

Reactions of Chloro(triphenylphosphine)gold(I) and [μ -1,2-Bis-(diphenylphosphine)ethane]-bis[bromogold(I)] with Oxopurine Bases. Molecular and Crystal Structure and Bonding of (Theophyllinato)-(triphenylphosphine)gold(I) †

Enrique Colacio,* Antonio Romerosa, and Jose Ruiz

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Pascual Román* and Juan M. Gutiérrez-Zorrilla

Departamento de Química Inorgánica, Universidad de País Vasco, 48080 Bilbao, Spain

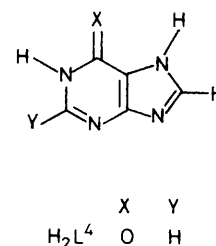
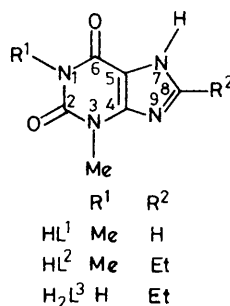
Martin Martínez-Ripoll

UEI Cristalografía, Instituto Rocasolano, C.S.I.C., 28006 Madrid, Spain

The interaction of chloro(triphenylphosphine)gold(I) and [μ -1,2-bis(diphenylphosphine)ethane]-bis[bromogold(I)] with oxopurine derivatives under basic conditions has been investigated. The resulting complexes, $[\text{Au}(\text{PPh}_3)\text{L}] [\{\text{Au}(\text{PPh}_3)\}_2(\mu\text{-L})]$, $[\text{LAu}(\mu\text{-dppe})\text{AuL}]$, and $[\text{Au}(\mu\text{-dppe})-(\mu\text{-L})\text{Au}]$ [$\text{L} = \text{purine anion}$, $\text{dppe} = 1,2\text{-bis(diphenylphosphine)ethane}$], containing one or two N-bonded gold(I) phosphine groups were characterized by means of ^1H and ^{13}C n.m.r. and i.r. spectroscopy. The crystal structure of the complex (theophyllinato)-(triphenylphosphine)-gold(I) was determined by X-ray crystallography. The compound is triclinic, space group $P\bar{1}$, with $a = 9.061(2)$, $b = 9.762(4)$, $c = 13.588(4)$ Å, $\alpha = 71.30(2)$, $\beta = 87.20(2)$, $\gamma = 86.10(2)^\circ$, and $Z = 2$. The structure was refined anisotropically to $R = 0.039$ and $R' = 0.044$, on the basis of 5 150 observed reflections. The crystal contains discrete $[\text{Au}(\text{PPh}_3)\text{L}]$ molecules ($\text{L} = \text{theophyllinato anion}$) with no unusually close intermolecular contacts. The co-ordination of the gold atom is almost linear, $\text{P-Au-N}(7)$ $176.1(2)^\circ$, with gold-nitrogen and gold-phosphorus bond distances of 2.047(6) and 2.231(2) Å, respectively. Other bond lengths and bond angles are normal. The $\text{Au}\cdots\text{O}(6)$ distance of 3.317(6) Å indicates that there is no significant gold-carbonyl bonding.

Interest in gold co-ordination chemistry has been growing in recent years with the successful use of gold(I) phosphine complexes such as 'auranofin' (2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranosato-*S*)(triethylphosphine)gold(I) and chloro-(triethylphosphine)gold(I) for the treatment of rheumatoid arthritis.^{1,2} Auranofin has also shown evidence of anticancer activity in 'in vivo' studies of P388 leukaemia in mice.^{3,4} These results prompted further efforts directed toward the preparation of gold(I) complexes analogous to auranofin⁵⁻¹² which might exhibit a broader spectrum of anticancer activity. Among these complexes, those of the general formula $[\text{Au}(\text{PPh}_3)\text{L}]$ ($\text{HL} = 2\text{-thiouracil}$, 5-fluorouracil, thymidine, or 6-mercaptopurine)‡ demonstrated significant antineoplastic activity against P388 leukaemia in mice.¹² Likewise, a number of analogous 1,2-bis(diphenylphosphine)ethane (dppe) gold(I) complexes have been reported to have good antitumour activity in a spectrum of transplantable tumour models.^{5,6,8,11}

On the other hand, absorption and circular dichroism spectroscopy and gel electrophoresis studies have revealed that



gold(I) complexes can bind to DNA 'in vitro' apparently via the guanine and cytosine bases.^{13,14} According to this, purine and pyrimidine bases could be utilized as model compounds for the interaction of gold(I) complexes with DNA in an attempt to explain their mechanism of action.

In view of all this, as a continuation of our studies on metal complexes of purine bases,¹⁵⁻¹⁹ in the current work we report on the interaction of chloro(triphenylphosphine)gold(I) and [μ -1,2-bis(diphenylphosphine)ethane]-bis[bromogold(I)] with theophylline (HL¹), 8-ethyltheophylline (HL²), 3-methyl-8-ethylxanthine (H₂L³), and hypoxanthine (H₂L⁴).§ The results reported complete a field of investigation where the information available is limited to only a few studies, including the preparation and characterization by ^1H , ^{13}C , and ^{31}P n.m.r. as well as i.r. spectroscopy of the products from the reactions of $[\text{AuClL}]$ ($\text{L} = \text{triphenyl- or tricyclohexyl-phosphine}$) with purine (adenine, guanine, azaguanine, theobromine, or theophylline) and pyrimidine bases (uracil, thymine, barbituric acid and some of its methyl derivatives),²⁰⁻²² and

† (3,7-Dihydro-1,3-dimethyl-1*H*-purine-2,6-dionato-*N*⁷)(triphenylphosphine)gold(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii-xx.

‡ Uracil = 1*H*,3*H*-Pyrimidine-2,4-dione; thymidine = 1-(2-deoxy- β -D-erythro-pentofuranosyl)-5-methyl-1*H*,3*H*-pyrimidine-2,4-dione.

§ Theophylline = 3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione; xanthine = 3,7-dihydro-1*H*-purine-2,6-dione; hypoxanthine = 1,7-dihydro-6*H*-purin-6-one; theobromine = 3,7-dihydro-3,7-dimethyl-1*H*-purine-2,6-dione; thymine = 5-methyl-1*H*,3*H*-pyrimidine-2,4-dione; barbituric acid = 1*H*,3*H*,5*H*-pyrimidine-2,4,6-trione.

Table 1. Analytical^a and physical data for the gold complexes

Complex	Analysis (%)				Yield (g, %)	M.p. ^b (θ/°C)
	C	H	N	Au		
(1) [Au(PPh ₃)L ¹]	47.1 (47.0)	3.5 (3.5)	8.9 (8.8)	30.9 (30.9)	(0.50, 78)	250—255
(2) [Au(PPh ₃)L ²]	48.7 (48.7)	4.0 (3.9)	8.0 (8.4)	29.0 (29.6)	(0.55, 82)	160—165
(3) [L ¹ Au(μ-dppe)AuL ¹]	41.6 (41.7)	3.3 (3.3)	8.8 (9.7)	34.5 (34.2)	(1.02, 89)	260—265
(4) [L ² Au(μ-dppe)AuL ²]	42.5 (43.8)	3.7 (3.8)	9.2 (9.3)	32.9 (32.7)	(1.10, 91)	360
(5) [Au(PPh ₃)(HL ³)]	47.8 (47.9)	3.7 (3.7)	8.4 (8.6)	29.5 (30.2)	(0.57, 88)	230—235
(6) [Au(PPh ₃) ₂ (μ-L ³)]	46.5 (47.6)	3.5 (3.5)	4.7 (5.0)	35.2 (35.5)	(0.91, 82)	130—135
(7) [Au(PPh ₃) ₂ (μ-L ⁴)]·3H ₂ O	45.8 (44.5)	3.4 (3.3)	5.0 (5.1)	35.2 (35.6)	(0.85, 77)	165—170
(8) [Au(μ-dppe)(μ-L ⁴)Au]·3H ₂ O	37.8 (38.0)	3.0 (3.3)	5.0 (5.7)	41.2 (40.2)	(0.72, 73)	290—295

^a Required values are given in parentheses. ^b With decomposition.

the crystal structures of (adeninato)(triphenylphosphine)-gold(I),²³ (1-methylthyminato)(triphenylphosphine)gold(I),²⁴ and 5,5-diethyl-1,3-bis[(triphenylphosphine)aurio]barbituric acid.²¹ Since the chosen purines generally exhibit biological activity,^{25,26} it was hoped that this would enhance the biological activity of the gold(I) complexes. For this reason, the new phosphine gold(I) complexes are being tested for anticancer activity.²⁷

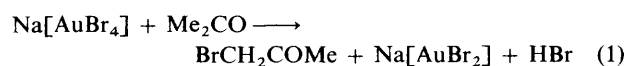
Experimental

Theophylline and hypoxanthine were purchased from Carlo Erba and Merck, respectively, and were used without further purification. The purine derivatives 3-methyl-8-ethylxanthine and 8-ethyltheophylline were prepared as described in the literature.²⁸ Triphenylphosphine and 1,2-bis(diphenylphosphine)ethane were purchased from Aldrich. The [Au(PPh₃)Cl] complex was prepared from Na[AuCl₄]·2H₂O and PPh₃ as previously described.²⁹

Microanalyses of C, H, and N were performed with a Perkin-Elmer 240C analyser. Gold was determined thermogravimetrically with a Mettler TG-50 thermobalance (Table 1). Infrared spectra were recorded in the 4 000—180 cm⁻¹ range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets. Proton and ¹³C n.m.r. spectra of the complexes dissolved in (CD₃)₂SO were recorded on a Bruker AM300 spectrometer.

Preparations.—[Au(PPh₃)L] (L = L¹, L², or HL³).—The general procedure for the synthesis of [Au(PPh₃)L] was as follows: a solution of [Au(PPh₃)Cl] (0.26 g, 1 mmol) in acetone (30 cm³) was added to one of the purine derivatives (1 mmol) in water (5 cm³) containing 1 mol equivalent of KOH. The resulting solution was refluxed for 15 min and then allowed to stand at room temperature for several hours, whereupon the white complex precipitated. The complex was filtered off, washed with water, acetone, and diethyl ether, and dried *in vacuo*. Crystals of [Au(PPh₃)L¹] suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in acetone-water (5:1, v/v) at 4 °C.

[AuBr₂(dppe)]. To a stirred solution of Na[AuCl₄]·2H₂O (2 g, 5 mmol) in water (15 cm³) was added NaBr (2.3 g, 22.5 mmol) over 15 min. The resulting red solution was treated with acetone (30 cm³) and heated at 70 °C until the solution became colourless. Addition of dppe (1 g, 2.5 mmol) with continuous stirring immediately gave a white precipitate, which was filtered off, washed with water and acetone, and dried with diethyl ether. Yield 90%, m.p. 275—280 °C. In this method, acetone was used as a reducing agent [equations (1) and (2)]. This procedure



presents some advantages over other published methods.²⁹⁻³¹ First, acetone is less expensive than the usual reducing agents thiodiglycol and dppe itself, and secondly acetone is a very clean reducing agent, since its oxidation product, bromoacetone, is volatile and thus easily eliminated. Furthermore, this method is general for the synthesis of μ-diphosphine-bis[bromogold(I)] complexes.

[LAu(μ-dppe)AuL] (L = L¹ or L²). A solution of [(AuBr)₂(dppe)] (1 mmol) in ethanol (30 cm³) was added to a solution of purine derivative (2 mmol) in water (5 cm³) containing 1 mol equivalent of KOH. The resulting solution was refluxed for 15 min and a white product formed, which was filtered off, washed with water and ethanol, and dried with diethyl ether.

[Au(PPh₃)₂(μ-L)] (L = L³ or L⁴). These complexes were prepared using the above method for [Au(PPh₃)L] but with a ratio purine derivative:[Au(PPh₃)Cl]:KOH of 1:2:2.

The complexes were also prepared by adding a solution of [Au(PPh₃)Cl] (1 mmol) in acetone (30 cm³) to one of the corresponding [Au(PPh₃)L] complex (1 mmol) in acetone-water (5:1) (30 cm³) containing KOH (1 mmol). In all cases, a white product precipitated immediately from solution. This was filtered off, washed with water, acetone, and diethyl ether, and dried *in vacuo*.

[Au(μ-dppe)(μ-L⁴)Au]·3H₂O. This white product was prepared by the same method as for [LAu(μ-dppe)AuL], using either a 1:1 or 1:2 [(AuBr)₂(dppe)]:H₂L⁴ molar ratio.

Crystal Structure Determination and Refinement of [Au(PPh₃)L¹] (1).—Crystal data. C₂₅H₂₂AuN₄O₂P, M = 638.4, a = 9.061(2), b = 9.762(4), c = 13.588(4) Å, α = 71.30(2), β = 87.20(2), γ = 86.10(2)°, U = 1 135.4(4) Å³ by a least-squares fit to 25 Bragg angles measured for both positive and negative values, space group P $\bar{1}$, Z = 2, D_c = 1.87, D_m = 1.84(1) g cm⁻³, F(000) = 620, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 67.80 cm⁻¹.

Intensity data collection. A colourless prismatic single crystal (dimensions 0.30 × 0.28 × 0.14 mm) was selected for data collection at 295 K on an Enraf-Nonius CAD4 diffractometer. A total of 6 559 independent reflections (with θ in the range 2—30°) was measured using the ω—2θ scanning technique at a scan rate of 1° min⁻¹, 5 150 of which with I > 3σ(I), were used in the structure analysis. The intensity data were corrected for Lorentz and polarization effects.

Structure analysis and refinement. The Au atom was located on a Patterson map, the remaining non-H atoms of the structure being located on successive Fourier syntheses. An empirical absorption correction was applied after isotropic refinement.³² The structure was then refined anisotropically. A

Table 2. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.) in parentheses for $[\text{Au}(\text{PPh}_3)\text{L}^1]$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Au	0.099 09(2)	-0.049 88(2)	0.216 03(2)	C(13)	0.497 0(8)	-0.429 7(9)	0.349 6(6)
P	0.186 9(2)	-0.213 9(2)	0.142 3(1)	C(14)	0.497 0(8)	-0.569 4(9)	0.348 6(6)
N(1)	0.220 1(5)	0.137 3(6)	0.499 2(4)	C(15)	0.396 5(9)	-0.606 0(8)	0.290 2(6)
C(1)	0.358 7(8)	0.097 6(10)	0.555 5(6)	C(16)	0.297 1(9)	-0.502 4(8)	0.229 7(6)
C(2)	0.115 6(7)	0.226 4(7)	0.533 2(5)	C(21)	0.034 5(6)	-0.297 8(6)	0.105 2(4)
O(2)	0.142 5(6)	0.272 7(6)	0.603 2(4)	C(22)	-0.065 1(8)	-0.372 0(8)	0.182 3(5)
N(3)	-0.015 5(6)	0.261 4(5)	0.481 8(4)	C(23)	-0.183 3(8)	-0.434 1(9)	0.154 9(7)
C(3)	-0.133 5(8)	0.347 0(9)	0.516 3(6)	C(24)	-0.205 0(7)	-0.417 7(8)	0.051 4(7)
C(4)	-0.039 0(6)	0.208 3(6)	0.402 0(4)	C(25)	-0.109 7(8)	-0.343 2(8)	-0.023 7(6)
C(5)	0.066 7(5)	0.122 9(6)	0.369 7(4)	C(26)	0.013 4(7)	-0.282 6(7)	0.002 3(5)
C(6)	0.204 8(6)	0.081 1(7)	0.416 6(5)	C(31)	0.301 4(6)	-0.147 0(6)	0.024 5(4)
O(6)	0.305 8(5)	0.006 4(6)	0.392 8(4)	C(32)	0.269 8(8)	-0.009 5(7)	-0.044 2(6)
N(7)	0.007 2(5)	0.091 6(5)	0.288 1(4)	C(33)	0.348 4(9)	0.037 4(9)	-0.138 4(6)
C(8)	-0.128 7(6)	0.157 5(7)	0.279 6(5)	C(34)	0.460 4(7)	-0.047 7(8)	-0.163 1(5)
N(9)	-0.163 0(5)	0.230 8(6)	0.346 3(4)	C(35)	0.492 3(8)	-0.182 7(10)	-0.094 5(6)
C(11)	0.299 2(6)	-0.359 8(6)	0.228 1(4)	C(36)	0.413 5(8)	-0.234 1(9)	-0.001 1(6)
C(12)	0.399 7(7)	-0.324 8(7)	0.290 4(5)				

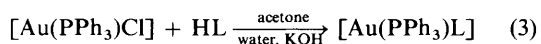
Fourier difference synthesis revealed the positions of all the hydrogen atoms close to those expected on geometrical grounds. A convenient weighting scheme of type $w = w_1 w_2$, with $w_1 = k_1 / (a + b|F_o|)^2$ and $w_2 = k_2 / [c + b \sin \theta / \lambda + e(\sin \theta / \lambda)^2]$, was used to obtain flat dependence in $\langle w \Delta^2 F \rangle$ vs. $\langle F_o \rangle$ and vs. $\langle \sin \theta / \lambda \rangle$; ³³ the coefficients used were: $k_1 = 0.62$, $k_2 = 0.81$, $a = 3.4$, and $b = -0.1$ for $F_o < 18$; $a = 1.8$ and $b = 0.0$ for $18 < F_o < 39$; $a = 0.3$ and $b = 0.0$ for $39 < F_o < 56$; $a = -0.8$ and $b = 0.1$ for $F_o > 56$; $c = 0.6$, $d = 0.8$, and $e = -0.7$ for $\sin \theta / \lambda > 0.05$. Last cycles of refinement (H atoms as fixed isotropic contributors) gave the discrepancy indices $R = 0.039$ and $R' = 0.044$. Most calculations were carried out using the X-RAY 76 system ³⁴ running on a MicroVAX II computer. Final atomic co-ordinates for non-H atoms are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Complexes of Theophylline and 8-Ethyltheophylline Derivatives.—From n.m.r. studies in dimethyl sulphoxide (dmsO) solution it was concluded that purine derivatives containing a weak acidic proton in the imidazole ring present a tautomeric equilibrium between N(7)-H and N(9)-H forms. ³⁵ In fact, both forms have been found in metal complexes which contain neutral theophylline as a ligand. ³⁶ When an imidazolic proton dissociates in a basic medium, either N(7) or N(9) might act as the co-ordination site to metal ions. However, in all metal complexes containing the theophyllinato anion, for which crystallographic results are available, co-ordination takes place through N(7). ³⁷ The steric hindrance from the N(3)-CH₃ group may explain why N(7) is favoured over N(9).

$[\text{Au}(\text{PPh}_3)\text{L}]$ complexes. Our results are in accord with the above considerations. When HL¹ and HL² were allowed to react in a basic medium with $[\text{Au}(\text{PPh}_3\text{Cl})]$ neutral 1:1 complexes were obtained in good yield, in which the imidazolic acidic proton is displaced by an Au(PPh₃) group [equation (3)].



These complexes had satisfactory elemental analyses and were further characterized by ¹H and ¹³C n.m.r. and i.r. spectroscopy (Tables 3–5). In addition to this, the X-ray crystal structure of $[\text{Au}(\text{PPh}_3)\text{L}^1]$ (1) was determined. This complex was

previously reported though prepared in a different way and only characterized by ¹H n.m.r. and i.r. spectroscopy. ²⁰

The ¹H n.m.r. spectra of these complexes lack the low-field signal due to a proton at either N(7) or N(9). The H(8) signal in (1) is masked by those of the phenyl protons occurring in the 7.57–7.71 range and, therefore, is shifted upfield with respect to that of neutral theophylline. This upfield shift of H(8) is similar to that observed for other theophyllinato complexes ^{38,39} and may be because the large amount of electron density delocalized around the imidazole ring has a shielding effect.

On the other hand, (triphenylphosphine)gold(I) seems to be a better electron-withdrawing group than the proton, as the signals due to the ethyl group in $[\text{Au}(\text{PPh}_3)\text{L}^2]$ (2) are shifted downfield (0.1) compared to those of the neutral ligand. The positions of the signals arising from methyl groups at N(1) and N(3) are similar for the two complexes and remain practically unaffected with respect to the corresponding ligand.

The ¹³C n.m.r. spectra of complexes (2) and $[\text{L}^1\text{Au}(\mu\text{-dppe})\text{AuL}^1]$ (3) show that the signals due to C(5), C(6), and C(8) are shifted downfield compared to those of the neutral ligands, with the most pronounced shift differences ($\Delta\delta$) occurring at C(5) (6.11 and 7.48 p.p.m., respectively) and C(8) (6.90 and 7.82 p.p.m., respectively), while the signals for the other carbons are affected to a much smaller extent. This observation is consistent with the binding of the (triphenylphosphine)gold(I) cation at N(7) in both complexes. Shift differences of the same sign and similar magnitude have been observed for the complex methyl(theophyllinato)mercury(II), ³⁹ for which an X-ray crystal structure analysis clearly shows methylmercury binding to the theophylline N(7) position. ⁴⁰

In good accord with the ¹³C n.m.r. data, the similarity of the i.r. spectra of (1) and (2) suggests an analogous co-ordination mode for L¹ and L² in the two complexes. The spectra show no bands due to N-H stretching vibration at 2 600–3 200 cm⁻¹ region, as expected. Although the crystal structure data for (1) (see below) rule out any direct interaction of the Au(PPh₃) moiety with the C(6)=O group, the bands for the ligand assigned to C=O, as well as C=C and C=N stretching vibrations in the 1 500–1 750 cm⁻¹ region, undergo shifts to lower frequency upon complex formation. These bands are primarily sensitive to the loss of the imidazolic proton, and they occur practically at the same positions for all N(7)-bonded theophyllinato complexes. ³⁷

Crystal structure of $[\text{Au}(\text{PPh}_3)\text{L}^1]$. The results of the crystal structure determination confirm the above proposed structure for this complex. The unit cell contains neutral monomeric

Table 3. Proton n.m.r. data (δ) for some of the isolated complexes

Compound	N ¹ -CH ₃	N ³ -CH ₃	N ⁷ -H	N ¹ -H	C ⁸ -H	C ⁸ -CH ₂ ^a	C ⁸ -CH ₃ ^b	Phenyl protons ^c
HL ¹	3.21	3.41	13.48		7.99			
(1)	3.24	3.43			<i>d</i>			7.58—7.70
HL ²	3.19	3.38	13.09			2.68	1.22	
(2)	3.22	3.38				2.78	1.31	7.58—7.71
H ₂ L ³		3.32	13.04	10.93		2.67	1.21	
(5)		3.33		10.65		2.76	1.30	7.57—7.70

^a Quartets. ^b Triplets. ^c Multiplets. ^d Included in the signal due to phenyl protons.

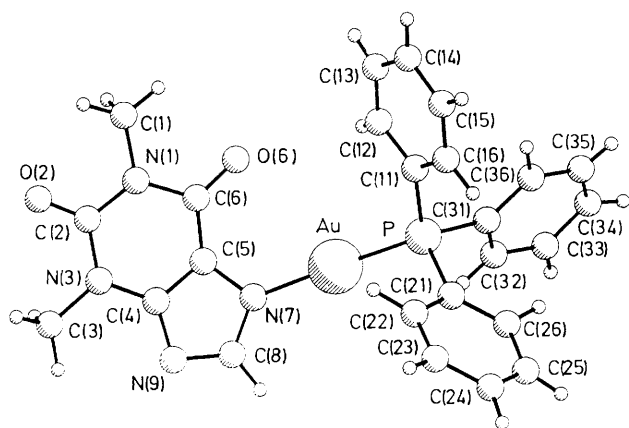
Table 4. Carbon-13 n.m.r. data (δ /p.p.m.) for compounds (1) and (2)

Compound	C ⁸ -CH ₃	C ⁸ -CH ₂	N ¹ -CH ₃	N ³ -CH ₃	C ²	C ⁴	C ⁵	C ⁶	C ⁸	Phenyl
HL ¹			27.60	27.90	151.10	147.74	106.34	154.32	140.38	
(1)			27.49	29.61	151.15	148.71	112.45	158.25	147.28	127.83—133.94
HL ²	12.00	21.58	27.47	29.50	153.81	151.02	105.82	155.12	147.85	
(2)	13.66	25.12	27.43	29.62	151.21	148.69	113.36	160.76	155.68	127.73—133.91

Table 5. Selected i.r. data (cm⁻¹) for the purine derivatives and their phosphinegold(i) complexes^a

Compound	ν (N-H)	ν (C ⁶ =O)	ν (C ² =O)	ν (C=C)	ν (C=N)
HL ¹	3 106—2 620 ^b	1 712	1 665	1 610	1 562
(1)		1 688	1 639	1 587	1 526
(3)		1 688	1 642	1 587	1 525
HL ²	3 150—2 950 ^b	1 704	1 643	1 598	1 560
(2)		1 688	1 643	1 589	1 517
(4)		1 689	1 641	1 585	1 517
H ₂ L ³	3 160—2 800 ^b	1 694	1 662	1 593	1 551
(5)	3 157—3 000 ^b	1 678	1 660	1 584	1 529
(6)		1 638	1 610	1 566	1 509
H ₂ L ⁴	3 259—2 500 ^b	1 665		1 579	
(7)		1 626		1 509	
(8)		1 625		1 510	

^a All complexes show intense bands at 1 479, 1 432, 1 101, 747, 720, and 692 cm⁻¹ due to the phosphine moiety. ^b Several bands.

**Figure 1.** A perspective view of the [Au(PPh₃)L¹] molecule with atom labelling

[Au(PPh₃)L¹] molecules in which the N(7)-H proton of theophylline has been substituted by a [Au(PPh₃)]⁺ cation. A perspective drawing of the molecule is shown in Figure 1 together with the atom labelling. Selected interatomic distances and bond angles are listed in Table 6.

The co-ordination around the gold atom is approximately linear as expected [P-Au-N(7) 176.1(2)°]. The Au-N(7) and Au-P bond lengths, 2.047(6) and 2.231(2) Å, respectively, are in the range usually found for other compounds containing a

P-Au-N linkage, such as (adeninato)(triphenylphosphine)-gold(i) [2.038(4) and 2.240(1) Å, respectively],²³ 5,5-diethyl-1,3-bis(triphenylphosphine)aurio]barbituric acid [2.022(1) and 2.233(5) Å, respectively],²¹ and (phthalimido)(triethylphosphine)gold(i) [2.238(6) and 2.05(2) Å, respectively].⁴¹ In the phosphine ligands, bond lengths and angles involving gold, phosphorus, and the phenyl rings (av. C-C and C-C-C 1.382 Å and 120.0°) compare reasonably well with results for other gold(i) triphenylphosphine complexes.^{21,23,42}

Bond lengths and angles of theophylline in the present compound do not significantly differ from those reported for free theophylline⁴³ and its N(7)-bonded complexes.³⁷ The nine atoms of the purine system are coplanar within 0.03 Å. The exocyclic atoms O(2), C(1), and C(3) are distant from this plane by 0.033(6), -0.044(9), and -0.059(9) Å. These deviations might be due to the steric interactions between the methyl groups at N(1) and N(3) and O(2) as is evidenced by the short C(1)···O(2) and C(3)···O(2) contact distances of 2.70(1) and 2.769(9) Å, respectively which are 0.6 Å less than the sum of their van der Waals radii.⁴⁴

As pointed out by some authors^{37,45} the existence of a significant M-O(6) interaction causes a dissymmetry in the exocyclic bond angles at N(7), so that the C(5)-N(7)-M angle is smaller than C(8)-N(7)-M. For instance, in the complexes bis(η⁵-cyclopentadienyl)(theophyllinato)titanium(III)³⁷ and (N-3,4-benzosalicylidene-N',N'-dimethylethylenediamine)-(theophyllinato)copper(II),⁴⁵ which contain the theophyllinato monocation co-ordinated in N(7),O(6) chelate mode, the C(8)-N(7)-M angle is larger than C(5)-N(7)-M by 50 and 21°, respectively. In the present compound, the Au-N(7) bond lies roughly along the expected lone-pair direction of N(7) since the C(8)-N(7)-Au angle [129.4(4)°] differs from C(5)-N(7)-Au [125.9(4)°] only by 3.5°, indicating that the Au···O interaction is very weak. In good accord with this, the distance Au···O [3.317(6) Å] is larger than 3.2 Å, the sum of the van der Waals radii of gold and oxygen.⁴⁴ The lack of any Au-O interaction is not surprising since the soft (class b) gold(i) shows a preference for the softer N donors over the hard oxygen atoms.

Figure 2 illustrates the arrangement of the [Au(PPh₃)L¹] molecules in the unit cell. Intermolecular contacts less than 3.5 Å are listed in Table 7 indicating that only van der Waals forces are present between molecules.

[LAu(μ-dppe)AuL] complexes. These complexes were prepared in good yield from the reaction of [(AuBr)₂(dppe)] and the corresponding purine ligand, at a 1:2 stoichiometry (Scheme 1). Attempts to obtain complexes of the type [LAu(μ-dppe)AuBr] at a 1:1 stoichiometry were unsuccessful. The i.r.

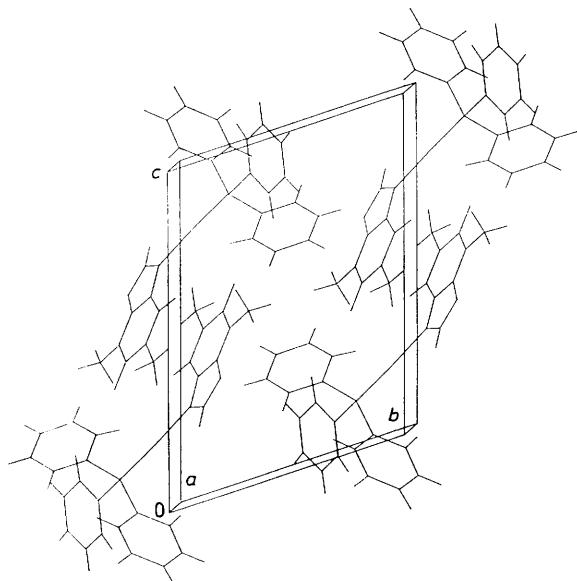
Table 6. Interatomic distances (Å) and bond angles (°) with e.s.d.s in parentheses

Au-P	2.231(2)	N(3)-C(4)	1.375(9)	C(11)-C(12)	1.403(9)	C(23)-C(24)	1.386(14)
Au-N(7)	2.047(6)	N(3)-C(3)	1.463(10)	C(11)-C(16)	1.386(10)	C(24)-C(25)	1.356(10)
P-C(11)	1.810(5)	C(4)-C(5)	1.375(8)	C(12)-C(13)	1.375(9)	C(25)-C(26)	1.407(10)
P-C(21)	1.822(6)	C(4)-N(9)	1.351(8)	C(13)-C(14)	1.368(13)	C(31)-C(32)	1.388(8)
P-C(31)	1.823(5)	C(5)-C(6)	1.407(7)	C(14)-C(15)	1.373(12)	C(31)-C(36)	1.383(10)
N(1)-C(2)	1.404(9)	C(5)-N(7)	1.382(8)	C(15)-C(16)	1.387(10)	C(32)-C(33)	1.391(11)
N(1)-C(6)	1.414(9)	C(6)-O(6)	1.227(8)	C(21)-C(22)	1.395(8)	C(33)-C(34)	1.365(11)
N(1)-C(1)	1.466(9)	N(7)-C(8)	1.343(8)	C(21)-C(26)	1.380(9)	C(34)-C(35)	1.370(10)
C(2)-N(3)	1.374(8)	C(8)-N(9)	1.337(10)	C(22)-C(23)	1.388(12)	C(35)-C(36)	1.388(10)
C(2)-O(2)	1.217(10)						
P-Au-N(7)	176.1(2)	C(2)-N(3)-C(3)	120.1(6)	N(7)-C(8)-N(9)	115.5(5)	C(21)-C(22)-C(23)	119.4(7)
Au-P-C(11)	113.2(2)	C(4)-N(3)-C(3)	120.0(5)	C(4)-N(9)-C(8)	102.4(5)	C(22)-C(23)-C(24)	120.1(7)
Au-P-C(21)	110.0(2)	N(3)-C(4)-C(5)	121.9(5)	P-C(11)-C(12)	118.1(5)	C(23)-C(24)-C(25)	120.4(7)
Au-P-C(31)	116.3(2)	N(3)-C(4)-N(9)	126.3(5)	P-C(11)-C(16)	123.0(5)	C(24)-C(25)-C(26)	120.7(7)
C(11)-P-C(21)	106.4(3)	C(5)-C(4)-N(9)	111.8(5)	C(12)-C(11)-C(16)	118.8(6)	C(21)-C(26)-C(25)	119.1(6)
C(11)-P-C(31)	104.8(3)	C(4)-C(5)-C(6)	122.9(5)	C(11)-C(12)-C(13)	120.3(7)	P-C(31)-C(32)	119.5(5)
C(21)-P-C(31)	105.4(3)	C(4)-C(5)-N(7)	106.3(5)	C(12)-C(13)-C(14)	120.6(7)	P-C(31)-C(36)	121.2(5)
C(2)-N(1)-C(6)	126.6(5)	C(6)-C(5)-N(7)	130.8(5)	C(13)-C(14)-C(15)	119.7(8)	C(32)-C(31)-C(36)	119.1(6)
C(2)-N(1)-C(1)	116.7(6)	N(1)-C(6)-C(5)	112.1(5)	C(14)-C(15)-C(16)	120.9(8)	C(31)-C(32)-C(33)	119.8(7)
C(6)-N(1)-C(1)	116.8(5)	N(1)-C(6)-O(6)	120.5(5)	C(11)-C(16)-C(15)	119.7(7)	C(32)-C(33)-C(34)	121.1(7)
N(1)-C(2)-N(3)	116.8(6)	C(5)-C(6)-O(6)	127.5(6)	P-C(21)-C(22)	118.8(5)	C(33)-C(34)-C(35)	118.9(7)
N(1)-C(2)-O(2)	121.0(6)	C(5)-N(7)-C(8)	104.0(5)	P-C(21)-C(26)	120.8(5)	C(34)-C(35)-C(36)	121.4(8)
N(3)-C(2)-O(2)	122.2(6)	C(5)-N(7)-Au	125.9(4)	C(22)-C(21)-C(26)	120.4(6)	C(31)-C(36)-C(35)	119.6(7)
C(2)-N(3)-C(4)	119.8(5)	C(8)-N(7)-Au	129.4(4)				

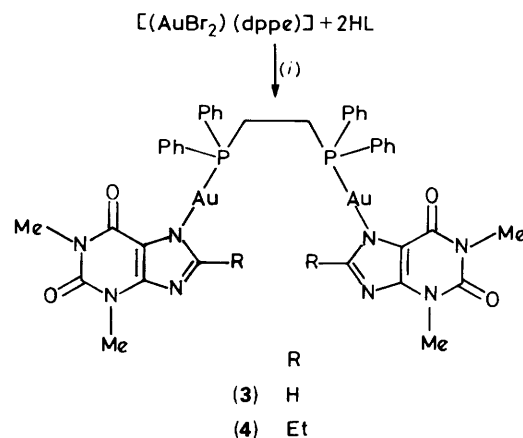
Table 7. Intermolecular contacts less than 3.5 Å in compound (1)

Au...O(2 ⁱ)	3.500(5)	C(1)...O(6 ⁱⁱⁱ)	3.178(8)
C(4)...C(6 ⁱ)	3.473(7)	C(22)...O(2 ⁱ)	3.384(10)
N(9)...C(23 ⁱⁱ)	3.466(9)	C(25)...C(25 ^{iv})	3.431(10)
C(3)...C(12 ⁱ)	3.443(10)		

Symmetry equivalent positions: I $-x, -y, 1-z$; II $x, 1+y, z$; III $1-x, -y, 1-z$; IV $-x, -1-y, -z$.

**Figure 2.** View of the unit cell of $[\text{Au}(\text{PPh}_3)_2\text{L}^1]$

spectra of complexes (3) and $[\text{L}^2\text{Au}(\mu\text{-dppe})\text{AuL}^2]$ (4) do not show significant differences in the positions of the ligand bands with respect to those in (1) and (2), respectively, suggesting also N(7) co-ordination of the purine ligand in both complexes.

**Scheme 1.** (i) EtOH, 2KOH

Therefore, the proposed structure for (3) and (4) as is depicted in Scheme 1.

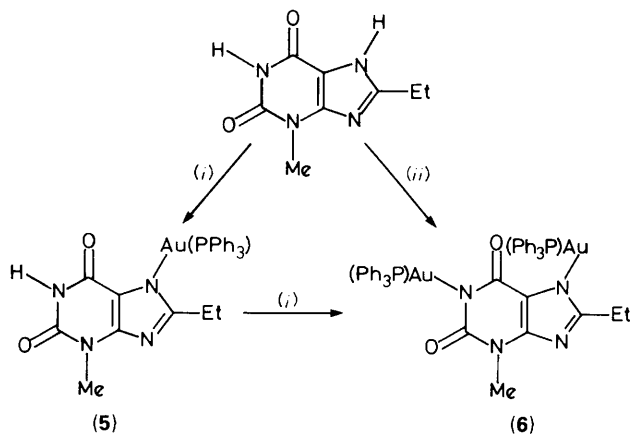
Complexes of 3-Methyl-8-ethylxanthine.—3-Methyl-8-ethylxanthine contains two ionizable protons, N(1)-H and that involved in the tautomeric equilibrium $\text{N}(7)\text{-H} \rightleftharpoons \text{N}(9)\text{-H}$. In a basic medium these protons can be replaced by $\text{Au}(\text{PPh}_3)$ groups. Owing to the higher acidity of the imidazolic proton¹⁶ and the steric hindrance from N(3)-CH₃, N(7) must be the first binding site of the $\text{Au}(\text{PPh}_3)$ group.

The complexes obtained from the interaction of 3-methyl-8-ethylxanthine with $[\text{Au}(\text{PPh}_3)\text{Cl}]$ are given in Scheme 2.

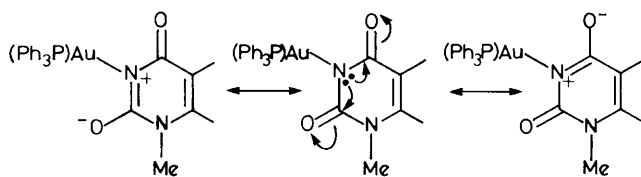
Complex (5) was obtained from the reaction of an equimolar mixture of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ and 3-methyl-8-ethylxanthine. The ¹H n.m.r. spectrum of complex (5) (Table 3) lacks the signal due to either the N(7)-H or N(9)-H proton. The positions of the signals for the protons associated with the 8-ethyl group are shifted downfield by 0.1 with respect to those of the neutral ligand. This downfield shift is similar to that observed for the same signals of (2), suggesting the binding of the $\text{Au}(\text{PPh}_3)$ group at the N(7) positions, as expected. According to this, the i.r. spectrum of complex (5) does not show significant differences

in the positions of the C=O, C=C, and C=N stretching vibrations with respect to those in (1)–(4).

The reaction of H_2L^3 with $[Au(PPh_3)Cl]$ and KOH at a 1:2:2 stoichiometry yielded complex (6). This complex was also obtained by the reaction of (5), which still contains an acidic proton, with an additional molar equivalent of $[Au(PPh_3)Cl]$. In the i.r. spectrum the absence of N–H stretching vibrations provide good evidence for Au(PPh_3) co-ordination at both N(7) and N(1). On going from (5) to (6) the positions of the C=O stretching bands are shifted to lower wavenumber by 40 cm^{-1} . This observation is consistent with the binding of the second Au(PPh_3) at N(1), since when the N(1)–H proton is substituted by an Au(PPh_3) ion the electron



Scheme 2. (i) KOH, $[Au(PPh_3)Cl]$; (ii) $2[Au(PPh_3)Cl]-2KOH$, acetone–water



Scheme 3.

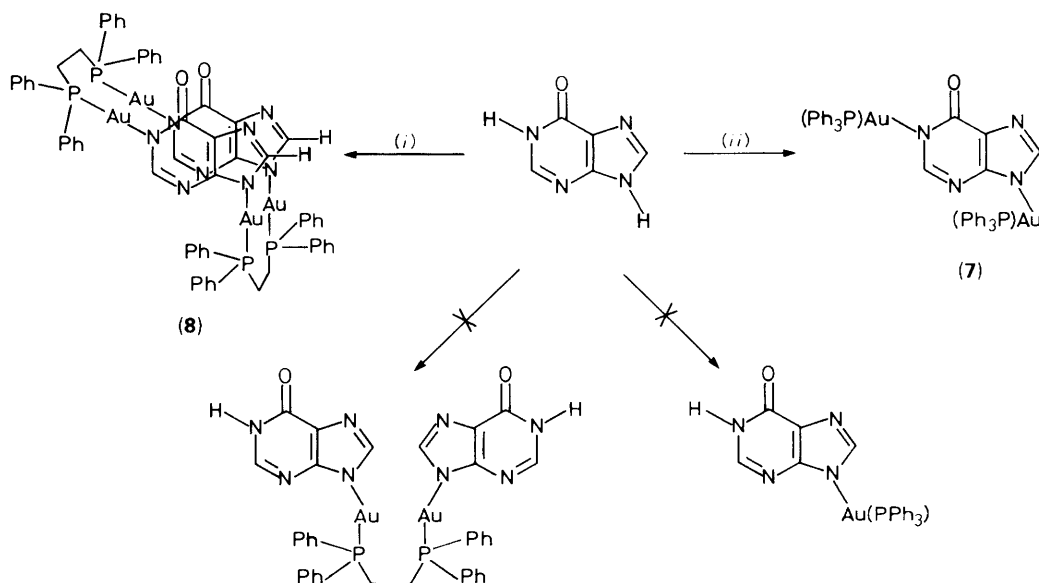
distribution in the N–C=O region approximates that of the anion, leading to a reduction of the C=O bond orders (Scheme 3).

The same effect on the C=O stretching vibration bands has also been observed for N(1)–HgMe complexes of xanthine⁴⁶ and xanthosine (3,9-dihydro-9- β -D-ribofuranosyl-1H-purine-2,6-dione).⁴⁷

Complexes of Hypoxanthine.—Hypoxanthine has two ionizable protons, which are involved in two types of tautomerism; prototropic N(7)–H \rightleftharpoons N(9)–H in the imidazole ring, and lactam–lactim, HN(1)–C(6)=O \rightleftharpoons N(1)=C(6)–OH, in the pyrimidine ring. Nevertheless, 1H and ^{13}C n.m.r. studies led to the conclusion that hypoxanthine exists in solution predominantly in the lactam form.^{35b} This tautomer has also been observed in the metal complexes of hypoxanthine.⁴⁸ Therefore, the likely Au(PPh_3) binding sites in this purine base must be N(1) and either N(7) or N(9).

The reactions of hypoxanthine with $[Au(PPh_3)Cl]$ and $[(AuBr)_2(dppe)]$ do not depend on the stoichiometry of the reactants. The complexes obtained from these reactions are given in Scheme 4.

All attempts to prepare complexes analogous to (1)–(4) failed. The evidence concerning the structures of the complexes (7) and (8) has been derived from i.r. absorption results, since the 1H and ^{13}C n.m.r. spectra could not be obtained because of the low solubility of the complexes in dmsO. The similarity of the i.r. spectra of (7) and (8) (the bands which originate from vibrations in the theophylline unit occur virtually at the same positions) suggest the same co-ordination mode for hypoxanthine in the two complexes. The band assignable to the C(6)=O stretching vibration is shifted to lower wavenumber by 40 cm^{-1} , which together with the absence of N–H stretching vibration bands supports the co-ordination of hypoxanthine through N(1) and either N(7) or N(9). Nevertheless, owing to the steric hindrance from C(6)=O, N(9) might be favoured over N(7). According to this, the proposed structures for (7) and (8) are as depicted in Scheme 4. For compound (8), a tetranuclear structure is proposed, since the geometric requirements of the Au(μ -dppe)Au group prevent its binding to both N(1) and N(9) positions of the same hypoxanthine moiety.



Scheme 4. (i) $[(AuBr)_2(dppe)]$, ethanol–water; (ii) $2[Au(PPh_3)Cl]-KOH$, acetone–water

Conclusions

Theophylline and 8-ethyltheophylline react with $[\text{Au}(\text{PPh}_3)\text{Cl}]$ and $[(\text{AuBr})_2(\text{dppe})]$, under basic conditions, affording $[\text{Au}(\text{PPh}_3)\text{L}]$ and $[\text{LAu}(\text{dppe})\text{AuL}]$ complexes, in which the binding of gold(i) phosphine occurs at the N(7) atom. However, with hypoxanthine the $[\text{Au}(\mu\text{-dppe})(\mu\text{-L}^4)\text{Au}]$ and $[\{\text{Au}(\text{PPh}_3)_2\}(\mu\text{-L}^4)]$ complexes are obtained, in which both N(1) and N(9) are involved in the co-ordination. All attempts to obtain the monoaurated complex were unsuccessful, thus indicating the tendency of hypoxanthine to replace all its N-H protons by gold(i) phosphine groups. Reaction of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ with 3-methyl-8-ethylxanthine, at 1:1 and 1:2 stoichiometries, affords $[\text{Au}(\text{PPh}_3)(\text{HL}^3)]$ and $[\{\text{Au}(\text{PPh}_3)_2\}(\mu\text{-L}^3)]$ complexes, respectively. In the first one the binding of the $\text{Au}(\text{PPh}_3)$ group takes place at N(7), while in the second one both N(1) and N(7) are involved in binding. To the best of our knowledge the diaurated complexes $[\{\text{Au}(\text{PPh}_3)_2\}(\mu\text{-L})]$ and $[\text{Au}(\mu\text{-dppe})(\mu\text{-L})\text{Au}]$ reported in this work are new types of purinegold(i) phosphine. Although a few purine complexes of $\text{Au}(\text{PPh}_3)$ were previously reported,²⁰ all were of the monoaurated $[\text{Au}(\text{PPh}_3)\text{L}]$ type.

Acknowledgements

The authors thank Professor K. Emerson for reviewing the manuscript. This work was partially supported by the Comisión de Investigación Científica y Técnica, which J. R. and E. C. gratefully acknowledge. P. R. and J. M. G.-Z. thank Iberduero, S.A. for financial support.

References

- B. M. Sutton, E. McGusty, D. T. Walz, and M. J. DiMartino, *J. Med. Chem.*, 1972, **15**, 1095.
- K. C. Dash and H. Schmidbaur, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1982, vol. 14, ch. 6.
- T. M. Simon, D. H. Kunishima, G. J. Vibert, and A. Lorber, *Cancer*, 1979, **44**, 1965; *Cancer Res.*, 1981, **41**, 94.
- C. K. Mirabelli, R. K. Johnson, C. M. Sung, L. Faucette, K. Muirhead, and S. T. Croke, *Cancer Res.*, 1985, **45**, 32.
- R. M. Snyder, C. K. Mirabelli, R. K. Johnson, C. M. Sung, L. F. Faucette, F. L. McCabe, J. P. Zimmerman, M. Whitman, J. C. Hempel, and S. T. Croke, *Cancer Res.*, 1986, **46**, 5054.
- S. J. Berners-Price, C. K. Mirabelli, R. K. Johnson, M. R. Mattern, F. L. McCabe, L. F. Faucette, C. M. Sung, S. M. Mong, P. J. Sadler, and S. T. Croke, *Cancer Res.*, 1986, **46**, 5486.
- C. K. Mirabelli, R. K. Johnson, D. T. Hill, L. F. Faucette, G. R. Girard, G. Y. Kuo, C. M. Sung, and S. T. Croke, *J. Med. Chem.*, 1986, **29**, 218.
- C. K. Mirabelli, B. D. Jensen, M. R. Mattern, C. M. Sung, S. M. Mong, D. T. Hill, S. W. Dean, P. S. Schein, R. K. Johnson, and S. T. Croke, *Anticancer Drug Design*, 1986, **1**, 223.
- D. T. Hill and R. K. Johnson, *Eur. P. Appl. E.P.* 198 696 (Cl. C07F9/50), 1986; *U.S. P. Appl.* 723 778, 1985 (C.A. 106, P50467k).
- D. T. Hill and R. K. Johnson, *Eur. P. Appl.* 202 854 (Cl. C07F9/50), 1986; *U.S. P. Appl.* 736 003, 1985 (C.A. 106, 84851w).
- C. K. Mirabelli, D. T. Hill, L. F. Faucette, F. L. McCabe, G. R. Girard, D. B. Bryan, B. M. Sutton, J. O. L. Bartus, S. T. Croke, and R. K. Johnson, *J. Med. Chem.*, 1987, **30**, 2181.
- K. C. Agrawal, K. B. Bears, D. Marcus, and H. B. Jonassen, *Proc. Am. Soc. Cancer Res.*, 1978, **19**, 23.
- C. E. Blank and J. Dabrowiak, *J. Inorg. Biochem.*, 1984, **21**, 21.
- C. K. Mirabelli, C. M. Sung, J. P. Zimmerman, D. T. Hill, S. Mong, and S. T. Croke, *Biochem. Pharmacol.*, 1986, **35**, 1427.
- J. M. Salas-Peregrin, M. N. Moreno-Carretero, and E. Colacio-Rodriguez, *Can. J. Chem.*, 1985, **63**, 3573.
- J. M. Salas-Peregrin, E. Sánchez-Martínez, and E. Colacio-Rodriguez, *Inorg. Chim. Acta*, 1985, **23**, 107.
- M. A. Romero, E. Colacio, J. Ruiz, J. M. Salas, and F. Nieto, *Inorg. Chim. Acta*, 1986, **33**, L23.

- V. Ravichandran, G. A. Ruban, K. K. Chacko, M. A. Romero-Molina, E. Colacio-Rodriguez, J. M. Salas-Peregrin, K. Aoki, and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1986, 1780.
- M. I. Moreno-Vida, E. Colacio-Rodriguez, M. N. Moreno-Carretero, J. Ruiz-Sánchez, and J. M. Salas-Peregrin, *Thermochim. Acta*, 1987, **115**, 45 and refs. therein.
- F. Bonati, A. Burini, and B. R. Pietroni, *Z. Naturforsch., Teil B*, 1985, **40**, 1749.
- F. Bonati, A. Burini, B. R. Pietroni, and B. Bovio, *J. Organomet. Chem.*, 1986, **317**, 121.
- F. Bonati, A. Cingolini, S. Calogero, and F. E. Wagner, *Inorg. Chim. Acta*, 1987, **127**, 87.
- N. Beck, U. Nagel, and J. Rosopulus, *Chem. Ber.*, 1985, **118**, 931.
- R. Faggiani, H. E. Howard-Lock, C. J. L. Lock, and M. A. Turner, *Can. J. Chem.*, 1987, **65**, 1568.
- T. W. Rail, in 'Las bases farmacológicas de la terapéutica,' 6th edn., L. S. Goodman and A. Gilman, Editorial Médica Sudamericana, Buenos Aires, 1980, ch. 6, p. 587 and refs. therein.
- G. A. LePage and J. P. Whitecar, jun., *Cancer Res.*, 1971, **31**, 1627.
- E. Colacio, A. M. Romerosa, J. Sánchez, M. Martínez-Ripoll, J. M. Gutiérrez-Zorrilla, P. Román, M. P. Arizti, and M. Martínez de Pancorbo, XXVI International Conference on Coordination Chemistry, Porto, 1988; M. P. Arizti, M. M. Pancorbo, A. Garcia-Orad, P. Román, J. M. Gutiérrez-Zorrilla, M. Martínez-Ripoll, E. Colacio, A. M. Romerosa, and J. Sánchez, Second International Conference of Anticancer Research, Saronis, 1988.
- J. H. Speer and A. L. Raymond, *J. Am. Chem. Soc.*, 1953, **75**, 114.
- C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1979, 1730.
- A. K. Al Sa'ady, C. A. McAuliffe, R. V. Parish, and J. A. Sanbank, *Inorg. Synth.*, 1985, **23**, 191.
- S. J. Berners-Price, A. M. Mazid, and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1984, 969.
- A. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- M. Martínez-Ripoll and F. H. Cano, PESOS, Program for the Automatic Treatment of Weighting Schemes for Least-squares Refinement, Instituto Rocasolano, CSIC, 1975.
- J. M. Stewart, The X-RAY 76 System, Computer Science Center, University of Maryland, 1976.
- (a) D. M. Cheng, L. S. Kan, P. O. P. T'so, C. Giessner-Rettre, and B. Puelman, *J. Am. Chem. Soc.*, 1980, **102**, 525; (b) M. T. Chenon, M. J. Pugmire, D. M. Grant, R. P. Panzina and L. B. Townsend, *ibid.*, 1975, **97**, 4636 and refs. therein.
- E. H. Griffith and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1979, 322; K. Aoki and H. Yamazaki, *ibid.*, 1980, 180; M. B. Cingi, A. M. M. Lanfredi, A. Tiripicchio, and M. T. Camellini, *Transition Met. Chem. (Weinheim, Ger.)*, 1979, **4**, 221.
- D. Cozak, A. Mardhy, M. J. Olivier, and A. L. Beauchamp, *Inorg. Chem.*, 1986, **25**, 2600 and refs. therein.
- E. Colacio-Rodriguez, J. M. Salas-Peregrin, and M. A. Romero-Molina, *Rev. Chim. Miner.*, 1984, **21**, 123; J. M. Salas-Peregrin, E. Colacio-Rodriguez, M. Moreno-Carretero, and J. D. López-González, *An. Quim.*, 1984, **80B**, 197.
- A. R. Norris, R. Kumar, E. Buncel, and A. Beauchamp, *J. Inorg. Biochem.*, 1984, **21**, 277.
- A. R. Norris, S. E. Taylor, E. Buncel, F. Bélanger-Gariépy, and A. L. Beauchamp, *Inorg. Chim. Acta*, 1984, **92**, 271.
- S. J. Berners-Price, M. J. DiMartino, D. T. Hill, R. Kuroda, M. A. Mazid, and P. J. Sadler, *Inorg. Chem.*, 1985, **24**, 3425.
- N. C. Baenziger, W. E. Bennett, and D. M. Soboroff, *Acta Crystallogr., Sect. B.*, 1976, **32**, 962.
- S. Nakao, S. Fujii, T. Sakaki, and K. I. Tomita, *Acta Crystallogr., Sect. B.*, 1977, **33**, 1373.
- J. E. Huheey, 'Inorganic Chemistry. Principles of Structure and Reactivity,' 3rd edn., Harper and Row, New York, 1983, pp. 258, 259.
- D. J. Szalda, T. J. Kistenmacher, and L. G. Marzilli, *J. Am. Chem. Soc.*, 1976, **98**, 8371.
- F. Allaire and A. Beauchamp, *Can. J. Chem.*, 1984, **62**, 2249.
- E. Buncel, B. K. Hunter, R. Kumar, and A. R. Norris, *J. Inorg. Biochem.*, 1984, **20**, 171.
- D. J. Hodgson, *Prog. Inorg. Chem.*, 1977, **23**, 211.