Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.637, T_{max} = 0.852
1376 measured reflections
1209 independent reflections
932 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.42°
$h = -6 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.133
S = 1.318
1209 reflections
98 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 1.5088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.023
$\Delta\rho_{max}$ = 0.663 e Å^{-3}
$\Delta\rho_{min}$ = −0.644 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	1/2	0	0	0.0275 (3)
Cl1	0.2851 (2)	0.1968 (2)	0	0.0389 (4)
N1	0.6270 (4)	0.1234 (4)	0.0856 (2)	0.0338 (7)
C1	0.5291 (6)	0.0927 (6)	0.1592 (2)	0.0421 (9)
C2	0.6709 (6)	0.3103 (5)	0.0743 (2)	0.0412 (10)
C3	0.7741 (9)	0.3335 (8)	0	0.0446 (14)
C4	0.7664 (11)	0.3865 (8)	0.1446 (4)	0.0693 (17)
Cl2	0	0	1/4	0.0433 (5)
O1	0.1143 (5)	0.0997 (5)	0.2026 (2)	0.0712 (11)

Table 2. *Selected geometric parameters (Å, °)*

Co1—N1	2.001 (3)	C1—C1^{i}	1.498 (9)
Co1—Cl1	2.2466 (14)	C2—C3	1.509 (6)
N1—C1	1.484 (5)	C2—C4	1.525 (7)
N1—C2	1.492 (5)	Cl2—O1	1.422 (3)
N1^{ii}—Co1—N1	180.0	C2—N1—Co1	118.4 (3)
N1—Co1—N1^{iii}	93.9 (2)	N1—C1—C1^{i}	107.7 (3)
N1—Co1—N1^{i}	86.1 (2)	N1—C2—C3	110.1 (4)
N1^{iii}—Co1—N1^{i}	180.0	N1—C2—C4	112.3 (4)
N1—Co1—Cl1^{ii}	87.72 (10)	C3—C2—C4	111.2 (5)
N1—Co1—Cl1	92.28 (10)	C2^{iii}—C3—C2	114.6 (5)
Cl1^{ii}—Co1—Cl1	180.0	O1^{iv}—Cl2—O1^{v}	108.9 (2)
C1—N1—C2	112.3 (3)	O1^{iv}—Cl2—O1	110.7 (4)
C1—N1—Co1	107.0 (2)	O1^{vi}—Cl2—O1	108.9 (2)

Symmetry codes: (i) $1-x, -y, z$; (ii) $1-x, -y, -z$; (iii) $x, y, -z$; (iv) $-x, -y, z$; (v) $-y, x, \frac{3}{2}-z$; (vi) $y, -x, \frac{3}{2}-z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL93*.

The authors thank the National Science Council for support under grants NSC87-2112-M007-009, NSC87-2811-M007-0048 and NSC87-2113-M007-041.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1261). Services for accessing these data are described at the back of the journal.

References

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Hay, R. W., Bembi, R. & House, D. A. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1921–1926.
Hay, R. W., Jeragh, B., Ferguson, G., Kaitner, B. & Ruhe, B. L. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1261–1266.
Kolinski, R. A. & Korybut-Daszkiewicz, B. (1975). *Inorg. Chim. Acta*, **14**, 237–245.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Tahirov, T.-H., Lu, T.-H., Liu, G.-S., Chi, T.-Y. & Chung, C.-S. (1995). *Acta Cryst.* C**51**, 2018–2020.
Wang, A., Lee, T.-J., Chi, T.-Y., Liao, F.-L., Liu, G.-S. & Chung, C.-S. (1996). *Acta Cryst.* C**52**, 806–807.

Acta Cryst. (1998). C**54**, 716–719

R_3PAuCN Complexes: [{Ph_2(cyclohexyl)P}AuCN] and [{(*m*-Tolyl)$_3$P}AuCN]

A. R. Al-Arfaj,[a] J. H. Reibenspies,[b] M. Sakhawat Hussain[a]† and A. A. Isab[a]

[a]*Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia, and* [b]*Department of Chemistry, Texas A & M University, College Station, Texas 77843, USA. E-mail: sakhawat@dpc.kfupm.edu.sa*

(*Received 22 September 1997; accepted 18 November 1997*)

Abstract

Linear complexes of cyanogold with cyclohexyldiphenylphosphine {cyano(cyclohexyldiphenylphosphine)-gold(I), [Au(CN)($C_{18}H_{21}P$)]} and tri(*m*-tolyl)phosphine {cyano[tri(*m*-tolyl)phosphine]gold(I), [Au(CN)($C_{21}H_{21}$-P)]} were synthesized and their crystal structures were compared with those of similar complexes. Irrespective of the differences in the anions (CN^- *versus* Cl^-) or in the steric and electronic requirements of the various

† Work carried out during sabbatical leave at Texas A & M University, College Station, Texas, USA.

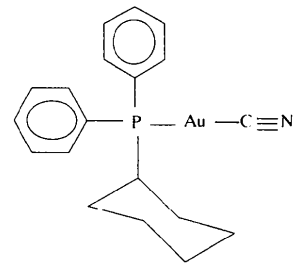
phosphines, the Au—C and Au—P distances are similar in all the compared AuCN complexes. The CN^- ligand in each of the two complexes reported here is tilted with respect to the P—Au—C axis, with the Au—C—N angle deviating by about 7.0 (1)° from linearity.

Comment

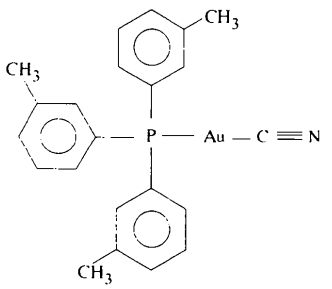
In recent years the synthesis, X-ray structures and solution equilibria of cyanogold complexes of a series of phosphines having general formula R_3P, with R = alkyl, aryl, cyclohexyl or 2-cyanoethyl, have been reported (Al-Arfaj *et al.*, 1997; Hussain *et al.*, 1996; Akhtar *et al.*, 1995). All phosphines studied so far (Al-Arfaj *et al.*, 1996; Harker & Tiekink, 1991) formed linear monomeric complexes with AuX (X = CN^-, Cl^- or Br^-), except tris(2-cyanoethyl)phosphine (CEP), which formed an ionic complex $[(CEP)_2Au][Au(CN)_2]$ (Hussain *et al.*, 1996), although it formed a linear species when AuCN was replaced by AuBr or AuCl (Al-Arfaj *et al.*, 1996; Fackler *et al.*, 1994). A large formation constant of $[Au(CN)_2]^-$ (Hancock *et al.*, 1972), aided by the unique electronic characteristics of CEP, are believed to cause ligand disproportionation of the initially formed monomer [CEPAuCN] to give the ionic complex of CEP. In addition to the steric and electronic requirements of phosphines, other factors, such as the concentration of the complex and the nature of the anion, also play a role in determining the extent of disproportionation.

The present study, dealing with the synthesis and X-ray structures of cyano(cyclohexyldiphenylphosphine)gold(I), (I), and cyano[tri(*m*-tolyl)phosphine]gold(I), (II), was undertaken in order to investigate the influence of steric and electronic characteristics of the ligands on the formation of monomeric *versus* ionic species.

The synthesis and characterization of complexes of AuCN is significant from a biological point of view (Sadler & Sue, 1995). Administration of anti-arthritic gold drugs to smokers is known to produce a higher concentration of gold {in the form of $[Au(CN)_2]^-$} in their red blood cells compared with non-smokers (Graham *et al.*, 1982, 1984; James *et al.*, 1982). Several recent studies were directed toward the determination of solution equilibria in R_2PAuCN complexes, where $[Au(CN)_2]^-$, generated as a result of ligand scrambling, is believed to enter the red blood cells (Hormann-Arendt & Shaw, 1990; Isab, 1992). ^{13}C, ^1H, ^{15}N and/or ^{31}P NMR studies in solution (Akhtar *et al.*, 1996, 1997) could not differentiate between the monomers and the ionic species, prompting us to perform the single-crystal structure analyses of the title complexes.



(I)



(II)

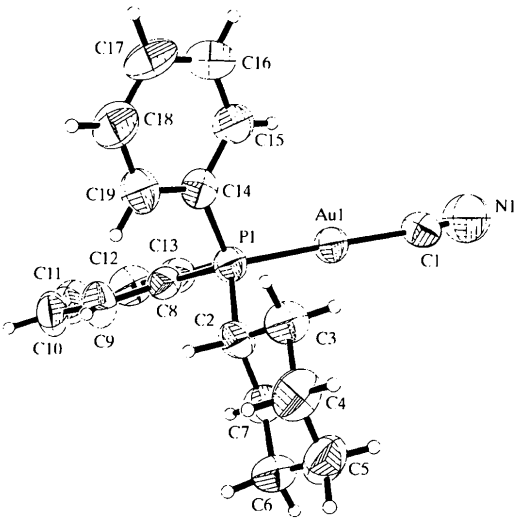


Fig. 1. View of [{Ph_2(cyclohexyl)P}AuCN] showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

The Au atom in each complex has linear coordination (Figs. 1 and 2) with an P1—Au1—C1 angle of 177.0 (4)° in (I) and 174.3 (3)° in (II). The C1 atom of the CN^- ion is at 2.07 (1) Å from Au1 in (I) and at 2.087 (10) Å from Au1 in (II). The Au1—P1 distance is 2.284 (3) Å in (I) and 2.286 (3) Å in (II). These distances are not significantly different from the corresponding distances in other tri(alkyl/aryl)phosphine complexes of AuCN or AuCl (Hancock *et al.*, 1972). For example, the Au—C and Au—P distances are, respectively, 1.85 (4) and 2.27 (3) Å in Ph_3PAuCN (Bellon *et al.*, 1969), 1.97 (2) and 2.288 (5) Å in Et_3PAuCN (Hormann *et al.*, 1986), and 2.00 (2)–2.06 (3) and 2.268 (6)–

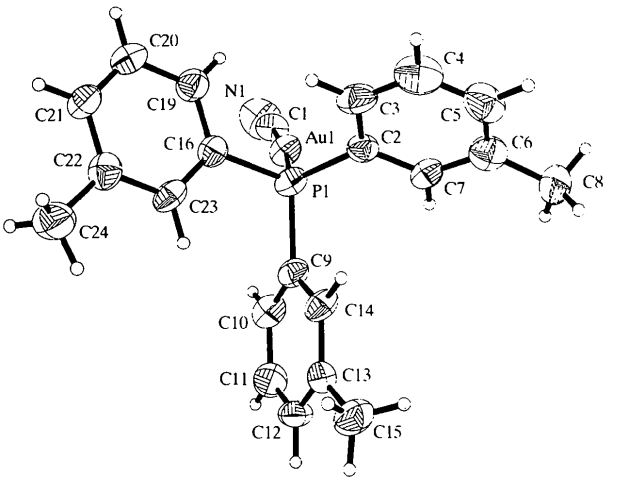


Fig. 2. View of [{(*m*-tolyl)$_3$P}AuCN] showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

2.279 (6) Å in Me_3PAuCN (Ahrland *et al.*, 1992). The P1 atom in each phosphine ligand [cyclohexyldiphenylphosphine and tri(*m*-tolyl)phosphine] has the usual tetrahedral bonding geometry. The cyclohexyl group in (I) has the usual chair conformation, similar to that found in tri(cyclohexyl)phosphine sulfide (Reibenspies *et al.*, 1996) and in [tri(cyclohexyl)phosphine]gold cyanide (Al-Arfaj *et al.*, 1997). The phenyl rings in complex (I) and the *m*-tolyl rings in (II) are planar, as expected. Contrary to the ligand disproportionation observed in the case of [CEPAuCN] forming an ionic [$(CEP)_2Au$]-[$Au(CN)_2$] complex in the liquid state as well as in the solid state, the crystal structures of (I) and (II) revealed no ionic species in the crystalline state. Neither any significant changes in the coordination sphere nor in the Au—P and Au—C distances were observed as a function of changing the functional groups of the phosphines.

Experimental

Initially, the chloro complexes [{Ph_2(cyclohexyl)P}AuCl] and [(*m*-tolyl)$_3$PAuCl] were prepared by the addition of cyclohexyldiphenylphosphine or tri(*m*-tolyl)phosphine to ethanolic solutions of $NaAuCl_4$, as reported earlier (Duddell *et al.*, 1970). The cyano complexes were then synthesized by adding solid KCN directly to ethanolic solutions of the corresponding chloro complex. In another method, a slurry of Me_2SAuCl in acetone, and the phosphine ligand and KCN, both in the solid state, were mixed in the dark, resulting in the title complexes in about 60–70% yield.

Compound (I)

Crystal data

[Au(CN)($C_{18}H_{21}P$)]
M_r = 491.30
Monoclinic
$P2_1/n$
a = 9.384 (2) Å
b = 17.237 (3) Å
c = 11.307 (2) Å
β = 94.50 (3)°
V = 1823.2 (6) Å^3
Z = 4
D_x = 1.790 Mg m^{-3}
D_m = 1.70 Mg m^{-3}
D_m measured by flotation in dibromoethane–CCl_4
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 15–30°
μ = 8.153 mm^{-1}
T = 293 (2) K
Plate
0.40 × 0.38 × 0.20 mm
Colourless

Data collection

Siemens *R3m* diffractometer
ω scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.152, T_{max} = 0.196
6424 measured reflections
3241 independent reflections
2340 reflections with $I > 2\sigma(I)$
R_{int} = 0.088
θ_{max} = 25.11°
h = −11 → 11
k = 0 → 20
l = −13 → 13
3 standard reflections every 97 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.132
S = 1.042
3241 reflections
199 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 11.409P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.009
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.93 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Au1—C1	2.073 (13)	P1—C14	1.813 (11)
Au1—P1	2.284 (3)	P1—C2	1.841 (11)
P1—C8	1.806 (12)	N1—C1	1.04 (2)
C1—Au1—P1	177.0 (4)	C2—P1—Au1	110.5 (4)
C8—P1—Au1	113.3 (4)	N1—C1—Au1	173.1 (4)
C14—P1—Au1	112.2 (4)		

Compound (II)

Crystal data

[Au(CN)($C_{21}H_{21}P$)]
M_r = 527.33
Orthorhombic
$P2_12_12_1$
a = 11.312 (2) Å
b = 12.996 (3) Å
c = 13.308 (3) Å
V = 1956.4 (7) Å^3
Z = 4
D_x = 1.790 Mg m^{-3}
D_m = 1.71 Mg m^{-3}
D_m measured by flotation in dibromoethane–CCl_4
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 18–25°
μ = 7.605 mm^{-1}
T = 293 (2) K
Needle
0.5 × 0.1 × 0.1 mm
Colourless

Data collection

Siemens *R3m* diffractometer
ω scans
Absorption correction:
ψ scan (North *et al.*, 1968)
T_{min} = 0.305, T_{max} = 0.467
1974 measured reflections
1972 independent reflections
1806 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 25.00°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.091$
$S = 1.060$
1959 reflections
227 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 1.0P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.736$ e Å^{-3}
$\Delta\rho_{min} = -0.811$ e Å^{-3}
Extinction correction:
*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
0.0008 (3)
Scattering factors from
International Tables for Crystallography (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (2)

Table 2. *Selected geometric parameters (Å, °) for (II)*

Au1—Cl	2.087 (10)	P1—C2	1.826 (10)
Au1—P1	2.286 (3)	P1—C16	1.833 (10)
P1—C9	1.814 (10)	N1—C1	1.02 (2)
C1—Au1—P1	174.3 (3)	C16—P1—Au1	107.5 (3)
C9—P1—Au1	113.8 (3)	N1—C1—Au1	172.9 (13)
C2—P1—Au1	116.9 (3)		

ω scans of several intense reflections were used to indicate acceptable crystal quality. The 2θ scan width was 2.0° + $K\alpha$ separation with a variable scan rate in θ between 1.5 and 14.6° min^{-1}. Background measurement was made by stationary crystal and stationary counter techniques at the beginning and end of each reflection for half the total scan time (Siemens, 1990*a*). Intensities were corrected for absorption using the ΔF empirical method (Walker & Stuart, 1983) in the case of compound (I) and by using ψ scans (North *et al.*, 1968) for compound (II). Correction of absorption in compound (I) was carried out by the ΔF method because the shape of the crystal was not suitable for using crystal faces and the ψ scan was unsuccessful. C-bound H atoms were placed in idealized positions [C—H = 0.96 Å and U(H) = 0.08 Å^2 (fixed)]. The H-atom parameters were not refined.

For both compounds, data collection: *P3VAX* (Siemens, 1990*a*); cell refinement: *P3VAX*; data reduction: *XDISK* (Siemens, 1990*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1990*c*); software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

We are thankful to the KFUPM Dhahran, Saudi Arabia. Thanks are also due to Dr N. Akhtar for synthesizing the compounds and the National Science Foundation (USA) for grant CHE-8513273.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1329). Services for accessing these data are described at the back of the journal.

References

Ahrland, S., Aurivillius, B., Dreisch, K., Noren, B. & Oskarsson, A. (1992). *Acta Chem. Scand.* **46**, 262–265.
Akhtar, M. N., Gazi, I. H., Isab, A. A., Al-Arfaj, A. R., Wazeer, M. I. M. & Hussain, M. S. (1995). *J. Coord. Chem.* **36**, 149–157.
Akhtar, M. N., Isab, A. A., Al-Arfaj, A. R. & Hussain, M. S. (1997). *Polyhedron*, **16**, 125–132.
Akhtar, M. N., Isab, A. A., Hussain, M. S. & Al-Arfaj, A. R. (1996). *Transition Met. Chem.* **21**, 553–555.
Al-Arfaj, A. R., Hussain, M. S., Isab, A. A. & Akhtar, M. N. (1996). *Acta Cryst.* C**52**, 550–553.
Al-Arfaj, A. R., Reibenspies, J. H., Hussain, M. S., Darensbourg, M. Y., Akhtar, N. & Isab, A. A. (1997). *Acta Cryst.* C**53**, 1553–1555.
Bellon, P. L., Manassero, M. & Sansoni, M. (1969). *Ric. Sci.* **39**, 173–175.
Duddell, D. A., Goggin, P. L., Goodfellow, R. J., Norton, M. D. & Smith, J. G. (1970). *J. Chem. Soc. A*, pp. 545–564.
Fackler, J. P. Jr, Staples, R. J., Kahn, M. N. I. & Winpenny, R. E. P. (1994). *Acta Cryst.* C**50**, 1020–1023.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Graham, G. G., Haavisto, T. M., Jones, H. M. & Champion, G. D. (1984). *Biochem. Pharmacol.* **33**, 1257–1262.
Graham, G. G., Haavisto, T. M., McNaught, P. J., Browne, C. D. & Champion, G. D. (1982). *J. Rheum.* **4**, 527–532.
Hancock, R. D., Finnkelstein, N. P. & Avers, A. (1972). *J. Inorg. Nucl. Chem.* **34**, 3747–3749.
Harker, C. S. W. & Tiekink, E. R. T. (1991). *Acta Cryst.* C**47**, 878–879.
Hormann, A. L., Shaw, C. F. III, Bennett, D. W. & Reiff, W. M. (1986). *Inorg. Chem.* **25**, 3953–3957.
Hormann-Arendt, A. L. & Shaw, C. F. III (1990). *Inorg. Chem.* **29**, 4683–4687.
Hussain, M. S., Al-Arfaj, A. R., Akhtar, M. N. & Isab, A. A. (1996). *Polyhedron*, **15**, 2781–2785.
Isab, A. A. (1992). *J. Inorg. Biochem.* **45**, 145–150, and references therein.
James, D. W., Ludvigsen, N. W., Cleland, L. G. & Milazzo, S. C. (1982). *J. Rheum.* **9**, 532–537.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Reibenspies, J. H., Draper, J. D., Struck, G. & Darensbourg, D. J. (1996). *Z. Kristallogr.* **211**, 400–401.
Sadler, P. J. & Sue, R. E. (1995). *Handb. Met.–Ligand Interact. Biol. Fluids: Bioinorg. Chem.* **2**, 1039–1051.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1990*a*). *P3VAX*3.42. *Program for R3m/V X-ray Diffractometer Control*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1990*b*). *XDISK*. *Program for Reduction of Data Collected on Siemens R3m/V Diffractometers*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1990*c*) *XP*. *Program for Molecular Graphics*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.