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

Ta(1)—I(3)	2.704 (1)	Ta(3)—Te(8ˢ)	2.850 (1)
Ta(1)—I(2ⁱ)	2.757 (1)	Ta(4)—Te(9ˢⁱ)	2.831 (1)
Ta(1)—I(1)	2.759 (1)	Ta(4)—Te(1ˢⁱⁱ)	2.843 (1)
Ta(2)—Te(6)	2.845 (1)	Ta(4)—Te(10ⁿⁱ)	2.853 (1)
Ta(2)—Te(8)	2.847 (1)	Ta(4)—Te(10)	2.860 (1)
Ta(2)—Te(2)	2.855 (1)	I(5)—Te(11)	3.215 (2)
Ta(3)—Te(4)	2.840 (1)	Te(9)—Te(10)	2.774 (1)
Ta(3)—Te(1)	2.842 (1)	Te(11)—Te(12)	2.811 (2)
Ta(2)—Ta(3ⁱⁱ)	3.397 (1)	I(5)—Te(8)	3.262 (2)
I(1)—Te(5ⁱⁱⁱ)	3.415 (2)	Te(6)—Te(7ˢⁱⁱⁱ)	3.586 (1)
I(2)—Te(2ⁱˢ)	3.433 (2)	Te(9)—Te(9ⁱˣ)	3.593 (2)
I(3ⁱ)—Ta(1)—I(1)	90.66 (4)	Te(6)—Ta(2)—Te(8)	78.41 (4)
I(3ⁱ)—Ta(1)—I(1ⁱ)	89.34 (4)	Te(6)—Ta(2)—Te(4)	77.15 (4)
I(2)—Ta(1)—I(2ⁱ)	180	Te(6)—Ta(2)—Te(2)	144.17 (4)
Te(3)—Ta(3)—Te(8ˢ)	90.36 (3)	Te(11ˢⁱⁱ)—Ta(4)—Te(12)	79.07 (4)
Te(3)—Ta(3)—Te(2)	107.22 (4)	Te(11ˢⁱⁱ)—Ta(4)—Te(11)	107.20 (3)
Te(7ˢ)—Ta(3)—Te(1)	77.05 (3)	Te(11ˢⁱⁱ)—Ta(4)—Te(10)	133.01 (4)
Te(7ˢ)—Ta(3)—Te(5ˢ)	80.39 (4)	Te(9)—Ta(4)—Te(12ˢⁱⁱ)	76.62 (3)
Te(1)—Ta(3)—Te(8ˢ)	84.38 (4)	Te(12)—Ta(4)—Te(10ⁿⁱ)	85.47 (4)
Te(1)—Ta(3)—Te(2)	58.15 (3)	Te(12)—Ta(4)—Te(10)	143.79 (3)
Te(9ˢⁱ)—Ta(4)—Te(12)	79.08 (4)	Te(2)—Te(1)—Ta(2)	61.22 (3)
Ta(3)—Te(3)—Ta(2)	73.03 (3)	Te(12)—Te(11)—I(5)	156.13 (4)
Te(8)—Te(7)—Ta(3ⁱⁱ)	60.93 (5)	Ta(2)—Te(7)—Ta(3ⁱⁱ)	73.52 (3)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 1-y, -z$; (v) $x, y, z-1$; (vi) $-x, 1-y, 2-z$; (vii) $-x, 1-y, 1-z$; (viii) $x-1, y, z$; (ix) $1-x, 1-y, 2-z$.

The structure was solved by direct methods (*MITHRIL*; Gilmore, 1983) and difference Fourier techniques, and refined by full-matrix least-squares methods (Peterse & Palm, 1966). Refined absorption corrections were compared to the cylindrical corrections and were deemed reliable for this fine needle crystal. The maximum and minimum peaks in the final difference Fourier map are near Ta sites. All calculations were performed on a MicroVAXII computer using *TEXSAN* software (Molecular Structure Corporation, 1985).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1093). Services for accessing these data are described at the back of the journal.

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Carbon Dioxide at 1.0 GPa

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Abstract

An X-ray diffraction study of single-crystal CO_2 has been undertaken at 1.00 (5) GPa pressure. The crystal exhibits $Pa\bar{3}$ symmetry with a cell edge of 5.4942 (2) Å and a C—O bond length of 1.168 (1) Å (corrected for thermal motion effects). The study demonstrates that an earlier claim of a new dry ice II phase at this pressure is unfounded.

Comment

Carbon dioxide is one of the most important gaseous compounds relevant to geological processes, both for the earth and other planetary bodies. As such, an understanding of its high-pressure phases and properties is of interest. For instance, an interpretation of near-surface emission spectra obtained from Jupiter requires a knowledge of the phases that could possibly exist there. The CO_2 gas phase, stable at room conditions, transforms directly to solid dry ice at 194.5 K and room pressure. The structure of a single crystal of dry ice has most recently been determined by Simon & Peters (1980) at 150 K, crystallizing in space group $Pa\bar{3}$ with the C atoms occupying special position $4a$ and the O atoms occupying $8c$.

With application of pressure while maintaining room temperature, however, the gas transforms to a liquid at around 7.5 MPa, and then to a solid at around 0.5 GPa (Bridgman, 1914). Liu (1983) claimed that this solid represents a new phase, which he called dry ice II, stable to 2.3 GPa, above which the solid transforms to dry ice. The evidence for the existence of the dry ice II phase was a 'poor quality' powder pattern. With further application of pressure above 10 GPa, dry ice appears to transform to a *Cmca* structure (Aoki *et al.*, 1994), again based on powder work. We report here the first single-crystal X-ray diffraction study of the structure of CO_2 at pressure, undertaken to determine the phase observed by Liu (1983). The results demonstrate that Liu's claim of the new dry ice II phase is unfounded.

The single-crystal X-ray analysis demonstrates that CO_2 exhibits cubic $Pa\bar{3}$ symmetry immediately upon

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transformation to a solid on the application of pressure. The unit-cell length of CO_2 at 1.0 GPa is 5.4942 (2) Å, compared with 5.624 (2) Å observed by Simon & Peters (1980). However, the C—O bond length appears to be constant under both sets of conditions. Its value, when corrected for simple rigid-bond thermal motion (Downs *et al.*, 1992) is 1.168 (1) Å [1.1486 (9) Å, uncorrected], compared with corrected values of 1.164 (Simon & Peters, 1980) and 1.162 Å (Karle & Karle, 1949, 1950) obtained by electron diffraction in the gas phase.

Experimental

CO_2 was obtained as a commercial product.

Crystal data

CO_2	Mo $K\alpha$ radiation
$M_r = 44.01$	$\lambda = 0.7107$ Å
Cubic	Cell parameters from 18
$Pa\bar{3}$	reflections
$a = 5.4942$ (2) Å	$\theta = 6.4–14.0°$
$V = 165.85$ (2) Å³	$\mu = 0.172$ mm⁻¹
$Z = 4$	$T = 293$ K
$D_x = 1.762$ Mg m⁻³	Disc
D_m not measured	0.25 mm (radius)
	Colourless

Data collection

Huber four-circle diffractom-eter	$R_{int} = 0.034$
	$\theta_{max} = 30°$
Profile data from $\theta/2\theta$ scans	$h = -6 \rightarrow 6$
Absorption correction: none	$k = -7 \rightarrow 7$
596 measured reflections	$l = -5 \rightarrow 5$
78 independent reflections	2 standard reflections
43 reflections with	frequency: 180 min
$I > 2\sigma(I)$	intensity decay: 9%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.041$	$\Delta\rho_{max} = 0.063$ e Å⁻³
$wR = 0.018$	$\Delta\rho_{min} = -0.082$ e Å⁻³
$S = 1.28$	Extinction correction: none
43 reflections	Scattering factors from
6 parameters	Doyle & Turner (1968)
$w = 1/[\sigma^2(F) + (0.0055F)^2]$	

Compressed CO_2 liquid was forced into a conventional four-pin Bassett high-pressure diamond anvil cell using a gas-loading apparatus at 8.3 MPa. This was conducted numerous times in order to ensure that the cell was well purged and the confined sample was pure. The cell was constructed with Be seats and 250 µm thick Inconel steel gaskets with a 250 µm diameter hole. The diamond culets were 500 µm in diameter. No pressure medium was included. The pressure in the cell was increased to 1.00 (5) GPa, as measured by the pressure-dependent positions of characteristic fluorescence peaks of small included ruby chips. The sample chamber was visually observed to contain several crystals. A precession photograph demonstrated that although the reflections showed strain broadening, they could be indexed with $Pa\bar{3}$ symmetry. A single crystal was obtained by heating the entire sample assembly in an oven at 473 K overnight. Attempts to obtain strain-free crystals at higher pressures failed, and most likely will require a pressure medium.

Intensities were measured using a Huber diffractometer and *SINGLE* software (Finger & Angel, 1990), which was also used for cell refinement. The peak profiles were quite sharp, indicating that the strain had been relieved during the heating process. Only peaks belonging to the $Pa\bar{3}$ structure could be found. The structure determination was initiated with the atomic parameters of CO_2 given by Simon & Peters (1980) and refined with a modified version of *RFINE* (Finger & Prince, 1975).

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A Niobium(V) Arsenate: Nb9AsO25

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Abstract

Nonaniobium arsenic pentacosaoxide contains 3×3 ReO_3-type NbO_6 octahedral columns extended along **c**. Each column is linked to four crystallographically identical columns through shared edges of NbO_6 octahedra and shared corners of AsO_4 tetrahedra.