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The Crystal Structure of Diisothiocyanatodiethoxy-(1,3-diphenylpropane-1,3-dionato)-niobium(V)

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The structure of $Nb(OC_2H_5)_2(NCS)_2(C_6H_5COCHCOC_6H_5)$ has been determined by Patterson and Fourier methods and refined by full-matrix least-squares calculations to a final R of 0·034 for 2353 independent reflexions. The crystals are triclinic, space group $P\overline{1}$, with $a=11{\cdot}085$ (4), $b=12{\cdot}688$ (5), $c=8{\cdot}690$ (3) Å, $\alpha=94{\cdot}07$ (5), $\beta=97{\cdot}72$ (5), $\gamma=77{\cdot}40$ (5)°, $Z=2$. Nb is involved in distorted octahedral coordination; the donor atoms are the N atoms of the isothiocyanato groups, and the O atoms of the ethoxy and of the dibenzoylmethane (dbm) groups.

Introduction

An X-ray analysis of diisothiocyanatodiethoxy-(1,3-diphenylpropane-1,3-dionato)niobium(V) was undertaken after the structural study by n.m.r. and infrared spectroscopy (Kergoat, Tocquer, Guerchais & Dahan, 1976) in order to confirm the monomeric structural unit and to determine the coordination of the Nb atom.

Experimental

The intensities were collected on a CAD-3 Enraf–Nonius diffractometer in the θ–2θ scan mode.

With Ni-filtered Cu $K\alpha$ radiation, 3435 reflexions up to $2\theta = 120°$ were measured. Throughout the data collection, two reference reflexions were recorded after each sequence of 40 measured reflexions. The intensities of the standards remained constant to within $\pm 2{\cdot}5\%$.

With $I \leq 3\sigma(I)$, 1082 reflexions were considered unobserved. Standard deviations $\sigma(I)$ were calculated from $\sigma(I) = [I + I_1 + I_2 + (0{\cdot}02[I - I_1 - I_2])^2]^{1/2}$ where I_1 and I_2 are the background and I the peak counts.

Table 1. *Crystal data*

$C_{21}H_{21}N_2NbO_4S_2$, M. W. 521·9
Space group $P\bar{1}$
$a = 11{\cdot}085$ (4), $b = 12{\cdot}688$ (5), $c = 8{\cdot}690$ (3) Å
$\alpha = 94{\cdot}07$ (5), $\beta = 97{\cdot}72$ (5), $\gamma = 77{\cdot}40$ (5)°
$U = 1180{\cdot}9$ Å^3, $Z = 2$
$D_m = 1{\cdot}47$ g cm^{-3} (by flotation in calcium nitrate)
$D_x = 1{\cdot}468$
Crystal size $0{\cdot}25 \times 0{\cdot}10 \times 0{\cdot}175$ mm
Linear absorption coefficient $\mu = 61{\cdot}9$ cm^{-1}[λ(Cu $K\alpha$) = 1·5418 Å]

Crystal data are given in Table 1.*

The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure determination

The structure was solved by the heavy-atom method. The Nb atom was located from a Patterson function. A Fourier map phased on Nb located all non-hydrogen atoms.

Calculations were performed on an IBM 370-168 computer with a local version of *ORFLS* (Busing, Martin & Levy, 1963) for refinement and with NRC programs (Ahmed, Hall, Pippy & Huber, 1966) for geometrical calculations.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Full-matrix least-squares calculation was used to refine the atomic coordinates and isotropic temperature factors of all non-hydrogen atoms. R fell to 0·13

Table 2. *Fractional atomic coordinates* (× 10⁴) *and thermal parameters* (× 10⁴)

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right].$$

Estimated standard deviations (× 10⁴) are in parentheses.

B (in Å^2) is $\frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab\cos\gamma + 2\beta_{13}ac\cos\beta + 2\beta_{23}bc\cos\alpha)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Nb	2890 (0)	7074 (0)	8679 (1)	109 (0)	87 (0)	283 (1)	8 (0)	61 (1)	69 (1)	6·20
N(1)	3248 (4)	8172 (4)	10560 (7)	132 (6)	89 (5)	388 (18)	8 (4)	41 (8)	60 (7)	7·78
C(S1)	3569 (5)	8756 (4)	11576 (8)	108 (7)	75 (5)	374 (22)	12 (5)	79 (10)	63 (8)	6·84
S(1)	3986 (2)	9538 (2)	12916 (3)	204 (3)	112 (2)	474 (7)	−25 (2)	76 (3)	2 (3)	10·05
N(2)	2316 (4)	6130 (4)	6764 (6)	125 (6)	108 (5)	287 (16)	2 (4)	26 (8)	66 (7)	7·06
C(S2)	2045 (5)	5585 (5)	5755 (8)	111 (7)	104 (7)	290 (20)	0 (5)	41 (10)	81 (9)	6·66
S(2)	1606 (2)	4836 (2)	4304 (3)	208 (3)	130 (2)	350 (5)	−22 (2)	114 (3)	19 (2)	9·13
O(1)	1913 (3)	8457 (3)	7648 (5)	109 (4)	98 (3)	352 (9)	4 (3)	90 (5)	102 (4)	6·94
O(2)	1179 (3)	7154 (3)	9327 (5)	115 (4)	81 (3)	356 (10)	−7 (3)	54 (5)	92 (4)	6·79
C(1)	844 (5)	9079 (4)	7768 (7)	101 (6)	71 (4)	339 (15)	−6 (4)	59 (7)	57 (6)	6·23
C(2)	122 (4)	7814 (4)	9235 (6)	96 (5)	78 (4)	172 (10)	−26 (4)	19 (6)	18 (5)	4·68
C(3)	−51 (5)	8810 (4)	8526 (6)	106 (5)	72 (4)	234 (12)	−12 (4)	53 (6)	36 (5)	5·29
C(4)	651 (4)	10132 (3)	6967 (6)	115 (5)	60 (4)	251 (12)	−10 (4)	37 (6)	65 (5)	5·36
C(5)	1633 (5)	10360 (4)	6359 (6)	130 (6)	70 (4)	227 (12)	−24 (4)	45 (7)	49 (5)	5·46
C(6)	1445 (6)	11378 (5)	5647 (9)	160 (8)	94 (5)	368 (17)	−44 (5)	67 (9)	46 (7)	7·66
C(7)	345 (6)	12128 (5)	5692 (7)	173 (8)	93 (5)	255 (14)	−33 (5)	38 (8)	38 (7)	6·90
C(8)	−602 (6)	11855 (4)	6274 (7)	151 (7)	78 (4)	229 (13)	2 (4)	24 (8)	23 (6)	6·32
C(9)	−465 (5)	10889 (4)	6991 (8)	135 (6)	68 (4)	333 (15)	−6 (4)	41 (8)	45 (6)	6·73
C(10)	−875 (5)	7503 (4)	9911 (7)	113 (6)	102 (5)	315 (15)	51 (4)	40 (7)	52 (7)	6·55
C(11)	−2044 (5)	8184 (6)	9997 (10)	83 (6)	135 (7)	595 (25)	−28 (5)	84 (9)	63 (10)	9·62
C(12)	−2943 (7)	7861 (7)	10691 (11)	144 (8)	195 (9)	524 (25)	−49 (7)	141 (11)	95 (12)	10·74
C(13)	−2700 (8)	6847 (8)	11293 (10)	220 (11)	246 (12)	318 (18)	−149 (10)	114 (12)	−19 (11)	10·51
C(14)	−1545 (7)	6154 (6)	11201 (8)	213 (10)	142 (7)	331 (17)	−108 (7)	96 (11)	28 (8)	8·60
C(15)	−658 (6)	6486 (5)	10597 (9)	163 (7)	107 (5)	323 (15)	−60 (5)	46 (8)	60 (7)	7·43
O(3)	3540 (3)	5975 (3)	9979 (5)	134 (4)	102 (3)	306 (9)	11 (3)	84 (5)	89 (4)	7·08
C(16)	3561 (6)	5362 (6)	11325 (8)	145 (7)	130 (6)	239 (14)	−25 (5)	19 (8)	71 (7)	7·15
C(17)	4310 (8)	5765 (6)	12689 (12)	189 (10)	105 (6)	496 (25)	−42 (6)	68 (13)	−8 (10)	9·77
O(4)	4256 (3)	7232 (3)	7850 (5)	106 (4)	96 (3)	461 (12)	9 (3)	72 (5)	105 (5)	8·03
C(18)	4679 (9)	7885 (7)	6820 (16)	231 (12)	133 (7)	791 (34)	24 (7)	285 (17)	136 (13)	13·55
C(19)	5845 (9)	7394 (9)	6309 (13)	249 (13)	179 (9)	406 (22)	−43 (9)	134 (13)	−2 (11)	11·20

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31306 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and was reduced to 0·056 with anisotropic thermal parameters $[R = \sum w(|F_o| - |F_c|)/\sum w|F_o|]$.

All H atoms were located on a difference synthesis. The refinement of their coordinates (the isotropic thermal parameters were those of the C atoms to which they are bonded) resulted in an R of 0·036.

During the last cycles of refinement, the weighting scheme was

$$w\Delta^2 = (0\cdot083|F_o| + 0\cdot550)^{-1} \text{ for } 0 \le |F_o| < 88\cdot0$$
$$w\Delta^2 = (0\cdot057|F_o| + 2\cdot894)^{-1} \text{ for } |F_o| \ge 88\cdot0$$

where $\Delta = |F_o| - |F_c|$.

The final R was 0·034. $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} =$ 0·038.

The final atomic and thermal parameters are listed in Tables 2 and 3.

Table 3. H *atom parameters* ($\times 10^3$) *with estimated standard deviations* ($\times 10^3$) *in parentheses*

The isotropic thermal parameters are those of the C atoms to which they are bonded.

	x	y	z
H(C3)	−85 (5)	923 (4)	872 (6)
H(C5)	255 (5)	970 (4)	634 (6)
H(C6)	212 (5)	1167 (5)	539 (7)
H(C7)	31 (5)	1298 (5)	538 (7)
H(C8)	−132 (6)	1225 (5)	632 (7)
H(C9)	−123 (5)	1076 (4)	758 (6)
H(C11)	−205 (6)	893 (5)	953 (7)
H(C12)	−380 (6)	830 (5)	1063 (8)
H(C13)	−326 (6)	666(5)	1185 (8)
H(C14)	−154 (6)	536 (5)	1157 (7)
H(C15)	−7 (5)	618 (5)	1064 (7)
H1(C16)	268 (6)	533 (5)	1164 (7)
H2(C16)	382 (6)	458 (5)	1107 (7)
H1(C17)	518 (7)	592 (6)	1241 (8)
H2(C17)	378 (6)	644 (6)	1330 (8)
H3(C17)	465 (6)	515 (6)	1364 (8)
H1(C18)	415 (7)	807 (6)	561 (8)
H2(C18)	486 (7)	853 (6)	732 (9)
H1(C19)	640 (7)	796 (6)	608 (9)
H2(C19)	638 (7)	696 (6)	725 (9)
H3(C19)	580 (7)	678 (6)	538 (9)

Description and discussion of the structure

Fig. 1 shows the structure viewed along **c**, with the atomic numbering. In Figs. 2 and 3, the bond lengths (Å) and angles (°) are given. The average standard deviations are 0·004 for Nb–O, 0·005 for Nb–N and 0·007 Å for other distances; 0·2° for angles around Nb and 0·5° for other angles.

The distances and angles involving H atoms are given in Table 4.

Intermolecular interactions are of the van der Waals type. The Nb atom is at the centre of a distorted octahedron of two *trans* N atoms of the isothiocyanato groups, and the O atoms of the ethoxy and of the 1,3-diphenylpropane-1,3-dionato groups.

The Nb–N bonds, *cis* to the alkoxy ligands, are 2·120 and 2·088 Å and may be compared to those found by Kamenar & Prout (1970) in tetraphenylarsonium oxopentathiocyanatoniobate(V). They are also very similar to the Mo–N bonds in $[Mo(NCS)_6]^{3-}$ (Knox & Eriks, 1968) and to Co–N bonds in octahedral complexes (Mangia, Nardelli & Pelizzi, 1974; Andreetti & Sgarabotto, 1972). The Nb–N–C angles are 173·3° and 177·0°, and the N–C–S angles 179·5° and 177·8°. None of the deviations from linearity in the Nb–N–C–S system is significant.

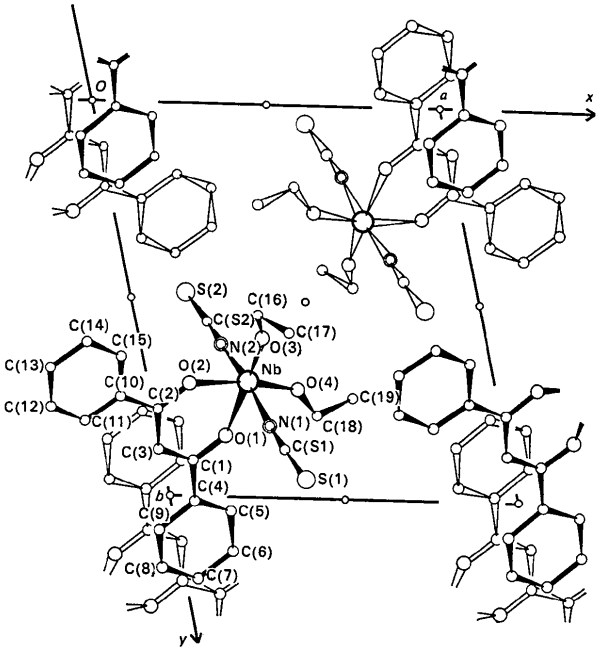


Fig. 1. Structure viewed along **c**.

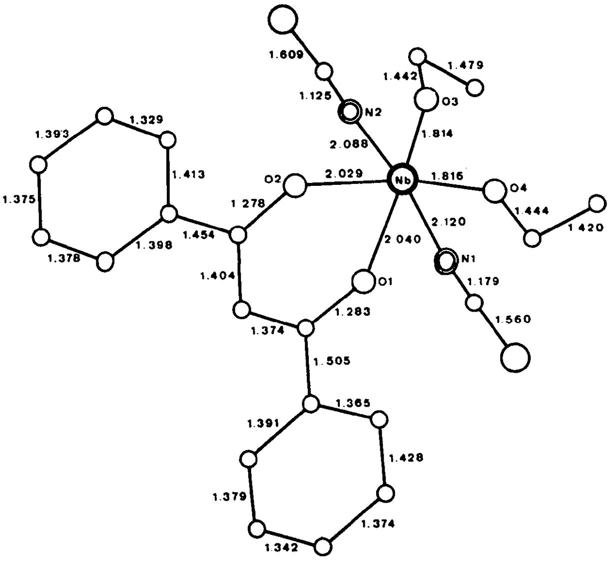
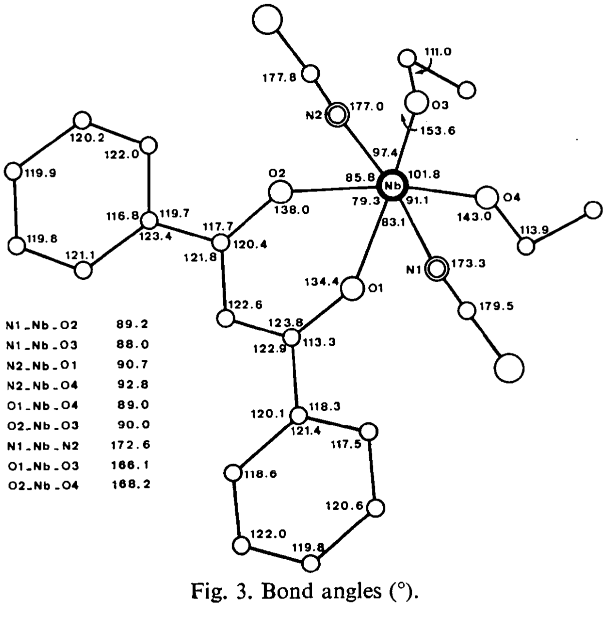


Fig. 2. Bond lengths (Å).

Table 4. *Distances* (Å) *and angles* (°) *involving* H *atoms*

Average standard deviations are 0·05 Å and 4°.

C(3)—H(C3)	0·96	C(1)——C(3)—H(C3)	129
		C(2)——C(4)—H(C3)	108
C(5)—H(C5)	1·17	C(4)——C(5)—H(C5)	120
		C(6)——C(5)—H(C5)	123
C(6)—H(C6)	0·96	C(5)——C(6)—H(C6)	123
		C(7)——C(6)—H(C6)	114
C(7)—H(C7)	1·12	C(6)——C(7)—H(C7)	118
		C(8)——C(7)—H(C7)	122
C(8)—H(C8)	0·85	C(7)——C(8)—H(C8)	126
		C(9)——C(8)—H(C8)	112
C(9)—H(C9)	1·10	C(8)——C(9)—H(C9)	118
		C(4)——C(9)—H(C9)	123
C(11)-H(C11)	1·05	C(10)——C(11)-H(C11)	109
		C(12)——C(11)-H(C11)	129
C(12)-H(C12)	0·99	C(11)——C(12)-H(C12)	121
		C(13)——C(12)-H(C12)	119
C(13)-H(C13)	0·91	C(12)——C(13)-H(C13)	120
		C(14)——C(13)-H(C14)	111
C(14)-H(C14)	1·08	C(13)——C(14)-H(C14)	121
		C(15)——C(14)-H(C14)	128
C(15)-H(C15)	0·78	C(14)——C(15)-H(C15)	120
		C(10)——C(15)-H(C15)	118
C(16)-H1(C16)	1·05	O(3)——C(16)-H1(C16)	116
C(16)-H2(C16)	0·99	O(3)——C(16)-H2(C16)	110
		C(17)——C(16)-H1(C16)	109
		C(17)——C(16)-H2(C16)	114
		H1(C16)-C(16)-H2(C16)	96
C(17)-H1(C17)	1·09	C(16)——C(17)-H1(C17)	113
C(17)-H2(C17)	1·07	C(16)——C(17)-H2(C17)	112
C(17)-H3(C17)	1·14	C(16)——C(17)-H3(C17)	114
		H1(C17)-C(17)-H2(C17)	113
		H1(C17)-C(17)-H3(C17)	102
		H2(C17)-C(17)-H3(C17)	102
C(18)-H1(C18)	1·14	O(4)——C(18)-H1(C18)	121
C(18)-H2(C18)	0·94	O(4)——C(18)-H2(C18)	112
		C(19)——C(18)-H1(C18)	96
		C(19)——C(18)-H2(C18)	101
		H1(C18)-C(18)-H2(C18)	110
C(19)-H1(C19)	1·08	C(18)——C(19)-H1(C19)	115
C(19)-H2(C19)	1·06	C(18)——C(19)-H2(C19)	106
C(19)-H3(C19)	1·08	C(18)——C(19)-H3(C19)	115
		H1(C19)-C(19)-H2(C19)	104
		H1(C19)-C(19)-H3(C19)	112
		H2(C19)-C(19)-H3(C19)	104



N1_Nb_O2	89.2
N1_Nb_O3	88.0
N2_Nb_O1	90.7
N2_Nb_O4	92.8
O1_Nb_O4	89.0
O2_Nb_O3	90.0
N1_Nb_N2	172.6
O1_Nb_O3	166.1
O2_Nb_O4	168.2

Fig. 3. Bond angles (°).

The bond distances and angles within the chelating dbm ring are in good agreement with values found in other β-diketone complexes: dioxobis-(1,3-diphenylpropane-1,3-dionato)molybdenum(VI) (Kojić-Prodić, Ružić-Toroš, Grdenić & Golič, 1974), hexa(acetylacetonato)aquotricobalt(II) (Cotton & Eiss, 1968) and 1,3-diphenylpropane-1,3-dionato-(1,6-dichlorocycloocta-1,5-diene)rhodium(I) (Ječný & Huml, 1974). The ring is planar, as are the two phenyl rings, within the limits of error (Table 5).

Table 5. *Equations of the mean planes and deviations* (Å) *of atoms from these planes*

Each plane is represented by an equation of the type $lX+mY+nZ-P=0$, referred to an orthogonal system of axes, which has X along **a**, Y in the *ab* plane and Z along **c***.

Plane 1: C(4), C(5), C(6), C(7), C(8), C(9)
$-0{\cdot}3077X-0{\cdot}3549Y-0{\cdot}8828Z+10{\cdot}4980=0$

Plane 2: C(10), C(11), C(12), C(13), C(14), C(15)
$-0{\cdot}3122X-0{\cdot}3478Y-0{\cdot}8840Z+10{\cdot}6359=0$

Plane 3: O(1), C(1), C(2), C(3), O(2)
$-0{\cdot}3507X-0{\cdot}4139Y-0{\cdot}8401Z+11{\cdot}0126=0$

Plane 1		Plane 2		Plane 3	
C(4)	0·010	C(10)	0·010	O(1)	0·017
C(5)	−0·012	C(11)	0·001	C(1)	−0·027
C(6)	0·024	C(12)	−0·014	C(2)	0·047
C(7)	−0·026	C(13)	−0·002	C(3)	−0·020
C(8)	0·026	C(14)	0·022	O(2)	−0·022
C(9)	−0·023	C(15)	−0·027		

The ethoxy ligands are *cis*. Nb–O single bonds to oxalato ligands lie between 1·96 and 1·98 Å (Mathern, Weiss & Rohmer, 1969). The Nb–O(3) (1·814 Å) and Nb–O(4) (1·816 Å) bonds indicate strong double-bond character, which is consistent with the very large Nb–O(3)–C(16) and Nb–O(4)–C(18) angles (153·6° and 143·0° respectively).

The Nb atom is hexacoordinated. The two ethoxy groups and the chelated dbm are in an equatorial plane, while the two isothiocyanato ligands are *trans*.

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The Structure of Hydroxyurea at Liquid-Nitrogen Temperature

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The crystal structure of *N*-hydroxyurea, $H_2NCONHOH$, first determined by Larsen & Jerslev [*Acta Chem. Scand.* (1966), **20**, 983] and independently by Berman & Kim [*Acta Cryst.* (1967), **23**, 180–181], has been reinvestigated at liquid-nitrogen temperature (−140°C) from densitometer-measured photographic data. The structural details reported in the above papers are confirmed, but the reduction in temperature has reduced the mean-square translational amplitudes of individual atoms by about 40% and has led to more precise values for bonds and angles. If the hydroxyl O is excluded, the remainder of the molecule vibrates as a rigid body.

Introduction

The crystal structure of *N*-hydroxyurea (Fig. 1) a substance used in cancer chemotherapy, was first determined by Larsen & Jerslev (1966) and later, independently, by Berman & Kim (1967). These were both X-ray investigations at room temperature, and the reported bonds and angles agree within the experimental errors. The present authors had also been working upon the structure of hydroxyurea when the above reports appeared. Our original data, collected at room temperature on Weissenberg films and measured by microdensitometer, refined to produce atomic positions which agreed well with both earlier studies. But an analysis of the thermal motions of the individual atoms showed that the molecule executes substantial librational motion with resulting errors in atomic coordinates. The substantial independent motion found for the hydroxyl oxygen [O(1), Fig. 1] means that the molecule as a whole does not vibrate as a rigid body and consequently the usual corrections (Cruickshank, 1956*a*) could not be applied, but the remaining four heavier atoms were found to vibrate as a rigid unit. It is not therefore possible to determine the bond lengths involving O(1) [particularly N(1)–O(1)] to the same precision as for the other bonds in the molecule, and a thermal analysis at best leads to an 'upper and lower bound' as described by Busing & Levy (1964). One way of reducing this kind of uncertainty is to reduce the vibrational amplitudes by taking data at a lower temperature; this is in addition to the other benefits which result from lowering the temperature such as improved resolution and reduction in the effects of thermal diffuse scattering. Further, hydroxyurea was found to decompose slowly at room temperature, but not at all at nitrogen temperature. For these reasons it was decided to investigate hydroxyurea at liquid-nitrogen temperature.

Experimental

Both room-temperature data and low-temperature data were taken from a pair of ground spherical crystals with Cu $K\alpha$ radiation. The first crystal of diameter 0·30 mm provided data about [010] and the second crystal of diameter 0·39 mm provided data about [100]. Both crystals were spherical to within ±1% as determined by a series of microscope photographs, and both specimens were sealed into Lindemann glass tubes after first being dipped several times into liquid nitrogen to reduce extinction. The lattice parameters were estimated from the separation of α_1 and α_2 spots of high-order reflexions on films. These are given in Table 1 for both temperatures, together with the previously reported values.

A comparison of the room and low temperature parameters reveals that the change in strain over the temperature range covered is markedly anisotropic. At both temperatures, four layers of data about [100] and five layers about [010] were recorded with a Nonius

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