

Two Crystalline Modifications of *cis-trans*-Dicarbonyl(1,10-phenanthroline)bis(trimethyl phosphite)manganese(I) Perchlorate

BY JOSÉ FAYOS*

Departamento de Rayos X, Instituto 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain

AND MITXEL ULIBARRI

Departamento de Cristalografía y Mineralogía, Colegio Universitario de Alava, Vitoria, Spain

(Received 7 June 1982; accepted 1 July 1982)

Abstract. $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OCH}_3)_3\}_2(\text{C}_{12}\text{H}_8\text{N}_2)]\text{ClO}_4$: crystal (I), monoclinic, $P2_1/c$, $a = 11.3770$ (5), $b = 13.4650$ (5), $c = 18.2880$ (5) Å, $\beta = 77.504$ (4)°, $Z = 4$, $D_x = 1.558$ Mg m⁻³, $R = 0.060$ for 3907 observed reflexions; crystal (II), monoclinic, $P2_1/n$, $a = 22.728$ (5), $b = 13.555$ (2), $c = 9.006$ (1) Å, $\beta = 76.45$ (1)°, $Z = 4$, $D_x = 1.580$ Mg m⁻³, $R = 0.066$ for 3265 observed reflexions. The title compound simultaneously forms, in the same crystallization process, two kinds of crystals, (I) and (II), having related crystal lattices. The geometries of the molecules in both crystals are alike except for one phosphite ligand, which is statistically disordered in crystal (II).

Introduction. Stereospecific reactions for some Mn^I coordination complexes have been postulated (Uson, Riera, Gimeno & Laguna, 1977) using IR spectroscopy. The following decarbonylation-carbonylation sequence has been proposed for the ClO_4^- salts: $[\text{Mn}(\text{CO})_3\text{phen}]\text{OClO}_3 \rightarrow \textit{cis-trans}$ - $[\text{Mn}(\text{CO})_2L_2\text{phen}]\text{OClO}_3 \rightarrow [\text{Mn}(\text{CO})L_3\text{phen}]\text{OClO}_3 \rightarrow \textit{cis-cis}$ - $[\text{Mn}(\text{CO})_2L_2\text{phen}]\text{OClO}_3$. In order to confirm this hypothesis, we have already determined the crystal structure of the last perchlorate salt with $L = \text{P}(\text{OMe})_3$ (Ulibarri & Fayos, 1982). In this paper we present the crystal-structure determination of the first intermediate salt, which has been carried out from two crystallographically independent crystals.

Crystals of *cis-trans*- $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2\text{phen}]\text{ClO}_4$ were a mixture of yellow prisms with two different habits, (I) and (II). Both selected crystals of ~0.25 mm in section are monoclinic with closely related crystal lattices. Graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) was used to collect the intensities of the 7900 independent reflexions on each crystal for $\theta < 30^\circ$. The experiments were done with a fully automatic single-crystal diffractometer, and no decomposition of

the crystals was observed. Some intensities were measured twice on two equivalent directions and showed an averaged experimental discrepancy less than 2% for both crystals. After background, Lorentz-polarization and absorption corrections ($\mu_1 = 7.89$, $\mu_2 = 8.01$ cm⁻¹), those reflexions with $I > 3\sigma(I)$ were considered as observed. There were 3907 observed intensities for crystal (I), while only 3265 for crystal (II).

The crystal structures of (I) and (II) were solved by the heavy-atom method. They are shown in Fig. 1. Positional and anisotropic thermal parameters were refined by full-matrix least squares. The scattering factors used were those given in *International Tables for X-ray Crystallography* (1974) and were corrected for anomalous dispersion. H atoms were found on difference maps except for those of some methyls where a geometrical disorder was assumed. Crystal (II) presents statistical disorder for the phosphite group P(2). In fact, after an anisotropic refinement of every atomic parameter, except those corresponding to this phosphite group, a difference map revealed two possible positions each for O(22) and O(23), *i.e.* four peaks with about the same electron-density values.

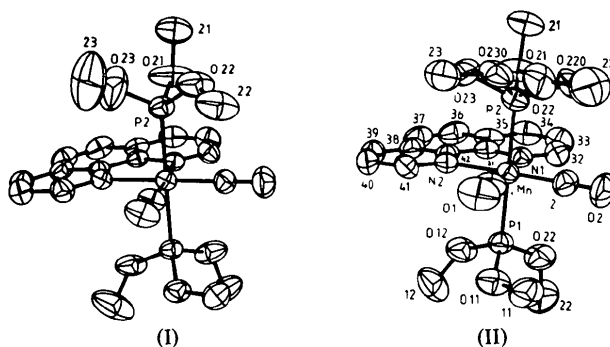


Fig. 1. Computer drawing of the molecules present in crystals (I) and (II). The atom nomenclature is the same for both molecules. The C atoms are named by their ordinal only.

* To whom correspondence should be addressed.

Table 1. Atomic fractional coordinates ($\times 10^4$) for non-H atoms and equivalent isotropic thermal parameters ($\times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \cos(a_i, a_j). \text{ E.s.d.'s in parentheses refer to the last significant digits.}$$

	x	y	z	U_{eq} (\AA^2)		x	y	z	U_{eq} (\AA^2)
Crystal (I)					Crystal (II)				
Mn	7508 (1)	2912 (1)	2886 (1)	37 (1)	Mn	3645 (1)	2867 (1)	6969 (1)	47 (1)
C(1)	7158 (5)	3769 (4)	3646 (3)	46 (1)	C(1)	3879 (3)	3752 (5)	8193 (7)	66 (2)
O(1)	6944 (4)	4325 (3)	4133 (2)	69 (2)	O(1)	4022 (3)	4320 (4)	8989 (6)	98 (2)
C(2)	9083 (5)	3005 (4)	2857 (3)	49 (2)	C(2)	2873 (3)	3263 (5)	7624 (7)	63 (2)
O(2)	10098 (4)	3066 (4)	2840 (3)	76 (2)	O(2)	2385 (2)	3516 (5)	8025 (7)	98 (2)
N(1)	7721 (3)	1936 (3)	2003 (2)	41 (1)	N(1)	3450 (2)	1786 (3)	5553 (5)	51 (1)
N(2)	5749 (3)	2742 (3)	2796 (2)	39 (1)	N(2)	4503 (2)	2352 (3)	6002 (5)	53 (2)
C(31)	6667 (4)	1686 (3)	1811 (2)	40 (1)	C(31)	3948 (3)	1300 (4)	4742 (6)	54 (2)
C(32)	8727 (5)	1523 (4)	1612 (3)	52 (2)	C(32)	2914 (3)	1496 (5)	5383 (7)	67 (2)
C(33)	8734 (6)	823 (5)	1044 (3)	62 (2)	C(33)	2847 (4)	695 (6)	4455 (9)	82 (3)
C(34)	7690 (6)	567 (4)	852 (3)	63 (2)	C(34)	3338 (4)	192 (5)	3647 (8)	79 (3)
C(35)	6607 (5)	1023 (4)	1225 (3)	49 (2)	C(35)	3914 (3)	510 (4)	3743 (7)	68 (2)
C(36)	5457 (6)	862 (5)	1039 (3)	64 (2)	C(36)	4470 (4)	87 (5)	2879 (8)	81 (3)
C(37)	4465 (6)	1332 (5)	1404 (3)	65 (2)	C(37)	5008 (4)	426 (6)	3037 (8)	81 (3)
C(38)	4502 (5)	1995 (4)	2014 (3)	50 (2)	C(38)	5050 (3)	1206 (5)	4075 (7)	67 (2)
C(39)	3489 (5)	2489 (5)	2440 (4)	59 (2)	C(39)	5593 (3)	1583 (7)	4326 (9)	84 (3)
C(40)	3624 (5)	3065 (5)	3026 (4)	62 (2)	C(40)	5592 (3)	2292 (7)	5405 (9)	81 (3)
C(41)	4759 (5)	3175 (4)	3191 (3)	52 (2)	C(41)	5033 (3)	2667 (5)	6234 (7)	64 (2)
C(42)	5614 (4)	2148 (3)	2215 (2)	39 (1)	C(42)	4514 (2)	1630 (4)	4951 (6)	52 (2)
P(1)	7707 (1)	4160 (1)	2058 (1)	44 (1)	P(1)	3771 (1)	3969 (1)	5046 (2)	55 (1)
O(11)	7891 (4)	5264 (3)	2321 (2)	59 (1)	O(11)	3888 (3)	5096 (4)	5361 (6)	86 (2)
C(11)	8899 (6)	5534 (5)	2625 (4)	72 (3)	C(11)	3455 (4)	5657 (6)	6444 (11)	95 (3)
O(12)	6603 (4)	4325 (3)	1681 (3)	79 (2)	O(12)	4340 (3)	3748 (4)	3694 (6)	88 (2)
C(12)	6136 (11)	5168 (7)	1430 (7)	133 (6)	C(12)	4764 (4)	4395 (8)	2767 (12)	111 (4)
O(13)	8829 (5)	3965 (3)	1394 (2)	77 (2)	O(13)	3225 (3)	3960 (4)	4243 (6)	88 (2)
C(13)	9268 (9)	4647 (7)	805 (4)	99 (4)	C(13)	3213 (5)	4541 (10)	2921 (11)	124 (5)
P(2)	7332 (1)	1633 (1)	3696 (1)	49 (1)	P(2)	3521 (1)	1745 (1)	8858 (2)	58 (5)
O(21)	7593 (7)	599 (3)	3284 (3)	108 (3)	O(21)	3460 (3)	659 (4)	8334 (6)	101 (3)
C(21)	7614 (9)	-344 (5)	3610 (5)	98 (4)	C(21)	3345 (5)	-180 (6)	9340 (9)	93 (3)
O(22)	8186 (5)	1536 (4)	4260 (3)	92 (2)	O(22)	3208 (7)	2005 (12)	10494 (11)	102 (6)
C(22)	8725 (9)	2288 (5)	4593 (5)	97 (4)	O(220)	2789 (4)	1648 (7)	9851 (12)	78 (4)
O(23)	6066 (5)	1427 (8)	4190 (4)	152 (4)	C(22)	2579 (6)	2296 (10)	11076 (12)	139 (5)
C(23)	5499 (11)	1689 (12)	4846 (8)	168 (7)	O(23)	4177 (4)	1391 (7)	9287 (11)	79 (4)
Cl	2047 (1)	2803 (1)	5169 (1)	66 (1)	O(230)	3761 (6)	1837 (10)	10279 (12)	85 (5)
O(31)	3151 (5)	3335 (5)	4927 (3)	102 (2)	C(23)	4448 (5)	1988 (7)	10151 (12)	108 (4)
O(32)	1743 (7)	2744 (7)	5947 (4)	139 (4)	Cl	3840 (1)	7283 (1)	10550 (2)	80 (1)
O(33)	2096 (9)	1873 (5)	4853 (5)	158 (4)	O(31)	3692 (8)	8062 (7)	11468 (12)	216 (8)
O(34)	1182 (6)	3365 (7)	4895 (6)	157 (4)	O(32)	3380 (5)	6830 (14)	10237 (20)	274 (9)
					O(33)	4205 (6)	7536 (11)	9178 (13)	220 (7)
					O(34)	4152 (7)	6606 (8)	11244 (15)	223 (8)

Nevertheless, only one peak each for C(22) and C(23) was found, as is shown in Fig. 1. This statistical disorder was also confirmed by anisotropic refinement of this model. The four population parameters for each position O(22), O(220), O(23) and O(230) converged to values between 47 and 52% when considered as free parameters. Disordered H atoms of methyls C(22) and C(23) were not included in the refinement. Although the phosphite group P(2) in crystal (I) is not disordered, its thermal motion is significantly high. The ClO₄⁻ anions presented difficulties in the refinement, as usual, due to the strong libration of the O atoms around Cl. After some trials, a non-disordered anisotropic model was considered more realistic and was included in the least-squares refinement for (I) and (II) (Stewart, Kundell & Baldwin, 1970). At the end of the refinement

a weighting scheme to prevent trends in $\langle w\Delta^2 F \rangle$ vs $\langle F_{obs} \rangle$ or $\langle \sin \theta / \lambda \rangle$ was introduced. The refinements converged to $R_{(I)} = 0.060$ and $R_{w(I)} = 0.066$, and $R_{(II)} = 0.066$ and $R_{w(II)} = 0.075$. Table 1 shows the atomic positional and thermal parameters for (I) and (II).* Bond lengths and selected bond angles are in Table 2. Table 3 shows some interesting torsional angles together with some of the *cis-cis* isomer (Ulibarri & Fayos, 1982) for comparison.

* The $F_o - F_c$ lists, anisotropic thermal parameters and fractional coordinates of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38051 (105 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) for crystals (I) and (II)

E.s.d.'s are in parentheses.

	(I)	(II)
Mn—C(1)	1.784 (5)	1.791 (7)
—C(2)	1.786 (5)	1.797 (6)
—P(1)	2.241 (1)	2.253 (2)
—P(2)	2.252 (2)	2.250 (2)
—N(1)	2.056 (4)	2.058 (5)
—N(2)	2.056 (4)	2.062 (4)
C(1)—O(1)	1.149 (6)	1.149 (9)
C(2)—O(2)	1.151 (7)	1.137 (8)
P(1)—O(11)	1.590 (4)	1.588 (5)
—O(12)	1.573 (6)	1.582 (5)
—O(13)	1.583 (4)	1.576 (7)
O(11)—C(11)	1.426 (9)	1.432 (10)
O(12)—C(12)	1.373 (12)	1.421 (11)
O(13)—C(13)	1.421 (9)	1.433 (11)
P(2)—O(21)	1.580 (5)	1.561 (6)
—O(22)	1.567 (7)	1.520 (10)
—O(220)	—	1.699 (9)
—O(23)	1.550 (6)	1.695 (11)
—O(230)	—	1.510 (13)
O(21)—C(21)	1.406 (9)	1.440 (9)
O(22)—C(22)	1.391 (11)	1.458 (19)
O(220)—	—	1.403 (15)
O(23)—C(23)	1.282 (15)	1.363 (15)
O(230)—	—	1.550 (18)
N(1)—C(31)	1.363 (7)	1.364 (7)
N(2)—C(42)	1.365 (6)	1.358 (7)
N(1)—C(32)	1.333 (6)	1.324 (8)
N(2)—C(41)	1.333 (6)	1.339 (8)
C(32)—C(33)	1.401 (8)	1.400 (11)
C(41)—C(40)	1.396 (9)	1.409 (9)
C(33)—C(34)	1.354 (10)	1.362 (11)
C(40)—C(39)	1.359 (9)	1.367 (12)
C(34)—C(35)	1.413 (8)	1.401 (12)
C(39)—C(38)	1.411 (7)	1.401 (11)
C(35)—C(31)	1.408 (7)	1.412 (8)
C(38)—C(42)	1.407 (7)	1.410 (8)
C(35)—C(36)	1.437 (10)	1.439 (11)
C(38)—C(37)	1.437 (9)	1.430 (10)
C(31)—C(42)	1.408 (6)	1.415 (8)
C(36)—C(37)	1.339 (9)	1.342 (13)
Cl—O(31)	1.431 (6)	1.335 (10)
—O(32)	1.393 (6)	1.299 (16)
—O(33)	1.375 (8)	1.360 (11)
—O(34)	1.416 (9)	1.394 (15)
C(1)—Mn—C(2)	91.8 (2)	90.3 (3)
—P(1)	90.8 (2)	91.5 (2)
—P(2)	90.5 (2)	89.5 (2)
—N(1)	173.8 (2)	174.8 (3)
—N(2)	94.4 (2)	95.7 (3)
C(2)—Mn—P(1)	88.5 (2)	89.6 (2)
—P(2)	91.1 (2)	90.8 (2)
—N(1)	94.3 (2)	94.6 (3)
—N(2)	173.4 (2)	173.5 (3)
P(1)—Mn—P(2)	178.63 (5)	178.94 (7)
—N(1)	88.3 (1)	90.2 (1)
—N(2)	89.2 (1)	87.8 (1)
P(2)—Mn—N(1)	90.4 (1)	88.8 (1)
—N(2)	91.0 (1)	91.7 (1)
N(1)—Mn—N(2)	79.5 (2)	79.5 (2)
Mn—C(1)—O(1)	179.3 (5)	179.2 (6)
—C(2)—O(2)	179.9 (5)	179.4 (6)
Mn—P(1)—O(11)	119.8 (2)	119.8 (2)
—O(12)	115.4 (2)	113.6 (2)
—O(13)	109.9 (2)	112.1 (2)

Table 2 (cont.)

	(I)	(II)
Mn—P(2)—O(21)	112.3 (2)	114.4 (2)
—O(22)	121.1 (2)	121.5 (6)
—O(220)	—	112.6 (4)
—O(23)	117.3 (4)	113.7 (3)
—O(230)	—	125.4 (5)
P(1)—O(11)—C(11)	121.7 (4)	121.0 (5)
—O(12)—C(12)	131.8 (6)	130.9 (6)
—O(13)—C(13)	124.6 (5)	123.2 (6)
O(11)—P(1)—O(12)	99.8 (2)	100.3 (3)
O(11)— —O(13)	104.5 (2)	105.8 (3)
O(12)— —O(13)	106.0 (3)	103.5 (3)
P(2)—O(21)—C(21)	127.8 (5)	124.8 (5)
—O(22)—C(22)	128.5 (5)	107.4 (8)
—O(220)—	—	118.5 (9)
—O(23)—C(23)	135.4 (9)	120.1 (7)
—O(230)—	—	120.3 (8)
O(21)—P(2)—O(22)	99.3 (3)	117.2 (6)
—O(220)—	—	86.6 (4)
O(21)—P(2)—O(23)	100.1 (5)	87.0 (4)
—O(230)—	—	114.2 (6)
O(22)— —O(23)	103.4 (3)	94.7 (7)
O(220)— —O(230)	—	93.7 (6)

Table 3. Some torsional angles (°) in the molecules of crystals (I), (II) and the *cis-cis* isomer

E.s.d.'s in parentheses refer to the last digit.

	(I)	(II)	<i>cis-cis</i>
N(1)—C(31)—C(42)—N(2)	4.9 (5)	3.9 (6)	−0.4 (7)
C(33)—C(34)—C(35)—C(36)	−175.7 (5)	−176.0 (6)	179.9 (7)
C(40)—C(39)—C(38)—C(37)	−177.2 (5)	−176.2 (7)	179.4 (7)
C(33)—C(32)—N(1)—C(31)	2.7 (5)	2.4 (8)	1 (1)
C(40)—C(41)—N(2)—C(42)	1.5 (7)	1.6 (7)	−0.8 (8)
C(1)—Mn—P(1)—O(11)	−17.9 (3)	−10.3 (4)	−8.6 (3)
—O(12)	101.4 (3)	108.0 (3)	103.1 (3)
—O(13)	−138.9 (3)	−135.1 (3)	−136.4 (3)
Mn—P(1)—O(11)—C(11)	−60.6 (5)	−60.1 (7)	−62.4 (6)
—O(12)—C(12)	−147.8 (7)	−141.9 (8)	−170.4 (5)
—O(13)—C(13)	174.8 (6)	184.4 (7)	168.0 (6)
C(1)—Mn—P(2)—O(21)	−180.9 (4)	−165.4 (4)	—
—O(22)	62.4 (3)	44.5 (7)	—
—O(220)	—	97.8 (5)	—
—O(23)	−65.7 (4)	−67.5 (4)	—
—O(230)	—	−14.5 (7)	—
Mn—P(2)—O(21)—C(21)	−177.2 (8)	−176.6 (7)	—
—O(22)—C(22)	−31.0 (7)	65 (2)	—
—O(220)—C(22)	—	−86 (1)	—
—O(23)—C(23)	93 (1)	78.0 (8)	—
—O(230)—C(23)	—	−57 (1)	—

Discussion. Apart from the disorder of the P(2) group in crystal (II), only slight differences are found between the molecules in crystals (I) and (II). Fig. 1 and Table 3 show these differences. Both phen groups present the same planarity deviation and the conformations around P(1) are similar and also comparable with those of the *cis-cis* isomer. Around P(2), the conformation of O(21)—C(21) does not change much between crystals (I) and (II). The pairs O(22), O(220) and O(23), O(230) are pseudosymmetrically disposed at both sides

of the planes Mn—P(2)—C(22) and Mn—P(2)—C(23) respectively.

We thank Professor S. García-Blanco for his support and Professor J. M. Amigó for the facilities provided for the use of the automatic diffractometer of the University of Bilbao, Spain. We also thank the Centro de Calculo de JEN, Madrid, for the facilities provided.

Acta Cryst. (1982). **B38**, 3089–3091

2-Chloro-4,4,6,6-tetramethyl-1,3,2-dioxarsenane

BY P. VAN NUFFEL, A. T. H. LENSTRA AND H. J. GEISE*

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

L. K. YULDASHEVA

A. M. Butlerov Scientific Research Chemical Institute at Kazan University, Leninstreet 18, 420008 Kazan, USSR

AND N. A. CHADAEVA

Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR, Kazan Branch, Arbusov Street 8, 420083 Kazan, USSR

(Received 18 May 1982; accepted 1 July 1982)

Abstract. C₇H₁₄AsClO₂, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.867$ (9), $b = 10.730$ (14), $c = 11.738$ (9) Å, $\beta = 92.67$ (5)°, $D_c = 1.614$ Mg m⁻³ at 150 K. The structure was solved by conventional techniques to $R_w = 0.041$ for 1005 observed reflections. The dioxarsenane ring adopts a twist-boat conformation with the As—Cl pointing in an axial direction.

Introduction. Recently, the spatial structure of six-membered cyclic esters containing CH₃ groups in the 4,4,6,6 positions was investigated by NMR and dipole-moment methods (Samitov, Yuldasheva & Anonimova, 1982). As a result of this work it was shown that 2-chloro-4,4,6,6-tetramethyl-1,3,2-dioxarsenane has a flexible conformation in solution. However, even at temperatures below 175 K the spectra gave no clear evidence about the type of flexible form. Therefore, an X-ray investigation of the solid phase was undertaken. This would give extra information about the title compound as well as information about dioxarsenane geometry. To our knowledge this is the first crystallographic report on a cyclic ester containing As.

The title compound was synthesized by a method

References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
 ULIBARRI, M. & FAYOS, J. (1982). *Acta Cryst.* **B38**, 952–954.
 USON, R., RIERA, V., GIMENO, J. & LAGUNA, M. (1977). *Transition Met. Chem.* **2**, 123–130.

described by Kamai & Chadaeva (1951) and purified by distillation *in vacuo* under argon (b.p. 365 K/1.47 kPa). It crystallized spontaneously upon standing (m.p. 316–317.5 K).

A total of 1198 independent reflections ($0 \leq \theta \leq 22^\circ$) was measured at 150 K on an Enraf–Nonius CAD-4 diffractometer employing Mo radiation ($\lambda = 0.7107$ Å), a monochromator and a pure ω scan. Even under a continuous stream of cold nitrogen gas, with the crystal sealed inside a Lindemann-glass capillary, a slight decrease in standard intensity was noticed and corrected for. Intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied in view of the size of the crystal ($0.2 \times 0.2 \times 0.2$ mm) and the absorption coefficient ($\mu = 3.84$ mm⁻¹ for Mo $K\alpha$).

A set of 1005 reflections with $I > 2\sigma(I)$ was used in the analysis. The structure was solved by conventional Patterson and (difference) Fourier techniques. Isotropic temperature parameters of the H atoms were fixed at $B_{150} = 2.5$ Å² during the least-squares refinement. A weighting scheme based on counting statistics was used. No extinction correction was made.

The refinement converged to $R_w = 0.041$, with R_w defined as $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ for observed reflections. The maximum noise level in the final

* Author to whom correspondence should be addressed.