

Table 2. Selected geometric parameters (Å, °)

Ta(1)—I(3)	2.704 (1)	Ta(3)—Te(8 [*])	2.850 (1)
Ta(1)—I(2 [†])	2.757 (1)	Ta(4)—Te(9 ^{††})	2.831 (1)
Ta(1)—I(1)	2.759 (1)	Ta(4)—Te(1 ^{†††})	2.843 (1)
Ta(2)—Te(6)	2.845 (1)	Ta(4)—Te(10 ^{††})	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(3 ^{††})	3.397 (1)	I(5)—Te(8)	3.262 (2)
I(1)—Te(5 ^{†††})	3.415 (2)	Te(6)—Te(7 ^{†††})	3.586 (1)
I(2)—Te(2 ^{††})	3.433 (2)	Te(9)—Te(9 ^{††})	3.593 (2)
I(3 [†])—Ta(1)—I(1)	90.66 (4)	Te(6)—Ta(2)—Te(8)	78.41 (4)
I(3 [†])—Ta(1)—I(1 [†])	89.34 (4)	Te(6)—Ta(2)—Te(4)	77.15 (4)
I(2)—Ta(1)—I(2 [†])	180	Te(6)—Ta(2)—Te(2)	144.17 (4)
Te(3)—Ta(3)—Te(8 [*])	90.36 (3)	Te(11 ^{†††})—Ta(4)—Te(12)	79.07 (4)
Te(3)—Ta(3)—Te(2)	107.22 (4)	Te(11 ^{†††})—Ta(4)—Te(11)	107.20 (3)
Te(7 [†])—Ta(3)—Te(1)	77.05 (3)	Te(11 ^{†††})—Ta(4)—Te(10)	133.01 (4)
Te(7 [†])—Ta(3)—Te(5 [†])	80.39 (4)	Te(9)—Ta(4)—Te(12 ^{†††})	76.62 (3)
Te(1)—Ta(3)—Te(8 [*])	84.38 (4)	Te(12)—Ta(4)—Te(10 ^{††})	85.47 (4)
Te(1)—Ta(3)—Te(2)	58.15 (3)	Te(12)—Ta(4)—Te(10)	143.79 (3)
Te(9 ^{††})—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(3 [†])	60.93 (5)	Ta(2)—Te(7)—Ta(3 [†])	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).

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References

- Allmann, R., Baumann, I., Kutoglu, A., Rösch, H. & Hellne, E. (1964). *Naturwissenschaften*, **51**, 263–264.
- Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, University of Glasgow, Scotland.
- Huang, C.-C. (1994). *Study on Transition Metal Chalcogenides with Low-Dimensional Structures*. Doctoral Dissertation of Fuzhou University, People's Republic of China.
- King, B. R. (1994). In *Encyclopedia of Inorganic Chemistry*, Vol. 2. New York: John Wiley.
- Li, J., Hoffmann, R., Badding, M. E. B. & DiSalvo, F. J. (1990). *Inorg. Chem.* **29**, 3943–3952.
- Liu, S.-X., Huang, D.-P., Huang, C.-C., Xu, F.-D. & Huang, J.-L. (1996). *Polyhedron*, **15**, 2295–2297.
- Minton, G. & Brill, J. W. (1987). *Phys. Rev. B*, **36**, 4254–4259.
- Molecular Structure Corporation (1985). *TEXSAN, TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Peterse, W. J. A. M. & Palm, J. H. (1966). *Acta Cryst.* **20**, 147–150.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
- Whittingham, M. S. & Jackson, A. J. (1982). In *Intercalation Chemistry*. New York: Academic Press.

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Carbon Dioxide at 1.0 GPa

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Abstract

An X-ray diffraction study of single-crystal CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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

CO₂ was obtained as a commercial product.

Crystal data

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

Data collection

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

Refinement

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

Compressed CO₂ 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 CO₂ given by Simon & Peters (1980) and refined with a modified version of *RFINE* (Finger & Prince, 1975).

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References

- Aoki, K., Yamawaki, H., Sakashita, M., Gotoh, Y. & Takemura, K. (1994). *Science*, **265**, 356–358.
- Bridgman, P. W. (1914). *Phys. Rev.* **3**, 153–203.
- Downs, R. T., Gibbs, G. V., Bartelmebs, K. L. & Boisen, M. B. Jr (1992). *Am. Miner.* **77**, 751–757.
- Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- Finger, L. W. & Angel, R. J. (1990). *SINGLE*. Unpublished program. Carnegie Institute of Washington, DC, USA.
- Finger, L. W. & Prince, E. (1975). *A System of Fortran IV Computer Programs for Crystal Structure Computations*, p. 128. Technical Note 854, US National Bureau of Standards.
- Karle, I. L. & Karle, J. (1949). *J. Chem. Phys.* **17**, 1052–1058.
- Karle, I. L. & Karle, J. (1950). *J. Chem. Phys.* **18**, 565.
- Liu, L. (1983). *Nature (London)*, **303**, 508–509.
- Simon, A. & Peters, K. (1980). *Acta Cryst.* **B36**, 2750–2751.

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A Niobium(V) Arsenate: Nb₉AsO₂₅

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Abstract

Nonaniobium arsenic pentacosaoxide contains 3×3 ReO₃-type NbO₆ octahedral columns extended along *c*. Each column is linked to four crystallographically identical columns through shared edges of NbO₆ octahedra and shared corners of AsO₄ tetrahedra.