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The Crystal and Molecular Structure of Carbonatodiamminecopper(II), $\text{Cu}(\text{NH}_3)_2\text{CO}_3$

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The crystal and molecular structure of carbonatodiamminecopper(II), $\text{Cu}(\text{NH}_3)_2\text{CO}_3$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in the space group $P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions $a=5.640$ (2), $b=10.579$ (3), $c=7.462$ (3) Å, and $\beta=97.49$ (1)°. The observed and calculated densities are 2.35 (2) and 2.372 g.cm⁻³. Least-squares refinement of the structure has yielded a final value for the conventional R factor, on F , of 0.032 for 934 data greater than their estimated standard deviations. The geometry at the copper atom is approximately a tetragonal pyramid whose basal plane consists of the two ammine nitrogen atoms and two oxygen atoms from a single carbonate. The copper atom of each formula unit is bonded to the adjacent unit through the terminal carbonate oxygen atom, with a Cu–O bond length of 2.303 (2) Å. The Cu–N distances are 1.971 (2) and 1.984 (2) Å. The Cu–O distances to the oxygen atoms in the bidentate carbonate are 1.986 (2) and 1.989 (2) Å. The N–Cu–N angle is 97.80 (12)°, while the chelated O–Cu–O angle is 66.38 (8)°. There is hydrogen-bonding between the ammine hydrogen atoms and the carbonate oxygen atoms of adjacent units.

Introduction

The structure of carbonatodiamminecopper(II), $\text{Cu}(\text{NH}_3)_2\text{CO}_3$, has been previously investigated by Hanic (1962, 1963), using two-dimensional X-ray data, and the spectroscopic properties of the complex have been discussed by Tomlinson & Hathaway (1968). Carbonatodiamminecopper(II) is also of considerable magnetic interest, as described in our recent examination of its low-temperature magnetic properties (Jeter, Hodgson & Hatfield, 1972).

The crystal structure reported by Hanic (1963) indicates that apparently chemically equivalent bonds, such as the two Cu–N bonds, have significantly different lengths. While it is true that two-dimensional data cannot be expected to give great precision in the atomic parameters, the reported values of these bond lengths are so disparate as to be either of enormous chemical interest or to cast doubt on the validity of the model. We have, therefore, undertaken an accurate three-dimensional single-crystal X-ray structural determination of the complex.

Experimental

Suitable crystals were obtained by adding 10 ml of 95% ethanol to a saturated solution of basic copper carbonate, $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2$, in 35 ml concentrated ammonium hydroxide solution and removing the resulting turquoise precipitate by filtration. The filtrate was allowed to stand for six days, after which the dark-blue, rhombic crystals were separated by filtration and were air-dried. The crystals were found to decompose slowly, turning green after a week's exposure to moist air; they could be preserved indefinitely in a desiccator.

On the basis of precession and Weissenberg photography, the crystals were assigned to the monoclinic system, and examination of the $0kl$, $hk0$, $h0l$, and hll zones demonstrated systematic absences of l odd in the $h0l$ zone and k odd for $0k0$ reflections; hence, the previous (Hanic, 1963) space group assignment of $P2_1/c$ was confirmed. The cell constants, obtained by the least-squares procedure described below, are $a=5.640$ (2), $b=10.579$ (3), $c=7.462$ (3) Å, and $\beta=97.82$ (1)°. The observations were made at 25°C, with the wavelength assumed to be $\lambda(\text{Mo } K\alpha_1)=0.7093$ Å. A density of 2.372 g.cm⁻³ calculated for four formula

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units in the cell is in acceptable agreement with the value of $2.35 (2) \text{ g.cm}^{-3}$ obtained by flotation in 1,2-dibromoethane/diiodomethane solution. Hence, no crystallographic symmetry need be imposed on monomeric species in the cell.

Intensity data were collected at 25°C on a Picker four-circle automatic diffractometer, using Mo $K\alpha$ radiation. The rhombic crystal chosen had faces $(0\bar{1}1)$, $(01\bar{1})$, (011) , $(1\bar{1}0)$, $(\bar{1}10)$, (011) , $(\bar{1}10)$, and (110) , the separations between all pairs of opposite faces being 0.020 cm . The crystal was mounted on a glass fiber roughly normal to the (010) planes. The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω -scan technique (Furnas, 1957); the widths at half-height for 12 strong reflections in various regions of reciprocal space were found to lie in the range 0.09 to 0.13° which, although larger than we would have desired, is acceptably low. Note that the common practice of examining the ω -scan of only one reflection is an insufficient test of the crystal mosaicity, and it is worthwhile to scan all the reflections that are used for the refinement of the crystal orientation. Twelve reflections from the crystal were accurately centered through a narrow vertical slit at a take-off angle of 1.0° . These observations formed the basis for the least-squares refinement of cell param-

eters and crystal orientation, which was effected with the logic documented by Busing & Levy (1967) in a PDP-8/L computer. The cell constants obtained by this procedure are in good agreement with those obtained by Hanic (1963).

Intensity data were collected at a take-off angle of 1.4° ; at this angle, the peak intensity was about 90% of the maximum value as a function of take-off angle. The counter aperture, chosen to minimize extraneous background, was 4.0 mm high by 4.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the θ - 2θ scan technique at a scan rate of 1° min^{-1} . Allowance was made for both $K\alpha_1$ and $K\alpha_2$ radiations by using a scan range of from 1.0° below the calculated $K\alpha_1$ peak to 1.0° above the calculated $K\alpha_2$ peak position. Stationary-counter stationary-crystal background counts of 10 sec duration were taken at each end of the scan.

The Mo radiation was filtered through a 3.0 mil Nb foil after diffraction from the crystal in order to remove the $K\beta$ radiation. Cu foil attenuators, giving attenuator factors of about 2.3, were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts per sec during the scan. These attenuator factors were determined as previously described (Hodgson & Ibers, 1969). The pulse-height analyzer

Table 1. *Positional parameters for $\text{Cu}(\text{NH}_3)_2\text{CO}_3$*

	This work			Hanic (1963)		
	X	Y	Z	X	Y	Z
Cu	0.1460 (1)*	0.0795 (1)	0.1892 (1)	0.3539 (8)	0.0795 (3)	0.1887 (5)
O(1)	0.3890 (3)	0.1415 (2)	0.0410 (2)	0.1008 (44)	0.1521 (14)	0.0362 (25)
O(2)	0.3611 (3)	0.3446 (2)	-0.0484 (2)	0.1424 (41)	0.3454 (15)	0.9494 (29)
O(3)	0.0779 (3)	0.2518 (2)	0.0884 (3)	0.4204 (30)	0.2547 (19)	0.0868 (26)
N(1)	0.2665 (5)	-0.0948 (2)	0.2257 (4)	0.7737 (41)	0.4044 (15)	0.2729 (28)
N(2)	-0.1598 (4)	0.0568 (3)	0.2891 (4)	0.6666 (56)	0.0575 (21)	0.2795 (40)
C	0.2794 (4)	0.2505 (2)	0.0225 (3)	0.2222 (38)	0.2486 (25)	0.0237 (33)
H(1)	0.3377 (70)	-0.1220 (35)	0.1522 (51)			
H(2)	0.1579 (80)	-0.1472 (59)	0.2180 (54)			
H(3)	0.3592 (75)	-0.1118 (47)	0.3136 (53)			
H(4)	-0.2080 (81)	-0.0065 (46)	0.3352 (56)			
H(5)	-0.0378 (158)	-0.0171 (111)	0.1930 (139)			
H(6)	-0.2853 (89)	0.0850 (35)	0.2099 (53)			

* The numbers in parentheses here, and elsewhere in this paper, refer to the e.s.d.'s in the least significant figure.

Table 2. *Thermal parameters for $\text{Cu}(\text{NH}_3)_2\text{CO}_3$*

The form of the anisotropic thermal ellipsoid is $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	β_{11} or $B (\text{\AA}^2)$	B_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.01184 (16)	0.00268 (15)	0.00844 (10)	0.00026 (3)	0.00271 (7)	0.00031 (2)
O(1)	0.1481 (5)	0.0033 (2)	0.0105 (3)	0.0020 (2)	0.0059 (3)	0.0011 (2)
O(2)	0.1778 (6)	0.0039 (2)	0.0095 (3)	-0.0021 (3)	-0.0002 (3)	0.0020 (2)
O(3)	0.0149 (6)	0.0037 (2)	0.0121 (4)	0.0026 (2)	0.0049 (3)	0.0013 (2)
N(1)	0.0140 (7)	0.0033 (2)	0.0099 (4)	0.0002 (3)	0.0023 (5)	0.0004 (2)
N(2)	0.0136 (8)	0.0058 (2)	0.0126 (4)	0.0001 (3)	0.0044 (5)	0.0030 (3)
C	0.0125 (7)	0.0028 (2)	0.0058 (4)	0.0002 (3)	-0.0002 (4)	-0.0003 (2)
H(1)	2.16 (67)					
H(2)	3.82 (94)					
H(3)	2.45 (89)					
H(4)	2.41 (86)					
H(5)	15.0 (29)					
H(6)	3.56 (82)					

was set for approximately a 90% window. A unique data set having $2\theta(\text{Mo}) \leq 55^\circ$ was gathered, a total of 1170 intensities being measured. As a check on crystal and electronic stability, the intensities of three standard reflections were measured after every 100 reflections; the intensities of these reflections remained essentially constant throughout the run, showing only the deviations from the mean predicted from counting statistics. There were very few intensities above background at values of $2\theta > 55^\circ$.

The data were processed by the method of Corfield, Doedens & Ibers (1967). A linear background correction was applied, and the intensities were assigned standard deviations according to the formula:

$$\sigma(I) = [C + 0.25(ts/tb)^2(B_H + B_L) + (pI)^2]^{1/2}$$

in our program *COPROC*. The value of p was selected as 0.045, since the crystal was of intermediate mosaicity; this term is included in the expression for the e.s.d. in order to prevent extremely high weight being given to very strong reflections in the least-squares refinement of the structure (Busing & Levy, 1957). The values of I , the intensity, and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption. The linear absorption coefficient, μ , for this compound is 50.1 cm^{-1} , and for the chosen sample the transmission coefficients evaluated by numerical integration, using our version of Hamilton's *GONO 9* program, were found to range from 0.20 to 0.33. Of the 1170 independent intensities measured, 934 were found to be greater than their e.s.d.'s.

Solution and refinement

An initial attempt was made to refine the atomic coordinates of Hanic (1963). All least-squares calculations in this analysis were carried out on F , the function minimized being $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes, and the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The full-matrix least-squares program used in this analysis was *NUCLS* (J. A. Ibers). In calculations of F_c , the atomic scattering factors for Cu were taken from Cromer & Waber (1965), those for H from Stewart, Davidson & Simpson (1965), and those for O, N, and C from the tabulation of Ibers (1962). The effects of anomalous dispersion were included in calculations of F_c (Ibers & Hamilton, 1964), the values of $\Delta f'$ and $\Delta f''$ for Cu being taken from Cromer (1965). Only the 934 data that were greater than their e.s.d.'s were used in the refinement of the structure. Four cycles of least-squares calculations, using Hanic's atomic parameters, yielded values of the normal agreement factors $R_1 = \sum |F_o - F_c| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.558 and 0.740 respectively. This was taken as evidence that Hanic's model is incorrect, and so this model was abandoned and the structure re-solved.

The copper atom was located in a three-dimensional Patterson function; three cycles of least-squares refine-

ment gave $R_1 = 0.360$ and $R_2 = 0.470$. The remaining nonhydrogen atoms were located in a difference Fourier synthesis, which was effected with a modification of A. Zalkin's program *FORDAP*. Least-squares refinement of these atoms, with isotropic thermal parameters assigned to all atoms, gave values of $R_1 = 0.086$ and $R_2 = 0.136$. Additional least-squares calculations, using anisotropic thermal parameters for all atoms, reduced these values to 0.052 and 0.084. The six ammine hydrogen atoms were located in a difference Fourier map which was run at this stage. Two cycles of least-squares calculation, with variable isotropic thermal parameters assigned to the hydrogen atoms and variable anisotropic thermal parameters assigned to all other atoms gave R_1 and R_2 values of 0.048 and 0.074. The improvement in R_2 is significant at any meaningful confidence level (Hamilton, 1964).

Examination of the data revealed that secondary extinction was significant, since for strong low-order reflections $|F_o|$ was systematically smaller than $|F_c|$.

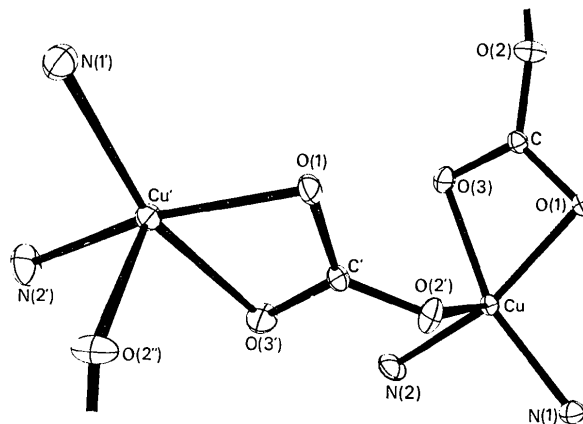


Fig. 1. View of the coordination around two neighboring copper atoms in $\text{Cu}(\text{NH}_3)_2\text{CO}_3$. Atoms C' , Cu' , etc., are related to C , Cu , etc., by the c glide; atom $\text{O}(2')$ is related to $\text{O}(2)$ by translation along c . The thermal ellipsoids are drawn at the 40% probability level.

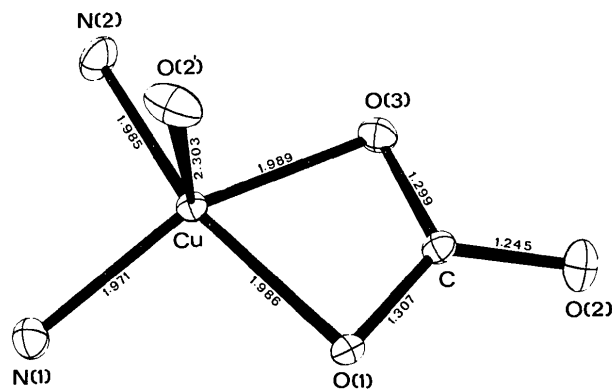


Fig. 2. View of the coordination around a single copper atom in $\text{Cu}(\text{NH}_3)_2\text{CO}_3$. Atom $\text{O}(2')$ is related to atom $\text{O}(2)$ by the c glide.

An extinction correction of the form:

$$F_o(\text{corr}) = F_o \{ c\beta(\theta)I + [1 + c^2\beta^2(\theta)I^2]^{1/2} \}^{1/2},$$

which is strictly valid for a spherical crystal (Zachariasen, 1968) and a good approximation for the rhombic sample used, was applied. The function minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|/g)^2$, where $g = \{c\beta(\theta)I + [1 + c^2\beta^2(\theta)I^2]^{1/2}\}^{1/2}$, c is the extinction coefficient, I the corrected intensity, and $\beta(\theta)$ is the function described by Zachariasen (1963). Three cycles of least-squares refinement gave R_1 and R_2 values of 0.032 and 0.043, respectively. In the final cycle, no parameter experienced a shift greater than its e.s.d., which was taken as evidence that the refinement had converged. The value of R_2 shows no dependence on $\sin \theta$ or on $|F_o|$, which indicates that our choice of $p=0.045$ is essentially correct. A final difference Fourier synthesis showed no peak greater than 0.62 e.Å⁻³, the peak height of a carbon atom in this analysis being about 10 e.Å⁻³.

The positional parameters derived from the last least-squares cycle, along with their associated standard deviations as estimated from the inverse matrix, are presented in Table 1; the relatively large values for the e.s.d.'s of the positional parameters of one of the ammine hydrogen atoms [H(5)] are indicative of our inability to satisfactorily refine the coordinates of this atom. Since H(5) is not involved in hydrogen bonding (see below), it is possible that there is some crystallographic disorder of the hydrogen atoms on N(2), but no evidence of this could be obtained from the final difference Fourier synthesis.

In Table 1 we also present the coordinates obtained by Hanic (1963), and it is readily apparent that while the y and z coordinates of all atoms are in reasonable agreement in the two analyses, the x coordinates differ in that Hanic's values are approximately 0.5 minus our values, *i.e.*, Hanic has replaced x by $\frac{1}{2} - x$. In $P2_1/c$ there is a center of symmetry at $(\frac{1}{2}, 0, 0)$, so

Hanic's parameters are equivalent to replacing $+x$ by $-x$. Hanic was able to satisfactorily refine his coordinates, because the data that he gathered (the $hk0$ and $0kl$ planes) are insufficient to unambiguously determine the structure. Information concerning the atomic x coordinates is obtained only from the $hk0$ data, but since $hk0$ is equivalent to $\bar{h}k0$ in a centrosymmetric monoclinic space group, it is impossible to distinguish between x and $-x$. Unfortunately, Hanic made the wrong assignment. This problem, of course, does not arise if data for either the $hk0$ and $h0l$ planes or the $0kl$ and $h0l$ planes are collected.

The thermal parameters, β_{ij} , of the atoms, along with their e.s.d.'s, are listed in Table 2. The final values of $|F_o|$, corrected for extinction effects, and $|F_c|$ (in electrons) are contained in Table 3; only the 934 intensities that were greater than their e.s.d.'s are listed in the Table. The final value of the extinction coefficient is $8.4(4) \times 10^{-7}$ (absolute units), and the estimated standard error in an observation of unit weight is 1.76.

Description of the structure

The structure consists of infinite polymeric chains of $\text{Cu}(\text{NH}_3)_2\text{CO}_3$ units; the polymeric linkages are formed through the terminal oxygen atom of one carbonate moiety bonding to an adjacent copper atom, whose terminal carbonate oxygen atom continues the chain. A view of the polymeric unit is shown in Fig. 1. The geometry at each copper atom is approximately tetragonal pyramidal, with the ammine nitrogen atoms and the chelating oxygen atoms of the carbonate ligand forming the basal plane, while the terminal carbonate oxygen atom of a neighboring copper atom occupies the axial site. The inner coordination sphere is shown in Fig. 2; both figures were drawn by C. K. Johnson's program *ORTEP*. The individual $\text{CuN}_2(\text{CO}_3)$ fragments are essentially planar, with no atom deviating from the weighted least-squares plane by more than 0.17 Å.

Table 4. Intramolecular distances and angles in $\text{Cu}(\text{NH}_3)_2\text{CO}_3$

	Distances (Å)			Angles	
	This work	Hanic (1963)		This work	Hanic (1963)
Cu—N(1)	1.971 (2)	2.02	O(1)—Cu—O(3)	66.38 (8)	67.0
Cu—N(2)	1.984 (2)	1.81	O(1)—Cu—N(1)	97.74 (10)	
Cu—O(1)	1.986 (2)	2.05	N(1)—Cu—N(2)	97.80 (12)	
Cu—O(3)	1.989 (2)	1.82	N(2)—Cu—O(3)	96.89 (10)	
Cu—O(2')	2.303 (2)	2.55	O(2')—Cu—O(1)	91.99 (8)	
Cu—C	2.375 (2)		O(2')—Cu—N(2)	96.16 (10)	
C—O(1)	1.307 (3)	1.15	O(2')—Cu—O(3)	93.14 (8)	
C—O(2)	1.245 (3)	1.22	O(2')—Cu—N(1)	94.38 (9)	
C—O(3)	1.299 (3)	1.32	O(1)—C—O(2)	123.62 (23)	114.5
N(1)—H(1)	0.84		O(1)—C—O(3)	113.25 (21)	119.9
N(1)—H(2)	0.81		O(2)—C—O(3)	123.12 (23)	125.5
N(1)—H(3)	0.90		H(1)—N(1)—H(2)	98.86	
N(2)—H(4)	0.92		H(1)—N(1)—H(3)	92.11	
N(2)—H(5)	1.07		H(2)—N(1)—H(3)	107.31	
N(2)—H(6)	0.93		H(4)—N(2)—H(5)	97.64	
			H(4)—N(2)—H(6)	95.68	
			H(5)—N(2)—H(6)	121.67	

The bond lengths and angles, as calculated using Busing, Levy & Martin's *ORFFE* program, are compared, in Table 4, with those obtained by Hanic. The Cu-N bond lengths of 1.971 (2) and 1.984 (2) Å are similar to the copper-ammine nitrogen distances found in sulfato and selenatotetraamminecopper(II) (Morosin, 1969), diammine-*o*-phthalato)copper(II) (Cingi, Guastini, Musatti & Nardelli, 1970), diazidodiamminecopper(II) (Agrell, 1966), hexaamminecopper(II) chloride (Distler & Vaughan, 1967), di- μ -hydroxobis(dimethylamine)copper(II) sulfate monohydrate (Iitaka, Shimizu & Kwan, 1966), bis(ethylenediamine)copper(II) thiocyanate (Brown & Lingafelter, 1964), and nitrate (Komiyama & Lingafelter, 1964) as well as in other molecules, all of which fall in the range 1.97 to 2.07 Å. The Cu-O(1) and Cu-O(3) bond lengths of 1.986 (2) and 1.989 (2) Å are within the range of 1.88 to 2.03 Å found in monopyridinecopper acetate (Barclay & Kennard, 1961), copper acetate monohydrate (van Niekerk & Schoening, 1953), acetylactone-mono-*o*-hydroxyanil)copper(II) (Barclay & Hoskins, 1965), azurite, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ (Gattow & Zemann, 1958), and other related molecules. The closest through-space Cu-Cu approach of 3.500 (1) Å is considerably longer than the values of 2.63 to 2.99 Å found for Cu-Cu bonds in copper dimers (van Niekerk & Schoening, 1953; Barclay & Kennard, 1961; Barclay & Hoskins, 1965), but it is not greatly different from the value of 3.722 Å which we have recently found for the non-bonded Cu-Cu approach in the $\text{Cu}_2\text{Cl}_8^{4-}$ dimer (Hodgson, Hale & Hatfield, 1971).

The bonding of the carbonate moiety in this complex is of great interest, since there are few proven examples of this kind of four-membered ring system. The geometry of the carbonate group is fundamentally similar to that in carbonatotetraamminecobalt(III) bromide (Barclay & Hoskins, 1962) and carbonatobis(triphenylphosphine)platinum(II) (Cariati, Mason, Robertson & Ugo, 1967), and to that found for the chelating acetate group in zinc acetate dihydrate (van Niekerk, Schoening & Talbot, 1953); this is in marked contrast to the structure of the free carbonate ion, in which all C-O distances are 1.294 Å and all O-C-O angles are 120° (Sass, Vidale & Donohue, 1957).

Hydrogen bonding

There are a number of relatively short N-H...O separations in this structure, and the possible hydrogen bonds are tabulated in Table 5. The N-H bond lengths found here are much shorter than the accepted values, as is usual in X-ray studies (Delaplane & Ibers, 1966; Hodgson & Ibers, 1969), but the N...O separations are valid and those listed in Table 5 fall within the range normally associated with hydrogen bonding (Hamilton & Ibers, 1968; Pimentel & McClellan, 1960). The bond angles subtended at the hydrogen atoms, while inaccurate because of the contraction of the N-H bonds (which is associated with the X-ray

technique), give some general indication as to the strength of these hydrogen bonds. Values in the 150 to 180° range are normally found for N-H...O and O-H...O hydrogen bonds (Hodgson & Ibers, 1969; Robertson, 1965; Raymond, Corfield & Ibers, 1968; Chidambaram, Sequeira & Sikka, 1964), from which we conclude that the interaction between O(3) and N(1) is, at best, very weak, but that the other interactions listed in Table 5 are quite strong.

Table 5. Possible A-H...B hydrogen bonds

A	H	B	A...B	Angle at H
N(1)	H(1)	O(1)	3.004 (3) Å	164°
N(2)	H(6)	O(1)	3.075 (3)	166
N(1)	H(3)	O(2)	3.043 (3)	174
N(2)	H(4)	O(2)	3.263 (3)	153
N(1)	H(2)	O(3)	3.014 (3)	138

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The Crystal and Molecular Structure of 2,7-Dichlorodibenzo-*p*-dioxin

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The crystal and molecular structure of 2,7-dichlorodibenzo-*p*-dioxin has been determined from three-dimensional single-crystal X-ray diffraction data. This compound crystallizes in the triclinic space group $P\bar{1}$ with lattice parameters $a = 3.878 \pm 0.003$, $b = 6.755 \pm 0.009$, $c = 10.265 \pm 0.015$ Å, $\alpha = 99.46 \pm 0.01$, $\beta = 100.63 \pm 0.03$, and $\gamma = 99.73 \pm 0.03^\circ$, giving a calculated density $\rho = 1.647$ g.cm⁻³ for C₁₂H₆O₂Cl₂ and $Z = 1$. The intensities of 1152 unique reflections were measured, using the θ - 2θ scan mode of a Picker automatic diffractometer (Mo $K\alpha$ radiation). The structure was solved from the Patterson function and was refined by full-matrix least-squares analysis to a final R value of 5.7% for the 1030 reflections above background. In the final model, Cl, O, and C atoms were assigned anisotropic thermal parameters, while the hydrogen atoms were restricted to isotropic thermal parameters. The molecules are situated on crystallographic inversion centers; because they are planar, the approximate molecular symmetry is C_{2h} . The C-Cl bond distance is 1.742 ± 0.004 Å, the C-O distances are 1.380 and 1.382 Å (± 0.004), and the six C-C distances vary between 1.370 and 1.397 Å (± 0.005). The C-O-C angle in the heterocyclic ring is $116.3 \pm 0.2^\circ$.

Introduction

As part of an effort to establish the chemical and biological properties of the chlorinated derivatives of dibenzo-*p*-dioxin, we are undertaking the structure determinations of key compounds in this series by X-ray diffraction. This paper describes the crystal and molecular structure of 2,7-dichlorodibenzo-*p*-dioxin. The preparation, isolation, and X-ray powder diffraction pattern of this compound are being communicated separately (Boer, van Remoortere & Muelder, 1972).

Although the primary purpose of this work is to assist researchers in making a rapid and positive identification of these materials, the molecular conformations are of some interest, since in principle the molecules are capable of folding along their transverse bisectors. Indeed, severe folding is encountered in

heterocyclic analogs containing sulfur, such as thianthrenes (Lynton & Cox, 1956; Rowe & Post, 1958) and thioxanthenes (Ternay, Chasar & Sax, 1967), and some slight folding is reported for 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (Cantrell, Webb & Mabis, 1969). On the other hand, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCBD) is planar (Boer, van Remoortere, North & Neuman, 1972).

Experimental

A sample of dichlorodibenzo-*p*-dioxin was received from W. W. Muelder. This material was isolated from sodium 2,4-dichlorophenolate that had been heated to 180°C for 16 hours. The dichlorodibenzo-*p*-dioxin forms colorless crystals of a lath-like habit, which tend to be very thin between the {010} faces and are