{1}$	1	AuC_2ClAu'	7.296 (9) 8.626 (9) 7.945 (8)	91.19 (8) 102.53 (8) 97.35 (8)	C 1.942 (5) Cl 2.359 (3) Au′ 2.597 (5)	2.597 (5)	[e]	187
$[Au^{II}\{Ph_2P(CH_2)S\}I]_2$ [e]	m	$P2_1/n$	4	AuCSIAu′	12.615 (4) 12.804 (2) 19.303 (3)	94.30 (1)	C 2.092 (15) S 2.370 (5) I 2.693 (2) Au′ 2.607 (1)	2.607 (1)	[c]	46
				AuCSIAu′			C 2.101 (15) S 2.369 (5) I 2.681 (1) Au′ 2.611 (1)	2.611 (1)	[c]	46
$[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4) \cdot Au^{I}_2(PPh_3)_2\}(BF_4)$	m	$P2_1/a$	4	AuCPFeAu′	14.460 (11) 30.539 (27) 9.509 (12)	92.61 (5)	C 2.28 P 2.29 Fe 2.82 Au′ 2.768 (3)	2.768 (3)	48 [f] 136 49 126	101, 102
				AuCPAu′ [g]						
$\{Os_4H_2(CO)_{12}(Au^{I}PPh_3)_2\}$	m	$C2/c$	8	$AuPOs_2Au'$	38.239 (15) 13.265 (5) 23.447 (10)	113.41 (3)	P [c] Os 2.889 (4, 115) Au′ 2.793 (4)	2.793 (4)	62.0 (1, 8) [h] 148.4 (6, 3.7) 61.1 (1, 3.1) 124.8 (4)	188
$[Ru_5WC(CO)_{17}(AuPEt_3)_2]$	or	$P2_12_12_1$	4	$AuPRu_2Au'$	13.217 (3) 16.265 (4) 19.422 (8)		P 2.27 (1) Ru 2.852 (5, 13) Au′ 2.808 (3)	2.808 (3)	[c]	113
				$AuPRu_3Au'$			P 2.29 (1) Ru 2.909 (5, 26)		[c]	

TABLE 8 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	Au–L (Å)	Au–Au′ (Å)	L–Au–L Au′–Au–L (°)	Ref.
$[Au^{I}_{2}Ru_3(\mu_3\text{-}S)(CO)_8\cdot(PPh_3)_3]\cdot 0.5(CH_2Cl_2)$	m	$P2_1/c$	4	$AuPRu_2Au'$	19.577 (12) 14.645 (11) 21.901 (8)	 102.15	P 2.310 (3) Ru 2.802 (2, 6) Au′ 2.915 (2)	2.915 (2)	65.6 (1) [i] 147.2 (1, 5.9) 128.8 (1)	189
				$AuPRu_3Au'$			P 2.305 (3) Ru 2.847 (2, 63)		61.6 (1, 3.4) [i] 143.0 (1, 11.8) 58.4 (1, 3); 105.2 (1) 119.5 (1)	
$[Au^{I}[(Ph_2P)_2CH_2\}Cl]_2\cdot$ (solvent)	tr	$P\bar{1}$	1	AuP_2ClAu'	11.76 (1) 10.60 (1) 11.72 (1)	92.40 (7) 112.60 (8) 87.69 (7)	P 2.307 (3, 21) Cl 2.771 (4) Au′ 2.962 (1)	2.962 (1)	155.9 (1) [j] 88.4 (1), 115.7 (1) 89.2 (1, 3.3) 97.0 (1)	190
$[Au^{III}_{2}Sr(OH)_8]$	tg	$I422$	2	AuO_4	5.588 (1) – 11.853 (3)		O 1.980 (8)	3.019 (3)	90 178.2 (4)	198
$[Au^{III}_{2}Ba(OH)_8]$				AuO_4	5.722 (2) – 12.104 (4)		O [c]	[c]	[c]	198
$[Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)\cdot(CO)_9(PPh_3)_2]$	tr	$P\bar{1}$	2	$AuCPRu_2$	13.016 (4) 13.803 (4) 15.124 (4)	102.26 (2) 108.73 (2) 100.15 (2)	C 2.665 (13, 1) P 2.316 (4) (2×) Ru 2.746 (1, 50)	3.176 (1)	101.2 (3, 6.5) [k] 42.2 (3, 1); 105.2 (3, 9) 146.7 (1, 13.6) 63.4 (1, 4)	189
$[Au^{III}\{N(CH_3)_2\}(CH_3)_2]_2$	m	$P2_1/c$	2	AuC_2N_2	7.196 (4) 11.537 (3) 8.174 (3)	 108.55 (4)	C 2.056 (6, 2) N 2.140 (5, 0) [l]	3.231 (1)	87.3 (2) [m] 82.0 (2) 95.4 (2, 4); 176.8 (2, 6) 98.0 (2)	191

$[Au^{II}_2O_6]Na_6$	tg	$P4_2/mnm$	4	AuO_4	9.465		O 2.12 (2×)	[c]	[c]	192
					–		O 2.17 (2×) [l]			
					4.506					
$[Au^{III}Cl_3]_2$	m	$P2_1/c$	4	$AuCl_4$	6.57		Cl 2.24 (0.1)	3.43	90 (4)	193
					11.04	113.3	Cl 2.34 (0.1) [l]			
					6.44					
$[Au^{III}Br_3]_2$	m	$P2_1/c$	4	$AuBr_4$	6.831 (6)		Br 2.398 (2, 15)	3.588 (1)	90.02 (5, 3.76)	194
					20.41 (1)	119.74 (7)	Br 2.462 (2, 9) [l]			
					8.105 (9)					
$[Au^{III}_2Br_4(CH_3)_2]^n$		$C2/c$	4	$AuBr_4$	12.202 (2)		Br 2.402 (2) (2×)	3.705 (1)	90.00 (7, 84)	195
					10.722 (2)	94.19	Br 2.453 (2) (2×) [l]			
					7.673 (2)					
				AuC_2Br_2			C 2.12 (1) (2×)		89.6 (5) [o]	
							Br 2.607 (2) (2×) [l]		82.68 (7)	
									93.9 (5)	
$[Au^{III}(Et)_2(Br)]_2$			2	AuC_2Br_2	9.63	121.10	C [c]	[c]	100 [p]	196
					9.33	89.6	Br 2.65 (10,1)		80	
					4.98	105.48				
$[Au^{III}(\mu\text{-}CH_2)\{Me_2P(CH_2)_2\}]_2$				AuC_3Cl			[c]	[c]	[c]	197
$Au^{III}_2Sr(OAc)_8 \cdot 2\,H_2O$	m	$C2/c$	4	AuO_4	12.332 (4)		O 1.975 (8,1)	3.58 (1)	89.8 (4, 1.4)	199
					11.487 (4)	101.97 (3)	1.992 (9)		173.9 (4,3)	
					19.496 (8)					
$[Os_8(CO)_{22}(Au^0PPh_3)_2]$	or	$Pna2_1$	4	$AuPOs_3$	26.192 (6)		P 2.289 (15, 14)	4.534 (1)	[c]	200
					25.030 (6)		Os 2.897 (3, 157)			
					10.404 (3)					

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of an e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Not given. [d] The value of Au–Pt–Au′ angle. [e] There are two independent molecules. [f] The values of Fe–Au–C, Au–Au–C, Fe–Au–P, and Au–Au–P angles. [g] Presented in Table 5. [h] The values of Os–Au–Os, Os–Au–P, Os–Au–Au and P–Au–Au angles. [i] The values of Ru–Au–Ru, Ru–Au–P, Ru–Au–Au and P–Au–Au angles. [j] The values of P–Au–P, P–Au–Cl, P–Au–Au and Cl–Au–Au angles. [k] The values of C–Au–P, C–Au–Ru, P–Au–Ru, Ru–Au–Ru angles and C–Au–Au = 54.1(2)° and 101.8(3)°; P–Au–Au = 124.7(1, 2.0)° and Ru–Au–Au = 69.1(1,19.6)°. [l] The bridged atoms. [m] The values of C–Au–C, N–Au–N, O–Au–N and Au–N–Au angles. [n] At −160°C. [o] The value of C–Au–C, Br–Au–Br and C–Au–Br angles. [p] The values of Br–Au–Br and Au–Br–Au angles.

TABLE 9

Structural data for tri-, tetra-, hexa- and polynuclear gold compounds with coordination number four [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	Au–L (Å)	Au–Au' (Å)	Au'–Au–Au'' L–Au–Au' (°)	Ref.
$[Au_3Ir(NO_3)(PPh_3)_5]\cdot(PF_6)$	m	$P2_1/c$	2	$AuPIrAu'_2$ (1×)	14.042 (3)		P 2.281 (1) [b]	2.766 (1)	115.24 (3)	114
					13.309 (2)	91.07 (2)	Ir 2.267 (1)		59.42 (3, 18);	
									139.0 (1, 1.1)	
					43.58 (1)		Au' 2.766 (1, 40)			
				AuPIrAu' (2×)			P 2.258 (0, 5)		[c]	
							Ir 2.623 (0, 30)			
							Au' 2.766 (1, 40)			
$[Au_3CoRu_3(CO)_{12}\cdot(PPh_3)_3]$	tr	$P\bar{1}$	2	$AuPRu_2Au'$	13.944 (2)	68.62 (2)	P [d]	2.784 (1)	[c]	201
					14.105 (3)	79.16 (2)	Ru 2.850 (3, 67)			
					20.365 (6)	63.89 (2)	Au' 2.784 (1)			
				AuPCoRuAu'			P [d]	2.836 (1)	[c]	
							Co 2.712 (4)			
							Ru 2.813 (2)			
							Au' 2.836 (1)			
				$AuPCoRu_2Au'_2$			P [d]	2.810 (1)	[c]	
							Co 2.726 (4)			
							Ru 2.952 (3, 102)			
							Au' 2.810 (1, 26)			
$(Ph_3PAu)_3V(CO)_5$		$P\bar{1}$	2	$AuPVAu'_2$	12.840 (6)	93.82 (3)	P 2.296 (2, 5)	2.817	60.00 (1, 1.7)	202
					19.088 (6)	117.26 (3)	V 2.733 (1, 24)		58.98 (2, 1.2);	
									129.72 (4, 9.0)	
					12.380 (4)	92.02 (3)	Au' 2.817 (0, 49)		168.12 (5, 11.0) [e]	
$[Au_3Ru_4(\mu\text{-}H)(CO)_{12}\cdot(PPh_3)_3]$	m	$P2_1/n$	4	$AuPRu_2Au'$ (2×)	22.31 (1)		P 2.284 (8, 5)	2.830	–	93
					18.54 (4)	113.33 (5)	Ru 2.833 (5, 11)		61.8 (1, 2.2);	203
									143.6 (2, 3.0)	
					18.76 (1)		Au' 2.830 (2, 8)		142.9 (2, 3.7) [f]	
				$AuPRu_3Au'_2$ (1×)			P 2.276 (6)		115.90 (5)	
							Ru 2.935 (2, 76)		75.5 (1, 33.2);	
									113.3 (2, 2.7)	
							Au' 2.830 (2, 8)			

$[Au_3Ru_4(\mu\text{-}H)(CO)_{12}\cdot(PPh_3)_3]$	m	$P2_1/n$	4	$AuPRu_2Au'$ (2×)	18.754 (3)		P 2.297 (7, 0)	2.836	–	206
					18.459 (5)	113.06 (2)	Ru 2.837 (2, 15)		63.7 (1, 3);	
									143.4 (1, 3.8)	
					22.317 (4)		Au′ 2.836 (2, 2)		63.6 (1, 5) [g]	
				$AuPRu_3Au'_2$ (1×)			P 2.288 (6)		115.9 (1)	
							Ru 2.939 (2, 10)		108.3 (1, 5);	
									113.3 (2, 3.0)	
							Au′ 2.836 (2, 2)			
$[Au_3Ru_4(\mu_3\text{-}C_{12}H_{15})\cdot(CO)_8(PPh_3)_3]$	m	$P2_1/c$	4	$AuPRuAu'_2$	13.574 (1)		P 2.261 (11)	2.852	61.4 (1)	204
					40.634 (4)	92.58 (1)	Ru 2.761 (3)		58.8 (1, 6);	
									140.9 (3, 6.1)	
					14.617 (2)		Au′ 2.852 (2, 13)		151.5 (3) [e]	
				$AuPRu_2Au'_2$			P 2.215 (16)	2.875	59.7 (1)	
							Ru 2.828 (4, 54)		58.2 (1, 7), 111.6 (1),	
									135.1 (4, 13.0)	
							Au′ 2.875 (3, 36)		140.1 (4, 13.9) [e]	
				$AuPRu_3Au'_2$			P 2.307 (11)	2.888	58.9 (1)	
							Ru 2.858 (4, 121)		58.8 (1, 5); 111.2 (1, 5.4)	
									108.6(3, 12.4)	
							Au′ 2.888 (3, 23)		141.8 (3, 11.5) [e]	
$[Au_3Ru_3(\mu_3\text{-}COMe)\cdot(CO)_9(PPh_3)_3]$	m	$P2_1/n$	4	$AuPRu_2Au'$ (2×)	15.103 (4)		P 2.311 (6, 2)	2.970	–	92
					17.650 (3)	90.59 (2)	Ru 2.820 (2, 24)		143.3 (2, 1.3)	93
					24.363 (6)		Au′ 2.970 (1, 40)		144.5 (2, 4.0) [e]	
									63.4 (2, 3) [g]	
				$AuPRu_3Au'_2$ (1×)			P 2.304 (6)		108.0 (1)	
							Ru 2.877 (2, 110)		112.6 (2, 3)	
							Au′ 2.970 (1, 4)		143.7 (2, 8.9) [e];	
									60.2 (1, 2) [g]	
$Au_4(dppmH)_3I_2$		$P\bar{1}$	2	$AuIAu'_3$ (1×)	12.305 (2)	94.85 (10)	I 2.593 (2)	2.744	57–64.6	205
					14.693 (2)	90.70 (12)	Au′ 2.744 (1, 27)		142.15 (5, 5.9)	
					21.238 (3)	67.90 (12)				
				$AuIP_2Au'_3$ (3×)			I 3.381 (2, 287)	2.821	50.38 (2, 2.1) [h]	
							P 2.354 (4, 37)			
							Au′ 2.821 (1, 126)			
$[Au^{III}(OH)(CH_3)_2]_4$	or	*Pbca*	32	AuC_2O_2	19.35 (3)		C 2.00 (0, 16)		[j]	207
					9.65 (2)		C 2.10 (0, 17)			
					19.59 (3)		O 2.08 (0, 21) [i]			
							O 2.23 (0, 17) [i]			

TABLE 9 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	Au–L (Å)	Au–Au′ (Å)	Au′–Au–Au″ L–Au–Au′ (°)	Ref.
$[Au_6(PPh_3)_4Co_2(CO)_8]$	tr	$P\bar{1}$	1	$AuPAu'_3$ (2×)	13.672 (6) 13.524 (4) 14.160 (5)	119.72 (2) 118.83 (3) 71.32 (2)	P 2.368 (24) Au′ 2.732 (7, 111)	2.732	60.7 (2, 3.8) 142.7 (8, 13.0)	208 209
				$AuCoAu'_3$ (2×)			Co 2.460 (16) Au′ 2.752 (7, 131)	2.752	59.8 (2, 3.6) 144.6 (6, 6.5)	
				$AuPAu'_5$ (2×)			P 2.282 (42) Au′ 2.773 (8, 118)	2.773	59.7 (2, 4.1) [k] 118.8 (8, 1.7); 178.6 (9)	
$[Au_6(PPh_3)_6](NO_3)_2 \cdot (CH_2Cl_2)_3$	m	$P2_1/n$	4	$AuPAu'_3$ (4×)	25.674 (5) 15.843 (10) 26.368 (4)	91.76 (2)	P [d] Au′ 2.762 (2, 99)	2.770	[d]	210
				$AuPAu'_5$ (2×)			P [d] Au′ 2.771 (2, 120)	2.779	[d]	
$[Au_6(1,3\text{-dppp})_4] \cdot (NO_3)_2 \cdot (CH_2Cl_2)_x$	tg	$P\bar{4}m2$	1	$AuPAu'_4$ (4×)	14.726 (5) 14.726 (5) 16.879 (4)		P 2.36 (8) Au′ 2.78 (1, 15)	2.78	– 175.0 (5)	211
				$AuP_2Au'_2$ (2×)			P 2.39 (8) Au′ 2.80 (1)	2.80	56.1 (4) 142.1 (9) [l]	
$Au^I_7P_{10}I$	trg	$P\bar{3}1m$	1	AuP_3I (1×)	6.180 (1) 11.122 (2)		P 2.339 (7) (2×) I 3.070 (7)		97.1 (1, 0) [c] 118.5 (2, 0) [l]	66(a)
				AuP_2 (6×)			P 2.328 (7, 7)		180.0 (2, 0) [l]	
$Au^I_7P_{10}I$	hx	$P\bar{6}2m$	1	AuP_3I (1×)	6.173 (7) – 11.107 (2)		P 2.324 (3×) I 3.067 (2)	3.069	106.0 [e] 98.2 [l]	66(b)
				AuP_2 (6×)			P 2.302		[d]	
$[Au_8(PPh_3)_7](NO_3)_2 \cdot (CH_2Cl_2)_2$	m	$P2_1/n$	4	$AuPAu'_3$ (6×)	25.444 (6) 17.332 (6) 28.795 (6)	90.0 97.66 (3) 90.0	P 2.28 (3, 4) Au′ 2.750 (5, 121)	2.750	– 165.3 (6, 5.2)	213
				$AuPAu'_4$ (1×)			P 2.31 (3, 5) Au′ 2.795 (5, 147)	2.795	– 155.0 (6, 22.0)	
				$AuAu'_7$ (1×)			Au′ 2.681 (5, 52)	2.681	60–178	

$[Au_8(PPh_3)_8](PF_6)_2 \cdot (CH_2Cl_2)_2$	tr	$P\bar{1}$	2	$AuPAu'_3$ (3×)	17.445 (2) 29.410 (5) 17.625 (3)	79.42 (2) 120.83 (1) 95.04 (2)	P 2.29–2.33 (3) Au′ 2.815 (8, 108)	2.815	– 165 (1, 2)	214
				$AuPAu'_4$ (4×)			P 2.29–2.33 (3) Au′ 2.825 (8, 190)	2.825	– 178 (1, 2)	
				$AuPAu'_7$ (1×)			P 2.42 (3) Au′ 2.696 (8, 61)	2.696	– 176 (1)	
$[Au_8(PPh_3)_8](aliz)_2$	or	*Pca*	2_1	$AuPAu'_3$ (3×)	25.28 (1) 17.90 (1) 34.61 (2)		P 2.30 Au′ 2.825 (5, 153)	2.825	– 171.3 (6)	215
				$AuPAu'_4$ (4×)			P 2.30 Au′ 2.817 (5, 230)	2.817	– 171.3 (6)	
				$AuPAu'_7$ (1×)			P 2.38 (2) Au′ 2.706 (5, 119)	2.706	– 175.8 (6)	
$Au_9(PPh_3)_8(PF_6)_3$		*Pbcn*			81.56 18.84 26.98					212
$[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8] \cdot (BF_4)_3$	or	*Pbca*	4	$AuPAu'_3$ (8×)	31.076 (4) 17.482 (2) 31.283 (4)		P [d] Au′ 2.741 (3, 97)	2.741	– 161–165	216
				$AuAu'_8$			Au′ 2.664 (2, 14)	2.664		
$[Au_9\{P(cy)_3\}_5(SCN)_3]$	m	12/*c*	8	$AuSAu'_3$ (1×)	44.488 (3) 22.089 (2) 23.407 (2)	91.35 (3)	S 2.35–2.43 (2) Au′ 2.764 (5, 80)	2.764	– 164 (1)	16
				$AuSAu'_4$ (2×)			S 2.35–2.43 (2) Au′ 2.779 (5, 106)	2.779	– 150 (1, 6)	
				$AuPAu'_4$ (4×)			P 2.26–2.29 (2) Au′ 2.836 (5, 332)	2.836	– 154 (1, 20)	
				$AuPAu'_5$ (1×)			P 2.26–2.29 (2) Au′ 2.894 (5, 274)	2.894	– 173 (1)	
				$AuAu'_8$			Au′ 2.707 (5, 64)	2.707	[d]	
$\{[Au^I(i\text{-}C_3H_7O)_2PS_2]_2\}n$	tr	$P\bar{1}$	4	$AuS_2Au'_2$	12.495 (4) 17.251 (4) 12.167 (4)	99.33 (3) 102.17 (5) 72.79 (2)	S 2.277 (9, 54) Au′ 2.914 (5)	3.040 [n]	173.6 (4, 4, 8) [m]	217
$\{Au^I_2P_3\}_n$	m	*C*2/*m*	4	$AuP_2Au'_2$	5.863 (1) 14.439 (3) 4.674 (1)	108.39 (1)	P 2.339 (8, 0) Au′ 2.932 (8, 0)	3.056 [n]	180.0 (8) [m]	66(a)
$\{Au^{III}_2O_3\}_n$	or	*Fdd*2	8	AuO_4	12.827 (3) 10.520 (3) 3.838 (1)		O 2.01 (2, 8)		89.8 (1.5, 4.0) [m]	218

TABLE 9 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	Au–L (Å)	Au–Au' (Å)	Au'–Au–Au'' L–Au–Au' (°)	Ref.
$\{Au_2^{III}(SeO_3)_2(Se_2O_5)\}_n$	m	$C2/c$	4	AuO_4	20.344 (5) 4.130 (1) 13.254 (3)	 115.88 (3) 	O 1.990 (10, 23)		90.0 (5, 2.5) [m] 180	219
$\{Au^{III}(SeO_3)Cl\}_n$	tr	$P\bar{1}$	4	AuO_4	4.185 (1) 9.756 (4) 10.608 (5)	 88.85 (2) 	O 1.985 (13, 13)		90.0 (5, 2.9) [m] 180.0 [m]	220
				AuO_3Cl			O 1.993 (14, 23)		86.2 (6, 6) [m]; 93.5 (4, 1.0) [c]	
				AuO_2Cl_2			Cl 2.250 (5) O 1.998 (16) Cl 2.277 (5)		168.8 (5); 177.0 (4) 90.0 (4, 2.5) 180.0	
$\{Au^{III}OCl\}_n$	trg	$R\bar{3}$	6	AuO_3Cl	8.148 (3)	113.45 (4)	O 2.02 (2, 5)		87.8 (8, 5.6) [m]; 92.4 (6, 1.5) [c]	221
							Cl 2.244 (4)		174.4 (8); 172.0 (5)	
$\{(Au^{III}Cl_4)_3 \cdot Ag_2Cl_5 \cdot (NH_4)_6\}_n$	or	$Immm$	2	$AuCl_4$	11.20 20.86 6.11		Cl 2.28		[d]	222

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] The data are presented in Table 5. [d] Not given. [e] The value of L–Au–L' angle. [f] The value of Ru–Au–P angle; Ru–Au–Ru = 63.7 (1, 4) °. [g] The value of Ru–Au–Ru angle. [h] The value of Au–I–Au angle. [i] The bridge atoms. [j] The C–Au–C = 82.5 (0, 2.0) and 85.3 (0, 3.6)°; O–Au–O = 87.4 (0, 4) and 84.7 (0, 2.3)°; C–Au–O = 94.6 (0, 11.3) and 94.7 (0, 2.9); Au–O–Au = 107.7 (0, 8) and 115(0, 4)°. [k] The other Au'–Au–Au'' angles are of 96.5 (2, 2) and 123.4 (3, 4)°. [l] The value of P–Au–P angle. [m] The value of L–Au–L angle. [n] The mean value between dimers in a chain.

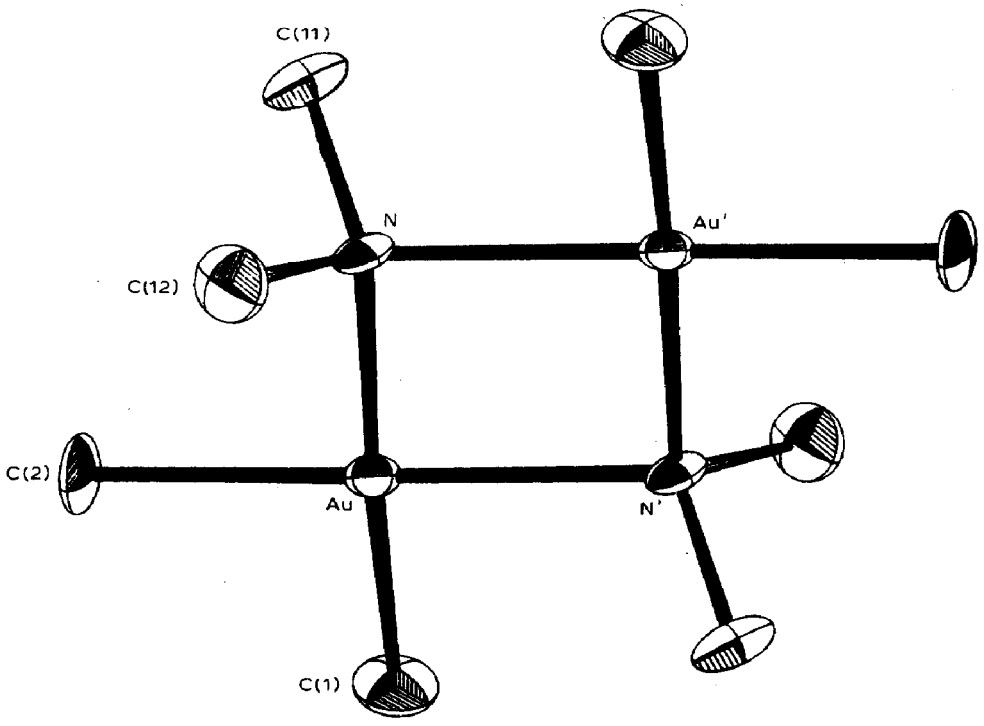

Fig. 10. Structure of $[Au^{III}\{N(CH_3)_2\}(CH_3)_2]_2$ [191].

$[Ru_5WC(CO)_{17}(AuPEt_3)_2]$ [113] and $[Au_2Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)_3]$ [189]. Two independent molecules in $[Au^{II}\{Ph_2P(CH_2)S\}I]_2$, differ mostly in their Au–L bond lengths, as well as in the Au–Au bond distance (Table 8); they are the only known examples of distortion isomers for Au(II) compounds.

There is a difference between the Au(III)–L bond lengths in mono- and binuclear compounds. The mean value of Au–N, 2.05 Å, found in mononuclear species is about 0.09 Å smaller than those found in binuclear species (2.14 Å); similarly Au–Cl is 2.28 compared to 2.29 Å; Au–C, 2.06 compared to 2.09 Å; Au–S, 2.32 compared to 2.39 Å, Au–Br, 2.46 compared to 2.50 Å, respectively, showing a trend for a longer Au(III)–L bond length in binuclear compounds.

(iv) Tri, tetra-, hexa- and polynuclear compounds

Structural data for oligonuclear gold compounds are given in Table 9. The structures are tabulated by increasing number of gold atoms and by increase of the Au–Au bond length.

In $[Au_3Ir(NO_3)(PPh_3)_5]^+$ [114] the three gold atoms are bound to the Ir atom in a nearly planar configuration. Each Au is also bound to a PPh_3 ligand, while the Ir is attached to two PPh_3 ligands and a chelate NO_3^-

group. The Au–Au separation (mean value 2.766(1) Å) is among the shortest of all the trinuclear gold compounds summarised in Table 9. The three gold atoms fall into two non-equivalent classes exhibiting different coordination patterns as well as different coordination numbers; one Au atom is four-coordinate and the other two are three-coordinate.

In $[Au_3CoRu_3(CO)_{12}(PPh_3)_3]$ [201] two gold atoms cap adjacent AuCoRu and $AuRu_2$ faces of the trigonal bipyramidal $AuCoRu_3$ core. Each Au is also bound to a PPh_3 ligand. One Au atom is four-, another is five- and the third is six-coordinate.

All three gold atoms in $(Ph_3PAu)_3V(CO)_5$ [202] are equivalent with a $AuPVAu_2$ chromophore. The four metal atoms (Au ($3\times$) and V) are arranged in a slightly distorted tetrahedral array with Au–Au–V, Au–Au–Au, and Au–V–Au angles close to the expected 60° (Table 9).

The crystal structure of $[Au_3Ru_4(\mu\text{-H})(CO)_{12}(PPh_3)_3]$ [93,203,206] shows the unusual bicapped trigonal bipyramidal $AuRu_4$ unit with two $AuRu_2$ faces capped by gold atoms. Each gold atom carries a PPh_3 ligand. Two independent measurements on the monoclinic $[Au_3Ru_4(\mu\text{-H})(CO)_{12}(PPh_3)_3]$ compound, show very similar structures, with two different coordination numbers about the gold atoms (distortion isomerism) (Table 9). The greatest differences in the interatomic distances were observed in the Au–P bonds. This distance is about 0.013 Å smaller [203] than those in [206].

Three gold atoms in $[Au_3Ru_3(\mu_3\text{-COMe})(CO)_9(PPh_3)_3]$ [92] have similar environments to those of $[Au_3Ru_4(\mu\text{-H})(CO)_{12}(PPh_3)_3]$.

$[Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$ [204] has the capped trigonal bipyramidal geometry, formed conceptually by the addition of a Au atom to a Ru_2Au face of a Ru_3Au tetrahedron, followed by capping of a Au_2Ru face of the resulting trigonal bipyramid. Each Au is also attached to a PPh_3 ligand, and falls into one of three, non-equivalent classes, with coordination number four, five and six, respectively (Table 9). The Au–Au bond distance is increasing monotonically with increasing coordination number (Table 9).

Four gold atoms in $Au_4(dppmH)_3I_2$ [205] form a slightly distorted tetrahedron. The top Au atom has a coordination number four ($AuIAu'_3$ chromophore) and the other three Au atoms, coordination number six ($AuIP_2Au'_3$ chromophore). The Au–Au distance of 2.744 Å (mean value) in $AuIAu'_3$ is about 0.077 Å shorter than those of $AuIP_2Au'_3$ (2.821 Å, mean value) (Table 9).

The crystal structure of $[Au(OH)(CH_3)_2]_4$ [207] is shown in Fig. 11. The molecule consists of an eight-membered ring where Au atoms are bridged by hydroxo groups. Four gold atoms have the same chromophore, AuC_2O_2, but, on the basis of Au–L lengths and L–Au–L(L') angles, can be divided into two groups. Au(1) and Au(3) have a mean value of Au–C, 2.10 Å and Au–O, 2.23 Å, with a sum of all the interatomic distances around Au(1) or

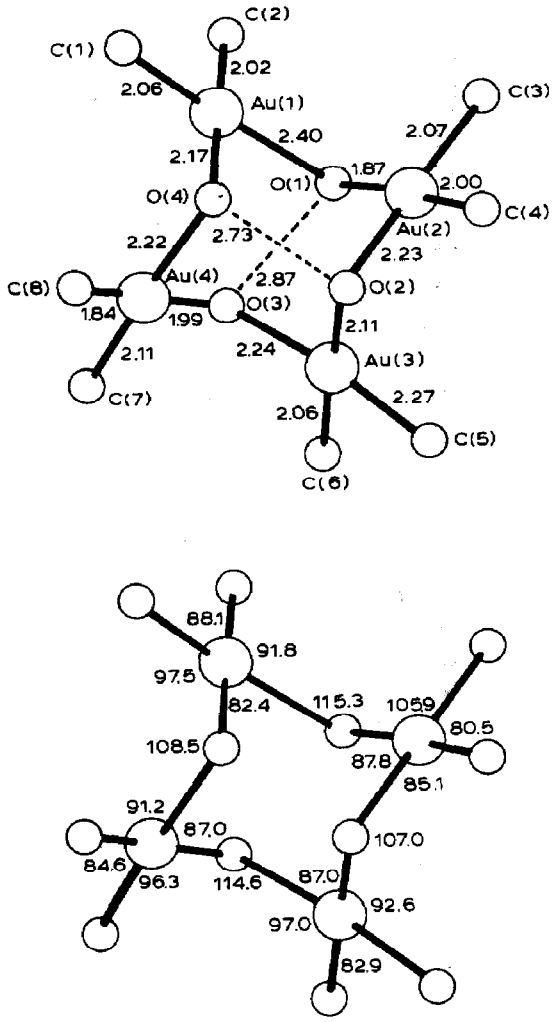

Fig. 11. Crystal structure of $[Au^{III}(OH)(CH_3)_2]_4$ [207].

Au(3) of 8.66 Å. These values are larger than those found about Au(2) and Au(4) which are 2.00, 2.08 and 8.16 Å, respectively. The C–Au–C, O–Au–O, and C–Au–O angles of 85.5, 84.7 and 94.7° in the former also differ from those found in the latter (82.5, 87.4 and 94.6°), respectively.

Six gold atoms in $[Au_6(PPh_3)_4Co_2(CO)_8]$ [209] fall into three non-equivalent groups; in $[Au_6(PPh_3)_6]^{2+}$ [210] and similarly in $[Au_6(1,3\text{-dppp})_4]^{2+}$ [211], there are two groups (Table 9). The Au–Au bond distance is sensitive to the coordination number and increases therewith.

Another example of distortion isomerism is hexagonal and trigonal $Au_7P_{10}I$ [66] (Table 9).

X-ray analysis of $[Au_8(PPh_3)_7]^{2+}$ [213] and $[Au_8(PPh_3)_8]^{2+}$ [214,215]

reveals that the octagold skeleton is a fragment of the centred icosahedron. Every peripheral gold atom has one triphenylphosphine ligand, including the central one in $[Au_8(PPh_3)_8]^{2+}$. The resulting coordination polyhedron around the central atom may be described as a deformed cube. The distances between peripheral gold atoms are distinctly longer than those between the centre-to-periphery (Table 9). On the other hand, the Au(centre)–P distance of 2.40 Å (mean value) is about 0.10 Å longer than those of Au(periphery)–P (2.30 Å). The lengthening reflects the smaller availability of the Au(centre) orbitals for this interaction.

The cationic enneagold clusters, $[Au_9(Pcy_3)_8]^{3+}$ [212] and $[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8]^{3+}$ [216] and neutral, $[Au_9\{P(Ch)_3\}_5(SCN)_3]$ [16] have a different symmetry. While the cationic enneagold cluster has metal geometries of D_{4d} symmetry, the neutral cluster has a metal arrangement of C_s symmetry. The metal–metal bond distances display the usual patterns, the centre-to-periphery being distinctly shorter than those in the periphery (Table 9).

Inspection of the data in Table 9 reveals that the Au–Au bond distance is dependent on the degree of aggregation. In the $AuXAu'_3$ chromophore, the mean value of the Au–Au distance is in the order: 2.74 Å (tetranuclear) < 2.76 Å (hexanuclear) < 2.79 Å (octanuclear) > 2.75 Å (nonanuclear). In the series of chromophores $AuPAu'_3$, $AuPAu'_4$, $AuPAu'_5$, and $AuPAu'_7$, the Au–Au bond length mean values are: 2.77 Å in the first, 2.81 Å in the second,m 2.77 Å in the third and 2.70 Å in the last.

In $\{Au^I_2P_3\}_n$ [66a] and $\{[Au^I(i\text{-}C_3H_7O)_2PS_2]_2\}_n$ [217], each gold(I) atom is surrounded by four atoms (Table 9), in a slightly distorted square-planar configuration. Dimers are joined together to form linear chains through the metal atoms in a staggered arrangement.

The structures of polynuclear gold(III) compounds (Table 9) reveal that each gold(III) atom has a square-planar coordination. The average Au–O length of 2.03 Å, is about 0.01 Å longer than the Au–O length (for O coordinated to two Au) with each O coordinated to three Au atoms [218,221]. A *trans* influence is seen in Au_2O_3 and AuOCl: the Au–O bond of 2.07 Å, *trans* to O (Au–O, 1.93 Å) in the former, and *trans* to Cl (Au–Cl, 2.244(4) Å), is significantly longer than the other Au–O bonds (2.01 and 2.04 Å, in the former; and 1.99 and 2.01(2) Å in the latter).

The average Au–L bond lengths (L = O or Cl) of 2.00 and 2.26 Å, found in polynuclear gold(III) compounds (Table 9) are smaller than those of 2.035 and 2.29 Å, found in binuclear species (Table 8) and in a mononuclear species (2.06 and 2.28 Å) (Table 7).

E. STRUCTURAL DATA FOR GOLD COMPOUNDS WITH COORDINATION NUMBER FIVE

(i) Mononuclear compounds

Structural data for mononuclear gold compounds with coordination number five are gathered in Table 10. Two types of gold(III) compounds are included. In $[AuCl_3(biq)]$ [224], the gold(III) atom is intermediate between the trigonal-bipyramidal and the square-pyramidal arrangement. This complex is the first example of five-coordinate gold(III) confirmed by X-ray structural analysis. In the other compounds (Table 10) the gold(III) atom has a distorted square-pyramidal geometry (Fig. 12). The gold(III) atom lies above the base plane 0.03–0.12 Å towards the apical ligand. The average values for the $Au–L_{eq}$ and $Au–L_{ax}$ bonds reveals that $Au–L_{ax}$ is significantly longer by about 0.31 Å(Cl) and 0.54 Å(N).

There is no example with five monodentate ligands. In [AuCl(tpp)] [223] the square plane is built up of a tpp ligand coordinated through its four N atoms, with the chlorine atom in the apical position. In $[AuCl(C_4Ph_4)(phen)]$ [227], the C_4Ph_4 coordinates through two carbon atoms in a plane together with a chlorine atom, and the remaining equatorial position is occupied by a

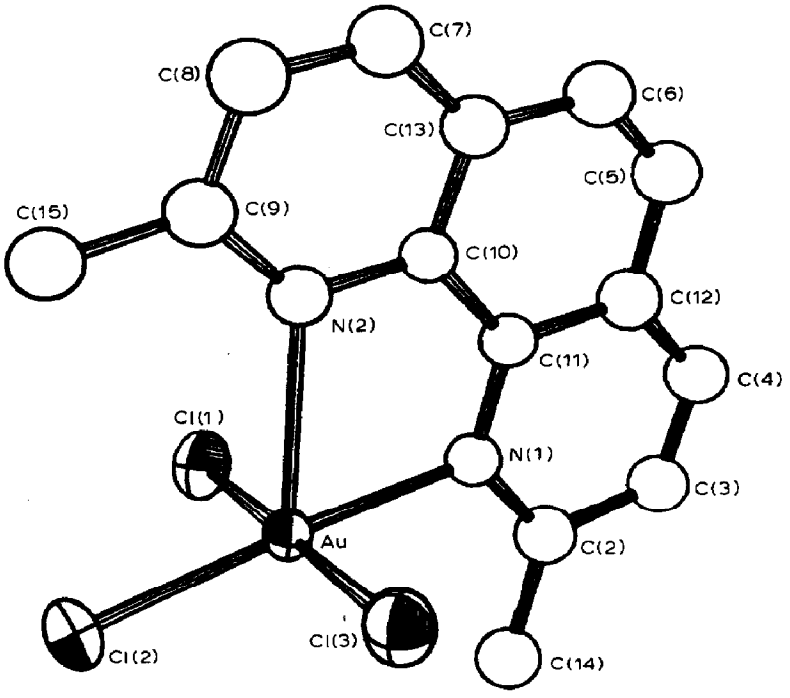

Fig. 12. Crystal structure of $[Au^{III}Cl_3(dmp)]$ [226].

TABLE 10

Structural data for mononuclear gold compounds with coordination number five [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L_{eq} (Å)	M–L_{ax} M–out-of-plane (Å)	L_{eq}–M–L_{eq} L_{eq}–M–L_{ax} (°)	Ref.
$[Au^{III}(Cl)(tpp)]$	m	$P2_1/c$	4	AuN_4Cl	12.06 (1) 22.35 (1) 16.66 (1)	 121.97 (5) 	N 2.00 (2, 4) [b]	Cl 3.01 (1) [b] 0.03	90.2 (0, 1.0) 90.4 (0, 9.3)	223
$[Au^{III}Cl_3(blq)]$	m	$C2/c$	4	$AuCl_3N_2$	18.84 9.67 13.63	 136.22	N 2.34 (0, 6) Cl 2.19	Cl 2.37 0.05	[c]	224
$[Au^{III}Cl_3(pq)]$		$P2_12_12_1$	4	$AuCl_3N_2$	7.711 (7) 10.04 (1) 19.34 (4)		N 2.11 (2) Cl 2.269 (4, 8)	N 2.68 (2) 0.04	90.0 (2, 1.8); 177.5 (3, 1.1) 90.8 (5, 23.8)	225
$[Au^{III}Cl_3(dmp)]$	m	$P2_1/c$	4	$AuCl_3N_2$	7.343 (1) 18.712 (3) 12.143 (3)	 112.29 (2)	N 2.09 (1) Cl 2.275 (5, 10)	N 2.58 (1) 0.08	90.0 (4, 1.2); 176.0 (3, 5) 91.8 (3, 19.4)	226
$[Au^{III}Br_3(pq)]$		$P2_12_12_1$	4	$AuBr_3N_2$	8.050 (4) 10.13 (2) 19.52 (1)		N 1.99 (2) Br 2.410 (3, 25)	N 2.64 (2) 0.08	89.9 (3.6); 175.8 (4, 6) 91.5 (6, 22.0)	225
$[Au^{III}Br_3(dmp)]$	m	$P2_1/c$	4	$AuBr_3N_2$	8.046 (1) 10.478 (3) 20.079 (5)	 92.56 (2)	N 2.08 (2) Br 2.409 (3, 11)	N 2.61 (2) 0.12	89.8 (4, 1.6); 173.9 (3, 2) 92.5 (7, 21.5)	226
$[Au^{III}Cl(C_4Ph_4)$-(phen)]	tr	$P\bar{1}$	2	AuC_2N_2Cl	11.040 (2) 12.283 (2) 13.670 (3)	99.76 (2) 113.58 (2) 101.94 (2)	C 2.042 (5, 4) N 2.184 (4) Cl 2.368 (2)	N 2.755 (4) 0.09	89.9 (2, 9.7); 174.5 (2, 7) 92.4 (2, 26.0)	227
$[Au(Et_2NCS_2)$-$(C_2B_9H_{11})]$ [d]	m	$P2_1/c$	4	AuB_3S_2	7.3710 (6) 11.0368 (9) 21.1564 (17)	 93.22 (4)	B 2.22 (2, 1) S 2.379 (4, 5)	 0.03	[e]	228 229
$[AuIr_3H_6(NO_3)$ $(dppe)_3]\cdot(BF_4)\cdot$ $(CHCl_3)_3$	tr	$P\bar{1}$	1	AuO_2Ir_3	13.656 (3) 14.310 (3) 13.234 (2)	95.88 (2) 116.06 (3) 71.77 (2)	O 2.36 Ir 2.704 (0, 14)	O 2.55	63.39 (2, 98) 53.7 (6)	114

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Not given. [d] There are C–Au–C lengths of 2.78 and 2.79 (1) Å. [e] The B–Au–B angle is 48.4 (6, 6)°; B–Au–C = 40.6 (5, 3)°; S–Au–S = 74.2 (1)° and C–Au–C = 30.5 (4)°.

N atom of the bidentate phen ligand, while the second N atom occupies the apical site. Similarly in $[AuX_3L]$ (X = Cl, Br; L = pq, dmp) a bidentate ligand links a plane and apical site [225,226]. This is reflected in the L_{eq}–Au–L_{ax} angles (Table 10).

(ii) Oligonuclear compounds

The gold(III) atoms in binuclear $[(Au_2B_8H_{10})(Et_2CNS_2)_2]$ [230] have a square-plane built up by two sulphur and two boron atoms. The third boron atom completes square-pyramidal geometry. There is no direct Au–Au bond (Table 11).

In tetranuclear $[Au_4I_2(PPh_3)_4]$ [231] (Fig. 13) a tetrahedral gold cluster is connected to four terminal PPh_3 ligands and two edge-bridging iodine ligands (Table 11).

The distorted centrosymmetric octahedron of $[Au\{P(tol)_3\}]_6^{2+}$ [233] is shown in Fig. 14. The distortion approximately corresponds to a squeezing of the octahedron along a C_3 axis.

The seven gold atoms in $[Au(PPh_3)]_7^+$ [232] fall into two non-equivalent sets, five are five-coordinate ($AuPAu'_4$) and two are seven-coordinate ($AuPAu'_6$) (Table 11). The Au_7 skeleton is a pentagonal bipyramid, where the average value of the Au–Au bond length in $AuPAu'_6$ (2.80 Å) is about

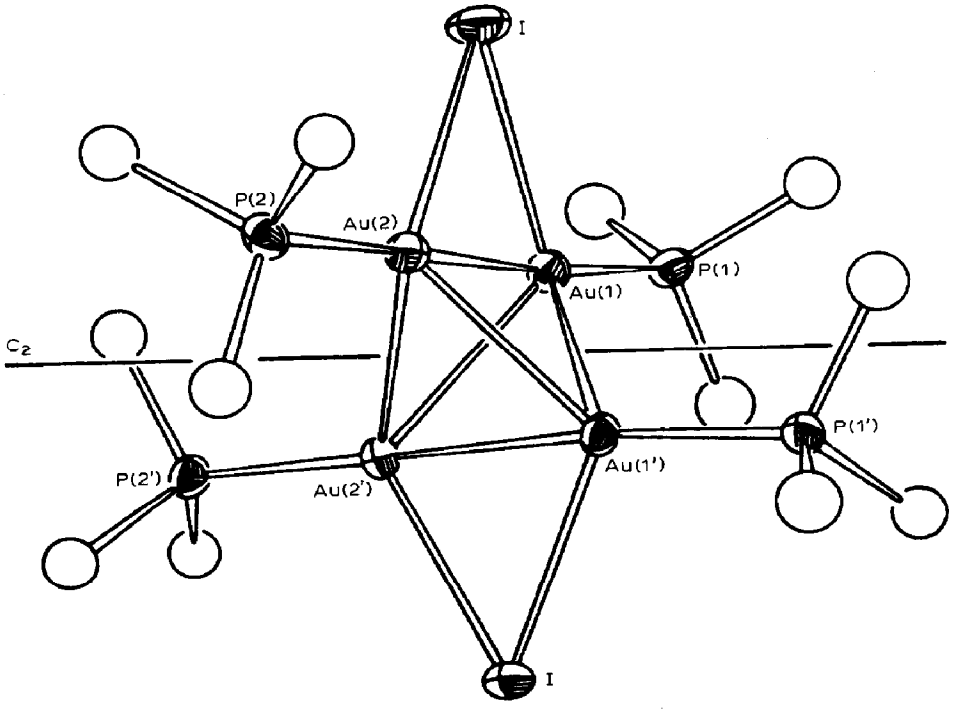

Fig. 13. Crystal structure of $[Au_4I_2(PPh_3)_4]$ [231].

TABLE 11

Structural data for oligonuclear gold compounds with coordination number five [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M′ (Å)	L–M–L L′–M–L (°)	Ref.
$[(Au_2B_8H_{10})(Et_2CNS_2)_2]$	m	$P2_1/m$	2	AuB_3S_2	6.862 (2)		B 2.229 (13, 26) [b]	3.581 (1)	74.4 (1); 61.2 (5, 26.1)	230
					17.751 (2)	92.82 (3)	S 2.399 (3, 2)		98.4 (4, 2.0); 141.4 (4, 2.0)	
					10.050 (3)				168.7 (4, 1.5)	
$[Au_4(\mu\text{-}I)_2(PPh_3)_4]$	m	$C2/c$	4	$AuPIAu'_3$	12.989 (4)		P 2.290 (3, 2)	2.748	175.1 (1, 1.2) [c]	231
					26.042 (11)	107.25 (2)	I 2.945 (1, 23)			
					20.543 (5)		Au′ 2.748 (1, 99)			
$[Au\{P(tol)_3\}]_6(BPh_4)_2$		$P\bar{1}$	1	$AuPAu'_4$	17.48 (3)	101.1 (1)	P 2.29 (1, 2)	3.020	[c]	233
					19.02 (3)	94.2 (1)	Au′ 3.020 (2, 86)			
					13.82 (2)	116.4 (1)				
$[Au_7(PPh_3)_7](OH)$	m	$C2/c$	16	$AuPAu'_4$ (5×)	68.18 (1)	89.99 (3)	P 2.29 (6, 9)	2.86	175 (2) [c]	232
					15.45 (2)	128.22 (3)	Au′ 2.86 (2, 14)		107.8 (4, 1.6) [d]	
					55.47 (1)	90.11 (3)				
				$AuPAu'_6$ (2×)			P 2.28 (6, 8)	2.80	158 (2, 19) [c]	
							Au′ 2.80 (2, 22)		63.3 (4, 1.9) [d]	
$[Au_9\{P(tol)_3\}_8](PF_6)_3$	tg	$P\bar{4}n2$	2	$AuPAu'_4$ (8×)	20.31 (1)		P 2.30 (1)	2.741	[e]	234
					–		Au′ 2.741 (3, 127)			
					20.34 (1)					
				$AuAu'_8$ (1×)			Au′ 2.709 (3, 20)	2.709	[e]	
$[Au_9\{P(tol)_3\}_8](NO_3)_3$	or	$Pbcn$	4	$AuPAu'_4$ (8×)	30.892 (6)		P [c]	2.745	[e]	235
					17.522 (7)		Au′ 2.745 (3, 98)			
					31.272 (10)					
				$AuAu'_8$ (1×)			Au′ 2.668 (2, 9)	2.668	[e]	
$[Au_9\{P(tol)_3\}_8](NO_3)_3$	tg	$P\bar{4}n2$	2	$AuPAu'_4$ (8×)	9.566 (7)		P [c]	2.787		235
					–		Au′ 2.787 (4, 112)			
					21.412 (7)					
				$AuAu'_8$ (1×)			Au′ 2.712 (2, 23)	2.712	[e]	
$Au_{10}(Pcy_2Ph)_6Cl_3]\cdot(NO_3)$	m	$P2_1/n$	4	$AuPAu'_4$ (6×)	16.118 (2)		P 2.710–2.740 (2)	2.813	[e]	236
					28.807 (8)	90.68 (2)	Au′ 2.813 (2, 128)			
					26.902 (8)					
				$AuClAu'_5$ (3×)			Cl 2.666–2.674 (1)	2.834	[e]	
							Au′ 2.834 (2, 168)			
				$AuAu'_9$ (1×)			Au′ 2.704 (2, 38)	2.704		

$Au_{11}\{P(p\text{-}ClPh)_3\}_7I_3$		$R\bar{3}c$		$AuPAu'_4$ (1×)	25.40 (3)	90	P [e]	2.98	[e]	237
					25.40 (3)	90	Au′ 2.612–3.165			
					79.65 (3)	120				
				$AuPAu'_5$ (3×)						
				$AuIAu'_5$ (3×)						
				$AuPAu'_6$ (3×)						
				$AuAu'_{10}$ (1×)			Au′ 2.68 (0, 70)	2.68		
$Au_{11}\{P(tol)_3\}_7(SCN)_3]$		$P\bar{1}$		$AuPAu'_4$ (1×)	17.61 (2)	91.4 (1)	[e]	[e]	[e]	237
					18.13 (2)	92.6 (1)				
					26.61 (3)	113.9 (1)				
				$AuPAu'_5$ (3×)						
				$AuSAu'_5$ (3×)						
				$AuPAu'_6$ (3×)						
				$AuAu'_{10}$ (1×)						
$[Au_{11}\{P(p\text{-}FPh)_3\}_7I_3]$	trg	$R3$	1	$AuPAu'_4$ (1×)	15.96 (2)	108.4 (1)	P 2.211 (1)	2.771	180 [c]	237, 238
							Au′ 2.77 (3, 171)		93.8 (1) [d]	
				$AuPAu'_5$ (3×)			P 2.283 (12)	2.895	176.3 (3) [c]	
							Au′ 2.895 (4, 250)		83.7 (1, 4) [d]	
				$AuIAu'_5$ (3×)			I 2.600 (5)	2.898	174.5 (1) [c]	
							Au′ 2.898 (4, 289)		71.4 (1, 26.1) [d]	
				$AuPAu'_6$ (3×)			P 2.295 (10)	2.977	174.2 (3) [c]	
							Au′ 2.977 (3, 306)		58.2 (1, 7.3) [d]	
				$AuAu'_{10}$ (1×)			Au′ 2.667 (3, 67)	2.667	70.0 (1, 23.3) [c]	
$[Au_{11}\{P(p\text{-}FPh)_3\}(SCN)_3]$		$R\bar{3}$			25.91 (3)	90				237
					25.91 (3)	90				
					16.72 (2)	120				
$[Au_{11}(PPh_3)_7(SCN)_3]$		$P2_1/m$		$AuPAu'_4$ (1×)	18.00		P [e]		[e]	212
					26.50	122.2				
					31.59					
				$AuPAu'_5$ (3×)						
				$AuSAu'_5$ (3×)			S [e]			
				$AuPAu'_6$ (3×)						
				$AuAu'_{10}$ (1×)			Au′ 2.67	2.67		
$\{AuAg(C_6F_5)_2(SC_4H_8)\}_n$	or	$Pccn$	8	AuC_2Ag_2Au'	11.185 (3)		C 2.058 (12, 1)	2.889	68.1 (1, 1);	239
									176.4 (7, 4)	
					22.475 (6)		Ag 2.722 (2, 4)		69.0 (4, 1.6);	
									107.8 (4, 1.2)	
					14.802 (4)		Au′ 2.889 (2)		91.7 (4, 2) [f];	
									145.9 (2, 1) [g]	

TABLE 11 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	M–M′ (Å)	L–M–L L′–M–L (°)	Ref.
$\{AuAg(C_6F_5)_2(C_6H_6)\}_n$	m	$C2/c$	8	AuC_2Ag_2Au'	24.231 (5)		C 2.057 (11, 6)	3.013	68.0 (2, 1.3); 176.1 (5, 1)	239
					7.570 (1)	117.49 (2)	Ag′ 2.747 (2, 45)		78.7 (3, 9.3); 101.0 (3, 6.0)	
					22.613 (5)		Au′ 3.013 (2)		90.0 (3, 2.0) [j]; 146.0 (3, 7) [g]	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] The value of Au′–Au–P angle. [d] The value of Au′–Au–Au′ angle. [e] Not given. [f] The value of Au′–Au–C angle. [g] The value of Au′–Au–Ag angle.

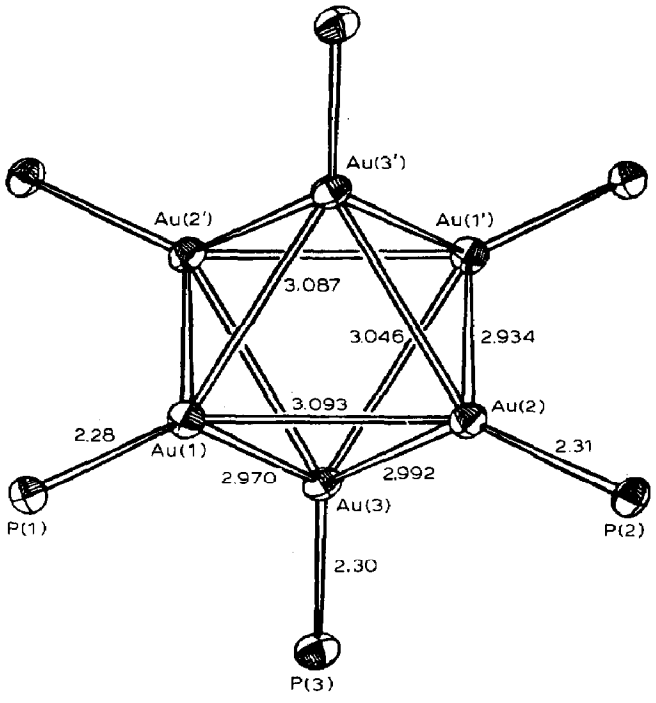

Fig. 14. A view of the $[Au\{P(tol)_3\}]_6^{2+}$ [233]. The phenyl groups are omitted.

0.06 Å shorter than that in $AuPAu'_4$ (2.86 Å). The latter value of 2.86 Å is significantly shorter than the mean value of 3.020 Å in $[Au\{P(tol)_3\}]_6^{2+}$ [233] with the same chromophore ($AuPAu'_4$).

Another example of distortion isomerism is $[Au_9\{P(tol)_3\}_8](NO_3)_3$ [235], which exists in tetragonal and orthorhombic forms (Table 11). Another tetragonal form has been prepared with the PF_6^- ion [234] (Table 11). In all three compounds, eight gold atoms have a coordination number five ($AuPAu'_4$) and one centre gold has eight-coordination ($AuAu'_8$). There are two crystallographically independent Au(centre)-to-Au(periphery) distances; 2.689(3) and 2.729(3) Å with a mean of 2.709(3,20) Å in the tetragonal form of $[Au_9\{P(tol)_3\}_8](PF_6)_3$; 2.689(2) and 2.735(2) Å with a mean of 2.712(2,23) Å in the tetragonal form $(NO_3)_3$; both show a greater variation than those for the orthorhombic form 2.659(2) and 2.677(2) with a mean of 2.668(2,9) Å. The peripheral Au–Au distances in the former fall between 2.752(3) and 2.868(3) (2.805 Å, mean); in the second between 2.751(2) and 2.899(2) (2.825 Å, mean); both tetragonal forms again show a greater variation than those in the orthorhombic form 2.810(3)–2.843(3) (2.823 Å mean). This can be attributed to the greater steric strain imposed on the skeleton by the bulky ligands in the more compact tetragonal structure. This observation, together with the recognition that the potential energy surfaces connecting alternative

polyhedral geometries were soft, necessitated a broad classification of gold clusters according to their gross topologies, with toroidal clusters characterised by a total of $12n + 16$ electrons (n is the number of peripheral gold atoms) e.g. nonagold clusters, and spherical clusters with a total of $12n + 18$ electrons, e.g. undecagold clusters.

Briant et al. [236] have studied the crystal structure of $[Au_{10}Cl_3(Pcy_2Ph)_6](NO_3)$. The $[Au_{10}Cl_3(Pcy_2Ph)_6]$ species has approximately D_{3h} symmetry with 6 $Au(Pcy_2Ph)$ and 3 AuCl fragments arranged around the central gold atom in a circular fashion. In common with other gold cluster compounds the central-to-peripheral Au–Au distances which fall in the range 2.666–2.740(2) Å with a mean of 2.704(2,38) Å are generally shorter than the peripheral Au–Au distances which fall in the range 2.738–2.941(2) Å with a mean of 2.849(2,111) Å.

Both radial and peripheral Au–Au bond lengths in the decagold cluster show a greater variation than those for an enneagold cluster, which are 2.659–2.735(3) (mean 2.696(3,39(Å) and 2.752–2.843(3) Å (mean 2.817(3,65) Å), respectively.

Five undecagold cluster compounds of the general formula $[Au_{11}L_7X_3]$ where L = P(*p*-ClPh)$_3$ or P(*p*-FPh)$_3$ and X = I [237,238]; and L = P(tol)$_3$; PPh_3 or P(*p*-PPh)$_3$ and X = SCN [212,237] are included in Table 11. The crystal structure of $[Au_{11}\{P(p\text{-}FPh)_3\}_7I_3]$, a representative example, is shown in Fig. 15. The undecagold cluster is based on a centred icosahedron, in which one triangular face has been substituted by a single gold atom. The eleven metal atoms fall into five nonequivalent classes: one is five coordinate, $AuPAu'_4$; six are six coordinate, $AuPAu'_5$ (3 ×) and $AuIAu'_5$ (3 ×); one is seven coordinate, $AuPAu'_6$, and the central gold atom is ten coordinate, $AuAu'_{10}$ (Table 11).

Both the Au–P and the mean of the Au–Au bond lengths increase with increase of coordination number in the order: $AuPAu'_4 < AuPAu'_5 < AuPAu'_6$ (Table 11). The radial and peripheral Au–Au distances in the undecagold cluster lie in the range 2.600–2.718(3) Å (mean 2.667(3,67) Å) and 2.836–3.187(3) Å (mean 2.981(3,206) Å) respectively. The radial Au–Au bond lengths in the undecagold cluster show a greater variation from the mean than those for the enneagold and decagold clusters, 2.659–2.735(3) Å (mean 2.696(3,39) Å) and 2.666–2.740(2) Å (mean 2.704(2.38) Å), respectively. However, the mean value of 2.667 Å is significantly smaller than those of 2.696 Å in the enneagold and 2.704 Å in the decagold cluster, respectively. On the other hand, the peripheral Au–Au distances in the undecagold cluster show not only a greater variation from the mean, but also the mean value is significantly greater than those found in decagold (2.738–2.941 (2) Å (mean 2.849(2,111) Å)) and enneagold clusters (2.752–2.843(3)) Å (mean 2.817(3,65) Å).

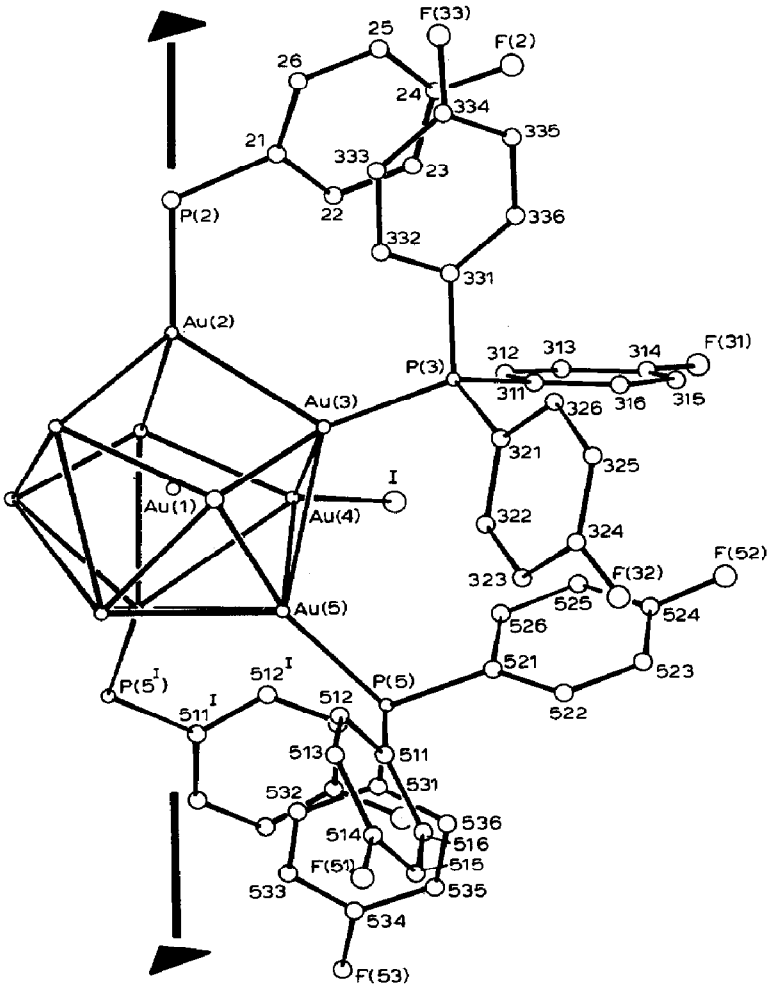

Fig. 15. Crystal structure of $[Au_{11}\{P(p\text{-}FPh)_3\}_7I_3]$ [238].

There is a discrepancy between the Au–P bond lengths and the degree of cluster aggregation. The Au–P of 2.30 Å in the enneagold cluster is comparable with those of 2.211–2.295(10) Å found in the undecagold cluster, but differs from those in the decagold cluster, which lie in the range 2.712–2.740(2) Å (Table 11). The Au–Cl distances of 2.666–2.674(1) Å in the last are even longer than the Au–I distance of 2.600(5) Å in the undecagold cluster.

Compounds of the general formula $\{AuAg(C_6F_5)_2L\}_n$ ($L = SC_4H_8$ or C_6H_6) [239,240] form polynuclear chains by repetition of the structural unit $[\ldots(C_6F_5)_2Au(\mu_2\text{-}Ag_2L_2)Au(C_6F_5)_2\ldots]_n$ through Au ... Au contacts (2.889(2) Å, $L = SC_4H_8$), which are longer (3.013(2) Å) when L is C_6H_6 (Table 11).

F. STRUCTURAL DATA FOR GOLD COMPOUNDS WITH COORDINATION NUMBERS SIX AND SEVEN

The only example where the oxidation state of a gold atom is greater than three is $[AuF_6]^-$ [241]. The crystal structure shows the gold(V) atom is essentially octahedral (Table 12).

The gold(III) atom in $[Au(pdma)_2I_2]^+$ [242,243] is in a tetragonal bipyramidal environment, with four arsenic atoms in a square-plane and two iodine atoms in the axial sites (Table 12). The compound $[Au(pdma)_2I_2]I$ exists in two isomeric forms.

Unusual for gold chemistry is the "slipped sandwich" structure where the gold(III) atom is six coordinate, found in $[3,3'\text{-}Au^{III}(1,2\text{-dcb})_2][Au^{III}(Et_2NCS_2)_2]$ [244] (Fig. 16, Table 12).

In $[Au_{13}(PPhMe_2)_{10}Cl_2]^{3+}$ [245], the lowest coordination number for twelve gold atoms is six ($AuPAu'_5$ (10 ×) and $AuClAu'_5$ (2 ×) and the central atom has a coordination number of twelve ($AuAu'_{12}$) (Table 12). The complex shows significant distortion from the idealised icosahedral geometry, probably arising from the different electronic and steric requirements of the chloro- and phosphine ligands.

Gold(III) fluoride [246] is a fluorine-bridged polymer, with gold(III)

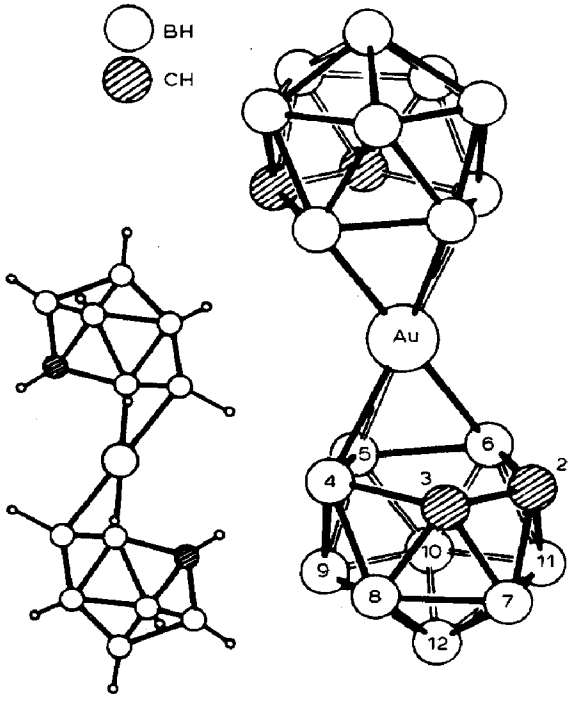

Fig. 16. Crystal structure of $[3,3'\text{-}Au^{III}(1,2\text{-dcb})_2]^-$ [244].

TABLE 12

Structural data for oligonuclear gold compounds with a coordination number six and seven [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L_{eq} (Å)	M–L_{ax} (A°)	L_{eq}–M–I_{eq} (°) L_{eq}–M–L_{ax} (°) L_{ax}–M–L_{ax} (°)	Ref.
$[Au^{V}F_6](Xe_2F_{11})$	or	*Pnma*	4	AuF_6	9.115 (6) 8.542 (25) 15.726 (20)		F [c b]	F [c b]	90.0 (6, 2.0) 90.4 (4) 179.1 (3)	241
$[Au^{III}(pdma)_2I_2]I$	m	*C2/c*	4	$AuAs_4I_2$	21.6 (2) 8.92 (4) 16.10 (8)	107 (1)	As 2.44 (3, 2)	I 3.35 (2) (2×)	90.0 (8, 4.0) 90.0 (6, 7.2)	242, 243
$[Au^{III}(pdma)_2I_2]I$	m	$P2_1$	4	$AuAs_4I_2$	16.57 (8) 18.28 (9) 9.20 (5)	97.7 (5)				243
$[3,3'\text{-}Au^{III}(1,2\text{-dcb})_2]\cdot[Au'''(Et_2NCS_2)_2]$ [d]	m	$P2_1/c$	2	AuB_6	8.3786 (9) 20.6068 (22) 10.0656 (11)	105.346 (8)	B 2.229 (10, 25)	B 2.273 (10) (2×)	[c]	244
				AuS_4			S [c]		[c]	
$[Au_{13}(PPhMe_2)_{10}Cl_2]\cdot(PF_6)_3$	tr	$P\bar{1}$		$AuPAu'_5$ (10×)	13.256 (2) 14.962 (2) 15.300 (2)	104.55 (2) 95.89 (1) 92.71 (3)	P [c] Au′ 2.716–2.949 (3)			245
				$AuClAu'_5$ (2×)			Cl [c] Au′ 2.716–2.949 (3)			
				$AuAu'_{12}$			Au′ 2.716–2.789 (2)			
$(Au^{III}F_3)_n$ [e]	hx	$P6_122$	6	AuF_6	5.149 – 16.26		F 1.91 (4) (2×) 2.04 (3) (2×)	F 2.69 (4) (2×)	90 (1.6, 2.0); 178 (1.6) 90 (1.6; 13) 175 (1.6)	246
$[Au_{13}(dppmH)_6]\cdot(NO_3)_n$	trg	$P\bar{3}m1$	2.86	$AuPAu'_6$ (12×)	28.998 (6) 28.998 (6) 15.643 (3)		P 2.46 (10, 6) Au′ 2.868 (11, 114)		[c]	117
				$AuAu'_{12}$			Au′ 2.786 (10, 32)			
$[Au_{13}(Ph_3P)_{12}Ag_{12}Cl_6]\cdot(Cl)_6\cdot(EtOH)_n$	m	$C2m$ ($C2$)	2	$AuPAg_3Au'_3$ (10×)	36.082 (10) 16.581 (10) 19.338 (11)	101.24 (5)	P 2.35 (6, 6) Ag 2.95 (2, 31) Au′ 2.82 (2, 22)		[c]	247
				$AuAg_5Au'_2$ (1×)			Ag 2.87 (2, 11) Au′ 2.79 (1)		[c]	
				$AuAg_6Au'_6$ (2×)			Ag 2.84 (2, 17) Au′ 2.73 (1, 16)		[c] [c]	
$\{KAu_4Sn_2\}_n$	tg	$I\bar{4}c2$	4	$AuSn_3Au'_4$	8.847 (4) – 8.178 (4)		Sn 2.875 (2, 115) Au′ 2.893 (2, 192)		[c]	248

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d. and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in these columns. [c] Not given. [d] There are Au–C distances of 2.760 (7) and 2.774 (9) Å. [e] There is Au ··· Au contact of 3.461 (1) Å; and Au–F–Au angles of 116 (2,6) and 148 (2.6)°.

atoms linked to square-planar arrangements of fluorine atoms (Au–F(bridging) = 2.04(3) Å). Two further bonds Au–F(non-bridging) = 1.91(4) Å, complete a tetragonally-elongated octahedral environment around each gold(III) atom (Table 12).

In three compounds, $[Au_{13}(dppmH)_6](NO_3)_n$ [117], $[Au_{13}(PPh_3)_{12}Ag_{12}Cl_6]Cl_6(EtOH)_n$ [247] and $\{KAu_4Sn_2\}_n$ [248] each gold atom shows a coordination number of seven (Table 12).

In icosahedral geometry ($[Au_{13}(dppmH)_6]^{n+}$), twelve gold atoms have a seven-coordinate geometry ($AuPAu'_6$) and the central atom is twelve coordinate, $AuAu'_{12}$ (Table 12). The radial Au–Au distances which fall between 2.754–2.813(10) Å (mean 2.786(10,32) Å), and the peripheral Au–Au distances 2.899–2.976(11) Å (mean 2.934(11,42) Å), show a smaller variation than those for $[Au_{13}(PPhMe_2)_{10}Cl_2]^{3+}$ (in which the lowest coordination number is six) (2.716–2.789(2) Å, variation of 0.073 Å, and 2.852–2.949(3) Å, variation of 0.097 Å).

Three different classes of gold atom are found in $[Au_{13}(PPh_3)_{12}Ag_{12}Cl_6]^{6+}$ [247]; the framework was described as a cluster containing 10 Au and 12 Ag atoms occupying corners of three interpenetrating icosahedra and three Au atoms completely encapsulated within the three icosahedral cages. There are $AuPAg_3Au'_3$ (10×), $AuAg_5Au'_2$ (1×) and $AuAg_6$ (2×) clusters. Both, Au–Ag and Au–Au′ bond lengths are shortened (Table 12) in the order: $AuPAg_3Au'_3 > AuAg_5Au_2 > AuAg_6Au'_6$.

In $\{KAu_4Sn_2\}_n$ [248] the gold atoms form a $AuSn_3Au'_4$ cluster (Table 12).

G. STRUCTURAL DATA FOR MIXED VALENCE, Au(I)–Au(III), COMPOUNDS

Structural data for mixed-valence, Au(I)–Au(III), compounds are summarised in Table 13. In $M_2Au^IAu^{III}X_6$ (M = K, Rb or Cs; X = Cl, Br or I) the crystal structure is built up by linear anions AuX_2^-, square-planar anions AuX_4^-, and M^+ cations. The coordination of the gold(I) and gold(III) atoms is completed by additional halogen atoms at longer distances (Table 13) to form compressed and elongated octahedra, respectively. The structures depend on the size of the alkali metals, more dense structures with smaller coordination numbers for the smaller alkali metals result from a rotation of the coordination octahedra of the gold atoms [163,250,252].

Denner et al. [251] have studied the influence of high hydrostatic pressure on the crystal structure of $Cs_2Au^IAu^{III}Cl_6$. The measurements showed a continuous decrease in the lattice constants with increasing pressure; however, they decrease in such a way that the unit cell ratio a/c remains constant in the measured pressure range ($P = (1.5–51.7) \times 10^8$ Pa). With increasing pressure the interatomic distances decrease and the coordination

octahedra of the gold atoms become more and more indistinguishable and, at the end of this process, have a formal valence of +2.

The Au(I)–X bond lengths are somewhat shorter than those of Au(III)–X (Table 13).

In $[Au^{III}(dtc)_2][Au^{I}Br_2]$ [254] the Au(1) atom is linearly coordinated by two Br^- ions, where the Au(I)–Br distance of 2.349(5) Å is significantly shorter than those in $Rb_2Au^{I}Au^{III}Br_6$ (Au(I)–Br = 2.402(8) Å). The Au(III) is in planar coordination with four S atoms (Table 13).

The crystal structure of $[Au'Au'''(PMe_3)_2(C_4F_6)]$ [255] is shown in Fig. 17. The coordination of $Au^{I}(2)$ is linear and that for $Au^{III}(1)$ is square planar (Table 13). There is contact between the Au(I) · · · Au(III) of 3.31 Å. Even shorter contact between Au(I) · · · Au(III) (3.050(3) Å) is found in $[Au^{I}\{Ph_2P(CH_2)S\}_2 \ldots Au^{III}I_2]$ [254] (Table 13).

In binuclear $[Au^{I}Au^{III}(C_6F_5)_3\{CH(PPh_2)\}_2]$ and trinuclear $[Au^{I}Au^{III}_2(C_6F_5)_4\{CH(PPh_2)_2\}_2]^+$ [256], the molecules possess crystallographic *m* symmetry; both gold atoms, the methanide CH, and C_6F_5 groups at Au(I) in the former and three gold atoms and the methanide C atom in the latter, lie in the mirror plane. The bond distances and angles are given in Table 13.

The crystal structure of tetranuclear $[Au^{I}_2Au^{III}_2Cl_8]$ [258] (Fig. 18) shows square-planar gold(III) and almost linear gold(I) centres in a chair-like

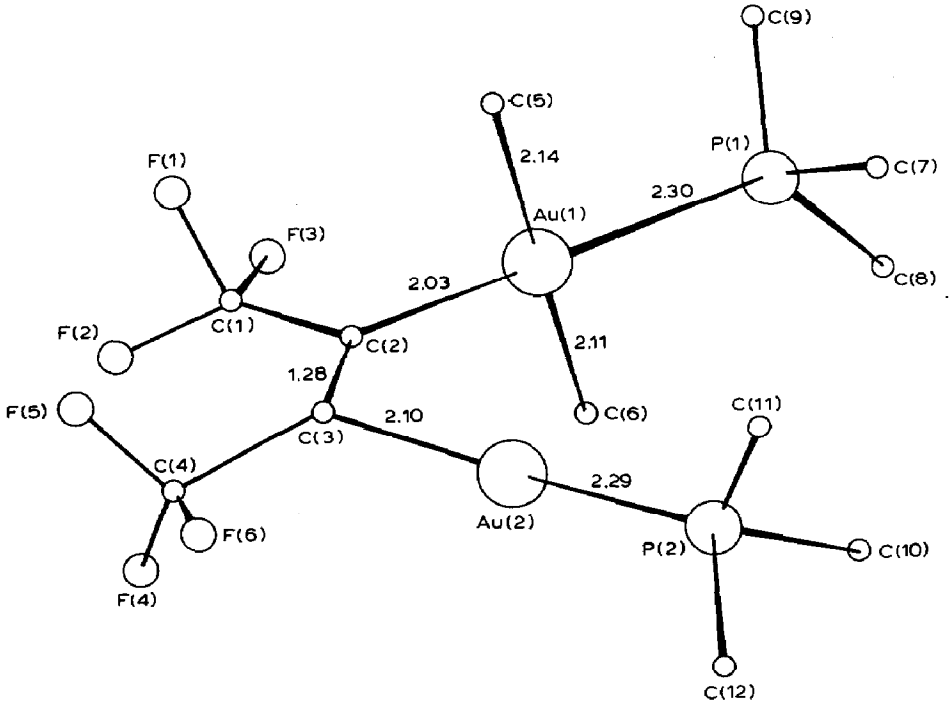

Fig. 17. Crystal structure of $[Au^{I}Au^{III}(PMe_3)_2(C_4F_6)]$ [255].

TABLE 13

Structural data for mixed valence, $Au(^{I})$–$Au(^{III})$, compounds [a]

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L(°) L–M–L'(°)	Ref.
$Cs_2Au^{I}Au^{III}Cl_6$	tg	*I4/mmm*	2	$Au^{I}Cl_2(Cl_4)$	7.49 (2) – 10.87 (2)		Cl 2.31 [b] (2.98)	[c]	249, 250
				$Au^{III}Cl_4(Cl_2)$			Cl 2.42 (3.05(0, 8))	[c]	
$Cs_2Au^{I}Au^{III}Cl_6$	tg	*I4/mmm*	2	$Au^{I}Cl_2(Cl_4)$	7.495 (1) – 10.880(2)		Cl 2.280 (3) (3.010(3))	[c]	251
				$Au^{III}Cl_4(Cl_2)$			Cl 2.29 (1) (3.150(3))	[c]	
$Cs_2Au^{I}Au^{III}Cl_6$ [d]		*P4/mmm*	2	$Au^{I}Cl_2(Cl_4)$	7.05 – 10.23		Cl 2.56(13) (2.49(11))	[c]	251
				$Au^{III}Cl_4(Cl_2)$			Cl 2.49 (11) (2.56 (13))	[c]	
$Rb_2Au^{I}Au^{III}Br_6$	m	*I2/m*	2	$Au^{I}Br_2(Br_4)$	8.520 (1) 7.243 (1) 11.210 (3)	101.24 (5)	Br 2.402 (8) (3.253 (5))	180.0	163
				$Au^{III}Br_4(Br_2)$			Br 2.438 (4) (3.360 (9))	89.26 (9)	
$Rb_2Au^{I}_2Au^{III}Cl_8$	m	*C2/c*	4	$Au^{I}Cl_2(Cl_4)$	12.02 (1) 7.522 (6) 18.29 (2)	97.62 (7)	Cl 2.26 (4, 1) (3.23 (3))	173.3 (4)	163
				$Au^{III}Cl_4(Cl_2)$			Cl 2.28 (3, 1) (3.19 (3))	89.7 (4)	
$K_2Au^{I}Au^{III}I_6$	m	$P2_1/n$	2	$Au^{I}I_2$ (I_4)	7.283 (3) 9.259 (3) 11.587 (5)	93.0 (1)	I 2.564 (3) (3.380 (5, 125))	[c]	252
				$Au^{III}I_4(I_2)$			I 2.644 (4, 5) (3.590 (5))	90.3 (1)	
$Rb_2AgAu^{I}_2Au^{III}I_8$	m	*C2/c*	4	$Au^{I}I_2(I_4)$	13.324 (4) 7.480 (2) 21.029 (6)	101.08 (2)	I 2.559 (9, 11) (3.641 (6, 146))	175.42 (3)	253
				$Au^{III}I_4(I_2)$			I 2.635 (5, 2) (3.598 (6))	89.23 (2)	

$[Au^{III}(dtc)_2]$-$[Au^{I}Br_2]$ [c]	m	$C2/c$	4	$Au^{I}Br_2$	22.38 (3) 15.80 (3) 8.11 (4)	98.2 (3)	Br 2.349 (5)	180	254
				$Au^{III}S_4$			S 2.332 (9) (2×) 2.333 (9) (2×)	75	
$[Au^{III}(dmg)_2]$-$[Au^{I}Cl_2]$	or	Pnm	2	$Au^{I}Cl_2$	11.52 10.59 6.52	Cl [c]	[c]		11
				$Au^{III}N_4$			N [c]	[c]	
$[Au^{I}\{Ph_2P(CH_2)S\}_2$-$Au^{III}I_2]$ [f]	m	$C2/c$	8	$Au^{I}S_2$	25.187 (4) 6.4465 (9) 42.5443 (11)	91.14 (2)	S 2.308 (13) 2.316 (13)	180	254
				$Au^{III}C_2I_2$			C 2.12 (5, 1) I 2.613 (4, 2)	[c]	
$[Au^{I}Au^{III}(PMe_3)_2$-$(C_4F_6)]$ [g]	or	$Pbca$	8	$Au^{I}CP$	20.68 (3) 19.20 (1) 10.47 (1)		C 2.10 P 2.29	180	255
				$Au^{III}C_3P$			C 2.09 (6) P 2.30	[c]	
$[Au^{I}Au^{III}(C_6F_5)_3$-$\{CH(PPh_2)_2\}]$	m	$P2_1/m$	2	$Au^{I}C_2$	10.003 (2) 17.389 (4) 11.754 (3)	103.53 (2)	C 2.048 (8) 2.094 (7)	177.0 (4)	256
				$Au^{III}C_3P$			C 2.075 (6) P 2.354 (2)	102.3 $(2)_1$ 172.1 (2)	
$[Au^{I}Au^{III}_2(C_6F_5)_4$-$\{CH(PPh_2)_2\}_2]\cdot$ $(ClO_4)\cdot(CHCl_3)_n$	m	$P2_1/m$	2	$Au^{I}C_2$	17.456 (6) 17.704 (6) 17.749 (8)	92.86 (5)	C 2.098 (28) 2.127 (29)	179.1 (11)	256
				$Au^{III}C_2P_2$			C 2.113 (11, 5) P 2.351 (7, 5)	87.7 (7, 1.3); 69.9 (4, 1.1) 100.9 (4, 2); 170.1 (4, 1.3)	
$Au^{I}_2Au^{III}_2Cl_8$ [i]	tr	$P\bar{1}$	1	$Au^{I}Cl_2$	7.015 (4) 6.830 (2) 6.684 (4)	94.4 (1) 107.5 (1) 88.4 (1)	Cl 2.29 (1) [h] Cl 2.31 (1) [h]	175.1 (5)	257, 258
				$Au^{III}Cl_4$			Cl 2.25 (0, 1) Cl 2.32 (0, 1) [h]	90.0 (5, 1.2); 178.8 (9, 2)	

TABLE 13 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L (Å)	L–M–L(°) L–M–L′(°)	Ref.
$[Au^{I}_{3}Cl_2(dppm)_2]\cdot[Au^{III}Cl(C_6F_5)_3]$ [j]	tr	$P\bar{1}$	2	$Au^{I}P_2$(1×)	12.170 (6) 14.448 (8) 23.780 (10)	102.29 (5) 90.01 (4) 93.68 (4)	P 2.322 (10) 2.323 (9)	166.9 (3)	174
				Au′PCl (2×)			Cl 2.294 (10, 7} P 2.241 (10, 2)	176.7 (3, 7)	
				Au‴C_3Cl			C 2.054 (24, 26) Cl 2.307 (10)	89.7 (10, 1.2); 177.4 (11) 87.8 (7); 177.9 (8)	
$[Au^{I}Cl_2]_3\cdot[Au^{III}(terpy)Cl_2]\cdot[Au^{III}Cl_4]$ [k]		$P\bar{1}$	1	$Au'Cl_2$ (3×)	9.703 (1) 15.351 (1) 7.813 (1)	92.05 (1) 106.58 (1) 107.102 (9)	Cl 2.275 (4, 2)	174.0 (1)	161
				Au‴N_3Cl (2×)			N 1.997 (8, 56) Cl 2.259 (3)	81.3 (4, 1); 162.6 (4) 89.5 (3, 11, 6); 178.6 (2)	
				Au‴Cl_4 (1×)			Cl 2.271 (3) (2×) 2.272 (3) (2×)	90.0 (1, 5)	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following is an averaged value of e.s.d., and the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] Not given. [d] High pressure data (52×10^8 Pa). [e] At −150°C. [f] There is Au(′)···Au(‴) contact of 3.050 (3) Å. [g] There is Au(′)···Au(‴) contact of 3.31 Å. [h] The bridging atoms. [i] There is Au(′)···Au(′) contact of 3.095 (4) Å. [j] There are Au(′)···Au(′) contacts of 3.067 and 3.164 (5) Å. [k] There is Au(′)···(Au(′) contact of 3.0932 (5) Å.

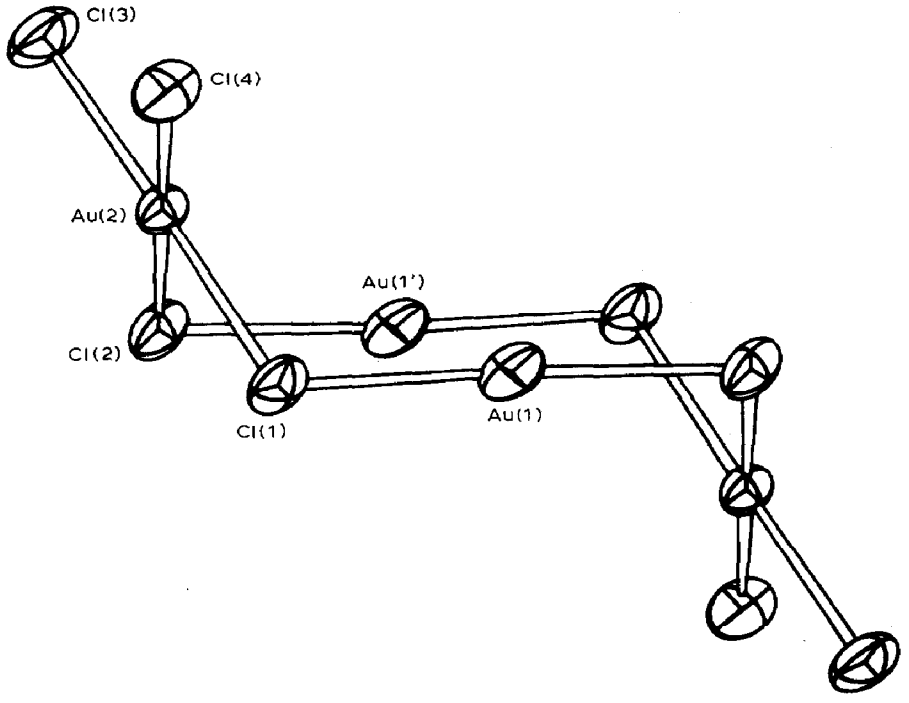

Fig. 18. Crystal structure of $[Au^{I}_{2}Au^{III}_{2}Cl_{8}]$ [258].

arrangement with Au(I) · · · Au(I) contacts of 3.095(4) Å (Table 13). Another example of tetranuclear Au(I)–Au(III) is $[Au^{I}_{3}Cl_{2}(dppm)_{2}]$ $[Au^{III}Cl(C_{6}F_{5})_{3}]$ [174]. There are 3 Au(I) and 1 Au(III) atoms. The three Au(I) atoms fall into two non-equivalent classes exhibiting different coordination patterns: two with AuClP and the central with a AuP_2 unit. There are Au · · · Au contacts between the central Au(I)(AuP_2) and the AuClP, from both sides of 3.067 and 3.164(5) Å, respectively (Table 13). The square-planar arrangement around Au(III) is built up by three C atoms and a chlorine atom.

X-ray analysis of $[Au^{III}Cl_4][Au^{I}Cl_2]_2[Au^{III}(terpy)Cl]_2$ [161] shows that a polynuclear · · · Cl–Au(III)–Cl · · · Au(III) · · · Au(I) · · · Au(I) · · · Au(I) · · · Au(III) · · · Cl–Au(III)–Cl · · · chain is present. Three $[AuCl_2]^-$ anions, arranged in a spiral, bridge two $[Au(terpy)Cl]^{2+}$ cations through long axial contacts (Au(I) · · · Au(III) = 3.300(1) Å). The other axial position of the $[Au(terpy)Cl]^{2+}$ cation is occupied by a chlorine atom of the $[AuCl_4]^-$ anion at a distance of 3.401(4) Å.

H. SUMMARY OF X-RAY DATA

This review has classified some 300 gold-containing structures showing gold in coordination numbers 2, 3, 4, 5, 6, 7 and even, in clusters, 12. The

TABLE 14

Review of mean Au–L bond lengths (Å)

Coordinate atom (ligand)	Au(I)			Au(III)	
	2 [a]	3 [a]	4 [a]	4 [a]	5 [a]
O	2.02			2.06	2.36 (2.55) [b]
N	2.02	2.28		2.09	2.11 (2.65) [b]
C [d]	2.05	2.21	2.47	2.065	2.275 (2.69) [b]
	2.10 [c]			2.09 [c]	
Cl	2.26	2.62	2.77	2.27	2.285 (2.69) [b]
	2.32 [c]			2.32 [c]	
S [e]	2.29	2.43	2.28	2.32	2.39
	2.31 [c]			2.33 [c]	
P [f]	2.27	2.31	2.39	2.33	
	2.29 [c]			2.34 [c]	
Br	2.385			2.46	2.41
	2.37 [c]			2.44 [c]	
I [g]	2.58	2.77	3.07	2.61	
	2.57 [c]			2.63 [c]	
Au′	2.84	2.81	2.80	2.81	2.83

[a] Coordination number, c.n. [b] The mean value of Au–axial ligand bond distance. [c] The mean value of Au(I)–L (Au(III)–L) bond distance found in a mixed valence, (Au(I)–Au(III)), compounds. [d] The mean value of Au(0)–C = 2.06 Å (5 c.n.) and 2.12 Å (6 c.n.). [e] The mean value of Au(0)–S = 2.39 Å (5 c.n. as well as 6 c.n.). [f] The mean value of Au(0)–P = 2.32 Å (2 c.n.); 2.29 Å (3 c.n. as well as 5 c.n.). [g] The mean value of Au(0)–I = 2.59 Å (4 c.n.); and 2.99 Å (5 c.n.).

more common oxidation states of the gold atom are Au(0) as in many organometallic and cluster complexes, Au(I), where the most prevalent coordination number is 2, and Au(III) where square planar four coordinate species are most common. Au(II) and Au(V) are very rare. Linear and trigonal planar stereochemistries are also fairly common both for Au(0) and Au(I).

A few examples of distortion isomerism exist in Au(0), Au(I), Au(II) and Au(III) species, e.g. in $[Au^{I}(C_6F_5)_2]^-$ [9], $[\{Au^{I}(PPh_3)\}_2Cl]$ [47], $[AuRu_3(\mu_2\text{-COMe})\cdot(PPh_3)(CO)_{10}]$ [92], $[Ru_5C(CO)_{15}\{\mu\text{-AuPPh}_3\}Cl]$ [94], $[Au'_2Ni_2(Pen)_4]^{2-}$ [106], $[Au^{I}(Ph_3Sb)_4]^+$ [10], $[Au^{III}Cl_4]^-$ [142, 144] and $[Au^{II}\{Ph_2P(CH_2)S\}I]_2$ [46] (see Sections B(i), (ii), C(i), (ii) and D(i)–(iii).

In Au(I) complexes, the Au(I)–L distance (Table 14) is sensitive to coordination number. Generally the Au(I)–L bond length increases with increasing coordination number as well as with the van der Waals' radius of L. This is also generally true for Au(III) species where the bond lengths in five-coordinate complexes are usually longer than in four-coordinate ana-

TABLE 15

Review of the Au–Au bond lengths (Å) of gold cluster compounds [a]

Coordination number [b]	X-nuclear	$AuPAu'_3$	$AuPAu'_4$	$AuPAu'_5$	$AuPAu'_6$	$AuPAu'_7$
3 [c]	5		2.70–3.01 (2.82)			
4	6	2.62–2.92 (2.76)		2.65–2.85 (2.77)		2.59–2.77 (2.70) [d,e]
	8	2.67–2.94 (2.79)	2.59–2.96 (2.81)			
	9	2.65–2.84 (2.74)	2.65–3.17 (3.02)	2.70–3.17 (2.89)		
5	6		2.93–3.09 (3.02)			
	7		2.74–3.00 (2.86)	2.58–2.90 (2.80)	2.58–2.90 (2.80)	
	9		2.66–2.90 (2.76)			
	10		2.70–2.94 (2.81)			
	11		2.60–2.94 (2.77)	2.68–3.14 (2.89)	2.67–3.19 (2.98)	
6	13			2.71–2.95 (2.83)		
7	13				2.75–2.97 (2.87)	
		$AuAu'_7$	$AuAu'_8$	$AuAu'_7$	$AuAu'_{10}$	$AuAu'_{12}$
4	8	2.63–2.72 (2.69) [d] 2.84–2.96 (2.89) [f]				
	9		2.65–2.77 (2.68) [d] 2.68–3.17 (2.84) [f]			
5	9		2.65–2.74 (2.69) [d] 2.80–2.90 (2.82) [f]			
	10			2.66–2.74 (2.70) [d] 2.74–2.94 (2.85) [f]		
	11				2.60–2.72 (2.67) [d] 2.86–3.19 (2.99) [f]	
7	13					2.75–2.81 (2.78) [d] 2.90–2.97 (2.93) [f]

[a] Mean value is given in parentheses. [b] Minimum coordination number in cluster. [c] There is no Au–Au bond. [d] The values of the radial Au–Au distances. [e] The peripheral Au–Au distances are in the range of 2.84–2.96 (2.89) Å. [f] The values of the peripheral Au–Au distances.

logs. Similarly in Au(I) phosphine species, the Au(I)–P distance increases with increasing size of the coordinating ligand (Section D(i)).

In general, Au–L distances are somewhat longer in oligonuclear species than in mononuclear species. Moreover in Au cluster species the Au–Au distance monotonically decreases with increasing coordination number and increases with decreasing oxidation state. In the listing of Au–Au bond lengths (Table 15) there are some interesting trends. The Au–Au bond lengths decrease in the sequence $AuPAu'_6 > AuPAu'_5 > AuPAu'_4 > AuPAu'_3$. The radial Au–Au bond lengths are generally shorter than the peripheral bond lengths (Table 15b). The variations in radial Au–Au distances in $AuAu'_n$ ($n = 7$–10) are greater than those in $AuAu'_{12}$. A similar trend is observed in the peripheral Au–Au distances, the smallest variation being in $AuAu'_{12}$. Evidently the icosahedral structure in tridecagold species is especially regular.

In mixed valence Au(I)–Au(III) compounds, both the Au(I)–L and Au(III)–L distances are somewhat longer than those in simple Au(I) and Au(II) compounds, respectively (Table 14). In the $M[Au(III)X_4]$ crystals, the axial ratio c/a increases with increase in radius of M.

I. MÖSSBAUER SPECTROSCOPY WITH GOLD

Mössbauer spectroscopy has proved to be one of the most powerful of the "sporting" methods for the characterisation of gold compounds. Using X-ray crystallographic data for model compounds, other physical data, and chemical common-sense, characteristic ranges of parameters have been established which allow definition of the oxidation state of the metal and the number and identity of the ligand donor atoms with some confidence.

The experimental methods and underlying theory are discussed in detail elsewhere [259, 260] and are not necessary to an understanding of the utility of the method. It suffices to say here that the Mössbauer method is a form of absorption spectroscopy which employs γ-radiation to excite energy-level transitions within the gold-197 nucleus [261]. The number and precise energy of these transitions reflect the symmetry and density of the electron cloud surrounding the nucleus and, hence, give chemical information. The γ-ray source used (platinum-197m) is highly monochromatic, and a suitable range of energies is obtained by Doppler modulation, i.e. the source is given a velocity relative to the sample. The energy experienced by the sample is then $E = E_\gamma(1 + v/c)$, where E_γ = gamma-energy of the stationary source (77.34 keV), v = applied velocity, and c = velocity of light. The velocity range required is about ± 20 mm s^{-1}. The data are normally quoted directly in mm s^{-1}: conversion factors for other units are 1 mm $s^{-1} = 25.8 \times 10^{-8}$ eV $= 2.49 \times 10^{-4}$ J $mol^{-1} = 62.4$ MHz.

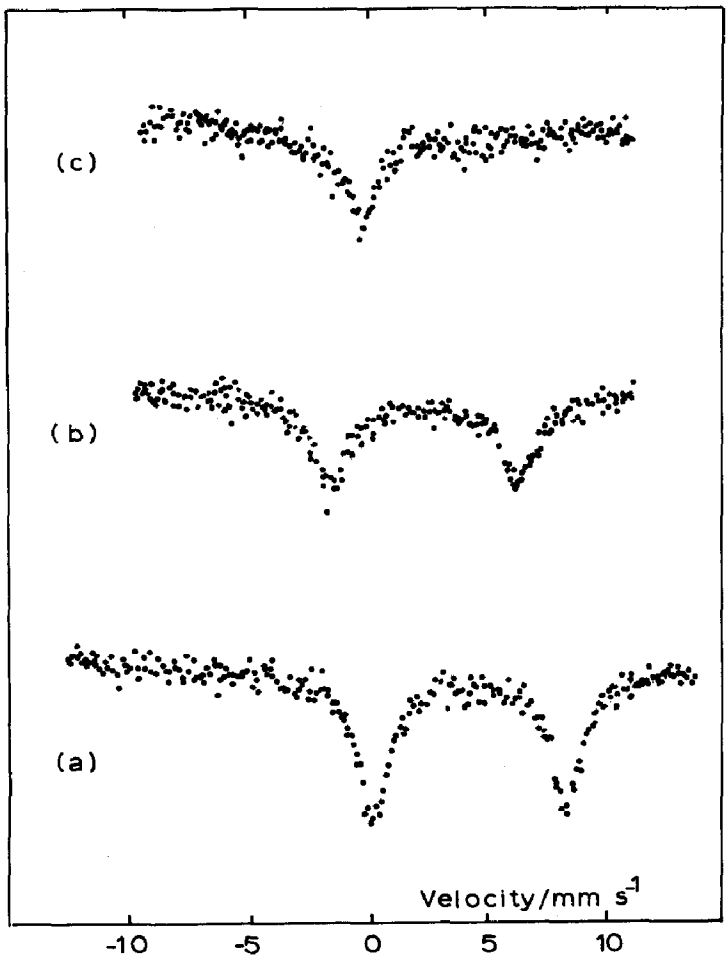

Fig. 19. ^{197}Au Mössbauer spectra for $[Au(PPh_3)_n]ClO_4$ with (a) $n = 2$. (b) $n = 3$. (c) $n = 4$.

The majority of spectra are simple absorption doublets, typical examples of which are shown in Fig. 19. The two major parameters are thus the centre of the doublet and the separation between the peaks, respectively known as the isomer shift (IS, usually measured relative to metallic gold) and the quadrupole splitting (QS). These cover the ranges $0 < IS < 7$ mm s^{-1} and $4 < QS < 12$ mm s^{-1} for gold(I) and $-0.5 < IS < 8$ mm s^{-1}, $-3 < QS < 8$ mm s^{-1} for gold(III). Since a typical linewidth is about 2 mm s^{-1}, the spectra are usually quite well-resolved.

For the two major oxidation states, both parameters increase with increasing covalency of the gold–ligand bonds, giving characteristic ranges for each type of ligand (Fig. 20). There is also a systematic dependence on coordination number.

The two parameters reflect the electron density surrounding the gold

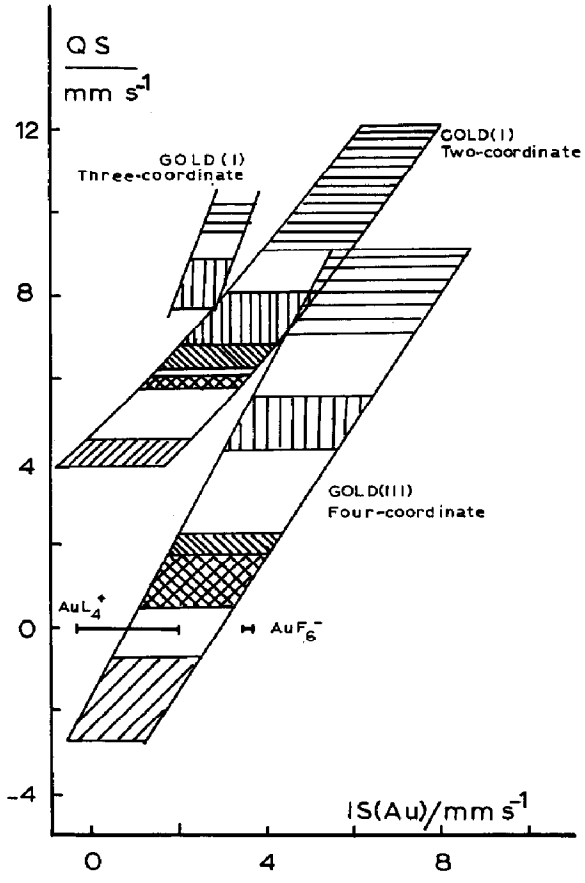

Fig. 20. IS–QS correlation diagram for gold-197 showing the regions characteristic of four-coordinate gold(III) and two-, three- and four-coordinate gold(I) complexes. The hatchings indicate corresponding sets of ligands [259,260].

nucleus, but in different ways. The IS is a measure of the total electron density at the gold nucleus. Increase in the *s* electron density causes a large increase in IS, while increases in *p* or *d* electron density give a smaller decrease. As the gold–ligand bonds become more covalent, therefore, the IS increases as electron density builds up on the gold atom. For a given ligand, however, increase in the coordination number results in a substantial decrease in IS, as *p* (or *d*) orbital participation increases in the hybridisation of the gold atom. Thus, for the three triphenylphosphine complexes shown in Fig. 19, the IS decreases from 5.40 to 2.99 to -0.17 mm s^{-1} as the coordination number increases from 2 to 4.

Compounds of gold(III) have similar IS to the corresponding two-coordinate compounds of gold(I). This similarity is the result of two opposing factors:

(a) The formal removal of two d electrons reduces the shielding and increases the s electron density at the nucleus.

(b) Since most gold(III) compounds are four-coordinate, the increased p and d orbital participation in the hybridisation increases the shielding.

If four-coordinate complexes involving the same ligand are compared, the IS is markedly higher for gold(III). These trends are continued in the (six-coordinate) compounds of gold(V).

The QS reflects the symmetry of the electron distribution about the gold nucleus or, more strictly, the electric-field gradient (EFG) at the nucleus. If the gold atom occupies a site of cubic (or higher) symmetry, the EFG and QS are zero, and a single-line spectrum results. This is the case for $[Au(PPh_3)_4]^+$ (tetrahedral, see Fig. 19), $[AuF_6]^-$ (octahedral) and the central gold atom in the icosahedral cluster compounds. All other ligand arrangements have lower symmetry, and a splitting of the spectrum is observed. In the majority of cases, the electron density in the gold–ligand bonds gives the major contribution to the EFG, and the QS therefore increases with increasing covalency.

For gold(I) (d^{10}) and gold(V) (d^6), the non-bonding electrons have spherical and cubic distributions respectively, and contribute nothing to the EFG. Gold(III), however, has a d^8 configuration which, in the usual square-planar coordination, leaves the $d_{x^2-y^2}$ orbital formally vacant (except insofar as it is repopulated by donation from the ligands). There is thus a contribution to the EFG which is of opposite sign to that from the ligands, and QS values for gold(III) compounds are smaller than those for corresponding gold(I) compounds.

A simple electrostatic treatment has been used to show that the QS for a planar three-coordinate gold(I) complex $[AuL_3]^+$ should be very similar to that for a linear two-coordinate complex with the same ligands, $[AuL_2]^+$ [260,262]. This effect is illustrated for $L = PPh_3$ in Fig. 19. In the three-coordinate system, the principal component of the EFG lies in the direction perpendicular to the coordination plane, and its value is independent of the bond angles within the plane. For two-coordination, the principal component lies along the molecular axis and is, in principle, sensitive to the bond angle; however, reduction in the bond angle even to 160° would be expected to reduce the QS by less than 5%, and such effects are usually undetectable. The associated rehybridisation might give a small reduction in IS.

J. CORRELATION OF STRUCTURAL AND MÖSSBAUER DATA

The ^{197}Au Mössbauer data for compounds of known structure are presented in Tables 16–20. They are best discussed in terms of the formal oxidation states and coordination numbers of the gold atom.

TABLE 16

Mössbauer data for gold(I) compounds

Compound	IS (Au) ($mm\ s^{-1}$)	QS ($mm\ s^{-1}$)	Donor atoms	Table for X-ray data	Ref.
1 $[AuCl]_n$	−0.40	4.34	2 μ-Cl	3	270
	−0.21	4.65			271
	−0.16	4.47			272
	0.0	4.6			273
2 $[AuI]_n$	0.00	3.91	2 μ-I	3	272
	−0.11	3.98			271
	−0.03	3.83			270
	−0.11	4.4			273
3 $[Au(Hdmg)_2][AuCl_2]$ [a]	1.58	6.03	2 Cl	1	266
4 $[Au(etu)_2]Cl \cdot H_2O$	2.74	7.22	2 S	1	274
5 $Na_3[Au(S_2O_3)_2] \cdot 2\ H_2O$	3.13	7.01	2 S	1	275
	3.13	6.98			276
6 $[AuS_2CNPr_2]_2$	3.00	6.39	2 S	5	277
7 $[AuS_2CCH_3]_4$	2.61	6.13	2 S	3	60
8 $[Au\{S_2P(O\text{-}Pr^i_2)_2\}]_n$	2.17	6.09	2 S	9	277
9 $[Au(OAc)(PPh_3)]$	4.5	7.6	P, O	1	273
10 $[AuCl\{P(OPh)_3\}]$	3.92	7.64	Cl, P	1	278
11 $[AuCl(PPh_3)]$	4.05	7.52	Cl, P	1	278
	4.17	7.47			273
	4.03	7.45			279
	4.04	7.34			280
	4.15	7.50			277
12 $[AuCl(PCl_3)]$	2.98	6.60	Cl, P	1	278
13 $ClAu(Ph_2PCH_2PPh_2)AuCl$	3.73	7.03	Cl, P	2	279
14 $ClAu(Ph_2PCH = CHPPh_2)AuCl$	3.42	6.94	Cl, P	2	279
15 $[Au(dtc)(PPh_3)]$	3.89	7.50	P, S	1	281
16 $[Au(tag)(PEt_3)]$	4.76	8.64	P, S	1	276
	4.80	8.77			275
17 $[AuS(CH_2)_2PEt_2]_2$	3.42	8.25	P, S	2	276
18 $[Au(PMePh_2)_2]PF_6$	4.75	9.69	2 P	1	278
19 $[Au(Pcy_3)_2]PF_6$	5.44	10.37	2 P	1	278
20 $[Au(CN)(PPh_3)]$	5.08	10.5	C, P	1	278
21 $[Au(CH_3)(PPh_3)]$	6.14	10.35	C, P	1	273
22 $Me_3PAuC(CF_3) = C(CF_3)AuMe_2PMe_3$ [b]	5.58	9.18	C, P	13	255
23 $K[Au(CN)_2]$	4.28	9.80	2 C	3	282
	4.46	10.21			271
	4.33	10.12			272
	4.35	10.12			283
24 $[Au(pdma)_2][Au(C_6F_5)_2]$ [a]	~5.3	~10.5	2 C	1	284
25 $[Au(SbPh_3)_4][Au(C_6F_5)_2]$ [a]	~5.4	~10.5	2 C	1	284
26 $[AuCH_2PEt_2CH_2]_2$	4.97	9.60	2 C	2	280
27 $\{[Ag(tht)][Au(C_6F_5)_2]\}_n$	4.59	9.23	2 C	11	284

TABLE 16 (continued)

Compound	IS (Au) (mm s^{-1})	QS (mm s^{-1})	Donor atoms	Table for X-ray data	Ref.
28 $[Au(bipy)(PPh_3)]PF_6$	2.81	6.76	N, P(N)	4	274
29 $[Au(SnCl_3)(PMe_2Ph)_2]$	4.18	8.39	2 P(Sn)	4	274
30 $[AuCl(PPh_3)_2]$	2.33	8.25	Cl, 2 P	4	279
	2.36	8.19			274
31 $[Au(SCN)(PPh_3)_2]$	2.46	8.42	2 P, S	4	274
32 $[AuCl(PPh_3)_3]$	1.18	4.38	Cl, 3 P	6	265
33 $[Au(pdma)_2][Au(C_6F_5)_2]$ [c]	0.8	1.1	4 As	6	284
34 $[Au(SbPh_3)_4][Au(C_6F_5)_2]$ [c]	1.11	0.00	4 Sb	6	284

[a] Data for anion. [b] Data for gold(I) atom. [c] Data for cation.

(i) Gold(I) compounds

The greatest amount of data is available for gold(I) compounds (Table 16). Those involving two-coordination are presented on an IS/QS correlation diagram in Fig. 21. The points form a compact band, regardless of the extent of aggregation and of the presence or absence of short Au–Au contacts.

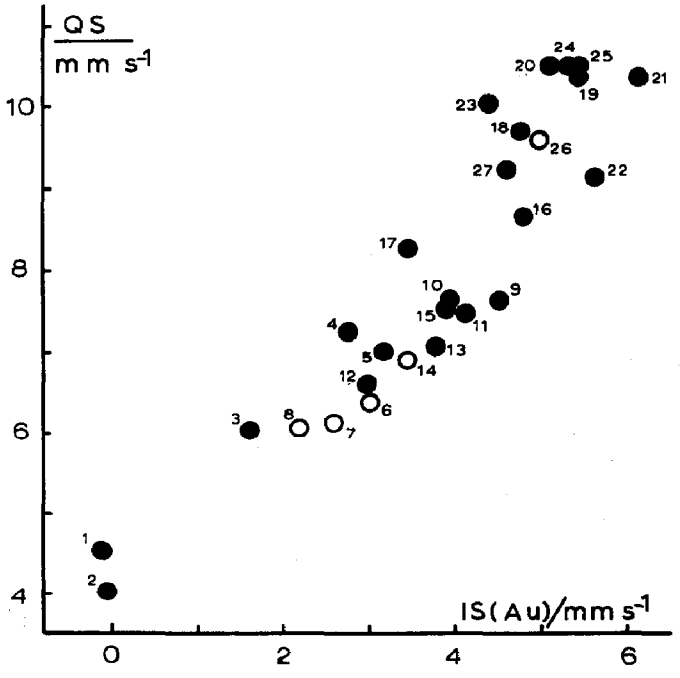

Fig. 21. Correlation diagram for gold(I) complexes. The numbering corresponds to Table 16. Open circles represent compounds in which close Au–Au contacts are observed.

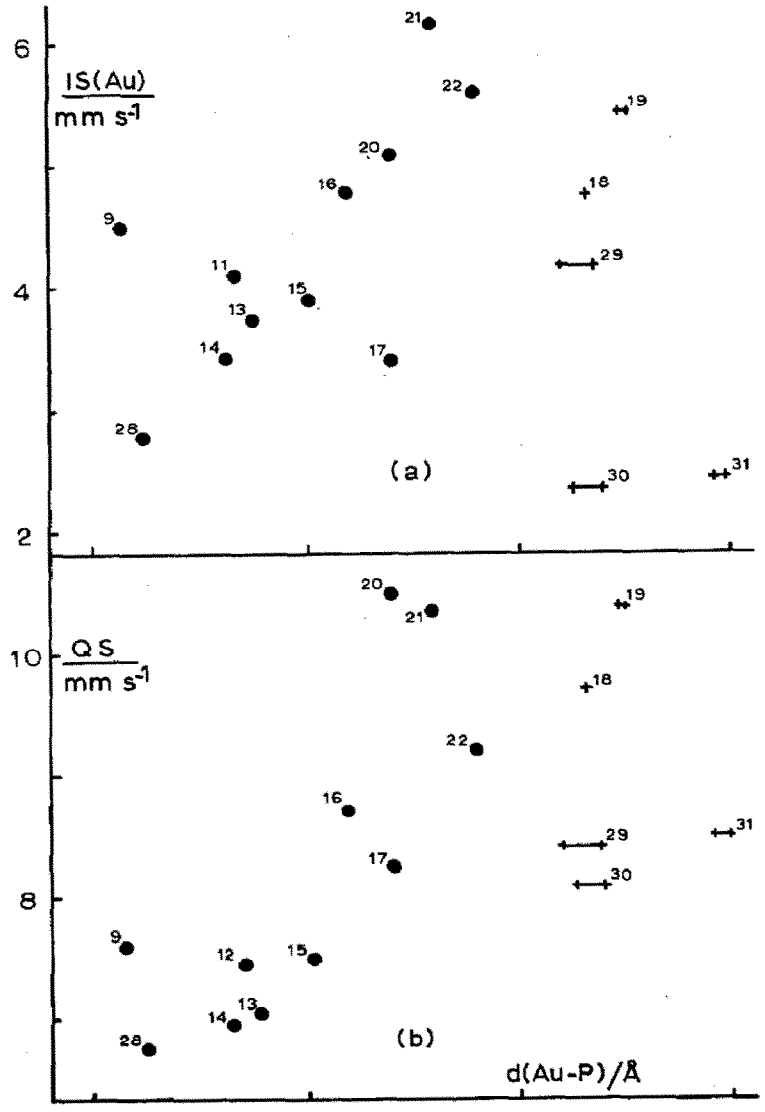

Fig. 22. Correlation of (a) IS and (b) QS with Au–P bond length for gold(I) complexes with tertiary organophosphines. The numbering corresponds to Table 16. Circles represent data for $[AuX(Ph_3)]$; crosses represent compounds with two Au–P bonds.

An important sub-set of two-coordinate compounds consists of those of the type $[AuX(PR_3)]$, where X may be an anionic ligand or another tertiary phosphine. In this series there is a reasonable positive correlation between the Mössbauer parameters and the Au–P bond length (Fig. 22). When X is anionic, the bond length increases as X changes from Cl^- or OAc^- to RS^- to CN^- or CH_3^-, demonstrating a clear *trans*-influence of the ligand X. The increase in IS indicates an increase in electron density on the gold atom, showing that any loss of donation from the phosphine ligand, as the Au–P

bond lengthens, is more than offset by donation from X. The change in QS may be similarly interpreted. Two compounds seem to be slightly out of line, $[Au(OAc)(PPh_3)]$ (F22.9) * and $[AuS(CH_2)_2PEt_2]_2$ (F22.17). For the former, both the IS and, to a lesser extent, the QS are higher than expected from the Au–P bond length, which is the shortest recorded for complexes of tertiary organophosphines with gold. The Au–O bond presumably has low covalency and high *p* character, allowing a considerable degree of *s* character to the Au–P bond. This results in a relative increase in the IS; it should be noted, however, that the IS and QS bear the normal relationship to each other (F21.9).

For the dimeric ring compound $[AuS(CH_2)_2PEt_2]_2$, the IS appears to be low while the QS is normal, especially when compared with other S–Au–P compounds (T16.15, 16); this is evident in both Figs. 21 and 22. The crystal structure [52] shows that the gold atoms are pulled together, to a distance of 3.104 Å, with distortion of the linearity of the S–Au–S system (173.5°), suggesting that the effective increase in coordination number might be responsible for the low IS. However, the compound $[AuS_2CNPr_2]_2$ (T16.6) has a similar dimeric structure and an even shorter Au–Au contact (2.76 Å [100]) (albeit with a smaller ring), but the Mössbauer parameters appear normal. It should perhaps be remarked that the IS of $[AuS(CH_2)_2PEt_2]_2$ is no lower in relation to its bond length than are those of $[Au(PMePh_2)_2]^+$ and $[Au(Pcy_3)_2]^+$ (F22.18, 19). It may well be that the apparent anomaly is simply the result of the relative paucity of data, and that interpretation in terms of unusual bonding is inappropriate. The bond lengths in all the bis-phosphine complexes are the largest recorded, and differ little between two-coordinate and three-coordinate complexes.

The compound $[Au(bipy)(PPh_3)]PF_6$ has Mössbauer parameters consistent with two-coordination (F21.28, F22.28), reflecting the asymmetry of binding of the bipyridyl ligand (Au–N = 2.166, 2.406 Å) [81]. The Au–P bond length is very short, also consistent with effective two-coordination, and it is evident that the second nitrogen contributes little to the bonding.

Another nominally three-coordinate compound is $[Au(SnCl_3)(PMe_2Ph)_2]$ (F21.29), for which the Mössbauer data lie well within the two-coordination region. This is consistent with the length of the Au–Sn bond (2.881 Å [86]) and the small extent of Au–Sn interaction indicated by the ^{119}Sn Mössbauer parameters [263,264]. The Au–P distances are indistinguishable from those for the linear cations $[Au(PMePh_2)_2]^+$ and $[Au(Pcy_3)_2]^+$, and the geometry

* Compounds will be referenced to the Table or Figure in which they appear by T or F followed by the Table (Figure) number and the entry (point) number. F22.9 thus indicates entry number 9 in Fig. 22.

of the $SnCl_3^-$ anion is close to that of the free ion [86]. This compound, like the bipyridyl complex, is effectively two-coordinate. Both have wide P–Au–P bond angles with almost identical values (153.8(2), 157.1(1)°) which are considerably greater than those in fully three-coordinate complexes.

Two compounds appear to be unambiguously three-coordinate, $[AuX(PPh_3)_2]$ (X = Cl, SCN (T16.30, 31)). These are immediately recognized by their IS values, which are about 1.5 mm s^{-1} lower than the two-coordinate compounds with similar QS. (As indicated earlier, the IS is the more sensitive parameter to change in coordination number.) When the bond lengths are considered (Fig. 22a), all the bis-phosphine complexes, whether two- or three-coordinate, lie on the low-IS side of the main band of data. This may indicate a saturation of the tendency to concentrate *s* character in the bonds to the softest ligands.

The trend to low IS is continued in four-coordinate compounds (T16.32–34). The cation $[Au(SbPh_3)_4]^+$ shows tetrahedral coordination, and the QS is zero. Regular tetrahedral coordination is not possible in $[Au(pdma)_2]^+$, and a small QS is resolved. The remaining compound, $[AuCl(PPh_3)_3]$, shows a QS which reflects the difference in donation to gold by Cl^- and PPh_3 ligands. Comparison with the two- and three-coordinate complexes $[AuCl(PPh_3)]$ and $[AuCl(PPh_3)_2]$ shows that the QS is slightly lower than might be expected [265], but it is consistent with the slight flattening of the coordination tetrahedron (P–Au–P = 117.4° [122]).

(ii) Gold(III) compounds

The data for gold(III) compounds are presented in Table 17 and Fig. 23. For four-coordinate compounds there is a remarkably good linear correlation between IS and QS, with only a few points deviating significantly. The two compounds farthest from the line (F23.15, 17) both involve dithiolate ligands which, in other systems, are "non-innocent"; that is, in complexes with metals in high formal oxidation states, part of the positive charge is delocalised onto the ligand. In the present cases, a reduction in QS results.

Data for several salts of the $[AuCl_4]^-$ anion are available (F23.2–9), which cover an appreciable range of IS and QS. There appears to be no correlation between the Mössbauer parameters and the Au–Cl bond lengths. However, in those compounds with low values of IS and QS (F23.2, 4, 5), the crystal structures clearly show close contacts between the chloride ligands and cations or water molecules, while the highest parameters are for $(Ph_4As)[AuCl_4]$ (F23.7), in which there are no short contacts. Interactions of this type polarise the chloride ligands and reduce their donor capacity to gold; the Mössbauer parameters thus approach the values for Au_2Cl_6 (F23.10) which contains two fully bridging chloride ligands.

TABLE 17

Mössbauer data for gold(III) compounds

Compound	IS(Au) ($mm\ s^{-1}$)	QS ($mm\ s^{-1}$)	Donor atoms	Table for X-ray data	Ref.
1 $Rb[AuF_4]$	1.26	0.17	4 F	7	272
2 $H[AuCl_4]\cdot 4\,H_2O$	1.87	0.94	4 Cl	7	272
3 $NH_4[AuCl_4]\cdot xH_2O$	2.07	1.7	4 Cl	7	285
4 $K[AuCl_4]$	2.02	1.11	4 Cl	7	272
	1.65	1.27			271
5 $K[AuCl_4]\cdot H_2O$	2.08	1.4	4 Cl	7	285
6 $Cs[AuCl_4]$	2.16	1.37	4 Cl	7	266
7 $(Ph_4As)[AuCl_4]$	2.30	1.88	4 Cl	7	285
8 $Cs_2[AgCl_2][AuCl_4]$	1.54	[a]	4 Cl	7	266
	1.53	0.86			286
9 $Cs_2[AuCl_2][AuCl_4]$ [b]	1.02	1.33	4 Cl	13	271
	1.51	0.84			287
	1.31	1.00			266
	1.56	0.95			266
	1.55	1.17			286
10 $[AuCl_3]_2$	0.64	(−)0.75	2 Cl, 2 μ-Cl	8	272
11 $[AuBr_3]_2$	0.42	(−)0.75	2 Br, 2 μ-Br	8	271
12 $[Au_2O_3]_n$	2.15	1.68	2 O, 2 μ-O	9	271
13 $Na_6[Au_2O_6]$	3.66	3.02	2 O, 2 μ-O	8	272
14 $[Au(dmg)_2][AuCl_2]$ [c]	3.88	4.04	4 N	13	266
15 $[Au(S_2CNBu_2)\{S_2C_2(CN)_2\}$	3.85	2.57	4 S	7	277
16 $[Au(S_2CNBu_2)_2]Br$	3.41	2.8	4 S	7	277
17 $(Bu_4N)[Au(S_2C_6H_3Me)_2]$	4.20	2.73	4 S	7	277
18 $[Au(S_2CNPr_2)_2][AuBr_2]$ [c]	3.2	2.7	4 S	13	288
19 $[Au(S_2CNBu_2)Br_2]$	2.68	2.20	2 Br, 2 S	7	277
20 $[Au(CH_3)_3(PPh_3)]$	5.91	8.87	3 C, P	7	289
21 $(Me_3P)Au(Me_2)C(CF_3)$ $= C(CF_3)AuPMe_3$ [d]	6.37	9.27	3 C, P	13	255
22 $[AuCl_3(dmp)]$	1.87	[e]	3 Cl, 2 N	10	266
23 $[AuBr_3(dmp)]$	2.07	[f]	3 Br, 2 N	10	266

[a] Not resolved. [b] Data for $[AuCl_4]^-$ anion. [c] Data for cation. [d] Data for gold(III) atom. [e] Not resolved (linewidth, 2.31 $mm\ s^{-1}$). [f] Not resolved (linewidth, 2.76 $mm\ s^{-1}$).

The compounds $[AuX_3(dmp)]$ (X = Cl, Br (T17.22, 23)) have IS values similar to the $[AuCl_4]^-$ salts, but show no resolvable QS. In these compounds, the gold atom is effectively five-coordinate, with the phenanthroline acting as an unsymmetrical bidentate (Au–N = 2.09, 2.58 and 2.08, 2.61 Å, respectively [226]). Conventional four-coordination is prevented by the methyl substituents which cause the bidentate ligand to twist out of the AuX_3 plane. The presence of the fifth ligand lowers the IS substantially

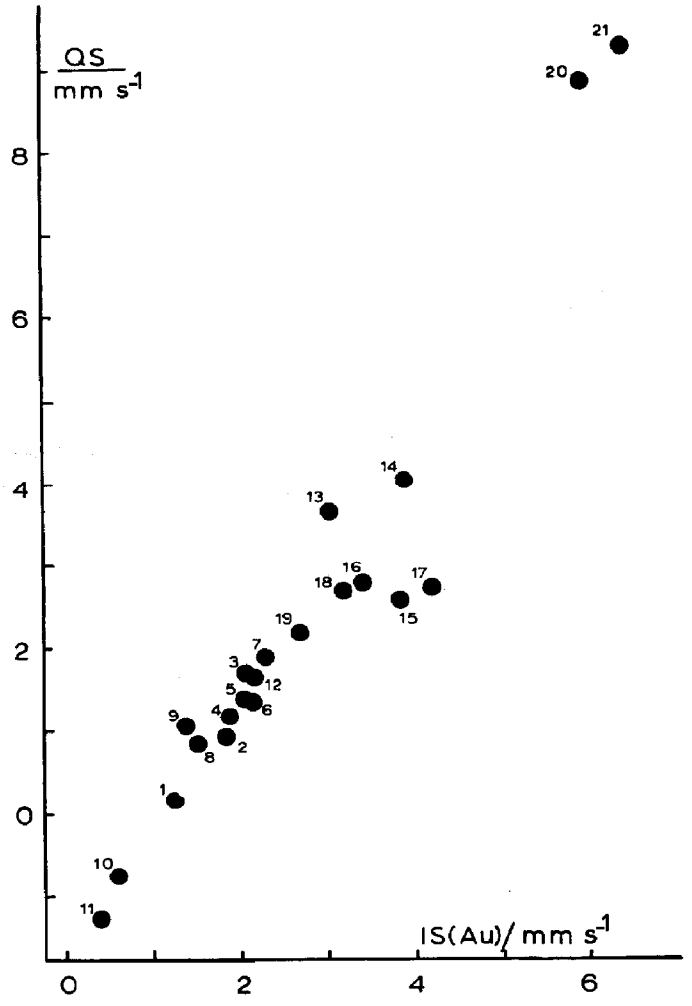

Fig. 23. Correlation diagram for gold(III) compounds. The numbering corresponds to Table 17.

compared to salts of $[AuCl_2(phen)]^+$, e.g. the perchlorate has IS 3.01 mm s^{-1} and a well-resolved QS of 1.95 mm s^{-1} [266].

(iii) Gold(V) compounds

Of the gold(V) compounds which have been characterised crystallographically, Mössbauer data are available only for $[Xe_2F_{11}][AuF_6]$: IS = 3.49 mm s^{-1}, QS = 0.0 mm s^{-1} [267]. The latter value reflects the octahedral symmetry of the six fluorine ligands and the six non-bonding d electrons. The IS is high because of the reduced shielding relative to gold(III) (d^8) and gold(I) (d^{10}).

(iv) Cluster compounds

Gold forms a wide variety of cluster compounds with nuclearities from 4 to 55. They may be divided broadly into two categories: (a) small clusters containing Au_4 tetrahedra with various capping groups (which may include other gold atoms); (b) metal-centered clusters which are icosahedral fragments.

The analysis of the Mössbauer spectra is difficult because of extensive overlapping of the lines. This is especially troublesome for the larger clusters, in which there may be up to five different types of gold atom, giving a nine-line spectrum (the central gold atom often gives only a single line). In these cases, and most of the others, satisfactory analysis of the spectrum can only be achieved on the basis of the known molecular structures; it is not yet possible to derive the structure from the spectrum. Even when the number of distinct gold sites is known, assumptions have to be made in assigning the lines: in principle, two sets of four lines can be paired in 24 ways. Some guidance is available from the relative intensities, which should reflect the numbers of each type of atom. Somewhat wider confidence limits than usual should therefore be placed on these data.

In only one case is it possible to see well-resolved signals for different gold atoms bearing phosphine ligands; the mixed-metal cluster $Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3$ [268]. Two gold atoms are adjacent to another gold atom and two ruthenium atoms, while the third gold atom has two gold atoms and three ruthenium atoms as neighbours [93,203]. The higher connectivity results in a dramatic decrease of both Mössbauer parameters from 2.90, 7.42 mm s^{-1} (IS, QS respectively) to 2.04, 4.90 mm s^{-1}. The second doublet is considerably broadened, with corresponding reduction in intensity, as the two chemically equivalent gold atoms are crystallographically different. The difference between the two sets of parameters is much more marked than for homonuclear clusters, presumably because of the considerable electronic difference between Au–L (L = PPh_3, halide) and $Ru(CO)_3$ groups.

The data for homonuclear clusters cover a wide range, and are best discussed in terms of the nuclearities of the clusters and the ligation of the individual gold atoms. In many cases the gold atoms are bound to phosphine ligands, and useful comparisons can be made with conventional gold(I)–phosphine complexes, providing a good opportunity to assess the influence on the Mössbauer parameters of additional gold–gold contacts.

(a) Tetrahedral clusters

Mössbauer data for homonuclear clusters with tetrahedral units are given in Table 18 and Fig. 24a. Most of the data lie in the parameter field for conventional two-coordination, regardless of whether the gold atom carries

TABLE 18

Mössbauer data for tetrahedral-based clusters (Au_4–Au_7)

	Coordination	IS(Au) ($mm\ s^{-1}$)	QS ($mm\ s^{-1}$)	Cluster	Table for X-ray data	Ref.
1	P, C, Au	4.8	9.0	$[Au_5(dppmH)_3(dppm)](NO_3)_2$	5	117
2	P, 4 Au	4.2	7.0	$[Au_6(1,3\text{-dppp})_4](NO_3)_2 \cdot x CH_2Cl_2$	9	211
3	P, 4 Au	3.7	6.7	$[Au_5(dppmH)_3(dppm)](NO_3)_2$	5	117
4	P, μ-I, 3 Au	2.6	4.2	$[Au_4(\mu\text{-}I)_2(PPh_3)_4]$	11	211
5	2 P, 2 Au	3.1	7.2	$[Au_6(1,3\text{-dppp})_4](NO_3)_2 \cdot x CH_2Cl_2$	9	211
6	2 P, 3 Au	2.6	7.4	$[Au_5(dppmH)_3(dppm)](NO_3)_2$	5	117
7	2 P, μ-I, 3 Au	1.9	6.2	$[Au_4(dppmH)_3I_2]$	9	205
8	I, 3 Au	1.6	5.6	$[Au_4(dppmH)_3I_2]$	9	205

one or two external ligands, and regardless of the number of Au–Au contacts.

Four data points lie well in the field of values for conventional two-coor-

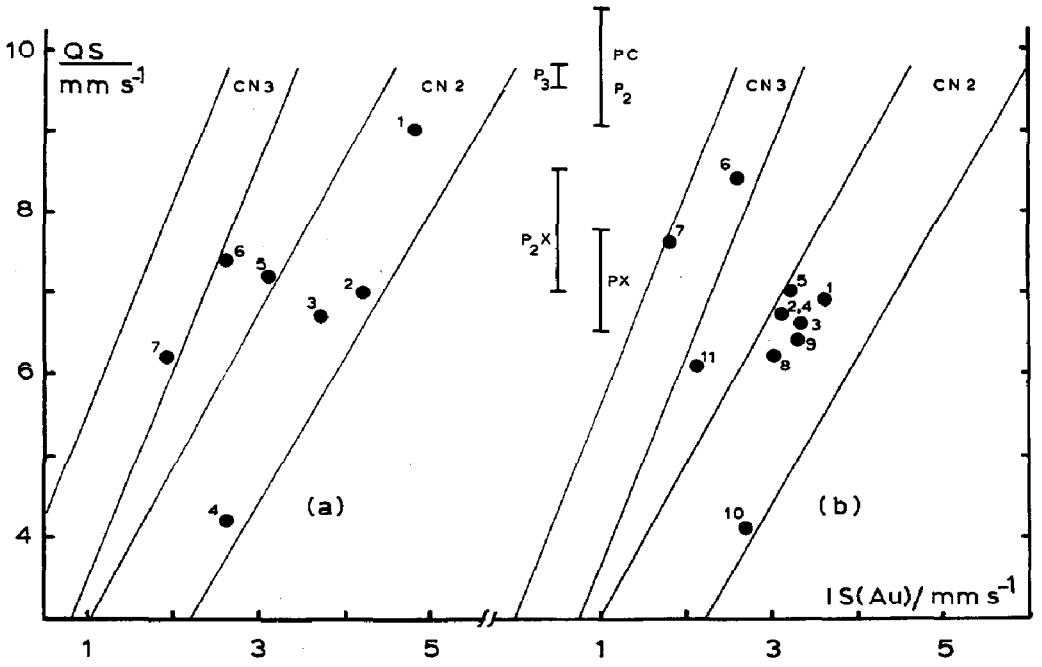

Fig. 24. Correlation diagram for (a) tetrahedral and (b) icosahedral cluster compounds. The numbering corresponds to Tables 18 and 20 respectively. The regions marked CN3 and CN2 are those found for conventional three- and two-coordinate gold(I)–phosphine complexes. The vertical bars indicate the ranges of QS values found for the conventional complexes with the donor-atom sets shown.

dination. The unique atom in $[Au_5(dppmH)_3(dppm)]^{2+}$ has linear P–Au–C coordination, and its parameters are at the low end of the range for monomeric complexes with similar coordination (F24a.1). The three equivalent basal atoms of this cluster (F24a.3) and those of the tetrahedral unit of $[Au_6(1,3\text{-dppp})_4]^{2+}$ (F.24a.2) have parameters similar to those of $[AuX(PR_3)]$ in which X is a weakly coordinating ligand, such as halide or acetate. The coordination of these atoms could be described as linear if one of the adjacent gold atoms is included, since all have one P–Au–Au angle of about 175°. The remaining point in this region (F24a.4) is for $[Au_4(\mu\text{-I})_2(PPh_3)_4]$; this also involves a linear P–Au–Au system (175°), but there is an additional, very long bond to the bridging iodide. The parameters are very low, comparable to $[AuX_2]^-$ or AuX(S) systems (X = halide), suggesting a relatively low charge density on these gold atoms. The average oxidation state and the Au–P bond lengths are, however, similar in each of the last three cases, and there is no obvious explanation for the low values.

(b) Icosahedral clusters

Most of the icosahedral-fragment clusters are metal-centred. In the Au_{11} clusters the central atom has high symmetry and shows no QS (Table 19). For Au_8 and Au_9 systems it is anticipated that a QS would be seen [213,290], but the signals cannot be resolved from those for the peripheral atoms. With the assumption that their parameters are similar to those of the peripheral atoms, the IS values of the central gold atoms are similar in all the clusters: 3.6–3.9 mm s^{-1}.

The peripheral atoms carry only a single ligand, and distinct sets of parameters are found for those bonded to phosphine ligands and those bound to anionic ligands.

TABLE 19

Mössbauer data for central gold atoms in icosahedral-fragment clusters

	Coordination	IS(Au) (mm s^{-1})	QS (mm s^{-1})	Cluster	Table for X-ray data	Ref.
1	7 Au	not resolved (~ 3.6	~ 6.9)	$[Au_8(PPh_3)_7](NO_3)_2$	9	213
2	7 Au	3.6	0	$[Au_8(PPh_3)_8](PF_6)_2 \cdot CH_2Cl_2$	9	290
3	8 Au	not resolved (~ 3.3	~ 6.6)	$[Au_9(PPh_3)_8](PF_6)_3$	9	290
4	10 Au	3.9	0.0	$[Au_{11}(PPh_3)_7(SCN)_3]$	11	269
5	10 Au	3.95	0.0	$[Au_{11}\{P(C_6H_4Cl)_3\}_7I_3]$	11	269
6	12 Au	0.1	0.0	$[Au_{55}(PPh_3)_{12}Cl_6]$		291

TABLE 20

Mössbauer data for icosahedral-fragment clusters (peripheral atoms)

Coordination	IS(Au) ($mm\ s^{-1}$)	QS ($mm\ s^{-1}$)	Cluster	Table for X-ray data	Ref.
1 P, 3 Au	3.6	6.9	$[Au_8(PPh_3)_7](NO_3)_2 \cdot CH_2Cl_2$	9	213
2	3.1	6.7	$[Au_8(PPh_3)_8](PF_6)_2 \cdot CH_2Cl_2$	9	290
3	3.3	6.6	$[Au_9(PPh_3)_8](PF_6)_3$	9	290
4 P, 4 Au	3.1	6.7	$[Au_8(PPh_3)_8](PF_6)_2 \cdot CH_2Cl_2$	9	290
5	3.2	7.0	$[Au_7(PPh_3)_7]OH$	11	232
6	2.6	8.4	$[Au_{11}\{P(C_6H_4Cl)_3\}_7I_3]$	11	269
7	1.8	7.6	$[Au_{11}(PPh_3)_7(SCN)_3]$	11	269
8 P, 5 Au	3.0	6.2	$[Au_{11}\{P(C_6H_4Cl)_3\}_7I_3]$	11	269
9	3.3	6.4	$[Au_{11}(PPh_3)_7(SCN)_3]$	11	269
10 P, 6 Au	2.7	4.1	$[Au_7(PPh_3)_7]OH$	11	232
11 P, 8 Au	2.1	6.1	$[Au_{55}(PPh_3)_{12}Cl_6]$		291
12 I, 6 Au	1.2	4.1	$[Au_{11}\{P(C_6H_4Cl)_3\}_7I_3]$	11	269
13 SCN, 6 Au	1.4	4.7	$[Au_{11}(PPh_3)_7(SCN)_3]$	11	269
14 Cl, 8 Au	1.1	4.2	$[Au_{55}(PPh_3)_{12}Cl_6]$		291

The data for the phosphine-coordinated atoms are shown in Fig. 24b. As for the similarly coordinated atoms of tetrahedral clusters, most of the points lie in the region associated with monomeric $[AuX(PR_3)]$. It is again possible to recognize approximately linear P–Au–Au units; in these cases the second gold atom lies at the centre of the icosahedron. Very low parameters are reported for the axial gold atoms in $[Au_7(PPh_3)_7]^+$ (F24b.10), which is a cluster with no central atom; however, these values must be regarded as approximate, in view of the very large linewidth ($3.7\ mm\ s^{-1}$). Similarly, the unique peripheral atoms in the Au_{11} clusters (F24b.6, 7) give low intensity signals, and their parameters are reported as "uncertain" [269]; no significance should be attached, therefore, to the fact that they appear to be well separated from the other points.

The gold atoms coordinated to anionic ligands have parameters which are considerably lower than the phosphine-bearing atoms, and lie in the neighbourhood of the $[AuX_2]^-$ anions.

The super-cluster $[Au_{55}(PPh_3)_{12}Cl_6]$ is a two-layer icosahedron [291]. The core consists of a complete, centred, Au_{13} icosahedron and is surrounded by a second shell of 42 gold atoms. Only 18 of the peripheral atoms carry ligands, the limitation being primarily steric. The core atoms have an IS close to that of elemental gold (T19.5). The uncoordinated peripheral atoms appear to show no QS, but have a somewhat higher IS of $2.3\ mm\ s^{-1}$. The

coordinated peripheral atoms have parameters similar to those for other icosahedral clusters, but with significantly lower IS.

(c) Discussion of cluster data

Two somewhat surprising facts emerge from consideration of the data for the peripheral gold atoms of clusters.

(a) Although the bonding must be molecular and not localised, the Mössbauer parameters can be treated in terms of recognizably different gold atoms.

(b) Although the oxidation states of the gold atoms in the clusters average to significantly less than unity, the majority of the Mössbauer parameters lie in regions characteristic of gold(I) compounds.

The first observation appears to indicate that the electron distributions about the gold atoms are independent of the Au–Au interactions, as was observed for conventional compounds. The metal–ligand bonding must be localised, in the same way as in conventional compounds, so that the Mössbauer parameters reflect principally the electron distribution in this bond. Indeed, when no such ligand is present, as in the Au_{55} cluster, the IS is low and no QS is seen even though this site has at best C_{6v} symmetry. It is noticeable that the data for the singly coordinated peripheral atoms are comparable to those for two-coordinate complexes involving similar ligands: the phosphine-coordinated atoms resemble $[AuX(PR_3)]$, and the anion-coordinated atoms resemble $[AuX_2]^-$. On this basis it has been suggested that these atoms should be regarded as *pseudo* two-coordinate, with another gold atom acting as the second ligand, LAuAu or XAuAu [269]. However, in the icosahedral clusters, the Au–Au distances to the central atom are little different from those to the other peripheral atoms, and it seems unlikely that the electronic interactions of these two sets of atoms would be different. This view is reinforced by the lack of QS for the uncoordinated atoms in the Au_{55} unit. It is also noticeable that the data correspond to those for conventional complexes in which the ligand X is an extremely weak donor. It is probably better, therefore, to regard the peripheral atoms as being effectively one-coordinate. The local symmetry of one- and two-coordinate systems is similar, given the generally large number of surrounding peripheral gold atoms, the same orbitals will be involved in the gold–ligand bonding, and the Mössbauer parameters would be expected to respond in similar ways to changes in the ligand. Donation by a single ligand would, naturally, be rather less than that from two ligands, and this would result in lower values for the Mössbauer parameters. Both these effects are observed.

The insensitivity of the parameters to the presence of Au–Au contacts could be interpreted by assuming that all the metal atoms have similar effective electronegativities, so that the formation of metal–metal bonds

results in little change in the distribution of electron density.

In all the clusters, the gold atoms coordinated to a single phosphine ligand have QS values in a narrow range, 6–7 mm s^{-1}. The IS values, however, decrease steadily from the tetrahedral clusters (F24a.2, 3) to the icosahedral clusters (F24b.1–5, 8, 9), to the Au_{55} cluster (F24b.11). Thus, as the nuclearity of the cluster increases, and the average oxidation state of the gold atoms decreases, the IS moves closer to that for metallic gold. Similar trends are seen for the anion-coordinated gold atoms. This indicates that Au–Au interactions do have a very small effect on the Mössbauer parameters, and therefore on the electron distributions. The direction of change would be consistent with transfer of a small amount of electron density from $6s$ to $6p$, i.e. to slight involvement of the $6p$ orbitals in the skeletal bonding. That such an effect is small would account for the insensitivity to single Au–Au contacts of the Mössbauer parameters for conventional compounds.

K. SUMMARY OF MÖSSBAUER DATA

The Mössbauer parameters allow diagnosis of the oxidation state and coordination number of gold, and give a good indication of the identity of the ligands. For compounds which do not crystallise, Mössbauer spectroscopy provides a good substitute to X-ray crystallography for structure determination. Additionally, within series of compounds, the electronic effects of the ligands can be probed. When structural data are also available, the subtler effects of solid-state interactions can be interpreted. The effect of gold–gold bond formation can be detected only in the larger clusters.

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NOTE ADDED IN PROOF

X-ray analysis data for several new gold compounds have been published recently and their structural data are given in Table 21. The structures are tabulated by increasing number of coordinated atom (ligand) and aggregation.

TABLE 21
Structural data for gold compounds [a]

Compound	Crystal class	Space group	Z	Chromophore	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Au–L [Å]	L–Au–L [°]	Au–Au [Å]	Ref.
$[Au^{II}(CH_2)_2PPh_2]_2$	m	$P2_1/n$	2	AuC_2	8.576 (1) 9.378 (2) 15.915 (3)	 96.48 (1) 	C [b] 2.088 (7, 3)	179.0 (3)	2.977 (1)	292
$[Au^{I}(Cy_3P)_2]Cl$	m	$P2_1/c$	2	AuP_2	9.504 (2) 17.421 (3) 11.607 (2)	 107.82 (2) 	P 2.321 (2) (2×)	180		293
$[Au^{I}(C_6H_5S)_2]\cdot(PPh_4)$	hx	$P6_1$	6	AuS_2	9.746 (3) 56.552 (11)	 	S 2.262 (8) S 2.271 (8)	179.0 (3)		294
$[Au^{I}(primt)_2]Cl$	m	$P2_1/n$	4	AuS_2	7.195 (7) 15.283 (3) 15.899 (6)	 91.7 (1) 	S	177.7 (1)		295
$[(Cy_3P)Au^{I}(2\text{-iPrim})]\cdot C_6H_6$	m	$P2_1/a$		AuNP	17.373 (3) 14.833 (2) 11.796 (1)	 99.17 (1) 	N 2.019 (3) P 2.255 (2)	177.0 (1)		296
$[(Ph_3P)Au^{I}(C_6H_5COO)]\cdot C_6H_6$	m	$P2_1/n$	4	AuOP	10.825 (2) 13.896 (3) 17.411 (4)	 94.43 (2) 	O 2.033 (6) P 2.213 (3)	173.7 (2)		297
$(Ph_3P)Au^{I}(mtim)$ [c]	tr	$P\bar{1}$	6	AuCP	21.710 (16) 17.235 (12) 10.316 (8)	77.9 (1) 104.7 (1) 95.4 (1)	C 2.056 (16) P 2.292 (5)	177.6 (5)		298
				AuCP			C 2.044 (18) P 2.284 (5)	178.1 (7)		
				AuCP			C 2.012 (16) F 2.282 (4)	177.0 (6)		
$(Cy_3P)Au^{II}Cl$	tr	$P\bar{1}$	2	AuClP	9.214 (3) 10.147 (3) 10.890 (3)	89.25 (2) 80.58 (2) 77.41 (2)	Cl 2.279 (5) P 2.242 (4)	177.0 (2)		293
$(primt)Au^{I}Cl$	m	$C2/c$	8	AuClS	10.164 (4) 14.836 (2) 13.590 (9)	 95.08 (5) 	Cl 2.27 (1) S 2.25 (1)	172.5 (4)		299
$[(Ph_3P)AuCo(CO)_3\cdot(Ph_3P)]$	m	$C2/c$	8	AuPCo	20.847 (4) 14.116 (6) 25.761 (4)	 110.78 (3) 	P 2.245 (2) Co 2.450 (1)	176.80 (7)		300

TABLE 21 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Au–L [Å]	L–Au–L [°]	Au–Au [Å]	Ref.
$[(Ph_3P)AuIr(dppe)_2]\cdot(BF_4)_2$	m	$P2_1$	2	AuPIr	11.647 (6) 19.359 (4) 15.952 (2)	 100.60 (2) 	P 2.219 Ir 2.625	168.7		301
$(Ph_3P)AuRe(CO)(CP)(p\text{-}N_2C_6H_4OMe)$	m	$P2_1/n$	4	AuPRe	10.960 (2) 14.313 (6) 18.856 (5)	 101.13 (2) 	P 2.271 (4) Re 2.615 (1)	175.3 (1)		302
$[\{(Ph_3P)Au\}_2\cdot SO_4]\cdot CH_3OH$	m	$C2/c$	4	AuOP	13.483 (2) 14.510 (2) 18.538 (3)	 99.90 (2) 	O 2.063 (5) P 2.216 (2)	177.6 (1)	3.318	303
$(dppe)Au^I_2Cl_2$	m	$P2_1/n$	4	AuClP	12.815 (2) 11.160 (2) 19.054 (4)	 109.33 (1) 	Cl 2.314 (5, 1) P 2.240 (6, 3)	174.3 (2, 1.2)	3.189 (1)	304
$[Au^{III}(CH_2)_2PPh_2]_2(CN)_2$	m	$C2/c$	4	AuC_3	13.481 (6) 12.089 (5) 17.645 (8)	90 101.98 (4) 90	C 2.086 (20) NC 2.046 (22)	171.4 (10) 88.6 (1)	2.637 (2)	306
$[Au^{III}(CH_2)_2PPh_2]_2\cdot(CH_3)Br$	m	C_c	4	AuC_3	13.385 (2) 12.340 (1) 17.360 (3)	 103.65 (1) 	C 2.117 (2, 1) H_3C 2.159 (2)		2.674 (1)	292
				AuC_2Br			C 2.057 (2, 50) Br 2.698 (3)			
[nido-μ-5,6-$(AuPCy_3)\cdot B_{10}H_{13}$]	m	$P2_1/a$	4	AuB_2P	11.6583 (20) 22.663 (6) 11.418 (3)	 118.061 (16) 				307
$Fe_4(AuPEt_3)(CO)_{12}\cdot(COCH_3)$	tr	$P\bar{1}$	2	$AuPFe_2$	14.764 (3) 9.574 (1) 11.094 (2)	87.26 (1) 82.33 (1) 112.13 (1)	P 2.278 (5) Fe 2.670 (2, 5)	149.6 (2, 3.2) 60.40 (8)		305
$(Ph_3P)AuRu_3(H)(CO)_9\cdot(\mu_3\text{-}S)$	m	$P2_1/n$	4	$AuPRu_2$	12.983 (2) 17.646 (4) 14.962 (2)	90 106.05 (1) 90	P not given Ru 2.748 (1, 12)	64.5 (1) [d]		308
$(Ph_3P)AuRu_3(CO)_9\cdot(\mu_3\text{-}SBu)$	tr	$P\bar{1}$	2	$AuPRu_2$	10.307 (4) 16.082 (2) 12.781 (3)	109.86 (2) 111.66 (2) 95.55 (2)	P not given Ru 2.769 (1, 4)	64.4 (1) [d]		308
$(Ph_3P)AuOs_3(CO)_{10}\cdot(\mu\text{-}CH{=}CHC_6H_5)$	tr	$P\bar{1}$	2	$AuPOs_2$	9.403 (4) 13.448 (3) 13.774 (4)	83.34 (2) 88.66 (3) 70.21 (3)	P 2.307 (4) Os 2.767 (1, 29)	not given		309

$(Ph_3P)AuOs_3(CO)_{10}$· (μ-CH=CHC$_6$F$_5$)	tr	$P\bar{1}$	2	$AuPOs_2$	9.081 (2) 13.291 (2) 17.419 (2)	84.49 (1) 76.20 (2) 75.81 (2)	P 2.315 (2) Os 2.772 (1, 6)	not given		309
$(ppn)_2Au^I_2Te_4$	m	$P2_1/n$		$AuTe_2Au'$	12.189 (4) 13.009 (4) 21.741 (6)	 105.16 (2)	Te 2.548 (1, 5) Au 2.908 (1)	176.64 [c] 88.56 (2.28)	2.908 (1)	310
[{$Au^I(PPh_3)$}$_2$(μ-C(PPh_3)· CO_2Et)]ClO_4	m	$P2_1/c$	4	AuCPAu′	18.666 (6) 17.490 (5) 16.413 (5)	 95.10 (3)	C 2.114 (10, 11) P 2.274 (4, 3) Au 2.892 (2)	174.5 (4, 3.8)	2.892 (2)	311
[$IrAu_2$(H)(PPh_3)$_4$· (NO_3)]BF_4	m	$P2_1/n$	4	AuPIrAu′	11.931 (3) 14.472 (8) 40.97 (1)	 91.09 (2)	P 2.272 (1, 14) Ir 2.670 (1, 3) Au′ 2.728 (1)	166.5 (1.7) 134.0 (1.3) 59.47 (55)	2.728 (1)	312
[($H_{12}B_{10}Au$)(μ-$AuPEt_3$)$_4$· ($AuB_{10}H_{12}$)]·(C_2H_3N)$_2$	m	$P2_1/c$	4	$AuPAu'_2$ (4×) $AuB_4Au'_4$ (2×)	16.817 (10) 16.067 (5) 21.798 (12)	 92.02 (4)				307
$[Au^{III}Cl_4](H)(npyNO)_2$ [h]	tr	$P\bar{1}$	4	$AuCl_4$	17.351 (11) 10.381 (9) 20.373 (8)	88.5 (1) 101.8 (1) 99.6 (1)	Cl 2.296 (5, 5)	179.1 (2) 89.8 (2, 1.1)		313
				$AuCl_4$			Cl 2.274 (5, 32)	179.5 (2) 90.4 (2, 1.6)		
(μ-CH_2)[$Au^{III}(CH_2)_2PPh_2$]$_2$· $(CN)_2$		$I4_1/a$	32	AuC_4	28.979 (6) 28.979 (6) 33.135 (5)	90.000 90.000 90.000	C 2.054 (20, 45)	173.7 (9) 87.3 (1)	3.167 (3)	306
$Au^{III}(PhCS_2)(Ph_2CCS_2)$	tr	$P\bar{1}$	2	AuS_4	18.094 (4) 11.371 (4) 4.912 (3)	87.40 (2) 98.93 (2) 96.33 (2)	S 2.295 (3, 1) S 2.369 (3, 0)	74.2 (1.9) 105.8 (1, 4) 177.7 (1, 5)		314
[Au^{III}(2-$C_6H_4CH_2NMe_2$)(py)$_2$] ·(BF_4)$_2$$CH_3COCH_3$	m	$P2_1/c$	4	AuN_3C	17.433 (7) 10.317 (4) 15.948 (6)	 107.04 (4)				315
[$Au^{III}Me_2$\{(pyl)(min)$_2$COH\}]· NO_3	tr	$P\bar{1}$	2	AuN_2C_2	11.393 (3) 10.859 (2) 7.927 (2)	89.16 (2) 74.11 (2) 89.87 (2)	N 2.106 (7, 8) C 2.027 (10, 3)	176.9 (3, 6) 90.0 (4, 5.5)		316
[$Au^{III}Me_2$\{B(pz)$_4$\}]	m	$P2_1/c$	4	AuN_2C_2	12.645 (2) 8.343 (2) 17.310 (4)	 99.14 (2)	N 2.098 (7, 3) C 2.04 (2, 1)	178.3 (6, 5) 89.8 (5, 3.4)		316
[$Au^{III}Me_2$(dpk·H_2O)]· (NO_3)	m	$P2_1/c$	4	AuN_2C_2	9.41 (1) 7.328 (7) 22.17 (2)	 97.85 (8)	N 2.127 (9, 9) C 2.03 (1, 1)	179.0 (5, 7) 90.0 (4, 5.3)		317

TABLE 21 (continued)

Compound	Crystal class	Space group	Z	Chromophore	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	Au–L [Å]	L–Au–L [°]	Au–Au [Å]	Ref.
trans-$[Au^{III}(NH_3)_2Br_2]\cdot Br$	m	$C2/m$	2	AuN_2Br_2	8.916 (2) 6.1134 (14) 6.6285 (14)	 98.003 (17) 	N 2.040 (7) Br 2.4277 (10)	90.0 (2, 2.5)		318
$[Me_2Au^{III}(NHCH_3)]_2$ [i]	m	$C2/c$	4	AuN_2C_2	17.517 (8) 3.983 (7) 18.688 (9)	 124.61 (4) 	N 2.138 (5, 2) C 2.039 (9, 0)	90.0 (3, 12.6)	3.0895 (6)	319
$[Me_2Au^{III}(NH_2)]_3$ [j]	or	$Ama2$	4	AuN_2C_2	16.534 (6) 18.444 (8) 4.481 (7)	 	N 2.150 (9, 1.4) C 2.03 (1, 4)	90.0 (5, 4.0)	3.554 (1, 9)	320
$[Ph_2P(CH_2)_2Au^{III}Cl_2]_2\cdot (CDCl_3)_2$	m	$P2_1/c$	4	AuC_2Cl_2	12.695 (2) 24.198 (5) 13.2279 (2)	 108.523 (11) 	C 2.12 (3, 8) Cl 2.316 (9, 44)	176.2 (7, 2) 90.0 (8, 2.0)		321
$[Ph_2P(CH_2)_2Au^{III}Br_2]_2$ $CDCl_3$	m	$C2/c$	4	AuC_2Br_2	11.657 (2) 13.244 (3) 26.374 (5)	 120.299 (13) 	C 2.13 (5, 1) Br 2.425 (3, 15)	171.5 (1, 7.2) 90.0 (8, 2.0)		321
$[Au^I(CH_3CSS)]_4$	tr	$P\bar{1}$	2	$AuS_2Au'_2$	12.087 (4) 9.698 (3) 8.862 (3)	95.50 (2) 110.57 (2) 92.65 (2)	S 2.296 (7, 26) Au 3.013 (1, 24)	167.7 (2, 3.6) [k] 94.3 (2, 9.8) 66.31 (113, 6(1, 3))	3.013 (1, 24)	314
$\{Au^I(tht)I\}_n$ [l]	or	$Pc2_1n$	8	$AuS_2Au'_2$	8.149 (2) 11.460 (4) 15.956 (3)	 	S 2.320 (7, 15) Au′ 2.974 (2, 7)	172.35 (23) [k] 90.82 (18, 8.28) 155.46 (4)	2.974 (2, 7)	322

				$AuI_2Au'_2$			I 2.565 (2, 0) Au 2.974 (2, 7)	177.57 (7) [m] 90.20 (6, 2.46) 161.25 (4)	2.974 (2, 7)	
$Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$	m	$P2_1/c$	4	$AuPRu_2Au'$	12.763 (3) 27.568 (5) 15.617 (4)	90 121.81 (2) 90	P not given Ru 2.802 (2, 19) Au' 2.967 (2)	64.6 (1)	2.967 (2)	308
				$AuPRu_3Au$			P not given Ru 2.844 (2, 27) Au' 2.967 (2)			
$[IrAu_2(H)_2(PPh_3)_6]\cdot BF_4\cdot(CH_2Cl_2)_{1.5}$	m	$C2/c$	8	$AuPIrAu'_2(2\times)$	55.46 (2) 14.270 (8) 29.228 (9)	90 113.12 (3) 90	P 2.264 (8, 9) Ir 2.724 (2, 29) Au' 2.861 (2, 146)	166.2 (2, 8) [n] 144.44 (5) 106.48 (5, 3.22)	2.861 (2.146)	323
				$AuPIrAu'_3(2\times)$			P 2.306 (8, 1) Ir 2.662 (2, 25) Au' 2.917 (2, 225)	172.8 (2, 3.2) [n] 72.33 (5) 66.58 (51.10)	2.917 (2, 225)	

$C_6H_5S^-$ = benzenethiolate; 2-iPrim = 2-isopropyl–imidazole; mtim = methoxy(*p*-tolylimino)methyl; primt = *N*-propyl-1,3-imidazolidine-2-thione; SBu = thiobutyl; ppn = $[(Ph_2P)_2N]^+$; npyNO = 2-nonylpyridine *N*-oxide; 2-$C_6H_4CH_2NMe_2$ = 2-{(dimethylamino)methyl}phenyl; mim = *N*-methylimidazol-2-yl; pyl = pyridin-2yl; $[(B(pz)_4]^-$ = tetrakis(pyrazol-1-yl)borate; tht = tetrahydrothiophene;

[a] Where more than one chemically equivalent distance or angle is present in the mean value is tabulated. The first number is parentheses is an e.s.d., the second number is a maximum deviation from the average number. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] There are three crystallographically independent molecules. [d] The value of Ru–Au–Ru angle. [e] The values of Te–Au–Te and Te–Au–Au' angles. [f] At 253 K. [g] The values of P–Au–Ir, P–Au–Au' and Ir–Au–Au' angles. [h] There are two crystallographically independent molecules. [i] At 198 K. [j] At 213 K. [k] The values of S–Au–S, Au'–Au–S and Au'–Au–Au' angles. [l] At 200 K. [m] The values of I–Au–I, Au'–Au–I and Au'–Au–Au' angles. [n] The values of Ir–Au–P, Au–Ir–Au and Au'–Au–Au' angles.

REFERENCES

1 P.J. Sadler, Gold Bull., 9 (1976) 110.
2 P.J. Sadler, Struct. Bonding, 29 (1976) 171.
3 D.T. Walz, M.J. Dimartino and B.M. Sutton, in R.A. Sherrer and M. Whitehouse (Eds.), Anti-inflammatory Agents, Academic Press, New York, 1974, Vol. 1.
4 H. Schmidbaur, Angew. Chem., 88 (1976) 830.
5 P.G. Jones, Gold Bull., 14 (1981) 102, 159; 16 (1983) 114.
6 N.A. Malik, P.J. Sadler, S. Neidle and G.L. Taylor, J. Chem. Soc., Chem. Commun., (1978) 711.
7 P.G. Jones, W. Clegg and G.M. Sheldrick, Acta Crystallogr., Sect. B, 36 (1980) 160.
8 G. Banditelli, F. Bonati, S. Calogero and G. Valle, J. Organomet. Chem., 275 (1984) 153.
9 R. Uson, A. Laguna, J. Vicente, J. Garçia, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1981) 655.
10 P.G. Jones, Z. Naturforsch., Teil B, 37 (1982) 937.
11 R.E. Rundle, J. Am. Chem. Soc., 76 (1954) 3101.
12 P.G. Jones, J.J. Guy and G.M. Sheldrick, Acta Crystallogr., Sect. B, 32 (1976) 3321.
13 H. Ruben, A. Zalkin, M.O. Faltens and D.H. Templeton, Inorg. Chem., 13 (1974) 1836.
14 J.J. Guy, P.G. Jones and G.M. Sheldrick, Acta Crystallogr., Sect. B, 32 (1976) 1937.
15 J.A. Muir, M.M. Muir and E. Lorca, Acta Crystallogr., Sect. B, 36 (1980) 931.
16 M.K. Cooper, G.R. Dennis, K. Henrick and M. McPartlin, Inorg. Chim. Acta, 45 (1980) L151.
17 M.I. Bruce, J.K. Walton, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1983) 809.
18 H. Jagodzinski, Z. Kristallogr., 112 (1959) 80.
19 J.J. Guy, P.G. Jones, M.Y. Mays and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1977) 8.
20 L.P. Bellon, M. Manassero and M. Sansoni, Ric. Sci., 39 (1969) 173.
21 R.W. Baker and P.J. Pauling, J. Chem. Soc., Dalton Trans., (1972) 2264.
22 P.D. Gavens, J.J. Guy, M.J. Mays and G.M. Sheldrick, Acta Crystallogr., Sect. B, 33 (1977) 137.
23 P.E. Riley and R.E. Davis, J. Organomet. Chem., 192 (1980) 283.
24 H. Werner, H. Otto, T. Ngo-Khac and Ch. Burschka, J. Organomet. Chem., 262 (1984) 123.
25 T.V. Baukova, Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organomet. Chem., 220 (1981) 125.
26 E.G. Perevalova, K.L. Grandberg, V.P. Dyadchenko and T.V. Baukova, J. Organomet. Chem., 217 (1981) 403.
27 J. Stahle, W. Hiller and W. Conzelmann, Z. Naturforsch., 396 (1984) 538.
28 P.G. Jones, Acta Crystallogr., Sect. C, 40 (1984) 1320.
29 P.B. Hitchcock and P.L. Rye, J. Chem. Soc., Dalton Trans., (1977) 1457.
30 N.W. Alcock, P. Moore, P.A. Lamje and K.F. Mok, J. Chem. Soc., Dalton Trans., (1982) 207.
31 N.C. Baenziger, W.E. Bennett and D.M. Soboroff, Acta Crystallogr., Sect. B, 32 (1976) 962.
32 G.J. Arai, Rec. Trav. Chim. Pays-Bas, 81 (1962) 307.
33 J.G. Wijnhoven, W.P.Y.H. Bosman and P.T. Beurskens, J. Cryst. Mol. Struct., 2 (1972) 7.
34 T.D. Hill and N.B. Sutton, Cryst. Struct. Commun., 9 (1980) 679.
35 F.W.B. Einstein and R. Restivo, Acta Crystallogr., Sect. B, 31 (1975) 624.

36 F.E. Simon and J.W. Lauher, Inorg. Chem., 19 (1980) 2338.
37 T.L. Blundell and H.M. Powell, J. Chem. Soc. A, (1971) 1685.
28 K.A.I.F.M. Mannan, Acta Crystallogr., 23 (1967) 649.
39 H. Lehner, D. Matt, P.S. Pregosin and L.M. Venanzi, J. Am. Chem. Soc., 104 (1982) 6825.
40 J.B. Wilford and H.M. Powell, J. Chem. Soc. A, (1969) 8.
41 R. Uson, A. Laguna, M. Laguna, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1981) 366.
42 P. Braunstein, W. Schubert and M. Bugard, Inorg. Chem., 23 (1984) 4057.
43 D.M.P. Mingos, Pure Appl. Chem., 52 (1980) 705.
44 H. Schmidbaur, J.E. Mandl, W. Richter, V. Bejenke, A. Frank and G. Huttner, Chem. Ber., 110 (1977) 2236.
45 H. Schmidbaur, H.P. Scherm and W. Schubert, Chem. Ber., 111 (1978) 764.
46 A.M. Mazany and J.P. Fackler, Jr., J. Am. Chem. Soc., 106 (1984) 801.
47 P.G. Jones, G.M. Sheldrick, R. Uson and A. Laguna, Acta Crystallogr., Sect. B, 36 (1980) 1486.
48 C. Lensch, P.G. Jones and G.M. Sheldrick, Z. Naturforsch., 376 (1982) 944.
49 C.J. Gilmore and P. Woodward, J. Chem. Soc., Chem. Commun., (1971) 1233.
50 H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama and G. Huttner, Chem. Ber., 110 (1977) 1748.
51 M.G.B. Drew and M.J. Riedl, J. Chem. Soc., Dalton Trans., (1973) 52.
52 W.S. Crane and H. Beall, Inorg. Chim. Acta, 31 (1978) L469.
53 P.G. Jones, Acta Crystallogr., Sect. B, 36 (1980) 2775.
54 R. Uson, L.A. Oro, J. Gimeno, M.A. Ciriano, J.A. Cabera, A. Tiripicchio and M. Tiripicchio Camellini, J. Chem. Soc., Dalton Trans., (1983) 323.
55 T.V. Baukova, Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organomet. Chem., 221 (1981) 375.
56 A.N. Nesmeyanov, E.G. Perevalova and Yu.T. Struchkov, J. Organomet. Chem., 201 (1980) 343.
57 P.G. Jones, G.M. Sheldrick and E. Haidicke, Acta Crystallogr., Sect. B, 36 (1980) 2777.
58 M.K. Cooper, K. Henrick, M. McPartlin and J.L. Latten, Inorg. Chim. Acta, 65 (1982) L185.
59 A. Tiripicchio, M. Tiripicchio Carmellini and G. Minghetti, J. Organomet. Chem., 171 (1979) 399.
60 O. Piovescana and P.F. Zanassi, Angew. Chem., 92 (1980) 579; B. Chiari, O. Piovescana, T. Tarentelli and P.F. Zanassi, Inorg. Chem., 24 (1985) 366.
61 Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organomet. Chem., 277 (1984) 143.
62 C.E. Briant, K.P. Hall and M.P. Mingos, J. Chem. Soc., Chem. Commun., (1983) 843.
63 H.N. Adams, W. Hiller and J. Stahle, Z. Anorg. Allg. Chem., 485 (1982) 81.
64 W. Conzelmann, W. Hiller, J. Strahle and G.M. Sheldrick, Z. Anorg. Allg. Chem., 512 (1984) 169.
65 P.G. Jones, C. Lensch and G.M. Sheldrick, Z. Naturforsch., Teil B, 37 (1982) 141.
66 (a) W. Jeitschenko and M.H. Moller, Acta Crystallogr., Sect. B, 35 (1979) 573.
(b) M. Binnervies, Z. Naturforsch., Teil B, 33 (1978) 570.
67 A. Rosensweig and D.T. Cromer, Acta Crystallogr., 12 (1959) 709.
68 N. Blom, A. Ludi, H.B. Burgi and K. Tichy, Acta Crystallogr., Sect. C, 40 (1984) 1767.
69 N. Blom, A. Ludi and H.B. Burgi, Acta Crystallogr., Sect. C, 40 (1984) 1770.
70 S. Esperas, Acta Chem. Scand., Ser. A, 30 (1976) 527.
71 E.M.W. Janssen, J.C.W. Folmer and G.A. Wiegers, J. Less Common Met., 38 (1974) 71.
72 P.W.R. Corfield and H.M.M. Shearer, Acta Crystallogr., 23 (1967) 156.

73 M.K. Cooper, L.E. Mitchell, K. Henrick, M. McPartlin and A. Scott, Inorg. Chim. Acta, 84 (1984) L9.
74 Interatomic Distances, Chem. Soc. Spec. Publ. No. 18, The Chemical Society, London, 1965.
75 M. Melnìk, Coord. Chem. Rev., 47 (1982) 239.
76 P. Braunstein, J. Rose, Y. Dusausoy and J.P. Mangeot, C.R. Acad. Sci., 294 (1982) 967.
77 P.G. Jones, Acta Crystallogr., Sect. B, 36 (1980) 3105.
78 P.T. Beurskens, R. Pet. J.N. Noordik, J.W.A. Van der Velden and J.J. Bour, Cryst. Struct. Commun., 11 (1982) 1039.
79 L.Y. Guggenberger, J. Organomet. Chem., 81 (1974) 271.
80 P.G. Jones, J. Chem. Soc., Chem. Commun., (1980) 1031.
81 W. Clegg, Acta Crystallogr., Sect. B, 32 (1976) 2712.
82 M. Barrow, H.B. Burgi, D.K. Johnson and L.M. Venanzi, J. Am. Chem. Soc., 98 (1976) 2356.
83 N.C. Baenziger, K.M. Dittmore and J.R. Doyle, Inorg. Chem., 13 (1974) 805.
84 M. Khan, C. Oldham and D.G. Tuck, Can. J. Chem., 59 (1981) 2714.
85 J.A. Muir, M.M. Muir and S. Arias, Acta Crystallogr., Sect. B, 38 (1982) 1318.
86 W. Clegg, Acta Crystallogr., Sect. B, 34 (1978) 278.
87 K. Burgess, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1983) 1661.
88 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, J. Chem. Soc., Chem. Commun., (1982) 314.
89 B.F.G. Johnson, D.A. Kaner, J. Lewis and P.R. Raithby, J. Organomet. Chem., 215 (1981) C33.
90 P. Braunstein, J. Rose, A.M. Manotti-Lanfredi, A. Tiripicchio and E. Sappa, J. Chem. Soc., Dalton Trans., (1984) 1843.
91 M. Green, K.A. Mead, R.M. Mills, I.D. Salter, F. Gordon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1982) 51.
92 L.W. Bateman, M. Green, K.A. Mead, R.M. Mills, I.D. Salter, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 2599.
93 L.W. Bateman, M. Green, J.A.K. Howard, K.A. Mead, R.M. Mills, I.D. Salter, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1982) 773.
94 B.F.G. Johnson, J. Lewis, J.N. Nicholls, J. Puga and K.H. Whitmire, J. Chem. Soc., Dalton Trans., (1983) 787.
95 M.J. Mays, P.R. Raithby, P.L. Taylor and K. Henrick, J. Organomet. Chem., 224 (1982) C45.
96 A.G. Cowie, B.F.G. Johnson, J. Lewis, J.N. Nicholls, P.R. Raithby and A.G. Swanson, J. Chem. Soc., Chem. Commun., (1984) 637.
97 M. Green, A.G. Orpen, I.D. Salter and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1982) 813.
98 M. Green, A.G. Orpen, I.D. Salter and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 2497.
99 G.A. Carriedo, D. Hodgson, J.A.K. Howard, K. Marsdan, F.G.A. Stone, M.J. Went and P. Woodward, J. Chem. Soc., Chem. Commun., (1982) 1006.
100 R. Hesse and P. Jennische, Acta Chem. Scand., 26 (1972) 3855.
101 P. Braunstein, H. Lehner, D. Matt, A. Tiripicchio and M. Tiripicchio-Camellini, Angew. Chem. Int. Ed. Engl., 23 (1984) 304.
102 V.G. Andrianov, Yu.T. Struchkov and E.R. Rossinskaya, J. Chem. Soc., Chem. Commun., (1973) 338; A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, D.A. Lemenovskii, T.V. Baukova and O.B. Apanassova, J. Organomet. Chem., 65 (1974) 131.

103 C.E. Briant, K.P. Hall and D.M.P. Mingos, J. Organomet. Chem., 229 (1982) C5.
104 E.I. Smyslova, E.G. Perevalova, V.P. Dyadchenko, K.I. Grandberg, Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organomet. Chem., 215 (1981) 269.
105 B.F.G. Johnson, J. Lewis, P.R. Raithby and A. Sanders, J. Organomet. Chem., 260 (1984) C29.
106 P.J.M.W.L. Birker and G.C. Verschoor, Inorg. Chem., 21 (1982) 990.
107 H. Schmidbaur, J.R. Mandle, J.M. Bassett, G. Blaschke and B. Zimmer-Gasser, Chem. Ber., 114 (1981) 433.
108 B.F.G. Johnson, D.A. Haner, J. Lewis and M.J. Rosales, J. Organomet. Chem., 238 (1982) C73.
109 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J.N. Nicholls, J. Puga, P.R. Raithby, M.J. Rosales, M. Schrober and M.D. Vargas, J. Chem. Soc., Dalton Trans., (1983) 2447.
110 K. Burgess, B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and A.S.A.B. Syed-Mustaffa, J. Chem. Soc., Chem. Commun., (1983) 455.
111 J.C. Huffman, R.S. Roth and A.R. Siedle, J. Am. Chem. Soc., 98 (1976) 4340.
112 P.G. Jones, G.M. Sheldrick, A. Fugner, F. Gotsfried and W. Beck, Chem. Ber., 114 (1981) 1413.
113 S.R. Burnkhall, H.D. Holden, B.F.G. Johnson, J. Lewis, G.N. Pain, P.R. Raithby and M.J. Taylor, J. Chem. Soc., Chem. Commun., (1984) 25.
114 A.L. Casalnuovo, L.H. Pignolet, J.W.A. van der Velden, J.J, Bour and J.J. Steggerda, J. Am. Chem. Soc., 105 (1983) 5957.
115 S. Gambarotta, C. Floriani, A. Chiesi Villa and C. Guastini, J. Chem. Soc., Chem. Commun., (1983) 1304.
116 J.W.A. van der Velden, J.J. Bour, F.A. Vollenbroek, P.T. Beurskens and J.M.M. Smits, J. Chem. Soc., Chem. Commun., (1979) 1162.
117 J.W.A. van der Velden, F.A. Vollenbroek, J.J. Bour, P.T. Beurskens, J.M.M. Smits and W.P. Bosman, Rec. Trav. Chim. Pays-Bas, 100 (1981) 148.
118 W. Stoeger and A. Rabenau, Z. Naturforsch., Teil B, 34 (1979) 685.
119 R.C. Elder, E.H.K. Zeiher, M. Onady and R.R. Whittle, J. Chem. Soc., Chem. Commun., (1981) 900.
120 S.J. Berners-Price, M.A. Mazid and P.J. Sadler, J. Chem. Soc., Dalton Trans., (1984) 969.
121 B.F.G. Johnson, D.A. Kaner, J. Lewis and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1981) 753.
122 P.G. Jones, G.M. Sheldrick, J.A. Muir, M.M. Muir and L.B. Pulgar, J. Chem. Soc., Dalton Trans., (1982) 2123.
123 J.A. Muir, M.M. Muir, S. Aria, Ch.F. Campana and S.K. Dwight, Acta Crystallogr., Sect. B, 38 (1982) 2047.
124 J.A. Muir, M.M. Muir, S. Arias, P.G. Jones and G.M. Sheldrick, Inorg. Chim. Acta, 81 (1984) 169.
125 J.W. Lauher and K. Wald, J. Am. Chem. Soc., 103 (1981) 7648.
126 B.F.G. Johnson, J. Lewis, W.J.J. Nelson, J. Puga, P.R. Raithby, D. Braga, M. McPartlin and W. Clegg, J. Organomet. Chem., 243 (1983) C13.
127 C.E. Briant, R.W.M. Wardle and M.P. Mingos, J. Organomet. Chem., 267 (1984) C49.
128 G.A. Carriedo, J.A.K. Howard, K. Marsden, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1984) 1589.
129 C.D. Garner and S.C. Wallwork, J. Chem. Soc., Chem. Commun., (1969) 108.
130 C.D. Garner and S.C. Wallwork, J. Chem. Soc., A (1970) 3092.
131 M. Weishaupt and J. Strahle, Z. Naturforsch., Teil B, 31 (1976) 554.
132 J.H. Kim and G.W. Everett, Jr., Inorg. Chem., 20 (1981) 853.

133 Ch.H. Park, B. Lee and G.W. Everett, Jr., Inorg. Chem., 21 (1982) 1681.
134 R.A. Penneman and R.P. Ryan, Acta Crystallogr., Sect. B, 28 (1972) 1629.
135 W.P. Fehlhammer and L.F. Dahl, J. Am. Chem. Soc., 94 (1972) 3370.
136 C. Kruger, J.C. Sekutowski, R. Goddard, H.J. Fuller, O. Gasser and H. Schmidbaur, Isr. J. Chem., 15 (1977) 149.
137 J.P. Fackler, Jr. and C. Pajarizon, J. Am. Chem. Soc., 99 (1977) 2363.
138 J. Stein, J.P. Fackler, Jr., C. Pajarizon and H.W. Chen, J. Am. Chem. Soc., 103 (1981) 2192.
139 H. Schmidbaur, G. Muller, K.C. Dash and B. Milewski-Mahrla, Chem. Ber., 114 (1981) 441.
140 R. Uson, A. Laguna, M.D. Villacampa, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 2035.
141 R. Hoppe and R. Hoffmann, Z. Anorg. Allg. Chem., 379 (1970) 193.
142 J.M. Williams and S.W. Peterson, J. Am. Chem. Soc., 91 (1969) 776.
143 M. Bonamico and G. Dessy, Acta Crystallogr., Sect. B, 39 (1973) 1737.
144 M. Bonamico and G. Dessy, Acta Crystallogr., Sect. B, 39 (1973) 1735.
145 F. Theobald and H. Amrani, Acta Crystallogr., Sect. B, 36 (1980) 2932.
146 G. Sleater, H. Barnighausen and G. Brauer, Z. Anorg. Allg. Chem., 372 (1970) 9.
147 W. Werner and J. Strahle, Z. Naturforsch., Teil B, 32 (1977) 741.
148 M. Elliott, J. Chem. Phys., 2 (1934) 419.
149 H.N. Adams and J. Strahle, Z. Anorg. Allg. Chem., 485 (1982) 65.
150 M.S. Hussain and E.O. Schlemper, J. Chem. Soc., Dalton Trans., (1980) 750.
151 M.R. Caira, L.R. Nassimbeni and A.L. Rodgers, Acta Crystallogr., Sect. B, 31 (1975) 1112.
152 P.G. Jones, J.J. Guy and G.M. Sheldrick, Acta Crystallogr., Sect. B, 31 (1975) 2687.
153 J. Vicente, M.T. Chicote, M.D. Bermudez, X. Solans and M. Font-Altaba, J. Chem. Soc., Dalton Trans., (1984) 557.
154 J.A. Cras, J.H. Noordik, P.T. Beurskens and A.M. Verhoeven, J. Cryst. Mol. Struct., 1 (1971) 155.
155 J.H. Noordik and P.T. Beurskens, J. Cryst. Mol. Struct., 1 (1971) 339.
156 J.H. Noordik, Th.W. Hummelink and J.G.M. van der Linden, J. Coord. Chem., 2 (1973) 185.
157 J.H. Noordik, Cryst. Struct. Commun., 2 (1973) 81.
158 J.H. Anemark and J.A. Ibers, Inorg. Chem., 7 (1968) 2636.
159 P.T. Beurskens, J.A. Cras and J.G.M. van der Linden, Inorg. Chem., 9 (1970) 475.
160 M.A. Mazid, M.T. Razi and P.J. Sadler, Inorg. Chem., 20 (1981) 2872.
161 L.S. Hollis and S.J. Lippard, J. Am. Chem. Soc., 105 (1983) 4293.
162 G. Nardin, L. Randaccio, G. Annibale, G. Natile and B. Pitteri, J. Chem. Soc., Dalton Trans., (1980) 220.
163 J. Strahle, J. Gelinek and M. Kolmel, Z. Anorg. Allg. Chem., 456 (1979) 241.
164 D.B. Dell'amico, F. Calderazzo, F. Marchetti and S. Merlino, Gazz. Chim. Ital., 108 (1978) 627.
165 G. Minghetti, C. Foddai, F. Cabiati, M.L. Ganadu and M. Manassero, Inorg. Chim. Acta, 64 (1982) L235.
166 N.W. Alcock, K.P. Ang, K.F. Mok and S.F. Tan, Acta Crystallogr., Sect. B, 34 (1978) 3364.
167 G. Bandoli, L. Cattalini, D.A. Clemente and G. Marangoni, Atti Accad. Peloritana Pericolanti, Cl. Sci. Fis., Mat. Nat., 52 (1972) 9.
168 G. Bandoli, D.A. Clementi, G. Marangoni and L. Cattalini, J. Chem. Soc., Dalton Trans., (1973) 886.

169 R. Uson, A. Laguna, M. Laguna, E. Fernandez, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1982) 1971.
170 D.S. Eggleston, D.F. Chodosh, D.T. Hill and G.R. Girard, Acta Crystallogr., Sect. C, 40 (1984) 1357.
171 S. Komiya, J.C. Huffman and J.K. Kochi, Inorg. Chem., 16 (1977) 2138.
172 A.J. Canby, N.J. Minchin, J.M. Patrick and A.H. White, Aust. J. Chem., 36 (1983) 1107.
173 A.J. Carty, N.J. Minchin, P.C. Healy and A.H. White, J. Chem. Soc., Dalton Trans., (1982) 1795.
174 R. Uson, A. Laguna, M. Laguna, E. Fernadle, M.D. Villacampa, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1983) 1679.
175 L. Manojlovic-Muir, J. Organomet. Chem., 73 (1974) C45.
176 L.R. Ocone, Struct. Rep., 20 (1956) 607.
177 L. Cattalini, G. Annibale, L. Canovese, G. Natile, M. Cingi-Biagini and A. Tiripicchio, Atti 12th Congr. Naz. Chim. Inorg., (1979) 71.
178 G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A.M. Manotti-Lanfredi and A. Tiripicchio, J. Chem. Soc., Dalton Trans., (1981) 2280.
179 A. Dunand and R. Gerdil, Acta Crystallogr., Sect. B, 31 (1975) 370.
180 P.T. Beurskens, J.A. Cras, Th.W. Hummelink and J.G.M. van der Linden, Rec. Trav. Chim. Pays-Bas, 89 (1970) 984.
181 P.T. Beurskens, J.A. Cres and J.J. Steggerda, Inorg. Chem., 7 (1968) 810.
182 F.Th.H.M. Wijnhoven, W.P. Bosman, J. Willemse and J.A. Cras, Rec. Trav. Chim. Pays-Bas, 98 (1979) 492.
183 R.W. Baker and P. Pauling, J. Chem. Soc., Chem. Commun., (1969) 745.
184 M. McPartlin and A.J. Markwell, J. Organomet. Chem., 57 (1973) C25.
185 M.A. Bennett, K. Hoskins, W.R. Kneen, R.S. Nyholm, P.B. Hitchock, R. Mason, G.B. Robertson and A.D.C. Towl, J. Am. Chem. Soc., 93 (1971) 4591.
186 C.E. Briant, D.I. Gilmour and M.P. Mingos, J. Organomet. Chem., 267 (1984) C52.
187 H. Schmidbaur, J.R. Mandl, A. Frank and G. Huttner, Chem. Ber., 109 (1976) 466.
188 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Taylor, Polyhedron, 1 (1982) 105.
189 L.J. Farrugia, M.J. Freeman, M. Green, A.G. Orpen, F.G.A. Stone and I.D. Salter, J. Organomet. Chem., 249 (1983) 273.
190 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, Chem. Ber., 110 (1977) 2751.
191 H.N. Adams, U. Grassle, W. Hiller and J. Strahle, Z. Anorg. Allg. Chem., 504 (1983) 7.
192 H. Klassen and R. Hoppe, Naturwissenschaften, 63 (1976) 387.
193 E.S. Clark, D.H. Templeton and C.H. MacGillavry, Acta Crystallogr., 11 (1958) 284.
194 K.P. Lobcher and J. Strahle, Z. Naturforsch., Teil B, 30 (1975) 662.
195 S. Komiya, J.C. Huffman and J.K. Kochi, Inorg. Chem., 16 (1977) 1253.
196 A. Burawoy, C.S. Gibson, G.C. Hampson and H.M. Powell, J. Chem. Soc., (1937) 1690.
197 P. Jandik, U. Schubert and H. Schmidbaur, Angew. Chem., 94 (1982) 74.
198 P.G. Jones and G.M. Sheldrick, Acta Crystallogr., Sect. C, 40 (1984) 1776.
199 P.G. Jones, Acta Crystallogr., Sect. C, 40 (1984) 804.
200 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, P.R. Raithby and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1983) 608.
201 M.I. Bruce and B.K. Nicholson, J. Chem. Soc., Chem. Commun., (1983) 1141.
202 J.E. Ellis, J. Am. Chem. Soc., 103 (1981) 6106.
203 J.A.K. Howard, I.D. Slater and F.G.A. Stone, Polyhedron, 3 (1984) 567.
204 M.I. Bruce, O.B. Shawkataly and B.K. Nicholson, J. Organomet. Chem., 275 (1984) 223.

205 J.W.A. van der Velden, J.J. Bour, R. Pet, W.P. Bosman and J.H. Noordik, Inorg. Chem., 22 (1983) 3112.
206 M.I. Bruce and B.K. Nicholson, J. Organomet. Chem., 252 (1983) 243.
207 G.E. Glass, J.H. Konnert, M.G. Miles, D. Britton and R.S. Tobias, J. Am. Chem. Soc., 90 (1968) 1131.
208 J.W.A. van der Velden, J.J. Bour, B.F. Otterloo, W.P. Bosman and J.H. Noordik, J. Chem. Soc., Chem. Commun., (1981) 583.
209 J.W.A. van der Velden, J.J. Bour, W.P. Bosman and J.H. Noordik, Inorg. Chem., 22 (1983) 1913.
210 C.E. Briant, K.P. Hall and D.M.P. Mingos, J. Organomet. Chem., 254 (1983) C18.
211 J.W.A. van der Velden, J.J. Bour, J.J. Steggerda, P.T. Beurskens, M. Roseboom and J.H. Noordik, Inorg. Chem., 21 (1982) 4321.
212 M. McPartlin, R. Mason and L. Malatesta, J. Chem. Soc., Chem. Commun., (1969) 334.
213 J.W.A. van der Velden, J.J. Bour, W.P. Bosman and J.H. Noordik, J. Chem. Soc., Chem. Commun., (1981) 1218.
214 F.A. Vollenbroek, W.P. Bosman, J.J. Bour, J.H. Noordik and P.T. Beurskens, J. Chem. Soc., Chem. Commun., (1979) 387.
215 M. Manassero, L. Naldini and M. Sansoni, J. Chem. Soc., Chem. Commun., (1979) 385.
216 K.P. Hall, B.R.C. Theobald, D.I. Gilmour, D.M.P. Mingos and A.J. Welch, J. Chem. Soc., Chem. Commun., (1982) 528.
217 S.L. Lawton, W.J. Rohrbaugh and G.T. Kokotailo, Inorg. Chem., 11 (1972) 2227.
218 P.G. Jones, H. Rumpel, E. Schwarzmann and G.M. Sheldrick, Acta Crystallogr., Sect. B, 35 (1979) 1435.
219 P.G. Jones, E. Schwarzmann, G.M. Sheldrick and H. Timpe, Z. Naturforsch., Teil B, 36 (1981) 1050.
220 P.G. Jones, M. Kraushaar, E. Schwarzmann and G.M. Sheldrick, Z. Naturforsch., Teil B, 37 (1982) 941.
221 P.G. Jones, H. Rumpel, E. Schwarzmann and G.M. Sheldrick, Acta Crystallogr., Sect. B, 35 (1979) 2380.
222 J.C. Bowles and D. Hall, J. Chem. Soc., Chem. Commun., (1971) 1523.
223 R. Timkovich and A. Tulinsky, Inorg. Chem., 16 (1977) 962.
224 R.J. Charlton, C.M. Harris, H. Patil and N.C. Stephenson, Inorg. Nucl. Chem. Lett., 2 (1966) 409.
225 C.J. O'Connor and E. Sinn, Inorg. Chem., 17 (1978) 2067.
226 W.T. Robinson and E. Sinn, J. Chem. Soc., Dalton Trans., (1975) 726.
227 R. Uson, J. Vincente, M.T. Chicote, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1983) 1131.
228 H.M. Colquhoun, T.J. Greenhough and M.G.W. Wallbridge, J. Chem. Soc., Chem. Commun., (1976) 1019.
229 H.M. Colquhoun, T.J. Greenhough and M.G.H. Wallbridge, J. Chem. Soc., Dalton Trans., (1978) 303.
230 M.A. Beckett, J.E. Crook, N.N. Greenwood and J.D. Kennedy, J. Chem. Soc., Dalton Trans., (1984) 1427.
231 F. Demartin, M. Manassero, L. Naldini, R. Ruggeri and M. Sansoni, J. Chem. Soc., Chem. Commun., (1981) 222.
232 J.W.A. van der Velden, P.T. Beurskens, J.J. Bour, W.P. Bosman, J.H. Noordik, M. Kolenbrander and J.A.K.M. Buskes, Inorg. Chem., 23 (1984) 146; R.E. Marsh, Inorg. Chem., 23 (1984) 3682.
233 P.L. Bellon, M. Manassero, L. Naldini and M. Sansoni, J. Chem. Soc., Chem. Commun., (1972) 1035.

234 P.L. Bellon, F. Cariati, M. Manessero, L. Naldini and M. Sansoni, J. Chem. Soc., Chem. Commun., (1971) 1423.
235 C.E. Briant, K.P. Hall and D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1984) 290.
236 C.E. Briant, K.P. Hall, A.C. Wheeler and D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1984) 248.
237 V.G. Albano, P.L. Bellon, M. Manassero and M. Sansoni, J. Chem. Soc., Chem. Commun., (1970) 1210.
238 P. Bellon, M. Manassero and M. Sansoni, J. Chem. Soc., Dalton Trans., (1972) 1481.
239 R. Uson, A. Laguna, M. Laguna, B.R. Mansano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 285.
240 R. Uson, A. Laguna, M. Laguna, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Chem. Commun., (1981) 1097.
241 K. Leary, A. Zalkin and N. Bartlett, J. Chem. Soc., Chem. Commun., (1973) 131.
242 V.F. Duckworth and N.C. Stephenson, Inorg. Chem., 8 (1969) 1661.
243 V.F. Duckworth, C.M. Harris and N.C. Stephenson, Inorg. Nucl. Chem. Lett., 4 (1968) 419.
244 H.C. Colquhoun, T.J. Greenhough and M.G.H. Wallbridge, Acta Crystallogr., Sect. B, 33 (1977) 3604.
245 C.E. Briant, B.R.C. Theobald, J.W. White, L.K. Bell and D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1981) 201.
246 F.W.B. Einstein, P.R. Rao, J. Trotter and N. Bartlett, J. Chem. Soc. A, (1967) 478.
247 B.K. Teo and K. Keating, J. Am. Chem. Soc., 106 (1984) 2224.
248 H.D. Sinnen and H.U. Schuster, Z. Naturforsch., Teil B, 33 (1978) 1077.
249 N. Elliott, J. Chem. Phys., 2 (1934) 419.
250 N. Elliott and L. Pauling, J. Am. Chem. Soc., 60 (1938) 1846.
251 W. Denner, H. Schulz and H. D'Amour, Acta Crystallogr., Sect. A, 35 (1979) 360.
252 J. Strahle, J. Gelinek, M. Kolmel and A.M. Nemecek, Z. Naturforsch., Teil B, 34 (1979) 1047.
253 W. Werner and J. Stahle, Z. Naturforsch., Teil B, 34 (1979) 952.
254 P.T. Beurskens, H.J.A. Bleauw, J.A. Cras and J.J. Steggerda, Inorg. Chem., 7 (1968) 805.
255 J.A. Jarvis, A. Johnson and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1973) 373.
256 R. Uson, A. Laguna, M. Laguna, B.R. Mansano, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 839.
257 D.B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, J. Chem. Soc., Chem. Commun., (1977) 31.
258 D.B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, J. Chem. Soc., Dalton Trans., (1982) 2257.
259 R.V. Parish, Gold Bull., 15 (1982) 51.
260 R.V. Parish, in G.J. Long (Ed.), Mössbauer Spectroscopy Applied to Inorganic Chemistry, Plenum, New York, 1984, Chap. 17.
261 R.V. Parish, Chem. Br., 21 (1985) 546, 740.
262 R.V. Parish, O. Parry and C.A. McAuliffe, J. Chem. Soc., Dalton Trans., (1981) 2098.
263 M.J. Mays and P.L. Sears, J. Chem. Soc., Dalton Trans. (1974) 2254.
264 R.V. Parish, Coord. Chem. Rev., 42 (1982) 1.
265 A.K.H. Al-Sa'ady, C.A. McAuliffe, R.V. Parish and R. Fields, J. Chem. Soc., Dalton Trans., (1984) 491.
266 M. Katada, Y. Uchida, K. Sato, H. Sano, H. Sakai and Y. Maeda, Bull. Chem. Soc. Jpn., 55 (1982) 444.

267 G. Kaindl, K. Leary and N. Bartlett, J. Chem. Phys., 59 (1973) 5050.
268 L.S. Moore, R.V. Parish, I.D. Salter and S.D.D. Brown, unpublished data.
269 E.A. Vollenbroek, P.C.P. Bouten, J.M. Trooster, J.P. van den Berg and J.J. Bour, Inorg. Chem., 17 (1978) 1345.
270 D.A. Shirley, R.W. Grant and D.A. Keller, Rev. Mod. Phys., 36 (1964) 352.
271 P.G. Jones, A.G. Maddock, M.J. Mays, M.M. Muir and A.F. Williams, J. Chem. Soc., Dalton Trans., (1977) 1434.
272 J.S. Charlton and D.I. Nicholls, J. Chem. Soc. A, (1970) 1484.
273 C.A. McAuliffe, R.V. Parish and P.D. Randall, J. Chem. Soc., Dalton Trans., (1977) 1426.
274 M.P.A. Viegers, Ph.D. Thesis, Nijmegen, Netherlands, 1976; quoted in P. Gütlich, R. Link and A. Trautwein, Mössbauer Spectroscopy and Transition Metal Chemistry, Springer Verlag, Berlin, 1978, p. 209.
275 D.T. Hill, B.M. Sutton, A.A. Isab, T. Razi, P.J. Sadler, J.M. Trooster and G.H.M. Calis, Inorg. Chem., 22 (1983) 2936.
276 J.D. Rush and R.V. Parish, quoted in ref. 260, p. 586.
277 E. Baggio-Saitovich, U. Wagner, F.E. Wagner and J. Danon, Proc. Int. Conf. Mössbauer Effect, Cracow, Vol. 1, 1975, p. 223.
278 H. Schmidbaur, J.R. Mandl, F.E. Wagner, D.F. van der Vondel and G.P. van der Kelen, J. Chem. Soc., Chem. Commun., (1976) 170.
279 M.O. Faltens and D.A. Shirley, J. Chem. Phys., 53 (1970) 4249.
280 H.D. Bartunik, W. Potzel, R.L. Mössbauer and G. Kaindl, Z. Phys., 240 (1972) 1.
281 G.C.H. Jones, P.G. Jones, A.G. Maddock, M.J. Mays, P.A. Vergnano and A.F. Williams, J. Chem. Soc., Dalton Trans., (1977) 1440.
282 A.K.H. Al-Sa'ady, K. Moss, C.A. McAuliffe and R.V. Parish, J. Chem. Soc., Dalton Trans., (1984) 1609.
283 W. Potzel and G.J. Perlow, Phys. Rev. Lett., 29 (1972) 910.
284 K. Moss, R.V. Parish, A. Laguna, M. Laguna and R. Uson, J. Chem. Soc., Dalton Trans., (1983) 2071.
285 M.P.A. Viegers, Ph.D. Thesis, Nijmegen, The Netherlands, 1976.
286 J. Stanek, J. Chem. Phys., 76 (1982) 2315.
287 H. Prosser, Diplomarbeit, Tech. Univ. Münich, 1973 (quoted in ref. 286).
288 M.P.A. Viegers, J.M, Trooster, P. Bouten and T.P. Rit, J. Chem. Soc., Dalton Trans., (1977) 2074.
289 J.D. Rush and R.V. Parish, quoted in ref. 259.
290 J.W.A. van der Velden, J.J. Bour, W.P. Bosman, J.H. Noordik and P.T. Buerskens, Rec. Trav. Chim. Pays-Bas, 103 (1984) 13.
291 G. Schmid, R. Pfeil, R. Boesa, F. Bandermann, S. Meyer, G.H.M. Calis and J.M. Trooster, Chem. Ber., 114 (1981) 3634.
292 J.D. Basil, H.H. Murray, J.P. Fackler, Jr., J. Tocher, A.M. Mazany, B. Trscimka-Bancroft, H. Knachel, D. Dudis, T.J. Delord and D.O. Marler, J. Am. Chem. Soc., 107 (1985) 6908.
293 J.A. Muir, M.M. Muir, L.B. Pulgar, P.G. Jones, and G.M. Sheldrick, Acta Crystallogr., Sect. C, 41 (1985) 1174.
294 P.A. Bates and J.M. Waters, Acta Crystallogr., Sect. C, 41 (1985) 862.
295 M.S. Hussain and A.A. Isab, Transition Met. Chem. (Weinheim, Ger.), 10 (1985) 178.
296 B. Borio, F. Bonati, A. Burini, and B.R. Pietroni, Z. Naturforsch., Teil B, 39 (1984) 1747.
297 P.G. Jones, Acta Crystallogr., Sect. C, 41 (1985) 905.
298 M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio, and F. Bonati, Acta Cyrstallogr., Sect. C, 41 (1985) 52.

299 M.S. Hussain and A.A. Isab, J. Coord. Chem., 14 (1985) 17.
300 J. Bashkin, C.E. Briant, D.M.P. Mingos, and R.W.M. Wardle, Transition Met. Chem., 10 (1985) 113.
301 A.L. Casalnuovo, T. Laska, P.V. Nilsson, J. Olofson, and L.H. Pignolet, Inorg. Chem., 24 (1985) 233.
302 C.F. Barrientos-Penna, F.W.B. Einstein, T. Jones, and D. Sutton, Inorg. Chem., 24 (1985) 632.
303 R. Hohbein, P.G. Jones, K. Meyer-Bäse, E. Schwarzmann, and G.M. Sheldrick, Z. Naturforsch., Teil B, 40 (1985) 1029.
304 P.A. Bates and J.M. Waters, Inorg. Chim. Acta, 98 (1985) 125.
305 C.P. Horwitz, E.M. Holt, C.P. Brock and D.F. Shriver, J. Am. Chem. Soc., 107 (1985) 8136.
306 H.H. Murray, A.M. Mazany and J.P. Fackler, Jr., Organometallics, 4 (1985) 154.
307 A.J. Wynd, S.E. Robins, D.A. Welch, and A.J. Welch, J. Chem. Soc., Chem. Commun., (1985) 819.
308 M.I. Bruce, O.B. Shawkataly and B.K. Nicholson, J. Organomet. Chem., 286 (1985) 427.
309 M.I. Bruce, E. Horn, J.G. Matisons, and M.R. Snow, J. Organomet. Chem., 286 (1985) 271.
310 R.C. Haushalter, Inorg. Chim. Acta, 102 (1985) L37.
311 J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheldrick, and P. Espinet, J. Chem. Soc., Dalton Trans., (1985) 1163.
312 A.L. Casalnuovo, T. Laska, P.V. Nilsson, J. Olofson, L.H. Pignolet, W. Bos, J.J. Bour, and J.J. Steggerda, Inorg. Chem., 24 (1985) 182.
313 M.G.B. Drew, L.R. Glaves and M.J. Hudson, J. Chem. Soc., Dalton Trans., (1985) 771.
314 B. Chiari, O. Piovesana, T. Tarantelli, and P.F. Zanazzi, Inorg. Chem., 24 (1985) 366.
315 J. Vicente, M.T. Chicote, M.D. Bermudez, P.G. Jones, and G.M. Sheldrick, J. Chem. Research S, (1985) 72.
316 P.K. Byers, A.J. Canty, N.J. Michin, J.W. Patrick, B.W. Skelton, and A.H. White, J. Chem. Soc., Dalton Trans., (1985) 1183.
317 P.K. Byers, A.J. Canty, L.M. Engelhardt, J.M. Patrick and A.H. White, J. Chem. Soc., Dalton Trans., (1985) 981.
318 K. Kaas and L.H. Skibsted, Acta Chem. Scand. Ser. A, 39 (1985) 1.
319 U. Grässle, W. Hiller and J. Strähle, Z. Anorg. Allg. Chem., 529 (1985) 29.
320 U. Grässle and J. Strähle, Z. Anorg. Allg. Chem., 531 (1985) 26.
321 D.S. Dudis and J.P. Fackler, Jr., Inorg. Chem., 24 (1985) 3758.
322 S. Ahrland, B. Norén and A. Oskarsson, Inorg. Chem., 24 (1985) 1330.
323 A.L. Casalnuovo, J.A. Casalnuovo, P.V. Nilsson, and L.H. Pignolet, Inorg. Chem., 24 (1985) 2554.