Preparations, Crystal Structures, and Molybdenum-95 Nuclear Magnetic Resonance Spectroscopic Studies of Triphenylphosphine–Gold–Tetrathiomolybdate(VI) Clusters†

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The preparation, spectroscopic properties, and *X*-ray crystal structures of two triphenylphosphine–gold–thiomolybdate clusters are reported. $[MoS_4(AuPPh_3)_2]$ crystallises in the triclinic space group $P\bar{1}$ with $a = 9.596(1)$, $b = 10.630(1)$, $c = 19.712(2)$ Å, $\alpha = 89.06(1)$, $\beta = 80.87(1)$, $\gamma = 66.99(1)°$, and $Z = 2$. $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ crystallises in the monoclinic space group $P2_1/c$ with $a = 21.251(2)$, $b = 10.535(1)$, $c = 23.167(2)$ Å, $\beta = 104.20(1)°$, and $Z = 4$. The structures have been solved from 5 748 and 7 476 unique observed diffractometer data and have been refined to $R = 0.031$ and 0.036, respectively. The ^{95}Mo n.m.r. spectra of these and related copper and silver tetrathiomolybdate(VI) clusters consist of a single resonance, whose chemical shift depends on the mole ratio of added PPh_3 to Mo in the solution.

The co-ordination chemistry of tetrathiomolybdate(VI) and related 'ligands' with various transition metals has been extensively investigated in the last 15 years,[1–6] with particular attention being focused on the formation of Cu–Mo–S clusters, which may be important in the biological antagonism between copper and molybdenum.[7] Recent ^{95}Mo n.m.r. studies[5,6] have shown that the molybdenum chemical shifts of these clusters are a sensitive probe of the co-ordination environment of the thiomolybdate ligands in solution. In this work we report the synthesis of several Au–Mo–S clusters, two of which have been characterised by *X*-ray crystallography, and show that ^{95}Mo n.m.r. spectroscopy can be used to monitor the behaviour of these and known Ag–Mo–S[8,9] and Cu–Mo–S[10,11] clusters in solution.

Experimental

Preparations.—1,3;1,3;2,3;2,3-*Tetra-μ-thio-*1,2-*bis*(*triphenylphosphine*)*digold*(I)*molybdenum*(VI), $[MoS_4(AuPPh_3)_2]$ (**1**). $[Au(PPh_3)Cl]$ (0.48 g, 1 mmol) was added under dinitrogen to a solution of $[NEt_4]_2[MoS_4]$ (0.24 g, 0.5 mmol) in dichloromethane (60 cm^3). After stirring for *ca.* 5 min, all of the solid had dissolved and the colour of the solution had changed from deep red to orange. The solvent was removed under vacuum, and the resulting orange powder was washed several times with portions of ethanol (30 cm^3) to remove $[NEt_4]Cl$ contamination. The remaining solid was dissolved in dichloromethane (30 cm^3) and filtered. Orange crystals of the product were obtained from this solution by careful addition of pentane, followed by cooling to 0 °C overnight. These crystals were collected by filtration, washed with pentane, and dried in air. Further product was recovered from solution by addition of more pentane. Yield 80% (Found: C, 38.0; H, 2.6; Mo, 8.9; P, 5.9; S, 10.9. Calc. for $C_{36}H_{30}Au_2MoP_2S_4$: C, 37.8; H, 2.6; Mo, 8.4; P, 5.4; S, 11.2%).

$[MoS_4(AuPPh_3)\{Au(PPh_3)_2\}]$. Triphenylphosphine (0.25 g, 1 mmol) was added to a solution of (**1**) (0.1 g, 0.08 mmol) in dichloromethane (20 cm^3). Careful addition of pentane yielded orange-red crystals of the product. These dissociate in solution to reform the starting materials, unless a large excess of triphenylphosphine is present. The elemental analyses indicated the presence of one molecule of solvent of crystallisation per molecule of complex. Yield *ca.* 40% (Found: C, 44.4; H, 3.1; Cl, 5.2; Mo, 6.9; P, 6.3; S, 7.7. Calc. for $C_{54}H_{45}Au_2MoP_3S_4 \cdot CH_2Cl_2$: C, 44.3; H, 3.2; Cl, 4.8; Mo, 6.4; P, 6.2; S, 8.6%).

3-*Oxo-*1,3;2,3-*di-μ-thio-μ*$_3$*-thio-*1,1,2-*tris*(*triphenylphosphine*)*digold*(I)*molybdenum*(VI), $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ (**2**). $[Au(PPh_3)Cl]$ (0.24 g, 0.5 mmol) was added under an atmosphere of purified nitrogen to a suspension of $Cs_2[MoOS_3]$ (0.12 g, 0.25 mmol) in dichloromethane (80 cm^3). After stirring overnight, the orange solution was filtered, to remove a white precipitate of caesium chloride. Some decomposition was observed since a metallic mirror of gold was deposited on the sides of the reaction vessel. The solution was evaporated to dryness under vacuum and the product recrystallised from dichloromethane–pentane. The first crop of crystals obtained was $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$. Yield *ca.* 50% (Found: C, 45.4; H, 3.2; Mo, 6.3; P, 6.9; S, 6.7. Calc. for $C_{54}H_{45}Au_2MoOP_3S_3$: C, 46.7; H, 3.3; Mo, 6.9; P, 6.7; S, 6.9%). Further addition of pentane gave a few crystals of $[MoS_4(AuPPh_3)_2]$ (**1**).

$[MoOS_3(AuPPh_3)_2]$. The previous reaction was repeated, but the reaction mixture was filtered after *ca.* 2 h, before any decomposition had occurred. A small amount of crystalline solid was obtained by adding pentane to the dichloromethane solution which analysed as $[MoOS_3(AuPPh_3)_2]$. In solution this compound slowly decomposed to give $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$, gold, and other unidentified products. Yield *ca.* 15% (Found: C, 38.0; H, 3.0; Mo, 8.8; P, 5.4; S, 8.4. Calc. for $C_{36}H_{30}Au_2MoOP_2S_3$: C, 38.4; H, 2.7; Mo, 8.5; P, 5.5; S, 8.5%).

Crystals of (**1**) and (**2**), prepared as described above, proved suitable for *X*-ray crystallographic studies.

Crystal Structure Determination.—Crystal data are summarised in Table 1. For both complexes, crystals were sealed in glass capillaries and examined at room temperature on a Stoe-Siemens AED diffractometer, with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). Unit-cell parameters were refined from 2θ values ($20 < 2\theta < 25°$) of 32 [complex (**1**)] and 36 [complex (**2**)] reflections.

Intensity data were measured by a real-time profile-fitting method.[12] Empirical absorption corrections were based on the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

measurement of sets of equivalent reflections at various azimuthal angles.[13]

The structures were solved by Patterson and Fourier techniques and refined with anisotropic thermal parameters, and with phenyl rings constrained as ideal hexagons (C–C 1.395 Å), to a minimum value of $\Sigma w\Delta^2$, with $w^{-1} = \sigma^2(F) + gF_o^2$; the value of g was optimised in each case during the refinement.[13] Hydrogen atoms were included in the refinements subject to the following constraints: C–H 0.96 Å, aromatic C–H on the external bisectors of C–C–C angles, U(H) = 1.2 U(C), where U(C) is the equivalent isotropic thermal parameter of a carbon atom, defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 1. Crystal structure determinations

	$[MoS_4(AuPPh_3)_2]$ (**1**) $C_{36}H_{30}Au_2MoP_2S_4$	$[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ (**2**) $C_{54}H_{45}Au_2MoOP_3S_3$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	9.596(1)	21.251(2)
b/Å	10.630(1)	10.535(1)
c/Å	19.712(2)	23.167(2)
α/°	89.06(1)	
β/°	80.87(1)	104.20(1)
γ/°	66.99(1)	
U/Å^3	1 825.0	5 028.1
Z	2	4
D_c/g cm^{-3}	2.079	1.834
F(000)	1 080	2 680
μ/cm^{-1}	86.7	63.0
Crystal size (mm)	0.65 × 0.42 × 0.27	0.55 × 0.55 × 0.27
$2\theta_{max.}$/°	50	50
Transmission factors	0.062—0.124	0.039—0.084
Reflections measured	8 947	9 556
Unique data $F > 4\sigma(F)$	5 748	7 476
R^a	0.031	0.036
R'^b	0.035	0.038
Weighting parameter, g	0.000 12	0.000 17

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $\Delta = |F_o| - |F_c|$. [b] $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$.

Atomic co-ordinates and selected bond lengths and angles are given in Tables 2—5.

N.M.R. Spectra.—Molybdenum-95 n.m.r. spectra were recorded on a Varian XL300 spectrometer operating at a frequency of 19.55 MHz, by the pulse Fourier-transform technique. The samples were dissolved in CH_2Cl_2 (saturated, *ca.* 0.01 mol dm^{-3}) and contained in cylindrical tubes (outside diameter 10 mm) rotated at *ca.* 20 Hz. The temperature was 19 ± 1 °C. Chemical shifts were referenced externally to a 2 mol dm^{-3} solution of $Na_2[MoO_4]$ in ^2H_2O at apparent pH 11.

Results and Discussion

Molecular Structures.—The molecular structures of complexes (**1**) and (**2**) are shown in Figures 1 and 2, respectively. In both compounds the molybdenum atom has an essentially tetrahedral co-ordination geometry. In (**1**) both of the gold atoms have trigonal geometry, and the P–Au–Mo–Au–P fragment is linear. In complex (**2**) one of the gold atoms has trigonal geometry, while the other is tetrahedrally co-ordinated.

The structure of (**1**) is very similar to that of the triethylphosphine analogue,[4] with comparable bond lengths and bond angles. The Mo–Au distances [average 2.81(1) Å] suggest the presence of a direct metal–metal interaction in this compound consistent with molecular orbital calculations for related systems.[1]

Complex (**2**) contains one triply bridging and two doubly bridging sulphur atoms [S(3), and S(1) and S(2), respectively]. The Au–S bond lengths are greater to the μ_3-S atoms than to the μ-S atoms. The Mo–Au distance is significantly greater for the four-co-ordinate gold atom [3.133(1) Å] than for the three-co-ordinate gold atom [2.838(1) Å]. Any direct metal–metal interaction in this complex will be less significant than in complex (**1**) and is likely to involve only the trigonal gold atom and the molybdenum atom.

Molybdenum-95 N.M.R. Spectroscopy.—The ^{95}Mo chemical shifts and linewidths at half-height of the two gold complexes and of some related silver(I) and copper (I) complexes are shown

Table 2. Atomic co-ordinates (× 10^4), with estimated standard deviations* in parentheses, for $[MoS_4(AuPPh_3)_2]$ (**1**)

Atom	x	y	z
Mo	4 045(1)	2 447(1)	2 424(1)
S(1)	6 200(2)	1 427(2)	1 689(1)
S(2)	2 575(2)	1 267(2)	2 501(1)
S(3)	4 640(2)	2 620(1)	3 450(1)
S(4)	2 782(2)	4 487(1)	2 048(1)
Au(1)	4 787(1)	−11(1)	1 675(1)
P(1)	5 594(2)	−2 026(1)	1 058(1)
C(112)	4 058(4)	−2 768(4)	125(2)
C(113)	2 800	−2 968	−45
C(114)	1 535	−2 792	461
C(115)	1 529	−2 417	1 137
C(116)	2 787	−2 218	1 306
C(111)	4 051	−2 393	801
C(122)	6 237(4)	−4 558(3)	1 697(2)
C(123)	7 049	−5 571	2 109
C(124)	8 239	−5 453	2 392
C(125)	8 617	−4 321	2 262
C(126)	7 804	−3 307	1 849
C(121)	6 614	−3 426	1 567
C(132)	7 196(4)	−1 053(3)	36(2)
C(133)	8 263	−1 178	−556
C(134)	9 111	−2 456	−894
C(135)	8 891	−3 610	−641
C(136)	7 824	−3 485	−49
C(131)	6 977	−2 207	289
Au(2)	3 222(1)	4 942(1)	3 169(1)
P(2)	2 370(2)	6 867(1)	3 863(1)
C(212)	212(5)	8 206(3)	3 030(2)
C(213)	−911	9 344	2 801
C(214)	−1 329	10 636	3 114
C(215)	−624	10 789	3 656
C(216)	500	9 651	3 884
C(211)	918	8 359	3 571
C(222)	4 620(5)	7 803(4)	3 416(1)
C(223)	5 676	8 379	3 479
C(224)	5 926	8 647	4 130
C(225)	5 120	8 339	4 717
C(226)	4 064	7 763	4 653
C(221)	3 814	7 495	4 003
C(232)	−66(4)	7 266(4)	4 952(2)
C(233)	−721	6 933	5 576
C(234)	184	5 894	5 950
C(235)	1 744	5 187	5 701
C(236)	2 398	5 520	5 077
C(231)	1 493	6 559	4 703

* Phenyl-ring carbon e.s.d.s are the same within each ring and are given only for the atom attached to phosphorus.

Table 3. Atomic co-ordinates (× 10^4), with estimated standard deviations* in parentheses, for $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	2 769(1)	3 217(1)	4 068(1)	C(211)	2 525	7 265	2 438
O	2 753(2)	2 750(4)	4 766(2)	C(222)	2 616(2)	3 593(4)	2 213(2)
S(1)	3 518(1)	2 040(1)	3 774(1)	C(223)	2 886	2 702	1 899
S(2)	1 807(1)	2 854(1)	3 462(1)	C(224)	2 909	2 947	1 313
S(3)	3 041(1)	5 306(1)	4 095(1)	C(225)	2 661	4 084	1 040
Au(1)	3 937(1)	4 166(1)	3 846(1)	C(226)	2 391	4 975	1 354
P(1)	4 883(1)	5 036(1)	3 738(1)	C(221)	2 368	4 730	1 940
C(112)	5 689(1)	6 921(3)	4 411(2)	C(232)	1 226(2)	7 185(4)	1 384(2)
C(113)	5 810	8 163	4 618	C(233)	636	7 452	983
C(114)	5 310	9 055	4 508	C(234)	68	6 865	1 046
C(115)	4 688	8 704	4 191	C(235)	91	6 011	1 510
C(116)	4 566	7 463	3 985	C(236)	681	5 744	1 912
C(111)	5 067	6 571	4 095	C(231)	1 249	6 331	1 849
C(122)	5 616(2)	3 323(4)	4 529(2)	P(3)	1 236(1)	6 078(1)	3 908(1)
C(123)	6 151	2 544	4 756	C(312)	741(2)	4 595(4)	4 722(2)
C(124)	6 660	2 492	4 475	C(313)	801	3 989	5 269
C(125)	6 636	3 220	3 967	C(314)	1 386	4 045	5 702
C(126)	6 102	4 000	3 740	C(315)	1 912	4 707	5 589
C(121)	5 592	4 051	4 021	C(316)	1 852	5 313	5 043
C(132)	5 283(2)	6 292(3)	2 820(2)	C(311)	1 267	5 257	4 610
C(133)	5 257	6 549	2 224	C(322)	−4(2)	7 085(3)	3 355(2)
C(134)	4 814	5 909	1 775	C(323)	−626	6 982	2 981
C(135)	4 396	5 012	1 921	C(324)	−852	5 809	2 736
C(136)	4 421	4 755	2 517	C(325)	−456	4 738	2 866
C(131)	4 864	5 396	2 967	C(326)	165	4 840	3 240
Au(2)	1 887(1)	5 289(1)	3 297(1)	C(321)	391	6 014	3 484
P(2)	2 009(1)	5 868(1)	2 362(1)	C(332)	1 092(2)	8 270(4)	4 557(2)
C(212)	3 186(2)	7 133(3)	2 474(2)	C(333)	1 237	9 519	4 742
C(213)	3 597	8 180	2 612	C(334)	1 691	10 208	4 524
C(214)	3 346	9 360	2 714	C(335)	1 999	9 647	4 122
C(215)	2 685	9 492	2 678	C(336)	1 854	8 397	3 937
C(216)	2 274	8 444	2 541	C(331)	1 400	7 709	4 155

* See footnote to Table 2.

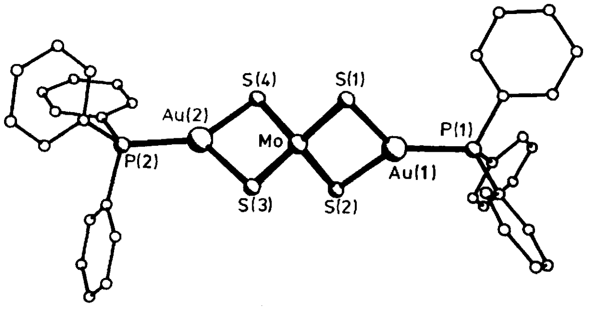

Figure 1. Molecular structure of $[MoS_4(AuPPh_3)_2]$ (**1**)

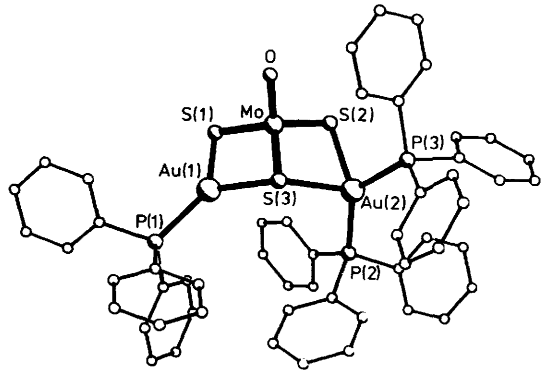

Figure 2. Molecular structure of $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ (**2**)

in Table 6. The ^{95}Mo n.m.r. chemical shifts for the two copper clusters correspond well with the values reported by Minelli *et al.*[5] for these thiomolybdate centres co-ordinated by two copper atoms. Clearly, silver and gold also shield the ^{95}Mo nucleus in $[MoS_4]^{2-}$ when co-ordinated to this entity. Furthermore, the differences in ^{95}Mo chemical shifts between similar complexes containing the $[MoS_4]^{2-}$ and $[MoOS_3]^{2-}$ centres are of the expected sign and magnitude.[6] Comparing the structurally analogous $[MoS_4(MPPh_3)\{M(PPh_3)_2\}]$ (M = Cu or Ag) complexes,[8,10] it is seen that replacing Cu by Ag leads to a *deshielding* of the ^{95}Mo nucleus by 121 p.p.m. A similar effect is seen in the ^{95}Mo and ^{183}W n.m.r. spectra of some Cu and Ag cyano–thiometalate complexes,[6] $[MS_4(M'CN)]^{2-}$ (M = Mo or W, M′ = Cu or Ag), where the ^{95}Mo chemical shifts are 1 854 p.p.m. for the Cu complex and 1 921 p.p.m. for the silver complex. Interestingly, the increased deshielding on going from Cu to Ag does not extend to the gold clusters. Thus, comparing the ^{95}Mo chemical shifts of the Mo nuclei in $[MoOS_3(MPPh_3)\{M(PPh_3)_2\}]$ (M = Cu or Au), the ^{95}Mo nucleus in the gold cluster is more *shielded* by 247 p.p.m.

It is known that tertiary phosphine ligands in complexes of this type are labile,[14,15] and it was therefore of interest to monitor the behaviour of the ^{95}Mo n.m.r. chemical shift of these complexes when additional phosphine was present. The dependence of the ^{95}Mo n.m.r. chemical shift, for three of the complexes studied, on the mole ratio of PPh_3 added to the solution is shown in Table 7. Clearly, addition of PPh_3 leads to a decrease in shielding of the ^{95}Mo nucleus; it is especially interesting to note that the chemical shifts for $[MoS_4\{Ag(PPh_3)_2\}_2]$, and for $[MoS_4(AgPPh_3)\{Ag(PPh_3)_2\}]$ plus one equivalent of PPh_3, are the same within experimental uncertainty (±3 p.p.m.).

Table 4. Selected bond lengths (Å) and interbond angles (°) for $[MoS_4(AuPPh_3)_2]$ (**1**), with estimated standard deviations in parentheses

Mo–S(1)	2.213(2)	Au(1)–P(1)	2.272(2)
Mo–S(2)	2.212(2)	Au(2)–S(3)	2.413(2)
Mo–S(3)	2.217(2)	Au(2)–S(4)	2.405(2)
Mo–S(4)	2.213(2)	Au(2)–P(2)	2.272(2)
Au(1)–S(1)	2.410(2)	Mo–Au(1)	2.801(1)
Au(1)–S(2)	2.392(2)	Mo–Au(2)	2.818(1)
S(1)–Mo–S(2)	111.5(1)	S(1)–Mo–S(3)	108.4(1)
S(2)–Mo–S(3)	108.9(1)	S(1)–Mo–S(4)	108.1(1)
S(2)–Mo–S(4)	108.7(1)	S(3)–Mo–S(4)	111.3(1)
S(1)–Mo–Au(1)	56.0(1)	S(2)–Mo–Au(1)	55.5(1)
S(3)–Mo–Au(1)	125.3(1)	S(4)–Mo–Au(1)	123.4(1)
S(1)–Mo–Au(2)	125.1(1)	S(2)–Mo–Au(2)	123.4(1)
S(3)–Mo–Au(2)	55.7(1)	S(4)–Mo–Au(2)	55.6(1)
Au(1)–Mo–Au(2)	178.5(1)	Mo–S(1)–Au(1)	74.5(1)
Mo–S(2)–Au(1)	74.8(1)	Mo–S(3)–Au(2)	74.8(1)
Mo–S(4)–Au(2)	75.1(1)	Mo–Au(1)–S(1)	49.6(1)
Mo–Au(1)–S(2)	49.7(1)	S(1)–Au(1)–S(2)	99.2(1)
Mo–Au(1)–P(1)	175.3(1)	S(1)–Au(1)–P(1)	126.0(1)
S(2)–Au(1)–P(1)	134.7(1)	Mo–Au(2)–S(4)	49.4(1)
Mo–Au(2)–S(3)	49.4(1)	Mo–Au(2)–P(2)	173.0(1)
S(4)–Au(2)–P(2)	133.3(1)	S(3)–Au(2)–S(4)	98.8(1)
		S(3)–Au(2)–P(2)	127.5(1)

Table 5. Selected bond lengths (Å) and interbond angles (°) for $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ (**2**), with estimated standard deviations in parentheses

Mo–O	1.701(4)	Mo–S(1)	2.251(2)
Mo–S(2)	2.211(2)	Mo–S(3)	2.271(2)
Mo–Au(1)	2.838(1)	Mo–Au(2)	3.133(1)
S(1)–Au(1)	2.402(2)	S(2)–Au(2)	2.604(2)
S(3)–Au(1)	2.437(2)	S(3)–Au(2)	2.684(2)
Au(1)–P(1)	2.277(2)	Au(2)–P(3)	2.360(2)
Au(2)–P(2)	2.325(2)		
O–Mo–S(1)	108.0(2)	O–Mo–S(2)	108.8(1)
S(1)–Mo–S(2)	109.0(1)	O–Mo–S(3)	108.6(2)
S(1)–Mo–S(3)	110.4(1)	S(2)–Mo–S(3)	112.0(1)
O–Mo–Au(1)	119.8(1)	S(1)–Mo–Au(1)	54.9(1)
S(2)–Mo–Au(1)	131.3(1)	S(3)–Mo–Au(1)	55.7(1)
O–Mo–Au(2)	126.5(1)	S(1)–Mo–Au(2)	125.5(1)
S(2)–Mo–Au(2)	55.1(1)	S(3)–Mo–Au(2)	56.9(1)
Au(1)–Mo–Au(2)	94.5(1)	Mo–S(1)–Au(1)	75.1(1)
Mo–S(2)–Au(2)	80.7(1)	Mo–S(3)–Au(1)	74.0(1)
Mo–S(3)–Au(2)	77.9(1)	Au(1)–S(3)–Au(2)	118.0(1)
Mo–Au(1)–S(1)	50.0(1)	Mo–Au(1)–S(3)	50.3(1)
S(1)–Au(1)–S(3)	100.2(1)	Mo–Au(1)–P(1)	175.1(1)
S(1)–Au(1)–P(1)	133.6(1)	S(3)–Au(1)–P(1)	126.1(1)
Mo–Au(2)–S(2)	44.1(1)	Mo–Au(2)–S(3)	45.2(1)
S(2)–Au(2)–S(3)	89.3(1)	Mo–Au(2)–P(2)	121.7(1)
S(2)–Au(2)–P(2)	114.9(1)	S(3)–Au(2)–P(2)	110.4(1)
Mo–Au(2)–P(3)	105.1(1)	S(2)–Au(2)–P(3)	101.0(1)
S(3)–Au(2)–P(3)	99.0(1)	P(2)–Au(2)–P(3)	133.0(1)

Table 6. Molybdenum-95 n.m.r. data (19.55 MHz) for triphenylphosphine–coinage metal–thiomolybdate clusters in CH_2Cl_2

Compound*	δ/p.p.m.	$\Delta\nu_{\frac{1}{2}}$/Hz
$[MoS_4(AuPPh_3)_2]$ (**1**)	1 521	200
$[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$ (**2**)	758	500
$[MoS_4(AgPPh_3)\{Ag(PPh_3)_2\}]$	1 848	100
$[MoS_4\{Ag(PPh_3)_2\}_2]$	1 863	50
$[MoS_4(CuPPh_3)\{Cu(PPh_3)_2\}]$	1 727	250
$[MoOS_3(CuPPh_3)\{Cu(PPh_3)_2\}]$	1 005	250

* Because the PPh_3 ligands dissociate from the complex in solution, the exact nature of the species producing the signal is unclear.

Table 7. Dependence of ^{95}Mo n.m.r. chemical shifts of triphenylphosphine–coinage metal–thiomolybdate clusters in CH_2Cl_2 on mole ratio of PPh_3 added

	Mole ratio (added $[PPh_3]:[Mo]$)				
Compound*	0	1	2	4	10
$[MoS_4(AuPPh_3)_2]$ (**1**)	1 521	1 522	1 526	1 539	1 565
$[MoS_4(AgPPh_3)\{Ag(PPh_3)_2\}]$	1 848	1 861	1 867	1 877	1 900
$[MoS_4(CuPPh_3)\{Cu(PPh_3)_2\}]$	1 727				1 737

* See footnote to Table 6.

Three conclusions can be drawn from these studies. First, the binding of Cu, Ag, and Au to a thiomolybdate unit influences the chemical shift of the molybdenum nucleus, but the change in chemical shift induced is not regular down the group of coinage metals, the extent of shielding varying as Au > Cu > Ag. Secondly, addition of PPh_3 to solutions of the complexes listed in Table 7 causes a decrease in shielding of the molybdenum nucleus in each case; since the binding of PPh_3 is remote from molybdenum, this change in chemical shift implies a direct interaction between the central molybdenum atom and the coinage metal. Thirdly, the simplest interpretation of the ^{95}Mo chemical shift data in Tables 6 and 7 supports the view[14,15] that the PPh_3 ligands of these complexes are labile since, in each case and irrespective of the mole ratio of added PPh_3 to Mo present, a single ^{95}Mo resonance is observed. This lability prevents a direct quantification of the number of PPh_3 molecules bound to the coinage metals of a particular Mo–S–M (M = Cu, Ag, or Au) cluster in solution by means of ^{95}Mo n.m.r. spectroscopy.

Acknowledgements

We thank the S.E.R.C. for the award of research studentships (to S. B. and J. R. N.) and a post-doctoral fellowship (to J. M. C.). Crystal structure determinations (by W. C.) were carried out at the University of Göttingen.

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Received 19*th February* 1986; *Paper* 6/353