In memory of T. A. Stephenson

Mixed-metal Phosphinito Complexes of Platinum(II) and Palladium(II) with Lanthanide and Actinide Elements. The Single-crystal *X*-Ray Structure of $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$†

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The synthesis of the phosphinito-bridged heteronuclear complexes $[M'\{(OPPh_2)_2M(S_2CNR_2)\}_n]$ ($M' = Ce^{III}$, Eu^{III}, Sm^{III}, or Nd^{III}, $n = 3$; $M' = Th^{IV}$, $n = 4$) and $[UO_2(OH_2)\{(OPPh_2)_2M(S_2CNR_2)\}_2]$ by reaction of $[M(S_2CNR_2)\{(Ph_2PO)_2H\}]$ (M = Pd or Pt, R = Et or Pr^i) with lanthanide and actinide salts is described. $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$ crystallises in the monoclinic space group *C*2/*c* with $a = 26.285(8)$, $b = 13.870(8)$, $c = 21.068(6)$ Å, $\beta = 90.042(8)°$, and $Z = 4$. The single-crystal *X*-ray structure of the complex shows a distorted pentagonal bipyramidal uranium(VI) ion lying on a crystallographic two-fold axis with the oxo ligands of the *trans*-UO_2 moiety, U=O = 1.774(7) Å, occupying apical sites. The structure confirms co-ordination of two $[(OPPh_2)_2Pd(S_2CNEt_2)]^-$ moieties around U^{VI}. The four phosphinito ligands bridge U^{VI} and the two Pd^{II} centres with U–O = 2.289(7) and 2.342(6) Å and Pd–P = 2.2642(24) and 2.2455(23) Å. An aqua ligand, U–O = 2.526(8) Å, completes the co-ordination sphere around the uranyl centre. The Pd^{II} centres are essentially planar, each being bound to two phosphinito and one bidentate dithiocarbamate ligand, Pd–S = 2.386(3) and 2.373(3) Å.

It is now well established that reaction of the hydrogen-bonded chelates $[M(S_2CNR_2)\{(Ph_2PO)_2H\}]$ (M = Ni, Pd, or Pt; R = Et or Pr^i) with various transition-metal and main-group metal acetylacetonates gives good yields of heterometallic complexes of general type $[M'\{(OPPh_2)_2M(S_2CNR_2)\}_n]$ ($M' = VO^{IV}$, Co^{II}, Cu^{II}, or Ni^{II}, $n = 2$; $M' = Mn^{III}$, $n = 3$).[1,2] The structures of these compounds have been assigned by spectral, magnetic, and analytical data[1,2] and in the cases of $[Co\{(OPPh_2)_2Pt(S_2CNEt_2)\}_2]$ and $[Co\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$ by single-crystal *X*-ray structural determinations.[2,3] For many of these complexes the exact conditions of preparation and choice of solvent were critical. Thus the preparation of $[Pd\{(OPPh_2)_2Ni(S_2CNR_2)\}_2]$ or $[Pt\{(OPPh_2)_2Ni(S_2CNR_2)\}_2]$ could be achieved by the reaction of $[Ni(S_2CNR_2)(OPPh_2)_2]$ with $[Pd(acac)_2]$ or $[Pt(acac)_2]$ (acac = acetylacetonate) in high boiling solvents such as *m*-xylene. The use of substituted phosphinito ligands R_2PO^- and R_2PS^- as bridging functions in polymetallic systems has been reported by several groups.[4–8]

We report herein a continuation of these studies and describe the reactions of $[M(S_2CNR_2)\{(Ph_2PO)_2H\}]$ (M = Pd or Pt, R = Et or Pr^i) with lanthanide and actinide salts in *m*-xylene or toluene to afford the mixed-metal complexes $[M'\{(OPPh_2)_2M(S_2CNR_2)\}_n]$ ($M' = Ce^{III}$, Eu^{III}, Sm^{III}, or Nd^{III}, $n = 3$; $M' = Th^{IV}$, $n = 4$) and $[UO_2(OH_2)\{(OPPh_2)_2M(S_2CNR_2)\}_2]$. The single-crystal *X*-ray structure of $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$ is described.

Results and Discussion

Reaction of $Na_2[MCl_4]$ (M = Pd or Pt) with $Na[S_2CNR_2]$ (R = Et or Pr^i) gives the complexes $[M(S_2CNR_2)_2]$ which react with Ph_2PCl under aqueous conditions to afford the species $[M(S_2CNR_2)\{(Ph_2PO)_2H\}]$. The single-crystal *X*-ray structure of $[Pd(S_2CNMe_2)\{(Ph_2PO)_2H\}]$ has been reported previously.[9] Reaction of $[M(S_2CNR_2)\{(Ph_2PO)_2H\}]$ with chloride, nitrate, or acetate salts of actinide or lanthanide elements in refluxing *m*-xylene–EtOH or toluene–EtOH gave good yields of heteronuclear complexes. These products were isolated by addition of a mixture of diethyl ether and light petroleum. They show little or no solubility in non-polar solvents or in MeOH, EtOH, or acetone, but can be recrystallised from $CHCl_3$. Solubility of the products was enhanced by use of the isopropyl dithiocarbamates. The purity of the compounds was confirmed by ^{31}P n.m.r. spectroscopy. Analytical data for the complexes are consistent with the formulation of the heteronuclear species $[M'\{(OPPh_2)_2M(S_2CNR_2)\}_n]$ ($M' = Ce^{III}$, Eu^{III}, Sm^{III}, or Nd^{III}, $n = 3$; $M' = Th^{IV}$, $n = 4$) and $[UO_2(OH_2)\{(OPPh_2)_2M(S_2CNR_2)\}_2]$. The i.r. spectra of the complexes show absorption bands near 1 050 and 1 530 cm^{-1} assigned to the phosphorus–oxygen, ν(P–O), and imine, ν(C=N), stretching vibrations. These results are indicative of bidentate $[S_2CNR_2]^-$ co-ordination.[10] The magnetic moments of the lanthanide complexes are consistent with the above formulation.

To confirm the stereochemistry and connectivity of the products, single crystals of $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$, suitable for diffraction studies, were grown from $CHCl_3$. The single-crystal *X*-ray structure of $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$ is illustrated in the Figure together with the numbering scheme adopted. Each molecule lies on a crystallographic two-fold axis which passes through the U atom and the co-ordinated oxygen of the water molecule. The U^{VI} ion shows a distorted pentagonal-bipyramidal stereochemistry

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† Aquabis[(*N*,*N*-diethyldithiocarbamato)bis(diphenylphosphinito-*P*)palladium(II)-*O*,*O*′]dioxouranium(VI).

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

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m^2.

with the oxo ligands of the *trans*-UO_2 moiety, U=O = 1.774(7) Å, occupying apical sites. Four phosphinito oxygen donors, U–O = 2.289(7) and 2.342(6) Å, and an aqua ligand, U–O = 2.526(8) Å, complete the co-ordination sphere around the uranyl centre. The structure confirms co-ordination of two $[(OPPh_2)_2Pd(S_2CNEt_2)]^-$ moieties around U^{VI}. The Pd^{II} centres are essentially planar with Pd–S = 2.386(3) and 2.373(3) Å and Pd–P = 2.2642(24) and 2.2455(23) Å. Bond lengths, bond angles, and fractional co-ordinates are given in Tables 1—3.

For the complexes $[M'\{(OPPh_2)_2M(S_2CNR_2)\}_3]$ (M′ = Ce^{III}, Eu^{III}, Sm^{III}, or Nd^{III}) octahedral geometry about M′ is proposed with the six $OPPh_2$ ligands bridging M and M′. For $[Th\{(OPPh_2)_2M(S_2CNR_2)\}_4]$ eight-co-ordination around the Th^{IV} centre appears likely. Our results are in agreement with the results of Sperline and Roundhill[4] who have previously reported the synthesis of the mixed-metal phosphinito complexes $[UO_2\{[OP(OMe)_2]_2PtCl(PEt_3)\}_2]$ and $[Th\{[OP(OMe)_2]_2PtCl(PPh_3)\}_4]$.

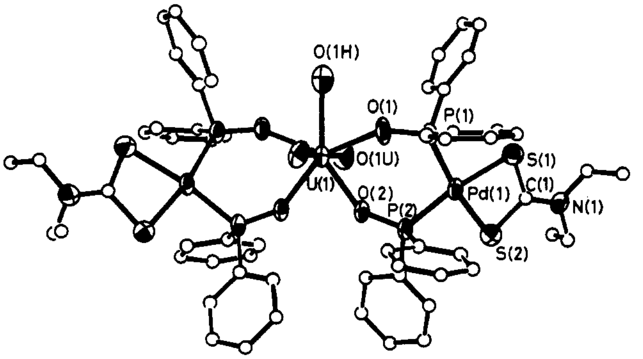

Figure. Structure of $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$ showing the numbering scheme

Table 1. Bond lengths (Å) with estimated standard deviations in parentheses

U(1)–O(1U)	1.774(7)	O(2)–P(2)	1.526(7)
U(1)–O(1H)	2.526(8)	P(2)–C(211)	1.810(6)
U(1)–O(1)	2.289(7)	P(2)–C(221)	1.807(7)
U(1)–O(2)	2.342(6)	S(1)–C(1)	1.727(10)
Pd(1)–P(1)	2.264 2(24)	S(2)–C(1)	1.688(10)
Pd(1)–P(2)	2.245 5(23)	C(1)–N(1)	1.341(13)
Pd(1)–S(1)	2.386(3)	N(1)–C(11)	1.462(14)
Pd(1)–S(2)	2.373(3)	N(1)–C(21)	1.449(16)
P(1)–C(111)	1.819(7)	C(11)–C(12)	1.587(18)
P(1)–C(121)	1.803(7)	C(21)–C(22)	1.536(24)
P(1)–O(1)	1.524(7)		

The ability of substituted phosphinito ligands R_2PO^- to bind to both soft and hard metal ions *via* P- and O-donors respectively has been demonstrated, and represents an important route to the synthesis of heteronuclear complexes.

Experimental

Microanalyses (C, H, or N) were carried out using a Carlo-Erba elemental analyzer and metal analyses using a Perkin-Elmer 373 atomic absorption spectrophotometer. Infrared spectra were recorded in the range 4 000—600 cm^{-1} on a Perkin-Elmer 257 spectrometer using KBr discs, while electronic spectra were obtained in the solid state on a Beckmann Acta M(IV) spectrophotometer. Magnetic measurements were made on a Newport variable-temperature magnetic balance using $Hg[Co(SCN)_4]$ as calibrant. ^1H N.m.r. spectra were obtained on a Perkin-Elmer R-12 spectrometer and ^{31}P n.m.r. spectra on a JEOL 60Q spectrometer. The light petroleum used was that fraction of b.p. 60—80 °C.

Structure Determination of $[UO_2(OH_2)\{(OPPh_2)_2Pd(S_2CNEt_2)\}_2]$.—*Crystal data.* $C_{58}H_{62}N_2O_7P_4Pd_2S_4U\cdot 2H_2O$, $M = 1\,638.1$, monoclinic, space group $C2/c$, $a = 26.285(8)$, $b = 13.870(8)$, $c = 21.068(6)$ Å, $\beta = 90.042(8)°$, $U = 7\,681$ Å^3, $T = 295$ K, $D_c = 1.416$ g cm^{-3}, $Z = 4$. Sample: pale yellow, columnar crystal, 1.4 × 0.56 × 0.56 mm: $F(000) = 3\,232$, $\mu(\text{Mo-}K_\alpha) = 26.81$ cm^{-1}.

Data collection and processing. STADI-2 diffractometer, ω scans with scan width $2.0 + 0.8(\sin\mu/\tan\theta)$, graphite-monochromated Mo-K_α X-radiation ($\bar{\lambda} = 0.710\,73$ Å); 6 874 reflections measured ($2.5 \leqslant \theta \leqslant 25°$, $\pm h$, $+k$, $+l$), 6 666 unique, giving 5 002 with $F \geqslant 6\sigma(F)$, no significant crystal decay or movement. Crystals could not be cut satisfactorily, and it was therefore necessary to use a long specimen and irradiate a constant volume.

Structure solution and refinement. Patterson synthesis (U) and iterative combination of least-squares cycles and difference Fourier syntheses located all the non-hydrogen atoms. At isotropic convergence, an empirical absorption correction[11] was applied (max. and min. corrections 1.327 and 0.764 respectively). Full-matrix least squares (F) with non-water H atoms in calculated positions[12] converged satisfactorily to give final $R,R' = 0.0610, 0.0862$ respectively. The weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0105F_o^{\,2}$ gave good agreement analysis; $(\Delta/\sigma)_{\text{max.}}$ in final cycle 0.01, maximum and minimum residues in the ultimate ΔF synthesis were 2.65 and −3.36 e Å^{-3}

Table 2. Angles (°) with estimated standard deviations in parentheses

O(1U)–U(1)–O(1)	88.8(3)	S(1)–Pd(1)–S(2)	73.96(9)	O(2)–P(2)–C(221)	106.3(3)
O(1U)–U(1)–O(2)	90.8(3)	Pd(1)–P(1)–C(111)	109.18(24)	C(211)–P(2)–C(221)	108.0(3)
O(1U)–U(1)–O(1U′)	178.9(3)	Pd(1)–P(1)–C(121)	112.2(3)	P(2)–C(211)–C(212)	115.0(4)
O(1U)–U(1)–O(1′)	92.0(3)	Pd(1)–P(1)–O(1)	119.2(3)	P(2)–C(211)–C(216)	125.0(5)
O(1U)–U(1)–O(2′)	88.9(3)	C(111)–P(1)–C(121)	103.7(3)	P(2)–C(221)–C(222)	122.0(5)
O(1H)–U(1)–O(1U)	89.5(3)	C(111)–P(1)–O(1)	106.4(4)	P(2)–C(221)–C(226)	117.7(5)
O(1H)–U(1)–O(1)	142.16(24)	C(121)–P(1)–O(1)	105.1(4)	Pd(1)–S(1)–C(1)	85.3(3)
O(1H)–U(1)–O(2)	68.82(24)	P(1)–C(111)–C(112)	120.1(5)	Pd(1)–S(2)–C(1)	86.6(3)
O(1)–U(1)–O(2)	73.41(23)	P(1)–C(111)–C(116)	120.0(5)	S(1)–C(1)–S(2)	113.9(5)
O(1)–U(1)–O(1′)	75.68(24)	P(1)–C(121)–C(122)	122.3(5)	S(1)–C(1)–N(1)	122.6(7)
O(1)–U(1)–O(2′)	148.89(23)	P(1)–C(121)–C(126)	117.7(5)	S(2)–C(1)–N(1)	123.4(7)
O(2)–U(1)–O(2′)	137.63(22)	U(1)–O(1)–P(1)	143.8(4)	C(1)–N(1)–C(11)	122.9(9)
P(1)–Pd(1)–P(2)	89.90(8)	U(1)–O(2)–P(2)	139.9(4)	C(1)–N(1)–C(21)	121.1(9)
P(1)–Pd(1)–S(1)	101.47(9)	Pd(1)–P(2)–O(2)	120.7(3)	C(11)–N(1)–C(21)	115.9(9)
P(1)–Pd(1)–S(2)	172.51(9)	Pd(1)–P(2)–C(211)	107.73(21)	N(1)–C(11)–C(12)	108.8(9)
P(2)–Pd(1)–S(1)	168.60(9)	Pd(1)–P(2)–C(221)	107.94(22)	N(1)–C(21)–C(22)	112.3(12)
P(2)–Pd(1)–S(2)	94.82(9)	O(2)–P(2)–C(211)	105.7(3)		

Table 3. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
U(1)	0.5	0.308 27(3)	0.25
O(1U)	0.478 3(3)	0.309 5(5)	0.329 7(3)
O(1H)	0.5	0.490 4(10)	0.25
Pd(1)	0.334 87(2)	0.234 51(5)	0.284 34(3)
P(1)	0.394 94(9)	0.138 82(15)	0.240 07(12)
C(111)	0.373 53(24)	0.100 6(6)	0.161 9(3)
C(112)	0.408 60(24)	0.088 8(6)	0.112 8(3)
C(113)	0.392 22(24)	0.058 9(6)	0.053 1(3)
C(114)	0.340 72(24)	0.040 8(6)	0.042 2(3)
C(115)	0.305 62(24)	0.052 6(6)	0.091 3(3)
C(116)	0.322 01(24)	0.082 5(6)	0.151 1(3)
C(121)	0.402 8(3)	0.027 2(4)	0.282 8(4)
C(122)	0.365 7(3)	−0.044 8(4)	0.282 6(4)
C(123)	0.373 4(3)	−0.129 3(4)	0.317 3(4)
C(124)	0.418 0(3)	−0.141 7(4)	0.352 1(4)
C(125)	0.455 1(3)	−0.069 7(4)	0.352 3(4)
C(126)	0.447 4(3)	0.014 7(4)	0.317 7(4)
O(1)	0.448 69(24)	0.178 0(4)	0.231 4(4)
O(2)	0.421 84(23)	0.369 3(5)	0.214 8(3)
P(2)	0.365 15(8)	0.360 92(16)	0.229 53(11)
C(211)	0.348 9(3)	0.469 2(4)	0.272 9(3)
C(212)	0.370 7(3)	0.476 5(4)	0.333 1(3)
C(213)	0.360 3(3)	0.556 3(4)	0.371 2(3)
C(214)	0.328 1(3)	0.629 0(4)	0.349 1(3)
C(215)	0.306 3(3)	0.621 7(4)	0.288 9(3)
C(216)	0.316 7(3)	0.541 9(4)	0.250 8(3)
C(221)	0.332 63(23)	0.364 7(5)	0.153 96(25)
C(222)	0.279 68(23)	0.367 7(5)	0.149 64(25)
C(223)	0.256 01(23)	0.359 7(5)	0.090 63(25)
C(224)	0.285 25(23)	0.348 7(5)	0.035 86(25)
C(225)	0.338 19(23)	0.345 6(5)	0.040 18(25)
C(226)	0.361 89(23)	0.353 6(5)	0.099 21(25)
S(1)	0.291 63(10)	0.123 27(17)	0.351 75(13)
S(2)	0.264 13(10)	0.319 27(17)	0.326 54(13)
C(1)	0.248 0(3)	0.214 9(7)	0.362 5(4)
N(1)	0.205 7(3)	0.204 1(6)	0.397 4(4)
C(11)	0.193 6(4)	0.114 8(9)	0.431 1(5)
C(12)	0.213 2(6)	0.123 5(11)	0.502 1(6)
C(21)	0.170 0(5)	0.282 7(9)	0.405 5(7)
C(22)	0.125 6(6)	0.277 5(14)	0.358 2(10)
O(1W)	0.436 0(4)	0.374 6(8)	0.490 2(5)
O(2W)	0.097 7(6)	0.709 9(12)	0.065 4(7)

respectively, $S = 0.810$. Molecular geometry calculations were performed using CALC.[13] The Figure was produced from ORTEPII.[14] Atomic scattering factors were inlaid (SHELX 76[12]) or taken from ref. 15.

Tris[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*palladium*(II)-O,O′]*cerium*(III).—[Pd(S_2CNEt_2){$(Ph_2PO)_2H$}] (1.0 g, 1.52 mmol) was refluxed in toluene (30 cm^3) for 10 min and $CeCl_3 \cdot 7H_2O$ (0.18 g, 0.48 mmol) dissolved in EtOH (20 cm^3) was added. The reaction mixture was refluxed for 8 h under N_2 and the solution reduced in volume before adding diethyl ether–light petroleum (50 cm^3, 50:50). The orange precipitate was filtered off, washed with diethyl ether, recrystallised from $CHCl_3$ and dried *in vacuo* (yield = 0.58 g, 50%) (Found: C, 47.9; H, 4.4; Ce, 6.4; N, 2.0; Pd, 14.9. Calc. for $C_{87}H_{90}CeN_3O_6P_6Pd_3S_6$: C, 49.5; H, 4.3; Ce, 6.6; N, 2.3; Pd, 15.1%); $\mu_{eff.}$ = 2.45 B.M. at 292 K. Electronic spectrum: 35 710 cm^{-1}. ^1H N.m.r.: δ, 6.8—7.8 (Ph), 3.5—3.9 (CH_2), 1.0—1.5 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 112.6 p.p.m.

Tris[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*palladium*(II)-O,O′]*neodymium*(III).—[Pd(S_2CNEt_2){$(Ph_2PO)_2H$}] (0.8 g, 1.2 mmol) was refluxed in *m*-xylene (30 cm^3) for 30 min and $NdCl_3 \cdot 6H_2O$ (0.17 g, 0.47 mmol) dissolved in EtOH (10 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether–light petroleum (50 cm^3, 70:30). The pale green precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (yield = 0.76 g, 77%) (Found: C, 49.0; H, 4.3; N, 1.9; Nd, 6.7; Pd, 14.8. Calc. for $C_{87}H_{90}N_3NdO_6P_6Pd_3S_6$: C, 49.4; H, 4.3; N, 2.0; Nd, 6.8; Pd, 15.1%); $\mu_{eff.}$ = 2.81 B.M. at 292 K. Electronic spectrum: 33 333, 18 870, 17 758, 11 500 cm^{-1}. ^1H N.m.r.: δ, 6.2—7.9 (Ph), 4.1—4.7 (CH_2), 1.0—1.9 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 138.7 p.p.m.

Tris[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*palladium*(II)-O,O′]*europium*(III).—[Pd(S_2CNEt_2){$(Ph_2PO)_2H$}] (0.9 g, 1.37 mmol) was refluxed in *m*-xylene (30 cm^3) for 15 min and $EuCl_3$ (0.13 g, 0.5 mmol) dissolved in EtOH (10 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether (50 cm^3). The solution was left to stand for 24 h and the pale yellow precipitate filtered off, washed with diethyl ether, and dried *in vacuo* (yield 0.7 g, 69%) (Found: C, 49.8; H, 4.3; Eu, 6.7; N, 1.8; Pd, 14.5. Calc. for $C_{87}H_{90}EuN_3O_6P_6Pd_3S_6$: C, 49.2; H, 4.3; Eu, 7.1; N, 2.0; Pd, 15.1%); $\mu_{eff.}$ = 3.91 B.M. at 296 K. Electronic spectrum: 29 850 cm^{-1}. ^1H N.m.r.: δ, 7.1—9.0 (Ph), 2.8—3.4 (CH_2), 1.0—4.0 p.p.m. (CH_3); ^{31}P n.m.r.: δ, −0.8 p.p.m.

Tris[(N,N′-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*palladium*(II)-O,O′]*samarium*(III).—[Pd(S_2CNEt_2){$Ph_2PO)_2H$}] (0.9 g, 1.37 mmol) was refluxed in *m*-xylene (30 cm^3) for 30 min and $SmCl_3 \cdot 6H_2O$ (0.18 g, 0.46 mmol) dissolved in EtOH (15 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether (50 cm^3). The white precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (yield = 0.65 g, 60%) (Found: C, 48.9; H, 4.3; N, 1.9; Pd, 15.2; Sm, 6.8. Calc. for $C_{87}H_{90}N_3O_6P_6Pd_3S_6Sm$: C, 49.3; H, 4.3; N, 2.0; Pd, 15.1; Sm, 7.1%); $\mu_{eff.}$ = 2.20 B.M. at 296 K. Electronic spectrum: 28 100 cm^{-1}. ^1H N.m.r.: δ, 6.6—7.6 (Ph), 3.6—4.1 (CH_2), 1.1—1.5 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 79.3 p.p.m.

Tetrakis[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*palladium*(II)-O,O′]*thorium*(IV).—[Pd(S_2CNEt_2){$Ph_2PO)_2H$}] (1.0 g, 1.52 mmol) was refluxed in *m*-xylene (30 cm^3) for 30 min and $Th(NO_3)_4$ (0.25 g, 0.52 mmol) dissolved in EtOH (15 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether (50 cm^3). The yellow precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (yield = 0.78 g, 62%) (Found: C, 48.5; H, 4.3; N, 2.0; Pd, 15.1; Th, 7.9. Calc. for $C_{116}H_{120}N_4O_8P_8Pd_4S_8Th$: C, 48.7; H, 4.2; N, 2.0; Pd, 14.9; Th, 8.1%); $\mu_{eff.}$ = 3.91 B.M. at 292 K. Electronic spectrum: 29 412 cm^{-1}. ^1H N.m.r.: δ, 6.7—8.0 (Ph), 3.4—3.9 (CH_2), 1.0—1.4 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 92.3 p.p.m.

Aquabis[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*palladium*(II)-O,O′]*dioxouranium*(VI).—[Pd(S_2CNEt_2){$Ph_2PO)_2H$}] (1.0 g, 1.52 mmol) was refluxed in toluene (30 cm^3) for 15 min and [$UO_2(CH_3COO)_2$] (0.31 g, 0.73 mmol) dissolved in EtOH (20 cm^3) was added. The reaction mixture was refluxed for 3 h under N_2 and the solution reduced in volume before adding diethyl ether (50 cm^3). The yellow precipitate was filtered off, washed with diethyl ether, recrystallised from $CHCl_3$, and dried *in vacuo* (yield = 1.2 g, 90%) (Found: C, 42.5; H, 3.6; N, 1.6; Pd, 12.9; U, 14.9. Calc. for $C_{58}H_{62}N_2O_7P_4Pd_2S_4U$: C, 43.5; H, 3.7; N, 1.8; Pd, 13.5, U, 14.9%). Electronic spectrum: 38 800 cm^{-1}. ^1H N.m.r.: δ, 7.0—8.1 (Ph), 3.45—4.0 (CH_2), 1.0—1.4 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 99.6 p.p.m.

Tris[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*platinum*(II)-O,O′]*cerium*(III).—[Pt(S_2CNEt_2){$(Ph_2PO)_2H$}] (1.0 g, 1.29 mmol) was refluxed in toluene (30 cm^3) for 15 min and $CeCl_3 \cdot 7H_2O$ (0.16 g, 0.43 mmol) dissolved in EtOH (20 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether (50 cm^3). The orange precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (yield = 0.78 g, 68%) (Found: C, 42.5; H, 3.7; Ce, 6.7; N, 1.6; Pt, 25.3. Calc. for $C_{87}H_{90}CeN_3O_6P_6Pt_3S_6$: C, 43.9; H, 3.8; Ce, 5.9; N, 1.8; Pt, 24.6%); $\mu_{eff.}$ = 2.12 B.M. at 292 K. Electronic spectrum: 34 480 cm^{-1}. ^1H N.m.r.: δ, 6.8—8.0 (Ph), 3.3—3.9 (CH_2), 1.0—1.5 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 83.1 p.p.m.

Tris[(N,N-*di-isopropyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*platinum*(II)-O,O′]*samarium*(III).—[Pt($S_2CNPr^i_2$){$(Ph_2PO)_2H$}] (0.78 g, 1.0 mmol) was refluxed in *m*-xylene (30 cm^3) for 30 min and $SmCl_3 \cdot 6H_2O$ (0.12 g, 0.33 mmol) dissolved in EtOH (15 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether–light petroleum (50 cm^3, 50:50). The cream precipitate was filtered off, washed with EtOH, and dried *in vacuo* (yield = 0.71 g, 74%) (Found: C, 45.6; H, 4.2; N, 1.7; Pt, 23.4; Sm, 5.9. Calc. for $C_{93}H_{102}N_3O_6P_6Pt_3S_6Sm$: C, 45.1; H, 4.1; N, 1.7; Pt, 23.7; Sm, 6.1%); $\mu_{eff.}$ = 2.18 B.M. at 296 K. Electronic spectrum: 31 250 cm^{-1}. ^1H N.m.r.: δ, 6.7—8.1 (Ph), 1.3—1.8 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 55.5 p.p.m.

Tris[(N,N-*di-isopropyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*platinum*(II)-O,O′]*europium*(III).—[Pt($S_2CNPr^i_2$){$(Ph_2PO)_2H$}] (1.0 g, 1.29 mmol) was refluxed in *m*-xylene (30 cm^3) for 15 min and $EuCl_3 \cdot 6H_2O$ (0.14 g, 0.54 mmol) dissolved in EtOH (15 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume before adding diethyl ether–light petroleum (50 cm^3, 70:30). The creamy precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (yield = 0.93 g, 86%) (Found: C, 45.3; H, 4.3; Eu, 5.9; N, 1.6; Pt, 23.4. Calc. for $C_{93}H_{102}EuN_3O_6P_6Pt_3S_6$: C, 45.1; H, 4.1, Eu, 6.1; N, 1.7; Pt, 23.7%); $\mu_{eff.}$ = 3.72 B.M. at 296 K. Electronic spectrum: 31 446 cm^{-1}. ^1H N.m.r.: δ, 7.1—9.1 (Ph), 1.0—1.2 p.p.m. (CH_3); ^{31}P n.m.r.: δ, −8.65 p.p.m.

Tetrakis[(N,N-*di-isopropyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*platinum*(II)-O,O′]*thorium*(IV).—[Pt($S_2CNPr^i_2$){$(Ph_2PO)_2H$}] (0.78 g, 1.00 mmol) was refluxed in *m*-xylene (30 cm^3) for 30 min and $Th(NO_3)_4$ (0.14 g, 0.29 mmol) dissolved in EtOH (15 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* (yield = 0.45 g, 41%) (Found: C, 44.2; H, 3.9; N, 1.7; Pt, 24.1; Th, 6.9. Calc. for $C_{124}H_{136}N_4O_8P_8Pt_4S_8Th$: C, 44.8; H, 4.1; N, 1.7; Pt, 23.4; Th, 7.0%). Electronic spectrum: 34 482 cm^{-1}. ^1H N.m.r.: δ, 6.7—8.2 (Ph), 1.1—1.7 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 65 p.p.m.

Aquabis[(N,N-*diethyldithiocarbamato*)*bis*(*diphenylphosphinito*-P)*platinum*(II)-O,O′]*dioxouranium*(VI).—[Pt(S_2CNEt_2)-{$(Ph_2PO)_2H$}] (1.0 g, 1.29 mmol) was refluxed in toluene (30 cm^3) for 15 min and $[UO_2(CH_3COO)_2] \cdot 2H_2O$ (0.28 g, 0.66 mmol) dissolved in EtOH (20 cm^3) was added. The reaction mixture was refluxed for 24 h under N_2 and the solution reduced in volume. The bright yellow precipitate was filtered off, washed with diethyl ether, recrystallised from $CHCl_3$, and dried *in vacuo* (yield = 1.1 g, 86%) (Found: C, 40.1; H, 3.4; N, 1.6; Pt, 22.3; U, 14.0. Calc. for $C_{58}H_{62}N_2O_7P_4Pt_2S_4U$: C, 39.1; H, 3.7; N, 1.6; Pt, 21.9; U, 13.4%). Electronic spectrum: 32 260 cm^{-1}. ^1H N.m.r.: δ, 7.0—8.0 (Ph), 3.2—3.7 (CH_2), 1.0—1.3 p.p.m. (CH_3); ^{31}P n.m.r.: δ, 74.4 p.p.m.

Acknowledgements

We thank the S.E.R.C. for support, and Johnson Matthey for generous loans of platinum metals.

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Received 24th February 1987; *Paper* 7/355